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Synthesis and crystal structure of some
novel phases involving metal-metal bonding

by

Douglas Guy Adolphson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
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Signature was redacted for privacy.

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1975

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INTRODUCTION

Much attention in recent years has been focused on compounds involving metal-metal bonding. While very few examples were known only a few years ago, it now appears that catenation is an important facet of the chemistry of the metallic elements.¹ In approximately the last decade it has been demonstrated that many metals, particularly the heavier ones in lower than normal oxidation states, show a propensity toward forming homonuclear metal to metal bonds. The occurrence of metal-metal bonds in compounds of the transition metals have been reviewed by several authors.²⁻⁵ Recently, Corbett has reviewed the homopolyatomic ions known for the post-transition elements,^{6a} and Gillespie and Passmore have presented a general review of the homopolyatomic cations of the elements.^{6b} Among the reasons for neglect of this field of chemistry until recently have been the nonexistence of good solvent systems for metallic systems, the range of composition that many such compounds exhibit, and the lack of a theory of valence to adequately describe such compounds.⁷ Cotton has emphasized that the surest indication of the existence of a metal-metal interaction is provided by the determination of the molecular structure.⁸ In this research X-ray crystallography was chosen as the method of structural elucidation.

The reduction of several of the rare earth metal halides by the respective metal has resulted in several unexpected and unusual compounds.⁹ The preparation and subsequent determination of the structure of gadolinium sesquichloride^{10,11} represents a rewarding investigation in this area. The overriding feature of the structure is the occurrence of chains of gadolinium atoms involving elongated octahedra sharing edges running parallel to the fiber axis. The chains dictate the structural arrangement and are separated by sheaths of chlorine atoms all of which occupy faces of metal atom triangles.

Research techniques developed in the study of the rare earth-rare earth metal halide systems have proven applicable to the investigation of other systems of experimental interest. A scarcity of information concerning the lower halides of zirconium and hafnium led to the study of the reduction characteristics of halides of the two elements by Struss and Corbett.^{12,13} The reaction of gaseous $HfCl_4$ from a reservoir at 450-550° with a large area of hafnium foil at 610-650° in a sealed tantalum tube gives a very small amount of metallic product $HfCl_{1+x}$ ($0 < x < .2$). The analogous reaction for $ZrCl_4$ at 600° produces $ZrCl_3$ and a small amount of $ZrCl_{1+x}$ mixed with $ZrCl_2$. Equilibration of either metallic product with the respective metal at 625 to 650° in a tantalum container gives the pure monochloride. While the reduction to zirconium monochloride is more facile, the two monochlorides are apparently

isostructural and metallic conductors.¹³ A previous preparation of zirconium(III) chloride, bromide and iodide resulted in better yields than for the corresponding hafnium(III) halides.¹⁴ Apparently the facility of the reduction of zirconium halides relative to those of hafnium is one of the few differences in the chemistry of the two elements. Larsen has proposed a separation scheme involving the reduction of zirconium tetrahalides containing hafnium in natural abundance to the appropriate zirconium trihalide by either metallic zirconium or aluminum in molten 76 mole percent aluminum trihalide at 260-310°.¹⁵ Under the same time and temperature conditions, the respective hafnium tetrahalide remains substantially unreduced and can be separated along with the aluminum halide solvent by sublimation from the nonvolatile zirconium trihalide. It remains to be seen if this approach is practicable, but the separation of zirconium and hafnium is of commercial significance as the disparate thermal neutron capture cross sections of the two elements enjoins the use of zirconium for cladding nuclear fuel and hafnium for control rods in nuclear reactors.¹⁶

The purity of several of the reported trihalide phases is questionable because of the use of powdered zirconium metal as the reducing agent or because of side reactions with silica containers.^{14,17,18} Newham and Watts reported the preparation of pure anhydrous zirconium trichloride, tribromide and

triiodide from passage of the appropriate tetrahalide vapor mixed with hydrogen through a glow discharge.¹⁹ Afterwards the product was freed from absorbed or unreduced contaminants by heating in vacuo. Struss and Corbett carried out their reactions between gaseous tetrahalide and the appropriate metal foil in sealed tantalum containers.^{12,13} Thus, side reactions with the container and cessation of the reaction by blockage of the surface of the metal particles were obviated. Zirconium dihalides of uncertain purity have been obtained from the disproportionation of the trihalides.^{20,21} Heating zirconium trichloride and metallic zirconium in a quartz tube lined with platinum foil resulted in zirconium dichloride of 95-99% purity.²² The homogeneity range of zirconium(II) chloride is presently being investigated in this laboratory.²³

The patent literature contains a reference to a product called "Zirklor"²⁴ made by electrolytic reduction of a $\text{SrCl}_2\text{-NaCl-ZrCl}_4$ melt (63:34:3) onto graphite. Its color, softness, graphitic character and analysis correspond to the properties of ZrCl , but the powder pattern data given in the patent are in poor agreement with the data reported by Struss and Corbett.¹³ Surprisingly, a sample of the material "Zirklor" was found to have substantially the same pattern as did ZrCl .¹³ A report of the synthesis of ZrCl and its powder pattern by Troyanov and T'sirelnikov²⁵ agrees generally with that of Struss and Corbett with the exception of the omission of the lowest angle line in the powder pattern by the former

authors. A subsequent crystal structure determination for ZrCl by Troyanov²⁶ is poorly refined and in error. The preparation of a suitable single crystal of ZrCl will be described in Chapter II of this thesis and the structure determination of ZrCl will be described in Chapter III.

Several years ago the X-ray investigation of the product of the reduction of molten bismuth chloride by bismuth metal revealed that the phase corresponded to the stoichiometry BiCl_{1.167}.²⁷ The structure determination resulted in the discovery of the homopolyatomic cation Bi₉⁵⁺ associated with the large complex anions [BiCl₅]²⁻ and [Bi₂Cl₈]²⁻ in the ratio 2:4:1. When the reduction is carried out in the aluminum chloride solvent system, two compounds Bi₅³⁺(AlCl₄⁻)₃ and (Bi⁺AlCl₄⁻)_n crystallize following reduction of the composition BiCl₃•AlCl₃ by a stoichiometric or excess quantity of bismuth, respectively.²⁸ Attempts to obtain a single crystal of either compound suitable for an X-ray structure determination were thwarted by the tendency to supercool and produce twinned crystals.²⁹ During the course of this research several attempts were made to prepare the compound Bi₅³⁺(AlBr₄⁻)₃ and isolate a single crystal suitable for a structural determination.

Over forty years ago, Zintl reported potentiometric evidence for solutions of polyatomic anions of antimony, bismuth, lead, tin and arsenic, among others, after reduction of a salt of the respective heavy metal with sodium metal in

liquid ammonia.³⁰⁻³³ The compounds indicated for Group IV and V elements are listed in Table 1. These unusual phases were

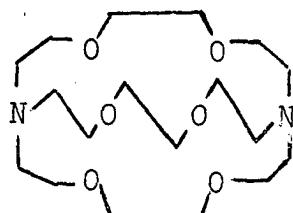
Table 1. Zintl phases

Na_3As	Na_4Sn_9	Na_4Pb_7
Na_3As_3	Na_3Sb	Na_4Pb_9
Na_3As_5	Na_3Sb_3	Na_3Bi
Na_3As_7	Na_3Sb_7	Na_3Bi_3

not further characterized because it was not possible to isolate them from the ammoniacal solutions in crystalline form. It is significant that two of the reported products, Na_4Sn_9 and Na_4Pb_9 , contain anions that are isoelectronic and presumably isostructural with the Bi_9^{5+} cation in BiCl_1 .¹⁶⁷⁶ Attempts to prepare solid phases containing these anions have been frustrated by their tendency to form the known and more stable intermetallic phase involving the heavy metal and the sodium counter cation. Some effort has been made to generate such species in molten salts, and the cryogenic evidence for Sb_3^{3-} in NaI is encouraging.³⁴ Exploratory work in this laboratory seeking to isolate stable cluster anions by varying the conditions, solvent and cation from those used by Zintl have been unsuccessful.³⁵ However, Kummer and Diehl have

recently reported isolation of a crystalline compound $\text{Na}_4\text{Sn}_9 \cdot 6\text{-}8$ ethylenediamine.³⁶ They present Mössbauer data, magnetic data and preliminary X-ray data, but they have yet to report a complete X-ray structure determination.

Recently, Dye has reported the preparation and crystal structure of a compound $\text{Na}_2\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ which contains a cryptated sodium cation and a sodium anion.^{37,38} Cryptates are a new type of complexing agent that wrap themselves around metal ions in solution thereby effectively hiding the metal ion from the solvent.³⁹ The compound $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ [I] is one of



I

a series of polyoxamacrobicycles synthesized by Lehn⁴⁰ consisting of a bicyclic ring system with two nitrogen bridgeheads and a defined number of ether-oxygen atoms in the bridges. The systematic designation is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane. While the shorter designation 2,2,2-crypt has the feature of specifying the number of ether oxygens in each bridge, in many cases it will be convenient to simply use the abbreviation C. Dye exploited 2,2,2-crypt to encapsulate the sodium cation in solutions of sodium in ethylamine which ultimately allowed

isolation of solid NaC^+Na^- .³⁷ One sodium cation was found to occupy the central cavity of the macrobicycle[I] as has been found for all of its complexes with alkali, alkaline earth and other metal ions so far studied.⁴¹ The sodium anion was found to be located outside of the cryptated cation at a large distance from all other atoms.³⁸ By comparison with the known crystal structure of (cryptated sodium) iodide⁴² the outside sodium is similar to the iodide ion in its placement, but distance comparisons suggest it is somewhat larger than the iodide ion.³⁸

Don Merryman and Frank Armatis have been involved in a series of synthetic attempts to prepare stable compounds containing homopolyatomic anions.⁴³ Typically, 18-crown-6 ether or the 2,2,2-crypt[I] was allowed to react with sodium alloys of heavy metals in amines to stabilize a salt containing the cryptated sodium cation and a presumed polyatomic anion. In the case of a 1:1 alloy of sodium and antimony, reaction with 2,2,2-crypt in ethylenediamine lead to the isolation of a dark brown crystalline solid on evaporation of the solvent. The X-ray structure determination reported here confirms that the compound involves three cryptated sodium cations and a Sb_7^{3-} cluster anion. The synthesis of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ will be described in Chapter II of this thesis. The details of the structure determination will be given in Chapter IV.

During the course of this work the goal of synthesizing a single crystal of zirconium monochloride suitable for a structure determination and solving the crystal structure has been realized. Now that the structure is known, the physical properties can be correlated with it. In fact, the layer structure determined for zirconium monochloride explains why it was so difficult to find a suitable single crystal. The synthetic work on the $\text{Bi}-\text{BiBr}_3-\text{AlBr}_3$ system did not produce such satisfactory results. While apparently crystalline material was obtained from two preparations and X-ray data sets were recorded for two different crystals, it has not been possible to solve the structure. Reasonable positions for the tetrabromoaluminate groups could be chosen by inspection of the Patterson map, but the positions of the bismuth atoms were more elusive. One interpretation of the problem involves packing of the Bi_5^{3+} units in alternative orientations. Despite the disappointment of not having solved the structure, the structure solution of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ has provided the opportunity to extend the idea of catenation of metal atoms to anions and to demonstrate the first example of a stable solid containing a well-characterized homopolyatomic cluster anion for a metallic element.

EXPERIMENTAL PROCEDURE

Preparation and Handling of Compounds

Preparation of zirconium monochloride

Struss and Corbett reported the formation of stable zirconium monochloride from the reaction of a partially reduced sample of zirconium chloride with zirconium metal at 625° in a closed tantalum container.¹³ The purpose of this research was to prepare a single crystal of ZrCl suitable for a structure determination. While the preparation of ZrCl was quite straightforward, the first several reactions resulted in polycrystalline products. The metal strips used had been cold-rolled to a 15-20 mil fold from crystal bar zirconium containing less than 0.05% hafnium. Typically two strips of foil about 8 cm long were reacted with 0.05 g of zirconium tetrachloride in a closed tantalum container. The tetrachloride had been prepared by treating the metal with HCl (Precision Gas Products) at an initial temperature of 300° and increasing to 500° followed by vacuum sublimation through a coarse frit.¹³ In order to determine the optimum temperature conditions, several preparations were carried out at various temperatures between 650 and 900°. The use of a 700-900° temperature gradient gave somewhat better results, but the reaction period of one week was apparently too short as the crystals were too small. A subsequent preparation was

carried out under similar conditions for 30 days. The half of a metal strip that had been at the cool end of the reaction tube was covered with gleaming black zirconium monochloride platelets while a dull grey powder clung to the other half of the strip. The powder pattern of the ZrCl₁ platelets compared favorably with that of Struss and Corbett,¹³ and the powder pattern of the grey powder established it as zirconium metal. It is reasonable that ZrCl would disproportionate to ZrCl₄ and the metal at 900°. Several platelets of ZrCl from this preparation were mounted and exposed to X-rays. Most were polycrystalline, but a few gave streaked spots. The layer line separation in these photographs gave a spindle axis of 3.42 \AA . The idea that the streaking indicated a disordering problem prompted the construction of a device capable of producing a continuously increasing potential that could be attached to the thermocouple input of a Brown temperature controller to enable the reaction tube to be cooled very slowly. The effect of electropolishing the metal was also contemplated, and a series of preparations was carried out to assess the merit of these proposals. The best crystals obtained from this series of reactions were grown on electro-polished metal in a 700-900° temperature gradient. Evidently electropolishing the metal does help to prevent nucleation, and electropolishing is the method of choice for cleaning zirconium because the high affinity of zirconium for oxygen

precludes cleaning it in oxidizing acid solutions or by induction heating. Finally, a preparation was undertaken in which electropolished strips of zirconium metal were heated with a small amount of zirconium tetrachloride in a sealed tantalum container in a 600-800° gradient for 24 days. The furnace was then cooled at an initial rate of $1.25^\circ \text{ day}^{-1}$ for four days. At this point the rate was increased to 5° day^{-1} . The scheme of slowly cooling the furnace was thwarted the next day by a power failure. Nonetheless, when the tube was taken into the dry box and cut open, bright, well-formed hexagonal platelets were found clinging to the center portions of the metal strips. No reaction had occurred at the cool end of the tube. As before, powdered zirconium metal was found on the surface of the strips at the hot end of the tube. Of the dozen crystals that were mounted, two gave sufficiently promising oscillation patterns that they were considered good enough to align. Oscillation photographs established that the spindle axis was 3.42\AA as before. However, the zero-level and first-level Weissenberg photographs of these two crystals were now of sufficient quality to allow construction of the reciprocal lattice. Plotting the spots from the two films on polar graph paper resulted in a primitive monoclinic cell having $a=9.19$, $b=3.42$, $c=5.92\text{\AA}$ and $\beta=103^\circ$. Unfortunately, by the time that priority for the diffractometer could be established, neither crystal diffracted

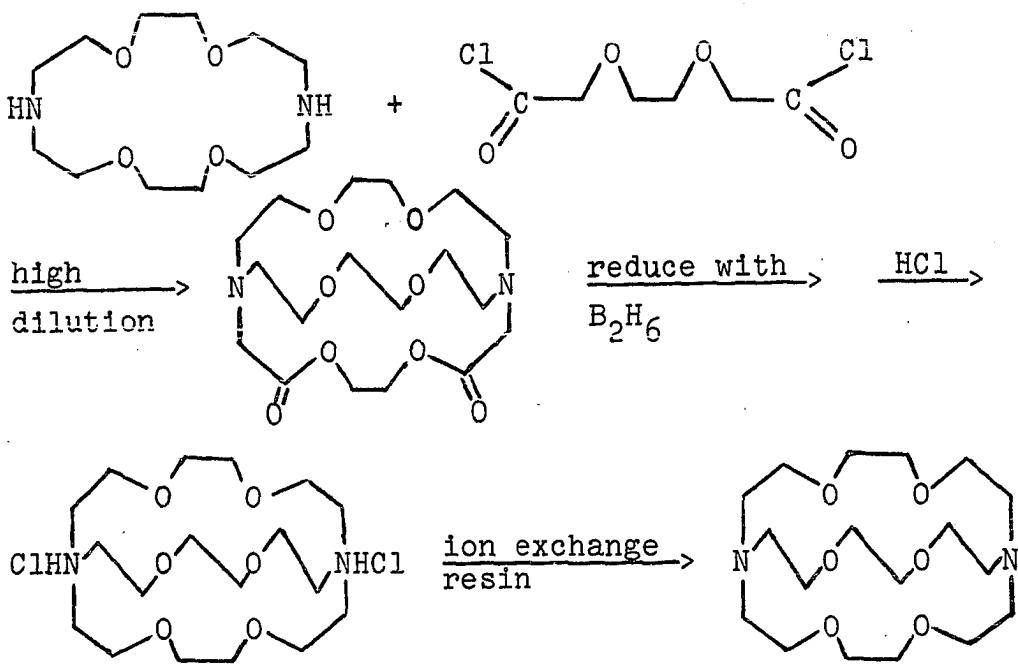
X-radiation. Since a search of the reaction product from which these two crystals had originally been obtained failed to produce a suitable crystal, the reaction was repeated using the same conditions. This reaction was apparently defeated by power failures during both the equilibration and cooling periods. After an appeal for an emergency power circuit had been heeded by the lab electricians, the reaction was repeated yet again. Following two sessions of mounting crystals from this reaction, capillary No. 215 was confirmed to contain a single crystal of zirconium monochloride.

Preparation of (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) sodium heptantimonide(-3)

Preliminary X-ray investigations were carried out on several phases expected to contain polyanions. In their synthetic work, Don Merryman and Frank Armatis employed the bicyclic amine 2,2,2-crypt or 18-crown-6 ether with sodium alloys of bismuth, lead and antimony in a solvent such as ethylenediamine or liquid ammonia to obtain a solid presumably containing a polyanion.⁴³ The first such solid investigated resulted from the reaction of NaSb and 2,2,2-crypt in ethylenediamine. Microscopic examination of the resultant solid product revealed dark brown crystals possessing regular external morphology in the form of needles on the order of tenths of millimeters in diameter and a millimeter in length. The first crystals that were mounted in capillaries in the

dry box were picked up with a wand greased with Vaseline. Two of six crystals mounted initially exhibited a diffraction pattern, but after several days they no longer diffracted X-rays. Crystals from a second preparation of this compound were mounted on another occasion using silicone lubricant rather than Vaseline. Several of these crystals gave good diffraction patterns. The reaction of NaSb_3 with 2,2,2-crypt in ethylenediamine produced a solid of similar morphology. Diffraction photographs obtained from these crystals had the same pattern as those obtained from the material prepared from the 1:1 alloy. Powder patterns of the two solids confirmed that they were the same compound. Several other compounds were examined with less success. A grey solid made by mixing NaBi and 2,2,2-crypt in ethylenediamine occurred as diamond shaped crystals adhering to the walls of the reaction tube. Once the tube was cracked open in the dry box, it was discovered the crystals had the consistency of Philadelphia cheese. None was successfully mounted in a capillary. A dark brown solid made from Na_4Pb_9 and 18-crown-6 ether occurred as large needles. While these crystals were easily scraped from the tube and mounted, most were found to be amorphous upon exposure to X-rays. A second preparation involving Na_4Pb_9 and 2,2,2-crypt in liquid ammonia gave slightly better formed crystals. However, these too were shown to be amorphous upon X-ray examination.

Since the antimony system seemed the most promising, further effort was concentrated on that system. Good crystals were readily obtained by reacting powdered NaSb with 2,2,2-crypt in ethylenediamine at room temperature for 12 hours.⁴³ The reaction was carried out in a Y-shaped reaction vessel which could be evacuated. Afterwards, the side arm was immersed in an ice bath and the ethylenediamine solvent was slowly distilled off over a twelve hour period. A deficiency of crypt was used to favor cryptation of sodium ions. The 1:3 alloy which was found to give the same product dissolved more slowly. Letting the solution stand longer or gently heating it to 40-50° was found to be equally satisfactory. The 2,2,2-crypt used in these syntheses was purchased from EM Laboratories, Inc. Its synthesis has been outlined by Truter and Pederson³⁹ as follows:



Dye, et al. have published a modification⁴⁴ of the original procedure of Lehn.⁴⁵

Mounting of crystals

A dry box designed primarily for mounting crystals was obtained from Blickman, Inc. It differs from the other dry boxes in the group in having a nearly horizontal window to facilitate the use of an external Bausch and Lomb "Stereozoom" microscope with a 7 inch focal length. To avoid the inconvenience of focusing the microscope from outside of the box, crystals to be mounted are placed on a lab jack which can be raised or lowered as needed to bring them into focus. This dry box has been equipped with a hot wire for sealing off capillaries which is operated by a foot switch. The moisture content of the box is monitored with a Beckman electrolytic hygrometer. Like the other dry boxes in the group, entrance is gained through an evacuable port. The box is flushed with dry nitrogen. An internal recirculating system consisting of a squirrel cage fan which pulls the incoming gas stream and the box atmosphere through a Molecular Sieve is capable of keeping the moisture content in the box below 30 ppm under most circumstances.

After crystals were sorted in the dry box, candidates for mounting were picked up on the end of a thin glass stalk tipped with Vaseline ($ZrCl_4$) or silicone lubricant ($[NaC^+]_3 Sb_7^{3-}$) and gently inserted into 0.2 mm i.d. Lindemann

(LiBeBO₃) glass capillaries. Once the stalk was inserted into the capillary, it was twisted to coat the walls with lubricant so that it could be removed leaving the crystal lodged in the capillary. The end of the capillary was then sealed off using the resistance wire inside the dry box, and the seal-off was checked visually with the microscope for the absence of pin-holes. When enough crystals had been mounted, the capillaries were removed from the dry box and sealed off to a length of about one cm on either side of the crystal using a fine tipped gas-oxygen flame. These shortened capillaries were then held in a brass pin 7 mm long by 3 mm o.d. with Apiezon W. Finally, the pin was placed in a goniometer head which could be attached to either X-ray cameras or the full-circle diffractometer.

X-Ray Diffraction Techniques

Camera techniques

Prior to the collection of intensity data, oscillation photographs were taken on a Weissenberg camera⁴⁶ in order to assess the diffraction characteristics of the crystal. If it is desired to proceed with further film work, the crystal is aligned so that the spindle axis is perpendicular to the X-ray beam. It is then possible to take Weissenberg photographs from which the reciprocal lattice can be constructed. The Weissenberg method involves translating the camera back and forth while the crystal oscillates. A screen with a

slit in it allows only one predetermined level of diffraction maxima to expose the film. In this manner the spots of the given diffracted cone are spread out over the film in a series of pinacoids which can be readily indexed. If, for example, the spindle axis corresponds to the b-axis, then the zero-level photograph contains all the $h0l$ reflections, the first level the $h1l$, the second level the $h2l$, and so forth. In order to examine the extinctions along the spindle axis it is either necessary to realign the crystal along another axis or to obtain photographs using a precession camera. The precession technique allows undistorted reproduction of the reciprocal lattice.⁴⁷ For a crystal having the b axis corresponding to the spindle axis, this is accomplished by aligning the crystal so that the $hk0$ or $0kl$ plane is normal to the X-ray beam. A flat piece of film opposite the beam from the crystal precesses while the crystal is slowly precessed. A screen with a circular slit enables diffraction maxima from a given layer to be recorded on the film. The spindle axis is then rotated by the angle β^* in order to record the diffraction maxima from the other plane.

Data collection

Intensity data for the reflections observed within one asymmetric unit of reciprocal space for a given crystal system can be obtained either by estimating intensities of spots on film or by using an automated diffractometer. X-ray data for

both of these compounds were taken at ambient temperature using a four-circle diffractometer interfaced with a PDP-15 computer.⁴⁸ The computer is programmed to control the diffractometer such that it is possible to take data from an unaligned crystal.⁴⁹ Several photographs are taken at arbitrary values of χ and ϕ . A few spots are chosen on each photograph, and their coordinates become input to the computer. The computer indexes these ten to fifteen reflections based on the fact that the indices must be whole small numbers. It then outputs a tentative unit cell and cell scalars which the user may transform if it is necessary. This unit cell assignment is verified by taking "oscillation" photographs aligned along the three crystallographic axes. Finally, three strong noncoplanar reflections are chosen as standard reflections. The instrument tunes on these reflections prior to undertaking data collection, and it checks these standards periodically while data are being collected. The X-radiation employed is Mo K α ($\lambda=7.0954\text{\AA}$) obtained using a graphite monochromator. Reflections are measured with a scintillation counter using a step scan technique⁵⁰ to obtain integrated intensities.

ZrCl Diffraction data for ZrCl were collected from a shiny black hexagonal platelet measuring 0.14 x 0.11 x 0.02 mm. The dataset was recorded on the basis of a monoclinic unit cell having $a=5.95$, $b=3.43$, $c=9.09\text{\AA}$ and $\beta=102.43^\circ$. This

compares with lattice constants $a=9.19$, $b=3.42$, $c=5.92$ and $\beta=103^\circ$ estimated from film work with a previous crystal that proved to be unsuitable for a complete structure determination. A total of 230 integrated intensities were obtained out of 416 reflections checked in the two octants hkl and $hk\bar{l}$. Refined unit cell parameters and their standard deviations were obtained by a least squares fit⁵¹ to twice the Ω angles of 16 independent reflections which were tuned by the diffractometer after the dataset had been recorded. Any error in the instrumental zero was eliminated by centering the reflection at $+\Omega$ and $-\Omega$. The final cell constants with errors for the last significant digits in parentheses are $a=5.943$ (6), $b=3.419$ (3), $c=9.087$ (18) Å, $\alpha=\gamma=90.00$ (0) and $\beta=102.50$ (12)°.

(NaC⁺)₃Sb₇³⁻ The needle used for data collection was an approximately regular rectangular prism having dimensions 0.1 x 0.2 x 0.6 mm. The compound crystallizes with monoclinic symmetry: $a=23.45$, $b=13.93$, $c=25.52$ Å and $\beta=108.73^\circ$. A total of 6717 integrated intensities were measured for reflections hkl and $hk\bar{l}$ out of 11,263 reflections scanned. Since a thirty per cent decrease in the intensities of the standards occurred during data collection, a dataset scaled linear in time to the initial sum of the intensities of the standards was prepared. Lattice constant refinement in the same manner as for ZrCl resulted in final cell constants $a=23.263$ (43), $b=13.776$ (4), $c=25.344$ (73) Å, $\alpha=\gamma=90.00$ (0) and $\beta=108.57$ (19)°.

Data reduction

After data collection, a series of steps collectively referred to as data reduction are carried out. Initially the data tape was read, and cards were punched with a record of the indices, theta, chi, phi, background count, total count and net count for each reflection. At this point the raw intensities were corrected for absorption. The extent to which an X-ray is absorbed in passing through a crystal of thickness t is given by⁵²

$$I=I_0 \exp(-\mu t) .$$

In this expression μ , the linear absorption coefficient, is defined as

$$\mu = \frac{n}{V} \sum_i (\mu_a)_i$$

where μ_a is the atomic absorption coefficient and n is the number of molecules in the unit cell with volume V . The absorption by a given crystal is thus a function of its shape and its orientation. No fully satisfactory method of evaluating the absorption correction for the general case has so far been described. The difficulty in making absorption corrections arises from having to calculate the absorption for the actual path length traveled within a crystal by the incident and diffracted beams for each infinitesimal volume element of the crystal dV and then to integrate these results

over the entire volume of the crystal.⁵³ While the linear absorption coefficients for ZrCl and $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ were both small, 66 and 25, respectively, the dimensions of both crystals were sufficiently different that it seemed appropriate to apply an absorption correction. The program TALABS⁵⁴ which was used calculates the absorption coefficient⁵⁵

$$A = \int \exp(-\mu L) dV .$$

The total path length L is equal to the sum of l_1 and l_2 where l_1 is the length of the path of the incident ray from its point of entry into the crystal up to the volume element dV and l_2 is the corresponding length of the path of the beam diffracted in dV . The integration is carried out over the volume V of the crystal. The program bases this calculation on the contribution to the diffracted intensity from a tetrahedron in which the path length of the rays is a linear function of the coordinates of the diffracting element.

After the absorption correction is carried out, each dataset was reduced using the program DATRED. This program divides each integrated intensity by its absorption coefficient, A , and also by a Lorentz and polarization factor⁵⁶ given by

$$L_p = \frac{\cos^2 2\theta_m + \cos^2 2\theta}{(1 + \cos^2 2\theta_m) \sin 2\theta} .$$

These corrected intensities are proportional to the square of the structure factor, F_o^2 . The estimated error in each intensity measurement is calculated by

$$(\sigma_I)^2 = [TC + BK + (K_T TC)^2 + (K_B BK)^2 + (KI)^2]/A^2$$

where TC is the total count, BK is the background count, I is the net intensity, A is the transmission factor, and K_T , K_B and K are fractional random errors in TC, BK and I, respectively.⁵⁷ The arbitrary value 0.03 was assigned to K_T , K_B and K. The estimated standard deviation in each structure factor is based on the finite difference method. The function used is

$$\sigma_F = \left| \frac{I/A + \sigma_I}{L_P} \right|^{\frac{1}{2}} - |F_o|$$

where all terms are as defined above.⁵⁷ In the case of ZrCl₂₀₃ reflections of the 230 integrated intensities collected were found to be statistically above background by more than $3\sigma_I$. Of the 6717 integrated intensities recorded for $(NaC^+)_3Sb_7^{3-}$, 4662 were more than $3\sigma_I$ above background.

Space group determination

Each reduced dataset was inspected for systematic conditions for reflection. For ZrCl the condition $h+k=2n$ for all reflections hkl was observed. This condition requires the cell to be C-centered. Since no other conditions were

noted, the space group choice included C2 No.5, Cm No.8 and C2/m No.12. In the case of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ no conditions were found for hkl reflections. The condition $k=2n$ found for $0k0$ reflections requires a 2-fold screw axis and the condition $h+l=2n$ for $h0l$ reflections requires an n-glide. These conditions serve to uniquely fix the space group as $P2_1/n$ (a non-standard setting of $P2_1/c$).

THE CRYSTAL STRUCTURE OF ZIRCONIUM MONOCHLORIDE

Structure Determination

Structure solution

The solution of a crystal structure from the intensities of a set of X-ray diffraction maxima depends upon recovering the phase relationships among the maxima. The intensity of scattered radiation is proportional to the absolute value of the square of the amplitude $|F(hk\ell)|^2$. The structure factor $F(hk\ell)$ represents the resultant amplitude of the waves scattered in the direction of the reflection hkl by the j atoms in the unit cell:

$$F(hk\ell) = \sum_j f_j \exp[2\pi i(hx_j + ky_j + \ell z_j)].^1$$

The value of the structure factor is determined by the atomic scattering factors f_j , which are a function of the number and distribution of electrons in the atoms and on the scattering angle θ , and by the exponential terms, which depend on the positions of the atoms. Since X-rays are scattered by electrons, solution of a crystal structure is equivalent to finding the electron density. The electron density is given

¹A more complete discussion can be found in any standard crystallographic text such as Buerger.⁴⁶

by the Fourier transform of the structure factors:

$$\rho(x, y, z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell} F(hkl) \exp[-2\pi i(hx + ky + \ell z)].$$

As stated earlier, it is necessary to devise a way to determine the phases of the structure factors in order to solve the crystal structure. No general solution to the phase problem exists. It has been found, however, that structures containing one or a few atoms that are markedly heavier than the remainder can be solved by locating the heavy atoms by methods which do not require a prior knowledge of the phases. The heavy atoms can then provide the principal phasing from which the lighter atom positions can be developed. Patterson pointed out that a Fourier calculation using the phaseless quantities $|F|^2$ results in peaks corresponding to all the interatomic vectors, with magnitudes proportional to the atomic numbers of the atoms involved.⁵⁸

A three dimensional Patterson map was calculated from the 203 observed structure factors for ZrCl using the program ALFF.⁵⁹ Interpretation of the Patterson map was very straightforward. Four strong peaks of equal intensity were located at $\frac{3}{4}, 0, \frac{1}{4}$, $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$, $\frac{1}{4}, 0, \frac{3}{4}$ and $\frac{3}{4}, \frac{1}{2}, \frac{3}{4}$. Inspection of the interatomic vectors for the general positions of the three possible space groups prompted the choice of C2 No.5 because of its intraset vectors $\pm(2x, 0, 2z; \frac{1}{2}+2x, \frac{1}{2}, 2z)$. The

peak at $\frac{3}{4}, 0, \frac{1}{4}$ was assigned as corresponding to a fourfold zirconium position. Three cycles of full matrix least squares refinement on the x and z coordinates of one zirconium at $\frac{3}{8}, 0, \frac{1}{8}$ using the program ORFLS⁶⁰ resulted in an unweighted residual¹ of 0.384. The chlorine position was located from an electron density map calculated using the program ALFF.⁵⁹ Other than the zirconium peak at $\frac{3}{8}, 0, \frac{1}{8}$ and the peak at $\frac{1}{8}, 0, \frac{3}{8}$ assigned as chlorine, the map was flat. Three cycles of refinement on the x and z coordinates of these two atom positions resulted in unweighted residual of 0.283.

Refinement

Refinement of the structure was carried out using the full matrix least squares program ORFLS.⁶⁰ The scattering factors used are those of Hanson et al.⁶¹ with corrections for both real and imaginary parts of anomalous dispersion.⁵² The reflections were weighted by σ_F^{-2} to account for the reliability of each measurement. A reduced dataset that had

¹The unweighted residual R and the weighted residual R_w used are defined by

$$R = \left| \sum |F_o| - |F_c| \right| / \sum |F_o|$$

and

$$R_w = \left[\sum_w (|F_o| - |F_c|)^2 / \sum_w |F_o|^2 \right]^{\frac{1}{2}}.$$

not been corrected for absorption was used in the initial stages of the refinement. A total of five cycles of refinement on the x and z coordinates of the two atom positions resulted in a residual of 0.146. Since the space group does not fix y, the y coordinate of one atom must be held constant. However, it was found to be necessary to constrain the y coordinates of both atoms in order to carry out the refinement using this dataset. The refinement of the x and z positional coordinates and the isotropic temperature factors of the two atoms converged in two cycles with $R=0.120$ and $R_w=0.150$. Final positional parameters and isotopic temperature factors are listed in Table 2. The specter of partial occupancy was

Table 2.. Atomic parameters^a from isotropic refinement of ZrCl

	Positional parameters			Isotropic thermal parameters $B(x10^3)$
	x	y	z	
Zr	0.3780(6)	0.0000(0)	0.1339(4)	893(123)
Cl	0.1100(17)	0.0000(0)	0.3295(10)	995(183)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

ruled out after varying the atom multiplier for zirconium. In two cycles of refinement the atom multiplier for zirconium

converged at 0.987(25) with $R=0.121$ and $R_w=0.150$. A difference electron density map was flat to ± 2 electrons/ \AA^3 . When the refinement was repeated using the absorption-corrected dataset it was possible to vary the y coordinate for the chlorine atom. However, since the same weighted residual of 0.165 for the converged positional and isotropic thermal parameters was obtained as in the case where y for chlorine was constrained to zero, the latter case is the preferable one according to the statistical test of Hamilton.⁶²

Conversion of the isotropic temperature factors to anisotropic temperature factors brought even more headaches. It was not possible to vary the anisotropic temperature factors¹ for either atom without their becoming not positive-definite. Refinement of the x and z positional parameters and the components of the anisotropic temperature factors β_{11} , β_{33} and β_{13} while damping the shifts in β_{22} and holding β_{23} and β_{12} identically zero using the original reduced dataset resulted in the parameters shown in Table 3 and $R=0.081$, $R_w=0.109$. The observed and calculated structure factors are listed in Table 4. In the refinement using the dataset that

¹The anisotropic temperature factors have the general form $\exp(-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

Table 3. Atomic parameters^a from anisotropic refinement of ZrCl

	Positional parameters			Anisotropic thermal parameters ($\times 10^4$)			
	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
Zr	0.3779(5)	0.0000(0)	0.1339(3)	58(10)	8 ^b	68(5)	11(5)
Cl	0.1104(14)	0.0000(0)	0.3306(9)	72(23)	5	69(10)	20(12)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

^bErrors indeterminant since shifts were damped.

had been corrected for absorption, the anisotropic temperature factors again became not positive-definite. For the case where the y coordinate for chlorine as well as β_{12} and β_{23} were constrained at zero and where the shifts in β_{22} were damped, residuals $R=0.081$ and $R_w=0.111$ were obtained.

Improving the refinement

Inquiry concerning the peculiarities encountered in the refinement of the dataset collected from this crystal disestablished their uniqueness. Apparently, the program controlling the data-taking procedure of the diffractometer contained a statistical error for the larger reflections which are normally counted for a shorter period of time than the

Table 4. Observed and calculated structure factors^a for ZrCl

L = 0						L = 3						L = -4						L = -8					
H	K	F0	FC	3	3	335	348	H	K	F0	FC	0	0	627	553	H	K	F0	FC				
2	0	60	71					4	0	583	606	L = 4	0	0	149	143	2	0	274	256			
4	0	111	103	H	K	F0	FC	6	0	111	103	2	0	202	214	4	0	453	501				
1	1	237	230	0	0	667	553	3	1	257	357	1	1	98	101	6	0	97	101				
3	1	140	152	2	0	267	304	5	1	152	140	0	2	146	130	1	1	334	359				
0	2	1136	890	4	0	338	315	0	2	1136	890	L = 10	1	1	211	200	3	1	171	191			
4	2	486	505	3	1	294	255	6	2	75	94	H	K	F0	FC	5	1	180	185				
6	2	170	161	5	1	176	172	1	3	170	170	0	0	123	117	2	2	213	200				
3	3	179	166	0	2	471	452	3	3	179	166	L = -1	2	2	227	227	4	2	396	433			
0	4	570	459	4	2	264	280	0	4	570	459	H	K	F0	FC	5	1	194	171				
				1	3	138	159	1	3	138	159	1	3	226	217	4	2	136	147				
				3	3	202	203	2	0	237	229	2	0	177	206	3	3	121	129				
								6	0	156	155	L = -5	6	2	83	92	H	K	FC	FC			
								1	1	55	72	H	K	F0	FC	0	0	158	143				
								3	1	780	866	0	0	363	382	1	1	147	158				
								4	0	381	382	0	2	374	363	2	0	243	358				
								6	0	135	128	2	2	198	213	4	0	222	231				
								1	1	812	817	4	2	221	215	6	0	115	117				
								3	1	174	165	1	1	357	384	1	1	274	301				
								5	1	428	439	3	1	218	226	3	1	494	432				
								0	2	342	363	5	1	200	196	5	1	154	162				
								2	2	180	175	0	2	269	254	0	2	272	255				
								4	2	207	201	2	2	169	198	4	2	203	202				
								1	3	536	525	1	3	189	194	1	3	189	201				
								3	3	102	112	1	3	266	283	2	0	834	804				
								0	4	177	151	2	0	309	334	3	1	112	121				
											L = 6	6	0	460	454								
											H	K	F0	FC	1	1	211	206	L = -6				
											0	0	313	275	3	1	271	349	H	K	FO	FC	
											0	0	258	232	5	1	155	151	0	0	295	275	
											2	0	695	656	2	0	228	254	2	0	388	369	
											4	0	208	186	4	1	241	247	4	0	194	211	
											6	0	210	197	6	1	228	216	6	0	257	301	
											1	1	291	292	1	2	228	227	1	1	220	225	
											3	1	211	209	3	2	181	222	3	1	272	240	
											5	1	221	211	5	3	177	196	5	1	137	140	
											0	2	184	168	0	4	116	105	0	2	233	228	
											2	2	502	534	L = ?	6	0	460	454	2	2	321	307
											H	K	F0	FC	1	1	211	206	4	2	176	188	
											0	0	296	244	L = -3	0	0	296	244	H	K	FO	FC
											1	3	223	206	H	K	F0	FC	1	3	165	171	
											3	3	147	135	2	0	177	196	3	3	179	192	
											0	4	115	105	4	0	227	208	2	0	292	284	
											1	1	210	211	1	1	210	211	1	1	220	225	
											3	1	163	151	4	0	159	166	4	2	176	188	
											6	0	144	148	L = -7	4	2	176	188	H	K	FO	FC
											0	2	243	212	1	1	748	655	0	0	277	244	
											2	2	247	217	3	1	169	164	2	0	251	237	
											2	0	314	363	5	1	485	481	4	0	184	177	
											4	0	190	182	L = 8	0	2	199	212	6	0	187	171
											6	0	211	192	H	K	F0	FC	1	1	213	246	
											1	1	261	261	4	2	137	140	3	1	226	215	
											3	1	506	450	2	0	147	163	5	1	255	249	
											5	1	185	193	1	1	231	229	0	2	218	213	
											0	2	151	208	3	1	135	132	2	2	207	208	
											2	2	230	252	3	2	158	147	4	2	159	157	
											4	2	147	157	2	2	120	148	1	3	161	194	

^aStructure factors have been multiplied by 10.

smaller ones and rescaled. When this problem was investigated it was also found that a set of parentheses missing in the program declaring the orientation matrix had the result of equating θ and Ω . A nonuniformity in the steps of the Ω scan was also discovered.⁶³ While the quantitative effect of these problems is difficult to assess precisely, it is considered fortunate that the refinement of this dataset went as well as it did. Particularly in view of the fact that the counting statistics were in question for the larger reflections it seemed appropriate to reweight the dataset. New weights were assigned to each reflection of the original reduced dataset using the program Omega.¹ All positional and thermal parameters converged after two cycles of refinement using the new weighting scheme. The final residual indices were $R=0.080$ and $R_w=0.087$. The parameters from this refinement are given in Table 5. The positional parameters for both zirconium and chlorine are within one standard deviation of those reported in Table 3 for the refinement using the original weighting scheme. However, the errors in these parameters

¹Omega is a local program written by C. R. Hubbard which calculates new weights for structure factors after refinement of a structure using ORFLS.⁶⁰

Table 5. Final parameters^a from the refinement of ZrCl using new weights

	Positional parameters			Anisotropic thermal parameters ($\times 10^4$)			
	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
Zr	0.3779(2)	0.0000(0)	0.1341(2)	31(7)	3(22)	63(3)	11(3)
Cl	0.1098(7)	0.0000(0)	0.3296(6)	43(13)	21(38)	67(5)	17(6)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

are improved by reweighting, as expected. Happily, the thermal parameters converged in this refinement without anomalous behavior on the part of β_{22} . Reweighting the reflections of the dataset that had been corrected for absorption and carrying out one cycle of least squares refinement resulted in the residuals $R=0.082$ and $R_w=0.098$.

A projection of the structure along the unique b-axis is presented in Figure 1. An alternate projection on the (001) plane is shown in Figure 2. The thermal ellipsoid plot program ORTEP⁶⁴ was used to prepare these drawings.

Interatomic distances and angles

Interatomic distances and angles were calculated using the function and error program ORFFE.⁶⁵ The estimated

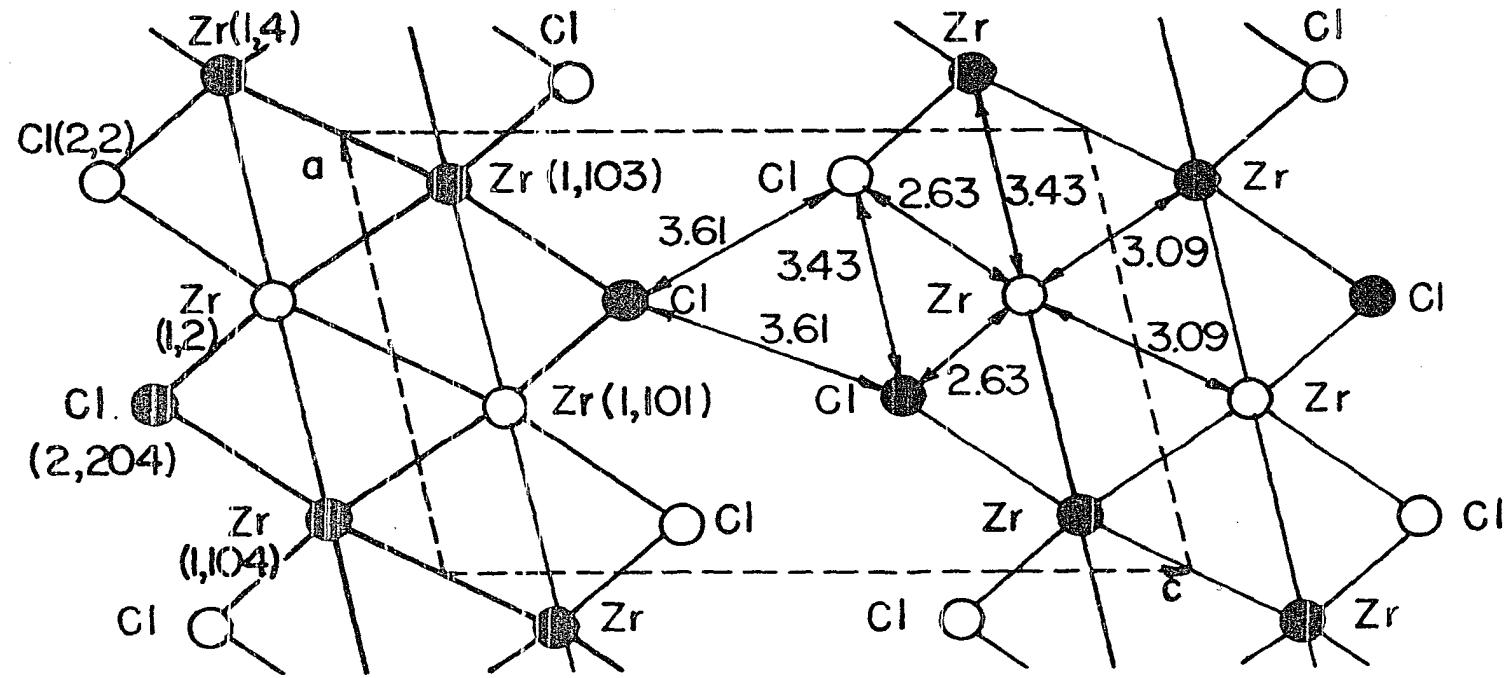
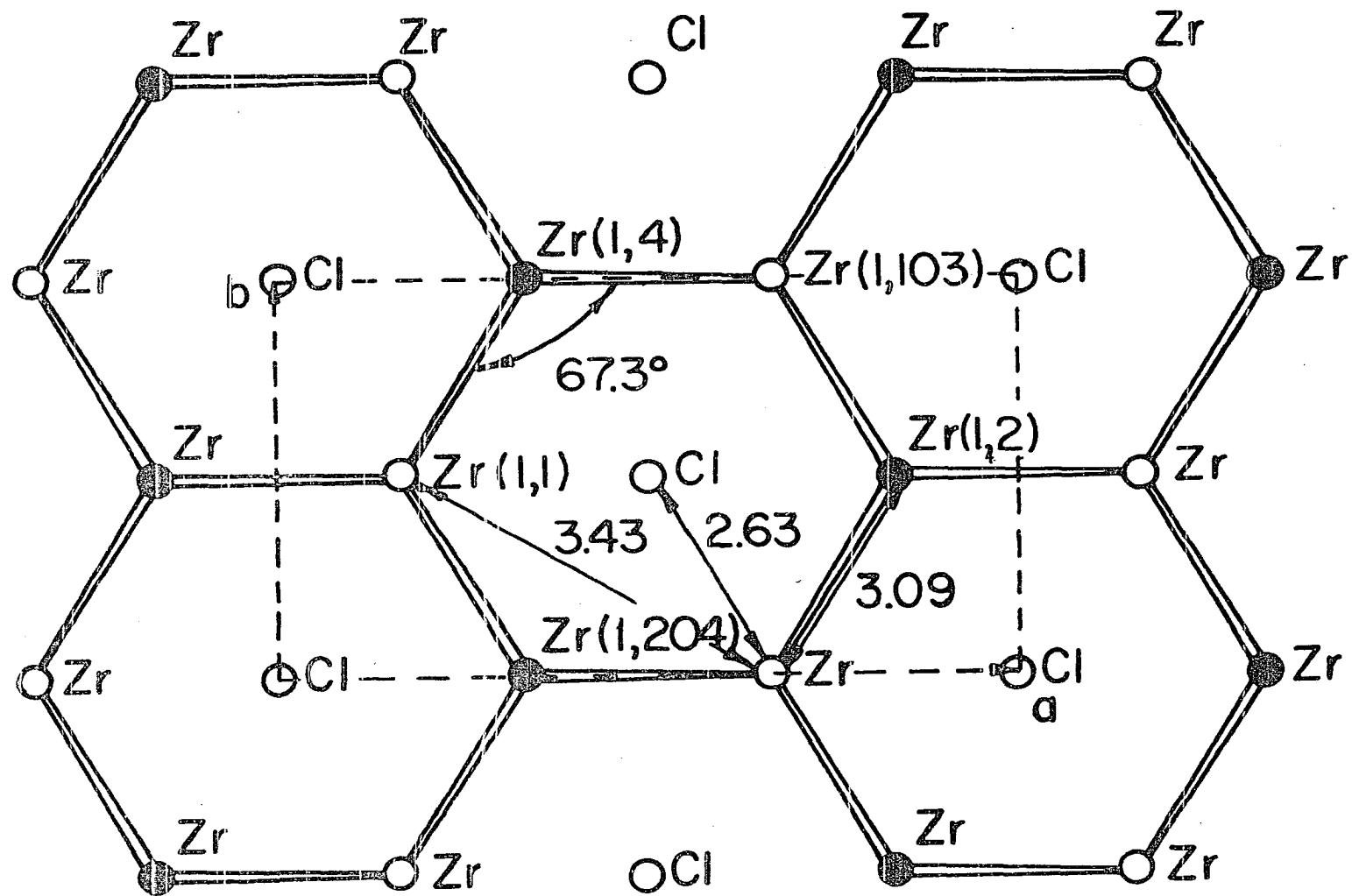


Figure 1. Projection of the structure of ZrCl on the (010) plane. Atoms at $y=0.0$ are represented by open circles while those at $y=0.5$ are shaded.

Figure 2. Projection of the structure of ZrCl on the (001) plane. Zirconium atoms at $z=0.1341$ are shaded while those at $z=-0.1341$ are represented by open circles. Chlorine atoms at $z=\pm 0.3296$ are superimposed.



standard deviations were calculated using the variance-covariance matrix from the final least squares cycle. These are tabulated for the anisotropic refinement using new weights in Table 6.

Table 6. Interatomic distances and angles^a from anisotropic refinement of ZrCl

Interatomic Distances ^b		Interatomic Angles ^c		
	Intralayer	Atom 1	Atom 2	Degrees
Zr-Zr	3.419(3) Å	Atom 1 Zr(1,1)	Zr(1,4)	Zr(1,103) 67.30(15)
	3.428(3)		Zr(1,2)	60.09(3)
Cl-Cl	3.419(3)	Zr(1,4)	Zr(1,104)	120.18(7)
	3.428(3)	Zr(1,4)	Zr(1,2)	Zr(1,101) 124(4)
		Zr(1,4)	Zr(1,2)	Zr(1,103) 56(4)
Interlayer		Zr(1,101)	Zr(1,2)	Zr(1,103) 67.30(15)
Zr-Zr	3.09(14)	Zr(1,104)	Zr(1,2)	Zr(1,103) 90(5)
	3.09(14)	Zr(1,104)	Zr(1,2)	Zr(1,101) 56(4)
Cl-Cl	3.61(13)	Cl(2,2)	Zr(1,2)	Zr(1,104) 131(3)
	3.61(17)	Cl(2,2)	Zr(1,2)	Zr(1,101) 171(1)
Zr-Cl	2.63(13)	Cl(2,2)	Zr(1,2)	Zr(1,103) 105(1)
	2.63(11)	Cl(2,2)	Zr(1,2)	Zr(1,4) 49(3)
		Zr(1,2)	Cl(2,2)	Zr(1,104) 81.3(4)
			Zr(1,2)	Cl(2,2) Zr(1,4) 81.3(4)

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

^bDifferences of pairs of distances are statistically insignificant.

^cReference numbers correspond to those shown in Figures 1 and 2.

Discussion

The remarkable layer structure found for ZrCl consists of approximately cubic-close-packed layers of either metal or chlorine in the sequence Cl-Zr-Zr-Cl. Each zirconium has three metal neighbors in the next layer at 3.09 Å, six metal neighbors in the same layer at 3.43 Å and three chlorine neighbors in the opposite layer at 2.63 Å. In zirconium metal there are twelve equal metal-metal distances of 3.19 Å. In Zr-Cl intralayer interatomic distances for chlorine are also 3.43 Å. Interlayer chlorine-chlorine distances are 3.61 Å. The sum of the usual atomic radii⁷ is 3.62 Å, but chlorine-chlorine approaches as close as 3.22 Å have been reported in GdCl₃ and Gd₂Cl₃.¹¹ The zirconium chlorine distances of 2.63 Å compare with three zirconium-chlorine distances 2.498, 2.655 and 2.307 Å found for ZrCl₄.⁶⁶ and a zirconium-chlorine distance of 2.44 Å in Rb₂ZrCl₆.⁶⁷

The short zirconium-zirconium interlayer distance suggests a strong interaction between zirconium sheets. Another measure of bond formation suggested by Pauling⁶⁸ involves calculating the bond order n from the equation

$$D(n) = D(1) - 0.60 \log n$$

where D(1) is twice the single bond radius. Using a single bond radius of 1.454 Å for zirconium,⁷ a bond order of 0.50 is obtained for the 3.09 Å interlayer distance while that for 3.43 Å intralayer distance is 0.13. For a chlorine

single bond radius of 0.99 Å⁷ a bond order of 0.023 is obtained for the 3.43 Å chlorine-chlorine intralayer distance and 0.005 for the 3.62 Å interlayer distance. The bond order for the zirconium-chlorine distance is 0.48. The sum of bond orders to a particular atom is given by $\Sigma N_i n_i$ where N_i is the number of bonds and their bond order is n_i . Thus, the sum of all bond orders to zirconium is 3.7 and to chlorine is 1.4. Similar bond orders and distances were found for Hf and S in Hf_2S by Franzen and Graham.⁶⁹ In Hf_2S each S atom is surrounded by six Hf atoms in trigonal prismatic coordination. The coordination polyhedron around each Hf is a distorted octahedron of three S and three Hf atoms. Around each S atom there are six equivalent Hf-S distances of 2.63 Å with a bond order of 0.56 and six S-S distances of 3.37 Å with bond order 0.008. Around each Hf atom there are three Hf-Hf distances of 3.06 Å with bond order 0.50 and six Hf-Hf distances of 3.37 Å with bond order 0.15. The sum of the bond orders to Hf is 4.08. A sum of bond orders of 3.36 to sulfur indicates substantial participation of 3d orbitals in bonding. It has been pointed out that the similar metal-metal and nonmetal-nonmetal nonbonded distances found in both structures may be dictated by close packing of the larger anions and may thus not necessarily be indicative of bond order.⁷⁰

During the course of this structural investigation a structure for $ZrCl$ was published by Troyanov.²⁶ Troyanov and

T'sirelnikov²⁵ had previously reported the synthesis of ZrCl and a powder pattern which agreed with that of Struss and Corbett¹³ except for the omission of a weak line with $d=9.73 \text{ \AA}$. Troyanov and T'sirelnikov indexed the powder pattern of ZrCl on the basis of a rhombohedral lattice having $a=9.12 \text{ \AA}$, $\alpha=21.62^\circ$ and $Z=2$. Troyanov proceeded with a single crystal structural determination using film methods. The choice of the space group $R\bar{3}m$ based on the improper indexing of the powder pattern is more likely the reason for the poor refinement he obtained than errors made in measuring the intensities from the films as he suggested. In any case the R factor did not drop below 0.29. Surprisingly enough the basic ordering and packing of layers Cl-Zr-Zr-Cl was properly deduced. The interatomic distances found of 3.41 \AA for either Zr-Zr or Cl-Cl within a layer are reasonable, but interlayer distances of 2.87 \AA for Zr-Zr, 2.81 \AA for Cl-Cl and 3.10 \AA for Zr-Cl are certainly unreasonable.

The layer structure found for ZrCl accounts well for the physical properties of the compound. Zirconium monochloride occurs as shiny black hexagonal platelets which are graphitic in character. Dean²⁴ has suggested the use of "Zirklor" as a lubricant; however, the use of a reduced compound for such a purpose is questionable. The reason for the difficulty encountered in finding a single crystal of ZrCl suitable for a structure determination is also apparent now that the

structure is known. The broad faces of the hexagonal platelets are parallel to the (001) planes whereas the thin dimension is roughly coincident with the c-axis. While there are strong interactions between Zr-Zr planes and Zr-Cl planes, the Cl-Cl interplanar distance of 3.62 Å indicates only weak van der Waals contacts. Therein lies the basis for the graphitic character of the compound and its propensity toward polycrystallinity.

Recently, ZrBr has been prepared in this laboratory from the reaction of $ZrBr_4$ and Zr turnings in a tantalum container heated in the final stages to 800° for 12 days.²³ ZrBr occurs as dark shiny platelets much like those of ZrCl although some needles of ZrBr have been observed. The powder pattern of ZrBr has been indexed by comparison with the powder pattern and the structure determined for ZrCl. Reasonable agreement between calculated and observed powder patterns has been obtained for ZrBr in the case where the coordination polyhedron around zirconium is a trigonal antiprism as in ZrCl; but the Br-Zr-Zr-Br four-layer sheets adopt an alternate packing to that of the Cl-Zr-Zr-Cl four-layer sheets in ZrCl.²³

Preliminary measurements have shown that ZrCl reacts reversibly with hydrogen even at room temperature to form a golden phase approximating $ZrClH_{0.5}^{71}$. Perhaps hydrogen enters the lattice filling the interstices between planes of

chlorines. No structural work has as yet been done, however, to confirm the hydrogen sites.

THE CRYSTAL STRUCTURE OF
 (4,7,13,16,21,24-HEXAOXA-1,10-DIAZABICYCLO[8.8.8]HEXACOSANE)
 SODIUM HEPTANTIMONIDE(-3)

Structure Determination

Structure solution

The heavy atoms were located using the program package MULTAN⁷² which is a system for solving crystal structures using direct methods. In this approach an attempt is made to determine the phases of the structure factors without first deriving a set of atomic positions. Any structure determination involves many more observations than there are parameters. Thus all the structure factors cannot be independent. In 1948 Harker and Kasper showed that inequality relationships existed between the structure factors and could occasionally lead to definite information about the phases of structure factors.⁷³

The Cauchy inequality

$$\left| \sum_{j=1}^N a_j b_j \right|^2 \leq \left(\sum_{j=1}^N |a_j|^2 \right) \left(\sum_{j=1}^N |b_j|^2 \right)$$

was applied to the unitary structure factor

$$U(hkl) = \sum_{j=1}^n n_j \exp\{2\pi i(hx_j + ky_j + lz_j)\}$$

by letting $a_j = \sqrt{n_j}$ and $b_j = \sqrt{n_j} \exp\{2\pi i(hx_j + ky_j + lz_j)\}$. By taking the symmetry elements of a given space group into account, relationships among the larger unitary structure

factors can be deduced. For a centric cell, the signs of a number of structure factors can be chosen arbitrarily because of the existence of a number of nonequivalent centers of symmetry which may be chosen as the origin. With three-dimensional data the selection and arbitrary assignment of signs to three strong reflections amounts to fixing the origin of the cell. Once progress in sign determination breaks down because of the inability to relate fresh signs to ones already determined, sign symbols are introduced. At the end of the sign-determining process the signs of the largest U's should have been determined in terms of a few sign symbols. If the number of symbols is n , there are 2^n possible sets of signs. The structure is sought by calculating Fourier syntheses for each of these sets and evaluating the respective electron density maps. In general, inequality relationships can be used only to solve simple structures. By definition the maximum value of the unitary structure factor $U(hkl)$ is 1. For N equal atoms in a centrosymmetric unit cell the average value of $|U(hkl)|^2$ is $1/N$. As the complexity of the structure increases, the fraction of the structure factors for which the inequality relationships are applicable declines.

In 1952 Sayre,⁷⁴ Cochran⁷⁵ and Zachariasen⁷⁶ independently showed that even when the $|U|$ values were smaller than necessary to satisfy the inequality relationships, the relationship

$$S(h)S(h')S(h-h') = +1$$

was probably true. Thus the sign S of $U(h'h', k+k', \ell+\ell')$ can be deduced from the known signs of $U(hk\ell)$ and $U(h'k'\ell')$ by taking the product of the signs of the latter two unitary structure factors. MULTAN⁶⁰ uses this relationship to develop a set of signs for the structure factors after first assigning arbitrary signs to a specified number of large $|U|$'s and relating the larger $|U|$'s using inequalities. A probability of correctness is given to each of the 2^n subsets arising from the n symbols used to relate the reflections. In the final step a Fourier synthesis is carried out on the most probable subset. The resulting electron density map is scanned automatically and the positional coordinates of the peaks are listed. Distances and angles among peaks within 1.9\AA of each other are printed out in order to facilitate assessment of the reasonableness of the model. Each time the Fourier step is repeated a Fourier synthesis is carried out on the next most probable subset.

In the present structure solution the seven strongest peaks output from the Fourier step of MULTAN⁶⁰ were located in a cluster having interpeak distances on the order of 2.8\AA . Following the assignment of these seven peaks as antimony atoms, three cycles of least squares refinement using ORFLS⁶⁰ resulted in a residual of 0.398. An electron density map calculated using the program ALFF⁵⁹ contained, in addition to the seven antimony atoms, three peaks of appropriate height for sodium atoms with smaller peaks appropriate to the

constituent carbon nitrogen and oxygen atoms of 2,2,2-crypt clustered about them. The 26 independent nonhydrogen atoms of the first crypt were readily located from a difference electron density map¹ phased by the seven antimony and three sodium atoms. The complete sets of atoms making up the other two independent crypts proved to be much more difficult to locate. Three cycles of least squares refinement of the 10 heavy atoms and the 26 atoms of the first crypt resulted in an agreement factor of 0.233. From a difference map phased with these 36 atoms, plausible positions for the 26 atoms of the second crypt were assigned. This turned out to be painstaking work as the programs used do not accommodate such a large problem well. After a cycle of least squares refinement was carried out on these 62 atoms, an agreement factor of 0.231 was obtained. Finally a third difference map was computed in order to locate the 26 independent atom positions of the third crypt. Locating the atoms of the final crypt proved to be even more difficult than for the second one. Only two thirds of the atoms comprising the molecule emerged in the difference map output by ORFURER.⁷⁷ Nitrogen and

¹Light atoms were located from electron density maps calculated using the program ORFURER.⁷⁷ ORFURER is an adaptation of the Fourier step from MULTAN⁷⁰ by M. Gifkins which calculates and searches electron density maps from the structure factors output from ORFLS.⁶⁰

oxygen atom positions were assigned after comparing the peaks in the difference map with those in the electron density map phased by only the heavy atoms and calculated using ALFF.⁵⁹ Carbon atom positions were less readily assigned as the peaks were broad and not very large, and in some cases there was evidence for disordering of the ethylene bridges.

Refinement

The initial stages of the refinement were carried out using the block-diagonal least squares program FBLS.⁷⁸ The calculation time for FBLS is about one fourth of that required for the full matrix least squares program ORFLS,⁶⁰ and the refined parameters obtained from FBLS normally agree with those from ORFLS within the respective estimated standard deviations. Pertinent to this refinement of 88 independent atoms is the fact that FBLS can accept 100 atoms while the maximum number of atoms that can be accommodated by ORFLS is 83. The scattering factors used in either program were those of Hanson *et al.*⁶¹ Scattering factors for antimony and sodium were corrected for both the real and imaginary components of anomalous dispersion.⁵² In either program the reflections were weighted by σ_F^{-2} to account for the reliability of each measurement. In the initial stages of refinement a reduced dataset which had not been corrected for absorption was used. Refinement of all 88 atoms with isotropic temperature factors using FBLS resulted in converged

positional and thermal parameters with an unweighted residual of 0.172. After converting the isotropic temperature factors of the heavy atoms to anisotropic temperature factors, three cycles of block-diagonal least squares using FBLS with the dataset that had been corrected for absorption resulted in well-behaved positional and thermal parameters with weighted and unweighted residuals 0.1304 and 0.1676, respectively.

A refinement of the parameters from FBLS using ORFLS⁶⁰ was attempted by refining only a part of the structure at a time after removing 5 carbon atoms from the atom list. Two cycles were carried out on the heavy atoms followed by two cycles on the first crypt, then two cycles on the second crypt and finally two cycles on the third crypt. Such a procedure is quite laborious as each cycle requires about 40 minutes of computer time, and jobs of this size do not enjoy daily turnaround at the computer center. This stepwise refinement resulted in converged parameters with $R = 0.113$ and $R_w = 0.139$. Conversion of the isotropic temperature factors of the light atoms of the first crypt to anisotropic temperature factors followed by two cycles of refinement using ORFLS did not produce a change in the unweighted residual. Thus the use of anisotropic temperature factors for the light atoms is unwarranted according to the statistical test of Hamilton.⁶²

Improving the refinement

Since it was considered imperative to use all 88 independent nonhydrogen atoms in the final refinement, a Fortran version of ORFLS was recompiled with atom arrays dimensioned at 120. After this had been done it was discovered that a 95 atom version of ORFLS was resident on disk under the program name ORFLSA.⁷⁹ Thereafter, the final refinement cycles were carried out using ORFLSA with all 88 independent nonhydrogen atoms in the atom list.

The dataset being used in this structure solution was collected just prior to that collected from the crystal of ZrCl so it is probable that the same instrumental problems affect both datasets. However, when the dataset was reweighted using OMEGA,⁶⁴ two cycles of full matrix least squares refinement using ORFLSA on the 10 heavy atoms with all 78 light atoms in the atom list resulted in converged parameters for the heavy atoms with a residual of 0.121 and a weighted residual of 0.161. Since this represents an increase of 0.02 in the weighted agreement factor, the absorption-corrected dataset with original weights was used in the final steps of refinement.

Estimated standard deviations for bond distances and angles calculated using the converged parameters from ORFLS contained significant contributions from errors in the lattice constants. Therefore the lattice constants were redetermined prior to the final refinement. The crystal from which the

X-ray reflection dataset had been collected was reoriented on the diffractometer and tuned values of the angles 2θ , Ω , χ and ϕ were measured on both sides of the instrumental zero for 24 strong reflections with $17.5 < 2\theta < 25^\circ$. A least squares fit to twice the average Ω angle using the program LCR2⁵¹ resulted in converged cell constants of $a=23.292(7)$, $b=13.791(6)$, $c=25.355(6)\text{\AA}$ and $\beta=108.56(2)^\circ$. These compare with $a=23.263(43)$, $b=13.776(4)$, $c=25.344(73)\text{\AA}$ and $\beta=108.57(19)$ obtained previously. One cycle of least squares refinement using ORFLSA with the more precise lattice constants was carried out on the ten heavy atoms with anisotropic temperature factors and on the nonhydrogen atoms of the first crypt with isotropic temperature factors. A file of the final parameters and the variance-covariance matrix was created in order to calculate bond distances and angles and their standard deviations. Two cycles of refinement on the nonhydrogen atoms of the second crypt with isotropic thermal parameters using ORFLSA resulted in converged parameters, and a file containing the final parameters and the variance-covariance matrix was created. It was not considered worthwhile to spend more time refining the third crypt since earlier refinements of this crypt using ORFLS had not resulted in improved standard deviations for the atomic parameters over those obtained from FBLS. Finally two cycles of refinement on the heavy atoms using ORFLSA with the refined light atom parameters as described above in the atom list resulted in

converged positional parameters for the heavy atoms with a conventional R of 0.111 and a weighted R of 0.134. The ratio of the largest shift to standard deviation in coordinate in the last refinement cycle was 0.07. A final calculation of structure factors was carried out after the last cycle. A difference Fourier map showed no features other than two ripples of less than 3 and 5 e⁻/Å³, respectively, in the vicinity of Sb(5) and one ripple of less than 3 e⁻/Å³ near Sb(6). This is not unreasonable since scattering factors for Sb⁰ were used. Otherwise, the map showed only a randomly fluctuating background of ± 1 e⁻/Å³. Since no discernable hydrogen peaks appeared in the difference map, these atoms were not included in the refinement. The calculated and observed structure factors for all 4662 observed reflections are tabulated in Table 7.¹ The final atomic and thermal parameters for the 88 independent nonhydrogen atoms are listed in Table 8.

Interatomic distances and angles

Interatomic distances and angles for the Sb₇³⁻ anion and the first two crypts were calculated using the function and error program ORFFE.⁶⁶ Standard deviations were estimated using the variance-covariance matrix from the appropriate

¹Structure factors shown in Table 7 have been multiplied by 10.

Table 7. Observed and calculated structure factors for $(\text{NaC}^+)_3\text{Sb}_7^{3-}$

L	C	1	4	1530	1654	1	8	783	665	3	1	3198	2931	16	4	575	493	6	10	1422	1410	8	2	619	766		
H	K	FC	FC	2	4	1383	1221	2	8	1072	1118	4	1	670	789	0	5	416	350	7	10	560	565	9	2	1892	1589
4	0	1537	1438	4	4	375	362	4	8	459	528	5	1	970	929	2	5	541	791	8	10	613	880	11	2	1885	1768
6	0	1349	1369	5	4	507	561	5	8	361	471	6	1	343	207	3	5	1351	1366	13	10	440	539	12	2	576	531
8	0	459	384	6	4	1128	993	7	8	893	749	7	1	1344	1717	4	6	3095	3128	6	11	1064	917	19	2	467	415
10	0	636	401	7	4	666	560	8	8	451	291	8	1	1002	1164	5	5	2319	2118	1	11	392	417	26	2	345	248
14	0	757	752	3	4	1120	952	9	8	1089	1084	9	1	980	1277	6	5	516	654	2	11	681	448	23	2	429	329
16	0	552	393	9	4	1315	1424	10	8	422	381	10	1	854	944	7	5	1239	1106	5	11	369	429	0	3	2353	1904
18	0	456	497	10	4	515	483	11	8	367	303	11	1	779	1008	8	5	895	877	7	11	538	641	1	3	1873	1813
20	0	1053	1189	11	4	1325	1131	13	8	381	198	12	1	1466	1439	10	5	963	884	10	11	396	416	2	3	662	604
22	0	334	374	12	4	1089	1005	14	8	386	300	13	1	410	462	11	5	728	836	12	11	440	383	3	3	4606	4316
24	0	332	147	13	4	949	816	15	8	542	513	18	1	722	673	12	5	936	863	13	11	483	361	4	3	2134	1816
1	1	761	689	15	4	1006	924	1	9	381	447	19	1	467	558	13	5	975	1079	0	12	326	244	5	3	4776	4742
2	1	244	437	16	4	661	531	2	9	782	724	20	1	517	593	14	5	1560	1600	1	12	466	339	6	3	519	473
3	1	577	602	18	4	377	430	3	9	964	887	6	2	2264	2037	15	5	462	516	2	12	398	362	7	3	4215	4049
4	1	957	1295	19	4	384	531	4	9	1764	1741	1	2	568	663	15	5	1017	1932	11	12	500	486	8	3	3314	3100
5	1	2558	3033	21	4	527	578	5	9	717	687	2	2	2049	2210	20	5	364	365	1	13	660	544	9	3	2744	2486
6	1	3917	3476	1	5	552	613	6	9	1546	1518	3	2	1079	990	21	5	503	461	3	13	388	302	10	3	2926	2891
7	1	687	816	2	5	741	733	7	9	834	754	4	2	6372	6047	9	6	492	511	11	13	375	285	11	3	1351	1603
8	1	839	664	3	5	1808	1681	8	9	736	613	5	2	478	438	1	6	396	463	2	15	378	196	13	3	748	763
9	1	2356	2260	0	9	1075	914	6	2	3866	3815	2	6	712	722	14	3	870	925								
10	1	1124	887	5	5	424	461	10	9	363	355	7	2	3158	3083	3	6	747	680	L	=	2	16	3	539	578	
11	1	2001	1914	6	5	1191	1193	11	9	402	368	8	2	1762	1717	4	6	700	718	H	K	F0	FC	25	3	299	63
13	1	453	395	8	5	287	318	14	9	507	631	9	2	4079	3859	5	6	1139	1289	C	0	6350	6599	0	4	539	643
15	1	512	525	9	5	1569	1367	16	9	450	517	10	2	625	564	7	6	518	6698	2	4	1619	1648				
16	1	661	679	10	5	515	502	1	10	550	559	11	2	2702	2544	11	6	414	552	4	0	1434	974	3	4	2103	2120
18	1	716	727	11	5	924	1090	2	10	355	143	12	2	839	874	12	6	536	525	6	0	1190	1341	4	4	604	744
19	2	2353	2361	13	5	527	468	3	10	418	359	14	2	811	988	13	6	1267	1360	8	0	963	1094	5	4	1287	1477
1	2	4553	4376	14	5	443	286	5	10	1073	1018	15	2	945	843	15	6	1076	1120	10	0	2314	2369	5	4	1786	1668
2	2	1472	1416	15	5	625	567	6	10	412	333	17	2	781	775	17	5	357	445	12	0	841	1070	8	4	1619	1609
3	2	1515	1091	16	5	415	358	7	10	511	899	19	2	375	309	0	7	1447	1539	14	0	381	270	9	4	834	673
4	2	1542	1361	0	6	478	647	9	10	605	684	0	3	803	559	1	7	1536	1617	16	0	365	461	11	4	807	644
5	2	2990	2840	1	6	2471	2328	11	10	357	265	1	3	1715	1450	3	7	2282	2383	18	0	1394	1529	12	4	473	456
6	2	775	792	12	6	2505	2584	12	10	545	497	2	3	376	397	4	7	346	237	20	0	733	964	13	4	1063	1069
7	2	1415	1216	3	6	2361	2226	17	10	352	212	4	3	265	212	5	7	1436	1381	24	0	346	245	15	4	984	850
8	2	1223	1363	4	6	4217	4094	5	11	703	694	5	3	1478	1415	8	7	715	714	0	1	1659	1550	16	4	498	532
9	2	864	731	5	6	1410	1464	7	11	605	667	7	3	502	361	9	7	494	441	1	1	1482	1292	19	4	559	679
11	2	1707	1367	6	5	3537	3552	0	12	1064	1059	8	3	1110	972	11	7	726	688	2	1	3156	3095	21	4	376	394
12	2	267	668	8	6	754	723	1	12	1065	889	16	3	1411	1238	13	7	1189	1126	4	1	322	916	0	5	417	292
13	2	787	815	9	6	349	220	2	12	735	646	11	3	432	365	15	7	888	964	5	1	1951	1710	1	5	829	723
14	2	254	372	12	6	414	353	3	12	616	580	12	3	1584	1550	16	7	372	389	6	1	976	1077	3	5	222	520
18	2	367	269	14	6	1980	1045	5	12	527	466	14	3	370	256	0	8	342	200	8	1	302	309	4	5	524	530
19	2	439	357	15	6	555	409	8	13	329	9	15	3	600	773	1	8	941	982	9	1	1718	1564	6	5	288	141
1	3	1397	1372	16	6	655	760	3	16	355	126	19	3	510	456	2	8	611	671	10	1	282	165	7	5	1314	1230
2	3	656	589	20	6	427	426			20	3	527	469	3	8	2126	2041	11	1	932	870	9	5	1987	1910		
3	3	4082	4209	1	7	368	S18	L	=	1	0	4	979	827	4	8	323	367	12	1	483	521	11	5	904	965	
4	3	1475	1511	2	7	1497	1491	H	K	F0	FC	2	4	3092	2895	5	8	1928	1973	13	1	552	698	12	5	371	414
5	3	4556	4215	3	7	1016	1002	1	0	2623	2188	3	4	2607	2285	7	8	1101	1053	14	1	514	371	13	5	486	514
6	3	1519	1339	4	7	1811	1749	5	0	3287	2496	4	4	1281	1162	8	8	652	630	15	1	409	501	14	5	903	1029
7	3	2396	2580	5	7	1294	1206	7	0	1581	1307	5	4	2907	2816	10	8	570	673	16	1	888	902	16	5	577	560
8	3	2048	1937	6	7	373	228	9	0	1727	1945	6	4	1868	1881	14	8	256	379	18	!	390	549	0	6	630	580
9	3	2471	2601	7	7	543	563	11	0	1845	1741	7	4	800	976	6	9	1226	1393	0	2	1369	1294	1	6	1711	1658
10	3	3673	3436	9	7	654	663	13	0	520	596	8	4	3938	4047</												

Table 7. (Continued)

10	6	930	875	L =	3	3	4	1728	1691	8	8	1063	1067	2	2	964	727	6	6	483	375	4	13	314	282				
11	6	552	506	H	K	4	4	1369	1206	10	8	893	765	3	2	1332	1058	7	6	549	656								
12	6	1422	1382	I	C	3220	2742	5	4	2337	2347	11	8	448	493	4	2	1182	1138	8	6	238	79	L =	E				
13	6	736	691	3	0	297	904	6	4	1037	1042	12	8	343	335	5	2	634	754	9	6	337	295	H	K				
14	6	1452	1666	5	0	729	719	7	4	686	666	1	9	493	359	7	2	429	851	10	6	296	445	1	0	1218	1541		
15	6	511	583	7	C	3142	2733	8	4	3103	2974	2	9	475	526	9	2	371	96	11	6	299	486	3	0	806	511		
16	6	911	978	9	6	673	557	9	4	1349	1484	3	9	619	545	10	2	559	398	12	6	1443	1546	5	3	546	452		
20	6	353	413	13	0	694	741	10	4	2370	2406	10	9	464	521	11	2	476	376	13	6	583	616	7	9	3010	2839		
0	7	418	622	15	0	316	254	11	4	948	994	12	9	376	368	13	2	676	739	14	6	1414	1571	9	0	916	868		
1	7	592	525	17	6	855	895	12	4	402	260	0	10	467	478	15	2	441	584	16	6	477	575	11	0	1755	1872		
3	7	1464	1419	C	1	2957	2884	14	4	490	455	1	10	321	269	17	2	675	574	20	6	376	281	13	0	1299	1425		
5	7	1384	1435	1	1	1935	1771	16	4	441	309	2	10	471	535	0	3	1298	1180	8	7	683	669	15	0	519	463		
7	7	377	397	2	1	365	551	18	4	405	427	3	10	560	633	1	3	3579	3337	1	7	409	461	17	0	367	287		
9	7	665	792	3	1	963	692	6	5	1151	1099	4	10	970	1081	2	3	1822	1885	2	7	1160	1141	0	1	636	533		
11	7	452	438	4	1	2638	1748	1	5	1696	1909	5	10	688	719	3	3	1765	1600	3	7	1141	1122	1	1	4551	3941		
12	7	651	796	5	1	2147	1955	2	5	1298	1122	6	10	762	826	4	3	3166	3150	4	7	1151	1034	2	1	4454	3918		
15	7	408	430	6	1	1199	1027	3	5	758	752	11	10	319	215	5	3	1302	1436	5	7	836	708	3	1	2764	2641		
14	7	362	447	7	1	2071	1997	4	5	442	417	13	10	314	357	7	3	1753	1817	6	7	379	458	4	1	3321	2811		
15	7	472	682	8	1	1392	1147	5	5	2299	2029	0	11	362	329	8	3	3344	3238	7	7	779	812	5	1	3735	3292		
21	7	319	85	9	1	1539	1597	7	5	1531	1353	1	11	608	610	9	3	1238	1258	8	7	292	137	5	1	300	110		
8	8	377	317	10	1	1488	1478	8	5	946	934	0	12	670	505	10	3	1925	1901	9	7	876	844	7	1	2265	2151		
1	8	622	363	11	1	1326	1412	10	5	390	415	1	12	803	705	11	1	962	859	12	7	365	433	9	1	1750	1561		
2	8	636	550	17	1	659	770	11	5	560	577	2	12	694	549	12	3	613	557	0	8	778	867	9	1	1220	1281		
3	8	315	305	18	1	682	735	12	5	1069	1196	3	12	494	466	14	3	601	588	1	8	292	451	10	1	735	597		
5	8	459	495	19	1	619	773	13	5	842	873	5	12	349	258	15	3	471	414	2	8	469	507	12	1	825	830		
7	8	655	650	6	2	311	311	14	5	1704	1712	7	12	425	293	16	3	517	494	2	8	600	636	13	1	775	777		
12	8	539	575	1	2	570	643	15	5	718	735	9	12	453	363	17	3	518	567	5	8	294	356	14	1	754	792		
13	8	389	405	2	2	1731	1626	16	5	610	718	9	13	394	323	18	3	421	376	7	8	796	395	17	1	813	880		
15	8	480	495	3	2	1371	1213	0	6	270	78	0	4	360	686	6	5	576	516	18	1	418	500						
1	9	1102	1241	4	2	423C	3973	1	6	1343	1758	L =	4	1	4	1457	1278	9	8	326	434	19	1	505	582				
2	9	1468	1543	5	2	323	396	2	6	320	219	H	K	F0	FC	2	4	646	658	11	8	494	466	0	2	489	470		
3	9	908	887	6	2	1769	1948	3	6	1347	1467	0	6	293	261	3	4	2622	2529	9	9	476	474	1	2	687	773		
4	9	1998	2151	7	2	1201	1219	5	6	1513	1810	2	6	2473	2860	4	4	952	766	1	9	882	943	2	2	2543	2313		
5	9	717	751	8	2	379	785	9	6	561	355	4	6	4273	3728	5	4	1857	1965	2	9	1784	1068	3	2	3308	3242		
6	9	1558	1563	9	2	3037	3163	11	6	324	529	6	6	2617	2320	6	6	1997	1901	3	9	370	448	4	2	2017	1790		
7	9	1072	1082	10	2	284	94	13	6	867	986	6	0	3082	3055	7	4	1340	1303	4	9	1551	1501	5	2	1384	1410		
8	9	316	281	11	2	1568	1517	15	6	343	330	10	0	1747	1754	8	4	1071	926	5	9	398	401	6	2	807	834		
9	9	859	801	12	2	1131	1142	16	6	462	410	16	0	456	647	9	4	1088	1249	6	9	490	423	8	2	1975	1888		
11	9	456	353	13	2	406	432	19	6	738	243	18	0	1121	1344	10	4	450	495	7	9	556	602	9	2	675	649		
1	10	576	505	14	2	739	836	5	7	500	499	20	0	516	618	15	4	802	817	8	9	576	558	10	2	653	723		
2	10	336	336	15	2	947	912	1	7	432	227	0	1	2321	2456	14	4	356	333	10	9	353	426	12	2	1066	1047		
3	10	333	405	17	2	917	876	2	7	278	223	1	1	827	832	15	4	545	582	0	10	704	683	13	2	874	822		
5	10	426	457	19	2	406	519	3	7	449	376	2	1	4420	3971	19	4	523	514	1	10	309	415	15	2	769	814		
6	10	448	484	3	3	2475	1957	4	7	870	663	3	2	2140	1910	0	5	1336	1275	2	10	617	589	17	2	455	544		
10	10	486	433	1	3	1028	1010	5	7	343	262	4	1	3336	3710	2	5	456	572	6	10	577	621	0	3	1311	1123		
12	10	558	570	3	3	2610	2873	7	7	393	508	5	1	611	666	3	5	2054	2169	7	10	550	394	1	3	826	778		
14	10	314	97	4	3	1444	1670	6	7	290	139	6	1	487	491	4	5	977	881	9	10	515	514	2	3	303	119		
1	11	322	160	5	3	477	343	9	7	680	732	7	1	1291	1239	5	5	944	1051	10	10	474	326	3	3	1455	1313		
5	11	324	493	6	3	1533	1845	11	7	732	779	9	1	622	529	7	5	1306	1223	12	10	427	281	5	3	656	607		
0	12	642	741	7	3	1142	1203	13	7	1367	1544	9	1	940	935	8	5	322	266	16	10	316	129	6	3	2148	2279		
1	12	514	356	8	3	1215	1324	15	7	1012	1066	10	1	285	485	9	5	1738	1569	11	11	551	384	7	3	975	862		
2	12	448	234	9	3	950	907	20	7	356	325	11	1	735	731	12	5	395	398	6	11	341	266	8	3	1329	1494		
11	12	413	449	12	3	363	518	6	8	39																			

Table 7. (Continued)

4	4	1951	1849	8	9	841	809	15	2	431	438	1	7	757	740	9	1	1510	1234	8	5	899	931	10	11	350	206		
7	4	1402	1400	10	9	744	826	17	2	355	355	2	7	640	504	1	1	3001	3152	9	5	497	496	12	11	394	408		
8	4	450	340	13	9	399	331	19	2	345	229	3	7	877	911	2	1	2620	2431	10	5	375	212	10	12	333	255		
9	4	1228	1376	0	10	747	723	1	3	720	704	4	7	813	669	3	1	1565	1813	11	5	419	519	1	13	583	482		
12	4	469	598	2	10	433	359	2	3	3199	2964	5	7	373	338	4	1	736	793	13	5	565	670	3	13	326	222		
14	4	705	709	3	10	664	740	3	3	938	763	7	7	1234	1277	5	1	1967	1948	15	5	359	359						
15	4	728	378	5	10	388	394	4	3	3479	3315	8	7	358	260	6	1	273	356	16	5	852	833	L =	8	H	K	F0	FC
18	4	333	375	6	10	358	275	5	3	2257	2282	9	7	1048	1279	7	1	1320	1333	18	5	370	444						
6	5	1366	1410	8	10	609	551	7	3	2303	2260	10	7	546	572	10	1	551	551	1	6	1337	1239	7	0	3145	3425		
1	5	1275	1502	6	11	350	223	8	3	1226	1354	14	7	516	558	11	1	1025	912	2	6	460	330	2	9	2842	3129		
2	5	528	675	1	11	469	451	9	3	1170	1178	16	7	578	562	12	1	1534	1580	5	6	1273	969	4	0	3819	4001		
4	5	761	822	2	11	712	635	10	3	354	441	6	8	995	1036	13	1	1541	1526	6	6	379	383	6	0	2493	2362		
5	5	1054	828	0	12	519	426	11	3	794	829	1	8	813	849	14	1	995	1028	7	6	969	1160	3	0	1355	1427		
6	5	1011	1035	2	12	634	528	12	3	490	462	2	8	1185	1185	15	1	524	465	8	6	359	369	10	0	1746	1576		
7	5	1468	1315	3	12	525	376	13	3	609	648	3	8	329	445	8	2	1178	1047	10	6	604	692	12	0	2826	2730		
11	5	437	594	5	12	354	273	14	3	490	492	4	8	655	697	1	2	1920	1823	13	6	516	555	14	0	1286	1272		
12	5	911	1506	7	12	481	408	16	3	436	457	7	8	313	325	2	2	2104	1892	15	6	700	673	6	1	965	984		
13	5	752	1012	1	13	506	493	18	3	558	511	8	8	543	398	2	2	4175	3907	17	6	415	368	1	1	2506	2292		
14	5	612	686	3	13	411	404	0	4	1443	1441	9	8	765	740	4	2	963	1017	7	0	359	387	2	1	427	98		
15	5	618	601	3	14	362	238	1	4	837	756	10	8	575	530	5	2	2912	2847	1	7	2226	2197	3	1	2328	2082		
18	5	410	422					2	4	1040	1040	11	8	416	501	6	2	2760	2659	2	7	496	495	4	1	1067	1070		
1	6	1504	1314	L =	6	3	4	407	423	17	8	387	403	8	2	1912	2103	3	7	1410	1674	5	1	375	372				
3	6	2660	2307	H	K	F0	FC	4	4	1396	1287	2	9	704	749	10	2	335	348	4	7	352	350	6	1	2335	2322		
4	6	297	280	~	0	5530	5284	5	4	1238	1307	3	9	397	412	11	2	477	518	5	7	991	998	7	1	1623	1605		
5	6	973	1187	2	0	6969	6807	6	4	1414	1337	6	9	824	791	13	2	535	669	7	7	458	436	8	1	520	686		
7	6	288	364	4	0	5455	5126	7	4	1719	1714	7	9	391	265	15	2	459	491	9	7	723	646	9	1	489	619		
9	6	334	364	6	0	3849	3810	8	4	565	483	8	9	1254	1353	18	2	367	339	12	7	347	290	10	1	511	406		
14	6	513	588	8	0	3464	3188	9	4	1553	1459	9	9	489	505	6	3	450	324	15	7	444	325	11	1	825	794		
16	6	375	375	10	0	455	454	10	4	351	287	10	9	573	672	1	3	1492	134*	17	7	311	344	12	1	685	584		
17	6	426	372	12	0	1913	1917	11	4	757	717	11	9	432	467	3	3	285	500	1	8	273	336	16	1	399	375		
0	7	554	594	14	0	940	814	12	4	455	383	0	10	983	893	4	3	1643	1679	2	8	642	634	17	1	363	420		
1	7	1733	1824	18	0	622	711	13	4	329	422	2	10	924	821	5	3	584	584	4	8	368	393	18	1	396	326		
2	7	504	614	0	1	1929	1869	16	4	348	427	6	10	409	451	6	3	1556	1614	5	8	683	692	0	2	939	743		
3	7	1400	1552	1	1	652	703	17	4	527	616	9	10	503	537	7	3	355	252	6	9	856	761	1	2	867	927		
5	7	1051	1329	2	1	1698	2069	0	5	855	804	11	10	724	652	8	3	980	1087	7	8	1223	1079	2	2	841	781		
6	7	314	368	3	1	1480	1399	1	5	1176	1038	13	10	446	521	10	2	957	916	8	8	568	639	3	2	1223	1176		
8	7	435	385	4	1	2344	2292	2	5	1408	1318	1	11	332	424	11	3	637	580	9	8	1286	1337	4	2	1356	1426		
9	7	307	54	6	1	3663	3440	3	5	1798	1697	5	11	372	454	12	3	682	633	11	8	636	648	6	2	681	763		
11	7	369	538	7	1	1946	1887	4	5	714	755	7	11	597	581	13	3	531	647	15	8	354	186	7	2	312	217		
12	7	339	219	8	1	1803	1815	5	6	1671	1489	1	12	761	674	14	3	325	446	0	9	847	879	9	2	529	586		
13	7	781	930	9	1	1172	1054	6	5	1087	922	2	12	332	344	17	3	444	559	1	9	757	767	11	2	1984	1960		
15	7	326	447	10	1	289	322	7	5	398	361	3	12	605	508	0	4	848	748	2	9	437	525	13	2	1343	1287		
0	8	556	576	11	1	777	754	10	5	489	510	4	12	488	314	1	4	1152	1227	3	9	434	373	0	3	1073	1133		
1	8	836	825	12	1	705	571	11	5	359	410	5	12	350	210	2	4	3242	3376	8	9	821	859	1	3	1623	1486		
2	8	933	652	13	1	944	958	12	5	477	601	1	13	357	284	3	4	1132	977	10	9	625	704	2	3	3903	3850		
3	8	515	594	17	1	408	438	15	5	368	409	3	13	384	338	4	4	2989	2734	11	9	347	357	3	3	2089	2259		
4	8	1030	1021	0	2	923	905	16	5	350	266					5	4	626	663	12	9	361	406	4	3	1981	1991		
6	8	397	377	1	2	4008	3275	0	6	3319	3401	L =	7	6	4	928	929	3	10	444	425	5	3	3341	3253				
7	8	602	602	3	2	748	582	1	6	1109	1323	H	K	F0	FC	7	4	1713	1681	4	10	541	577	5	3	385	450		
8	8	1062	1071	4	2	399	384	2	6	2237	2193	1	0	1162	800	8	4	604	591	6	10	966	1014	7	3	3141	2865		
9	8	953	1085	5	2	277	574	3	6	1747	1753	3	0	1209	1291	9	4	1600	966	7	10	332	378	8	3	353	394		
10	8	479	568	6	2	296	207	4	6	1193	1472	5	0	1801	1955	10	4	1266	1284	8	10	774	852	9	3	2005	1954		
11	8	566	574	7	2	318	86	5	6	1164	1262	7	0	1822	1733	12	4	929	973	10	10	476	446	17	3	309	536		
0	9	526	605	8	2	354	487	7	6	475	596	9	0	352	436	0	5	2325	2214	0	11	643	561	11	3	820	883		
1	9	782																											

Table 7. (Continued)

3	4	445	290	5	9	451	390	3	4	2085	1894	L = 10	17	4	336	353	3	1	1334	1632	1	7	781	827	
4	4	319	359	6	9	1244	1265	1	4	568	526	H K FC FC	1	5	660	620	4	1	590	537	3	7	421	561	
5	4	359	451	7	9	726	654	2	4	2781	2613	0	0	815	623	4	5	805	663	5	7	734	813		
6	4	1016	886	8	9	1153	1236	3	4	1162	1214	2	6	1669	1293	5	5	1062	1091	6	1	274	93		
7	4	1111	1122	9	9	567	611	4	4	1655	1495	4	6	309	286	6	5	937	1176	6	1	745	632		
8	4	795	621	10	9	507	578	5	4	632	679	6	6	614	835	7	5	341	368	10	1	1369	1424		
11	4	360	189	11	9	335	355	6	4	592	448	8	6	799	465	8	5	501	499	11	1	1092	1034		
14	4	454	524	10	10	654	789	7	4	809	866	10	0	2013	1964	9	5	456	573	12	1	577	760		
16	4	465	532	2	10	476	737	8	4	504	524	12	0	2319	2257	0	6	266	173	16	1	313	340		
17	4	410	523	11	10	353	390	10	4	1126	1048	14	0	981	889	1	6	386	361	0	2	999	855		
6	5	311	391	13	10	392	399	12	4	493	509	0	1	1412	1414	4	6	454	544	1	2	1734	1655		
1	5	1056	725	5	11	354	497	15	4	331	323	1	1	3072	2991	5	6	321	405	2	2	1140	1125		
2	5	471	369	7	11	371	421	17	4	493	472	2	1	1021	1185	6	6	1211	1236	3	2	885	774		
3	5	1329	1125	9	12	347	304	0	5	323	114	3	1	1136	1104	7	6	435	441	4	2	910	870		
4	5	387	247	1	12	487	486	1	5	789	844	4	1	744	682	8	6	702	940	5	2	416	368		
7	5	300	52	2	12	419	363	6	5	897	932	5	1	741	E71	11	6	318	349	6	2	862	969		
9	5	575	623	6	12	307	178	7	5	535	493	6	1	341	361	16	6	434	594	7	2	692	732		
10	5	398	169					8	5	719	764	7	1	767	714	9	7	526	641	8	2	461	460		
11	5	598	664	L = 9		11	5	427	470	8	1	313	315	1	7	545	606	9	2	655	784	6	12	325	305
15	5	321	291	H K FC FC		13	5	453	588	10	1	684	577	2	7	859	681	11	2	492	476	1	13	370	274
16	5	499	492	1	0	2835	2429	14	5	463	534	0	2	1785	1491	4	7	1284	1342	0	3	889	1002		
18	5	374	275	3	0	1945	2226	16	5	814	826	2	2	1124	968	5	7	777	761	1	3	906	865		
6	2133	2769	5	0	1227	1255	0	6	593	512	3	2	900	965	6	7	793	1020	2	3	624	712			
1	6	908	891	7	0	1118	1097	3	6	1036	992	4	2	523	693	7	7	773	746	4	3	359	219		
2	6	1792	1596	9	1	1189	1089	5	6	1473	1516	5	2	287	293	9	7	354	368	5	3	263	270		
3	6	1130	1114	11	0	779	737	7	6	1030	1248	6	2	473	470	10	7	516	459	6	3	416	412		
4	6	1388	1242	13	0	456	416	8	6	644	592	7	2	741	650	12	7	276	144	8	3	807	794		
5	6	902	796	15	0	421	282	10	6	374	367	8	2	596	669	14	7	311	185	9	3	669	737		
6	6	350	423	17	6	417	438	11	6	385	208	9	2	481	453	1	6	318	455	10	3	730	613		
8	6	742	820	0	1	1348	1301	15	6	392	374	10	2	597	646	7	8	486	489	11	3	674	650		
9	6	411	341	1	1	1027	1243	6	7	581	588	11	2	824	945	11	8	343	352	12	3	707	576		
10	6	360	175	3	1	256	372	1	7	701	651	12	2	357	251	1	9	461	446	14	3	374	387		
12	6	346	424	5	1	694	866	2	7	554	591	13	2	365	494	2	9	307	256	15	3	512	580		
13	6	549	557	6	1	517	397	3	7	835	792	14	2	402	279	4	9	375	397	0	4	2020	1939		
15	6	533	481	7	1	1554	1291	7	7	843	869	16	2	321	367	5	9	365	332	1	4	876	885		
16	6	705	625	8	1	310	346	8	7	322	228	17	2	337	229	6	9	665	609	2	4	658	718		
0	7	738	808	9	1	692	568	9	7	620	664	0	3	2462	2245	8	9	416	390	3	4	657	559		
1	7	744	766	10	1	1455	1602	15	7	451	555	1	3	1355	1253	9	9	340	423	4	4	686	642		
3	7	536	547	11	1	1590	1585	6	8	498	419	2	3	2743	2456	12	9	294	27	6	4	861	910		
4	7	583	772	12	1	1560	1651	1	8	464	524	3	3	2037	1767	C 10	340	378	11	4	299	9			
5	7	685	700	13	12	1264	1132	2	8	396	416	4	3	465	385	3	10	486	472	17	4	317	320		
6	7	536	608	15	1	331	369	5	8	398	391	5	3	1202	1139	4	10	456	421	0	5	1740	1741		
7	7	1261	1428	0	2	1047	991	6	8	684	732	6	3	759	745	5	10	626	547	1	5	255	171		
9	7	815	924	1	2	2578	2386	7	8	948	975	7	3	1107	1123	6	10	277	188	2	5	710	852		
14	7	495	577	2	2	860	754	9	8	782	779	8	3	443	373	7	1C	355	356	4	5	635	806		
16	7	397	379	3	2	3111	2918	10	8	482	393	9	3	731	728	1	11	354	181	5	5	514	553		
8	6	602	532	4	2	965	924	0	9	942	1015	11	3	548	533	0	13	484	443	6	5	1053	1172		
1	8	553	608	5	2	710	767	1	9	368	382	16	3	467	383	2	13	439	305	10	5	567	425		
2	8	934	908	6	2	2652	2562	4	10	455	528	17	3	326	276	11	5	482	594	8	2	755	851		
4	8	374	366	7	2	405	352	6	10	727	740	0	4	1521	1505	L = 11	13	5	340	326	10	2	893	906	
7	8	607	642	8	2	1202	1303	7	10	330	305	1	4	578	680	H K FC FC	17	5	329	288	13	2	575	538	
8	8	503	529	10	2	326	328	8	10	719	636	2	4	856	943	1	0	4402	4190	C 6	6	699	712		
9	8	393	538	0	3	362	494	5	11	369	464	3	4	562	691	3	0	670	671	1	6	475	339		
10	8	423	441	1	3	1447	1344	7	11	386	417	4	4	382	255	7	0	578	598	2	6	844	909		
12	8	432	458	3	3	324	321	1	12	535	444	6	4	432	321	9	0	809	831	3	2	2111	1911		
C	9	337	116	4	3	974	959	3	12	461	324	9	4	557	367	11	0	696	721	4	6	701	755		
I	9	437	465	11	3	911	817	8	12	320	206	11	4	1021	956	0	1	1217	1296	5	6	2274	2305		
3	9	673	720	15	3	484	593	14	4	430	590	1	1	2886	2538	7	6	976	933	4	3	661	493		
4	9	386	192	17	3	400	444	15	4	456	475	2	1	754	769	8	6	389	426	5	3	589	571		

Table 7. (Continued)

6	3	1153	1244	L = 13	7	6	394	464	3	4	592	568	8	3	466	438	3	3	687	564	5	6	413	321			
7	3	1209	1269	H K FO FC	13	6	397	327	5	4	520	638	9	3	907	912	4	3	581	501	5	6	470	400			
8	3	538	615	1 6 1645 1705	1	7	1079	933	7	4	410	428	10	3	422	394	5	3	672	714	7	6	512	464			
9	3	642	674	3 0 355 230	3	7	941	847	9	4	1014	1082	0	4	335	245	6	3	367	279	1	7	530	671			
10	3	474	456	5 0 331 128	5	7	913	976	10	4	426	275	1	4	325	372	7	3	637	460	1	9	376	410			
0	4	1083	1138	7 0 300 412	7	7	651	496	11	4	785	785	2	4	1058	949	9	3	394	280	0	10	326	199			
1	4	415	489	9 0 363 497	10	7	484	507	13	4	313	212	4	4	1403	1358	14	3	369	340							
2	4	295	586	6 1 775 915	11	7	329	314	14	4	315	136	6	4	1126	1935	0	4	372	379	L = 18						
3	4	838	870	1 1 3233 2947	0	8	644	723	0	5	487	384	8	4	703	669	5	4	401	296	H K FO FC						
4	4	667	663	2 1 1280 1213	1	8	463	456	2	5	551	564	10	4	394	339	6	4	472	601	0	0	876	841			
5	4	789	855	3 1 1777 1512	2	8	397	293	3	5	1322	1211	2	5	621	564	8	4	753	674	2	0	1329	1287			
6	4	416	501	6 1 532 526	3	8	759	660	4	5	1225	1309	3	5	626	494	9	4	452	645	4	5	1140	1164			
7	4	500	357	9 1 382 362	5	8	380	308	5	5	855	834	4	5	972	906	1	5	292	254	6	5	482	410			
9	4	1256	1218	10 1 345 548	7	8	338	246	6	5	864	932	5	5	748	633	3	5	349	393	8	0	379	280			
10	4	318	203	14 1 524 537	11	8	313	239	0	6	1181	1006	7	5	329	304	8	5	295	51	1	1	465	531			
11	4	1276	1224	16 1 356 372	2	9	667	419	1	6	614	453	8	5	640	682	10	5	309	286	2	1	976	919			
13	4	450	421	0 2 1357 1280	4	9	630	566	2	6	1030	850	10	5	738	756	4	6	581	443	3	1	772	822			
15	4	305	289	3 2 603 715	6	9	439	395	2	6	413	303	12	5	326	244	6	6	318	159	4	1	911	899			
0	5	514	421	5 2 994 1187	8	9	434	429	4	6	1305	1205	1	6	452	327	8	6	449	518	6	1	425	433			
2	5	604	827	7 2 1146 1286	6	10	291	241	5	6	330	301	3	5	424	456	10	6	423	480	8	1	346	333			
3	5	1217	1053	8 2 364 380	6	6	844	702	11	6	326	311	0	7	327	280	9	1	354	151							
4	5	1247	1234	9 2 762 891	L = 14	10	6	561	549	1	7	277	55	1	7	631	605	1	2	989	949						
5	5	1437	1328	11 2 572 695	H K FO FC	1	7	919	845	3	7	551	404	0	8	447	501	3	2	1011	959						
6	5	1230	1179	1 3 967 1028	C 0 3274 3157	2	7	623	671	5	7	452	249	2	8	585	514	9	2	366	348						
7	5	551	518	3 3 299 287	2 0 1587 1590	4	7	911	863	8	7	374	309					4	3	330	142						
8	5	612	617	4 3 594 497	8 0 524 372	7	8	457	411	11	7	325	265	L = 17		1	3	521	428								
13	5	287	116	5 3 280 432	14 0 677 729	9	8	496	531	0	8	512	567	H K FC FC		1	4	381	218								
6	6	967	911	6 3 787 747	16 0 463 396	11	8	332	171	1	8	414	462	1	0	1226	1197	6	4	652	731						
1	6	474	558	7 3 304 350	0 1 1331 1344	8	0	486	433	3	8	394	346	3	0	1936	1804	8	4	543	568						
2	6	1128	981	8 3 782 633	1 1 475 541	2	9	321	288	1	9	374	315	5	0	1297	1183	5	5	463	425						
3	6	782	794	9 3 853 909	3 1 633 476	5	10	461	434	2	9	531	466	7	0	594	598	7	5	322	295						
4	6	1354	1467	10 3 980 968	5 1 643 709	7	12	385	235	4	9	336	299	1	1	465	302	10	5	336	244						
5	6	766	828	11 3 308 433	6 1 504 537	1	12	474	401	6	9	317	323	1	1	563	701	0	6	622	640						
6	6	1395	1324	12 3 598 633	8 1 603 862	L = 15	0	10	362	396	2	1	903	947	1	6	453	422									
7	6	389	439	8 4 862 285	10 1 529 583	C 12	332	141		3	1	867	966	0	7	329	133										
10	6	4C5	461	1 4 459 512	0 2 572 562	H K FC FC				4	1	1456	998	4	7	454	304										
1	7	733	806	2 4 549 487	1 2 451 603	L = 16	5	1	394	482	6	7	410	393													
2	7	577	1032	4 4 1829 1691	2 2 417 370	C 0 1730 1599	H K FC FC			0	2	323	246	0	2	575	684										
4	7	1338	1330	5 4 327 374	4 2 391 300	5 0 1048 1015	H K FO FC			0	6	994	980	1	2	306	75	2	8	464	495						
5	7	434	376	6 4 1322 1469	5 2 671 568	9 1 290 337	4 0 1087 1164	2	2	327	453																
6	7	705	614	7 4 469 509	7 2 312 234	1 1 1123 1078	6 0 448 501	4	2	404	357	L = 16															
11	7	371	318	8 4 766 816	8 2 463 553	3 1 319 251	8 0 317 249	12	2	338	232	H K FO FC															
8	8	369	431	10 4 358 454	9 2 306 313	4 1 780 672	12 0 392 474	C 3	3	893	768	1	0	955	908												
9	8	416	390	0 5 1434 1368	10 2 550 607	12 1 482 488	14 0 546 570	2	3	319	369	3	0	1016	1053												
11	8	338	376	2 5 1274 1300	11 2 384 276	14 1 587 551	0 1 297 337	3	3	530	426	5	0	826	855												
0	9	354	312	3 5 765 717	13 2 613 633	0 2 808 774	1 1 475 457	6	3	342	263	7	0	353	528												
1	9	269	143	4 5 1264 1205	15 2 506 473	3 2 454 390	2 1 641 658	7	3	449	545	0	1	785	749												
2	9	342	373	5 6 820 664	0 3 804 847	5 2 998 1012	3 1 997 1019	9	3	365	520	1	1	825	826												
10	9	329	339	6 5 668 831	1 3 531 495	6 2 396 466	4 1 496 437	11	3	302	83	2	1	1032	987												
3	10	445	426	7 5 436 488	3 3 910 940	7 2 893 1072	5 1 420 405	0	4	286	181	3	1	1116	1073												
5	10	513	569	9 5 386 413	4 3 868 865	8 2 606 453	1 2 645 575	2	4	475	616	4	1	816	755												
7	10	526	529	10 5 778 816	5 3 1535 1453	9 2 614 713	2 2 427 407	4	4	36F	382	5	1	467	439												
1	11	328	323	11 5 470 607	6 3 473 470	11 2 309 328	3 2 879 804	0	5	792	759	2	2	362	434												
1	12	567	357	12 5 360 248	7 3 1204 1209	15 2 343 241	5 2 690 773	3	5	450	399	3	2	434	396												
2	12	302	204	0 6 555 500	8 3 506 604	0 3 1005 829	10 2 291 184	5	5	479	470	5	2	366	488												
3	12	359	301	2 6 998 866	9 3 1013 1050	2 3 374 205	11 2 304 171	8	5	656	661	6	2	382	451												
				3 6 1260 1234	10 3 431 597	3 3 652 717	0 3 347 341	10	5	335	301	7	2	492	364												
				4 6 649 599	11 3 677 526	5 3 591 502	1 3 616 510	1	6	595	408	0	3	43													

Table 7. (Continued)

3	3	446	372	3	2	437	379	13	1	1508	1535	1	5	1215	1257	5	9	805	647	2	2	822	902	10	6	765	680	
6	3	434	424	1	3	461	489	15	1	1376	1431	2	5	1460	1403	6	9	1540	1446	12	2	439	525	11	6	599	571	
7	3	522	565	7	3	339	343	16	1	640	615	3	5	375	270	7	9	351	149	13	2	741	497	12	6	414	336	
8	3	492	342	4	4	314	299	17	1	740	846	4	5	2980	2952	8	9	1605	1474	14	2	569	740	13	6	786	706	
10	3	348	249					20	1	560	672	5	5	2082	1815	10	9	842	701	15	2	365	531	14	6	459	297	
6	4	448	427	L = 22		22	1	410	445	6	5	1816	1822	13	9	419	499	17	2	674	724	20	6	465	462			
8	4	434	400	H K FO FC	C	2	1881	2037	7	5	2387	2347	17	9	376	377	22	2	414	291	9	7	329	622				
0	5	649	551	0	0	310	274	1	2	353	552	9	5	633	538	2	10	336	251	6	3	2026	1904	1	7	479	578	
2	5	409	335	2	0	566	432	2	2	1258	1066	11	5	324	331	4	10	485	268	1	3	2523	2743	2	7	270	2842	
4	5	285	240	6	0	365	399	3	2	620	765	13	5	334	307	5	10	530	486	2	3	1899	1930	4	7	2491	2557	
6	5	398	480	0	2	388	457	4	2	551	721	16	5	463	504	6	10	1008	804	3	3	3704	3225	5	7	717	651	
4	6	455	259	1	4	463	470	5	2	556	494	19	5	561	531	7	10	524	517	4	3	2629	2137	7	7	428	443	
6	6	381	335	2	4	276	49	6	2	3677	3055	21	5	477	497	8	10	617	535	5	3	808	474	8	7	680	612	
7	6	388	260	1	6	358	103	7	2	1564	1413	0	6	526	512	11	10	440	243	6	3	3498	3228	10	7	387	338	
8	6	318	222	3	7	334	214	8	2	976	902	1	6	2008	2351	0	11	676	917	7	3	602	586	11	7	773	707	
1	7	709	631	1	7	324	187	9	2	2934	2613	2	6	1023	1008	1	11	556	547	11	3	3085	2991	12	7	565	432	
3	7	447	439			10	2	1761	1675	3	6	1312	1353	2	11	735	543	12	3	1972	1955	15	7	667	546			
4	7	298	103	L = 23		11	2	2125	2160	4	6	344	414	7	11	614	619	13	3	659	666	17	7	375	390			
5	7	357	327	H K FO FC	12	2	964	808	5	6	389	330	13	11	413	327	14	3	525	566	18	7	416	309				
5	8	377	275	C	3	472	365	13	2	571	415	7	6	923	824	1	13	845	719	15	3	656	792	0	8	313	317	
1	9	442	324	1	3	462	513	14	2	484	628	8	6	863	708	3	13	456	312	16	3	1027	996	1	8	704	700	
3	9	331	242	2	3	381	366	15	2	504	658	9	6	669	644					17	3	503	546	3	9	411	331	
				C	5	379	338	16	2	754	700	10	6	663	620	L = -2				19	3	421	694	6	8	741	630	
				H K FO FC	1	6	368	290	17	2	421	455	11	6	425	198	H K FC FC	20	3	358	349	7	8	653	493			
0	0	979	1059	L = 24		21	2	373	342	12	6	714	666	0	0	6436	6599	21	3	634	667	9	8	1055	911			
2	0	1223	1181	H K FO FC	0	3	704	559	14	6	615	618	4	0	2615	1670	1	4	3974	4017	17	8	515	576				
4	0	560	538	2	0	311	249	1	3	1934	1897	15	6	1131	1077	6	0	1065	857	2	4	535	557	1	9	385	557	
0	1	588	501	4	0	465	399	2	3	2960	2424	17	6	372	333	10	0	3505	3216	3	4	1870	1720	4	9	428	396	
2	1	954	852	0	2	546	477	3	3	2061	2049	0	7	1428	1540	12	0	2105	2218	4	5	559	684	6	9	628	603	
4	1	553	660	2	2	326	261	4	3	2565	2082	1	7	717	708	14	0	1685	1740	9	4	1514	1268	10	6	580	610	
6	1	563	524	1	4	504	486	5	3	1517	1324	2	7	967	828	16	0	1772	1913	11	4	873	755	12	9	458	475	
0	2	435	275			6	3	1738	1365	3	7	2021	1925	18	0	547	446	12	4	1104	1168	14	6	509	556			
1	2	687	753	L = 25		7	3	1048	874	5	7	2835	2628	20	0	556	525	13	4	505	308	15	9	311	168			
2	2	373	346	H K FO FC	8	3	1529	1469	7	7	1461	1460	22	0	510	529	14	4	359	511	16	9	701	728				
3	2	341	356	1	1	317	281	9	3	1485	1334	9	7	365	433	0	1	1494	1550	15	4	482	428	19	9	425	365	
7	2	502	461		10	3	2427	2242	10	7	498	404	1	1	205	233	16	4	431	381	1	10	329	459				
4	3	379	273	L = -1		12	3	1490	1402	11	7	394	339	2	1	1816	1562	18	4	437	364	3	10	376	344			
7	3	454	453	H K FO FC	13	3	623	755	14	7	434	400	3	1	2638	2508	21	4	384	424	5	10	1678	954				
9	3	420	312	1	0	167	593	14	3	431	323	16	7	521	566	5	1	1940	1837	6	5	331	292	7	10	1514	1417	
4	4	306	316	3	0	2840	2790	17	3	573	514	18	7	375	300	6	1	3245	2276	1	5	974	1141	9	13	484	579	
6	4	460	455	5	0	637	497	21	3	370	418	19	7	373	395	7	1	1602	1454	2	5	1223	1161	9	10	753	679	
2	5	279	86	7	C	874	902	0	4	820	827	0	8	276	200	8	1	2015	1537	3	5	982	1297	5	11	358	224	
0	6	625	508	9	0	845	1037	1	4	1100	1000	1	8	581	625	9	1	1247	1269	4	5	1760	1936	7	11	363	370	
1	6	408	336	11	0	3105	3372	3	4	1332	1338	2	8	477	499	10	1	385	430	5	4	494	303	10	11	379	153	
3	6	353	261	13	0	1074	1327	5	4	1650	1562	3	8	1604	1570	11	1	3171	2930	7	5	2061	1868	9	12	737	741	
4	6	335	158	15	0	577	765	6	4	503	348	5	8	1301	1256	12	1	713	556	13	5	414	361	1	12	755	646	
4	7	343	209	17	0	614	514	7	4	602	563	6	8	962	892	13	1	632	568	14	5	369	275	2	12	613	551	
0	8	387	358	6	1	3177	3197	8	4	1397	1565	7	8	753	714	15	1	408	502	15	5	734	699	3	12	519	443	
2	8	326	325	1	1	5861	5550	9	4	900	1038	8	8	432	240	17	1	334	268	17	5	370	325	12	12	400	213	
					2	1	4364	3996	10	4	1847	1648	12	8	647	621	22	1	390	363	0	6	633	580	0	13	475	441
				L = 21	3	1	5626	5410	11	4	1241	1073	11	8	425	286	0	2	1271	1294	1	6	744	735				
				H K FO FC	4	1	307	225	12	4	1251	1270	12	8	450	394	1	2	2023	2079	3	6	1140	1129	L = -3			
3	0	413	339	6	1	2186	1982	13	4	528	482	14	8	471	462	2	2	425	997	4	6	2428	2275	H K FO FC				
9	0	327	111	7	1	377	676	14	4	445	282	17	8	620	624	3	2	1531	1369	5	6	1159	981	1	0	2453	2541	
0	1	497	521	8	1	526	450	15	4	640	678	0	9	292	194	4	2	1522	1159	6	6	3172	3046	3	0	447	455	
2	1	571	516	9	1	445	275	17	4</td																			

Table 7. (Continued)

15	9	654	690	6	4	2653	2246	6	8	902	805	4	1	1022	1319	10	4	476	373	19	8	490	411	19	1	542	570	
17	6	564	537	7	4	970	915	7	8	400	354	5	1	1634	1547	11	4	278	136	6	9	473	474	22	1	432	412	
9	1	2836	2884	3	4	2819	2925	8	8	751	701	7	1	294	120	12	4	784	817	1	9	815	974	6	2	569	470	
1	1	5518	5392	9	4	432	593	9	8	946	921	11	1	1971	2068	14	4	623	850	2	9	414	458	1	2	4383	3894	
2	1	2581	2290	10	4	440	363	10	9	629	726	12	1	305	269	17	4	364	409	3	9	668	659	2	2	901	937	
3	1	820	703	11	4	862	868	11	8	907	811	13	1	1012	1090	18	4	441	400	4	9	663	687	3	2	4173	4066	
4	1	1626	1587	12	4	418	518	13	8	327	237	15	1	580	521	9	5	1056	1275	5	9	856	765	4	2	4569	4651	
5	1	3836	3214	15	4	1290	1186	15	8	399	439	16	1	405	256	1	5	640	544	6	9	503	615	5	2	3869	3822	
6	1	2717	2514	17	4	860	834	16	8	428	415	17	1	601	645	2	5	1207	1499	7	9	1150	1073	6	2	2721	2819	
7	1	759	515	18	4	439	368	17	8	904	854	18	1	413	489	5	5	1225	1169	8	9	369	488	7	2	3687	3606	
9	1	1040	928	20	4	408	501	19	8	496	492	21	1	453	326	7	5	1944	1865	9	9	969	957	8	2	811	852	
10	1	1738	1854	6	5	1068	1190	1	9	297	300	22	1	364	252	8	5	664	556	10	9	974	998	9	2	830	831	
11	1	2792	2643	1	5	1127	1246	2	9	692	503	24	1	293	153	9	5	1736	1607	12	9	769	832	10	2	1984	1932	
12	1	585	587	2	5	765	800	4	9	891	763	9	2	1574	1538	12	5	458	471	16	9	752	628	11	2	504	422	
13	1	2630	2613	3	5	899	1151	5	9	1225	1020	1	2	2140	2385	13	5	471	322	18	9	594	484	12	2	2471	2424	
14	1	668	704	5	6	1753	1386	6	9	1022	842	3	2	846	735	14	5	1139	1120	1	10	596	682	13	2	465	499	
15	1	1772	1908	6	5	2474	2333	7	9	542	614	4	2	3483	2905	16	5	620	504	5	10	612	513	14	2	269	306	
16	1	826	849	7	5	2152	1691	8	9	1232	931	5	2	1566	1606	17	5	363	387	7	10	1065	879	16	2	915	800	
17	1	858	1018	8	5	1236	1231	9	9	405	327	6	2	406	489	19	5	388	248	9	10	500	341	17	2	561	534	
18	1	454	511	9	5	1299	1128	10	9	893	728	7	2	1982	1530	8	6	2542	3349	14	10	423	321	18	2	543	533	
20	1	429	462	10	5	450	306	14	9	311	69	8	2	493	661	1	6	729	912	1	11	325	274	21	2	477	495	
21	1	584	558	11	5	369	173	16	9	379	277	9	2	937	1004	2	6	2704	3042	5	11	405	530	0	3	1262	1123	
22	1	692	639	12	5	1276	1352	18	9	350	265	17	2	282	57	3	6	483	685	6	11	356	292	1	3	825	761	
1	2	616	776	14	5	1123	1142	0	10	406	478	11	2	876	931	6	5	3151	2825	13	11	318	194	2	3	1987	1589	
3	2	3231	3172	17	5	456	781	2	10	564	741	12	2	581	729	7	6	554	436	2	12	502	462	3	3	2267	2298	
5	2	3769	3506	19	5	424	406	6	10	572	622	13	2	439	564	8	6	2743	2521	9	12	582	536	4	3	744	563	
7	2	1325	1330	1	6	1690	2019	8	10	355	293	14	2	629	872	10	6	897	740	11	12	370	371	5	3	1298	945	
8	2	961	1191	2	6	323	596	9	10	540	535	17	2	592	554	11	6	849	671	11	12	464	487	6	3	1144	1270	
9	2	605	622	3	6	1715	1939	11	10	753	727	21	2	651	663	12	6	1095	878	12	12	453	386	7	3	384	428	
10	2	2200	2255	4	6	1343	1369	16	10	416	365	23	2	585	512	13	6	914	805	0	13	567	537	8	3	500	719	
11	2	1442	1196	5	6	1506	1572	18	10	426	394	0	3	1130	1180	14	6	1146	1050	2	13	327	251	10	3	1324	1339	
12	2	2286	2262	6	6	686	550	1	11	429	457	1	3	2616	2622	15	6	842	830	13	3	700	642					
13	2	471	623	7	6	958	829	2	11	375	474	2	3	2301	2263	16	6	414	341	L = -5	14	3	521	491				
14	2	357	266	8	6	998	899	6	11	440	372	3	3	4908	4767	19	6	347	247	H K FC FC	15	3	466	447				
16	2	1228	1257	9	6	1088	923	7	11	405	303	4	3	3249	2934	22	6	395	370	1	0	3257	3473	16	3	423	263	
18	2	479	375	10	6	777	904	12	11	443	235	5	3	4854	4314	0	7	637	669	3	0	410	919	17	3	600	614	
19	2	527	505	11	6	684	796	C	12	552	505	6	3	1864	1812	2	7	1446	1556	5	0	2524	2379	19	3	512	625	
21	2	525	534	12	6	628	611	1	12	612	479	7	3	3293	3308	4	7	1573	1721	7	6	1218	1194	20	3	390	431	
23	2	346	361	14	6	508	479	3	12	332	173	8	3	1041	903	6	7	327	303	9	0	2798	2592	0	4	1553	1531	
3	3	2304	1957	19	6	342	308	7	12	462	382	9	3	2494	2443	7	5	595	436	15	6	1096	894	2	4	2734	2850	
1	3	3041	2983	0	7	446	499	9	12	371	412	10	3	1132	1050	8	7	983	875	17	0	1089	1100	3	4	516	428	
2	3	1635	1690	1	7	897	1240	11	3	1637	1583	9	7	387	317	19	0	326	162	4	4	3214	3219					
3	3	3119	2470	2	7	1480	1515	L = -4	12	3	1926	2026	10	7	781	780	0	1	643	534	5	4	637	680				
4	3	2903	2594	3	7	466	370	H K FO FC	14	3	336	249	11	7	850	1003	1	1	1621	1210	6	4	4615	4642				
6	3	2593	2530	5	7	2385	2230	0	0	273	261	16	3	1187	1222	12	7	333	406	2	1	1367	1472	8	4	4334	4248	
7	3	1163	1017	6	7	638	616	2	0	1605	1665	17	3	699	599	13	7	805	973	3	1	1726	1852	10	4	2139	2191	
8	3	2294	2227	7	7	1732	1487	4	0	524	616	18	3	426	433	14	7	362	430	4	1	1227	950	11	4	1092	1114	
9	3	1010	627	8	7	401	372	6	0	5787	5770	19	3	571	576	16	7	326	316	5	1	2426	2333	14	4	424	348	
10	3	634	1041	9	7	892	834	8	0	1087	1012	20	3	386	432	17	7	615	467	6	1	1732	1041	15	4	964	853	
12	3	798	734	11	7	1313	1123	10	0	2997	2955	22	3	381	389	18	7	487	491	7	1	2068	1954	17	4	1115	1120	
13	3	1326	1526	12	7	536	595	12	0	3521	3632	0	4	302	686	20	7	383	271	8	1	942	786	0	5	1218	1410	
14	3	504	408	13	7	1369	1287	14	0	3117	2872	1	4	3788	3909	0	8	761	867	10	1	1593	1725	1	5	2895	3510	
17	3	498	487	14	7	317	264	16	0	2748	2180	2	4	361	73	1	8	754	710	11	1	3126	2940	2	5	3832	4124	
0	4	2723	2563	15																								

Table 7. (Continued)

9	5	1864	1526	4	10	1119	1183	20	2	573	624	2	7	541	383	L = -7	6	4	737	748	12	8	369	453
10	5	1342	1397	5	10	660	724	21	2	480	448	3	7	371	374	H	K	FC	FC	1	4	1575	1422	
11	5	561	493	6	10	1260	1217	23	2	419	448	4	7	691	630	3	9	897	807	2	4	1846	1997	
12	5	1917	1943	8	10	760	780	1	3	1445	1320	5	7	634	545	5	3	2944	3005	3	4	552	639	
13	5	589	493	10	10	560	524	2	3	2806	2566	6	7	351	13	7	3	1084	1000	4	4	2326	2572	
14	5	1245	1242	11	10	580	585	3	3	3247	3281	8	7	1060	1206	9	0	3203	3396	5	4	494	547	
15	5	415	377	12	10	610	608	4	3	2731	2690	10	7	475	470	11	0	1603	1596	6	4	1784	1695	
1	6	732	773	13	10	461	498	5	3	3790	3828	11	7	904	1028	13	0	746	711	8	4	2077	2173	
2	6	862	824	1	11	512	473	6	3	1805	1607	12	7	639	739	15	0	417	367	9	4	1673	1947	
3	6	1805	1674	3	11	347	303	7	3	3337	3536	13	7	820	939	17	0	813	629	10	4	825	865	
4	6	704	766	7	11	364	330	8	3	1295	1223	14	7	909	958	19	0	787	769	11	4	680	806	
5	6	1112	1192	10	11	524	504	9	3	2654	2511	16	7	457	506	0	1	1434	1234	12	4	543	283	
6	6	653	636	12	11	537	484	10	3	378	44	17	7	571	501	1	1	1765	1720	13	4	735	792	
7	6	915	997	0	12	357	426	11	3	2201	1345	18	7	381	373	3	1	773	838	14	4	610	623	
8	6	756	856	7	12	444	455	12	3	1080	1052	19	7	47	364	4	1	853	799	15	4	425	413	
9	6	535	514	9	12	663	555	13	3	1179	1086	0	8	840	1036	5	1	2815	2784	17	4	654	665	
10	6	427	463	11	12	393	266	16	3	1049	1095	2	8	492	667	6	1	1477	1331	18	4	811	749	
11	6	1148	1074	11	13	476	342	18	3	793	795	3	8	1101	1224	7	1	3174	3224	20	4	385	374	
13	6	1553	1618	5	14	361	277	0	4	1385	1441	7	8	1021	1062	8	1	1472	1271	0	5	2076	2214	
15	6	1613	961	1	4	1575	1546	9	8	797	753	11	1	1211	947	1	5	2076	2522	12	10	472	300	
16	6	338	159	L = -6	2	4	1239	1270	10	8	324	239	12	1	1220	1204	2	5	3370	3736	13	10	347	347
19	6	334	255	H	K	FO	FC	3	4	3135	3268	15	8	499	301	13	1	704	684	3	5	1085	1040	
0	7	570	593	0	C	5463	5282	4	4	622	403	1	9	641	622	14	1	442	408	4	5	2011	2191	
1	7	2071	2649	2	0	4225	3831	5	4	543	462	3	9	952	828	18	1	388	483	5	5	771	824	
2	7	652	636	6	0	4174	4303	4	4	1033	814	4	9	312	334	20	1	341	330	6	5	396	590	
7	7	1886	2247	8	0	3776	3548	7	4	2808	2781	5	9	964	805	21	1	424	286	7	5	1159	1096	
4	7	294	25	10	0	1157	1147	8	4	461	418	6	9	823	905	0	2	1100	1147	8	5	1616	1497	
5	7	428	86	12	0	2797	2462	9	4	1191	1211	7	9	1307	1203	1	2	882	870	9	5	1634	1442	
6	7	893	852	14	0	2138	2224	16	4	407	457	8	9	633	696	2	2	350	260	10	5	635	613	
7	7	1111	1009	16	0	943	864	14	4	1139	1073	9	9	1081	994	3	2	3050	3578	11	5	432	365	
8	7	812	702	18	0	407	515	16	4	523	366	10	9	924	947	4	2	1937	1994	13	5	558	812	
9	7	1368	1128	22	C	460	423	17	4	378	477	12	9	1003	986	5	2	3267	2995	15	5	530	596	
11	7	942	766	0	1	1823	1866	19	4	572	550	14	9	388	424	6	2	1166	1099	17	5	349	357	
13	7	1006	764	1	1	630	784	0	5	792	804	19	9	439	444	7	2	1530	1555	22	5	377	348	
15	7	892	925	2	1	1654	1467	1	5	501	671	0	10	870	893	8	2	517	489	4	6	928	920	
0	8	456	576	3	1	1077	1053	2	5	985	814	1	10	390	567	10	2	416	495	5	6	691	449	
2	8	616	654	4	1	2355	2435	3	5	808	959	3	10	507	622	11	2	334	515	5	6	705	532	
4	8	475	392	6	1	639	724	4	5	314	460	6	10	392	254	12	2	1070	1021	7	6	693	436	
5	8	365	411	7	1	1855	970	6	5	435	732	13	10	444	466	13	2	756	844	8	6	578	390	
6	8	586	556	8	1	941	1006	7	5	1331	1775	3	11	508	475	14	2	828	773	11	6	611	576	
7	8	1225	1162	16	1	1311	1396	8	5	1292	1182	5	11	586	567	17	2	971	972	12	6	459	490	
9	8	556	486	13	1	1252	1243	9	5	1170	1305	10	11	357	333	19	2	491	448	13	6	1842	1894	
9	8	1374	1413	16	1	888	794	17	5	572	767	12	11	399	237	22	2	558	537	14	6	497	389	
10	8	332	129	17	1	929	979	12	5	808	780	16	11	333	51	0	3	471	325	15	6	1395	1398	
11	8	901	813	18	1	735	593	13	5	851	817	1	12	580	664	2	3	822	596	6	7	343	387	
13	8	416	392	21	1	414	309	14	5	878	806	3	12	352	386	3	3	1922	1770	1	7	2574	2958	
15	8	507	450	0	2	849	902	16	5	700	628	6	12	349	318	4	3	2200	2465	3	7	1808	2172	
16	8	413	324	1	2	886	903	0	6	2971	3401	9	12	339	278	5	3	2084	2288	5	7	1027	1140	
17	8	644	650	2	2	4147	4154	1	6	1689	1867	11	12	403	372	6	3	1192	1602	7	7	743	623	
19	8	445	438	3	2	974	1165	2	6	4308	4837	13	12	362	206	7	3	1676	1580	8	7	906	894	
0	9	454	604	4	2	2323	2124	3	6	1185	1335	14	12	329	94	8	3	1855	2352	9	7	337	75	
1	9	299	178	5	2	448	142	4	6	2322	2849	0	13	402	333	9	3	1106	1110	11	7	493	588	
3	9	302	175	7	2	724	477	5	6	833	1076	4	13	358	233	10	3	2115	2301	2	8	925	1050	
5	9	361	155	9	2	671	604	6	6	973	908	10	13	420	416	12	3	307	306	4	8	347	364	
7	9	591	651	11	2	1365	1423	8	6	1733	1532	12	13	405	205	14	3	414	26	7	8	552	559	
14	9	371	494	12	2	752	543	10	6	656	540	6	14	284	118	16	3	816	614	8	8	494	483	
18	9	518	372	13	2	599	769	13	6	699	768	19	3	726	942	9	8	956	991	15	1	368	289	
0	1	681	723	14	2	502	428	15	6	720	692	20	3	365	212	10	8	341	355	17	1	640	669	
2	10	740	809	18	2	682	705	0	7	457	325	24	3	318	119	11	8	762	843	19	1	435	449	

Table 7. (Continued).

0	2	908	743	15	5	665	719	5	11	444	278	5	3	1249	1290	5	7	972	952	17	1	297	26	5	6	412	459
1	2	1301	913	15	5	356	294	9	11	514	462	6	3	2569	2765	6	7	363	313	18	1	587	545	6	6	834	741
3	2	1597	1908	19	5	459	539	11	11	480	427	8	3	1863	1978	8	7	575	644	19	1	565	569	9	6	582	505
4	2	733	814	c	6	1873	2069	2	12	325	304	9	3	1442	1248	10	7	553	579	6	2	1710	1491	10	6	509	475
5	2	1361	1573	1	6	427	605	1	12	522	617	10	3	550	643	11	7	1344	1522	1	2	571	726	11	6	748	685
6	2	580	634	2	6	2664	3096	5	12	335	179	14	3	386	295	13	7	1346	1397	2	2	884	896	12	6	1651	1844
7	2	689	774	3	6	1417	1272	8	12	504	423	16	3	565	449	15	7	687	733	3	2	1847	1938	13	6	820	894
8	2	477	223	4	6	2374	2422	10	13	469	375	19	3	563	645	0	8	295	419	4	2	322	125	14	6	1679	1732
9	2	663	481	5	5	709	867			21	3	411	416	2	8	442	459	5	2	2593	2793	15	5	485	565		
10	2	812	610	7	6	433	418	L = -9		0	4	1824	1894	4	8	414	413	6	2	707	778	16	6	678	673		
11	2	474	521	8	6	675	708	H	K	F0	FC	1	4	403	591	5	8	872	966	8	2	1015	923	19	6	318	123
12	2	419	312	9	6	574	563	1	0	2871	2641	2	4	591	514	7	8	317	156	9	2	1151	1214	0	7	546	640
15	2	492	601	11	6	370	330	3	0	2801	2667	3	4	1985	2121	14	8	418	456	10	2	791	853	2	7	385	347
16	2	390	532	12	6	1237	1490	7	0	2451	2434	5	4	557	428	18	8	462	455	11	2	606	586	3	7	756	805
18	2	798	787	13	6	349	276	9	0	2789	2723	6	4	1396	1316	0	9	881	1015	18	2	396	431	5	7	861	881
20	2	428	646	14	6	1147	1156	11	0	2255	2327	7	4	545	495	2	9	1206	1216	19	2	474	390	6	7	527	373
3	9	983	1133	16	6	513	523	15	0	796	903	8	4	980	1205	3	9	854	990	20	2	352	314	7	7	335	388
2	3	1383	1564	c	7	617	806	17	5	427	263	9	4	828	677	4	9	573	590	21	2	542	508	8	7	372	244
4	3	1512	1498	3	7	914	958	19	c	619	591	12	4	420	609	5	9	1324	1438	c	3	2272	2245	19	7	550	697
5	3	635	812	4	7	487	256	r	1	1398	1300	13	4	569	611	6	9	476	299	1	3	2013	2076	14	7	404	466
7	3	1713	1595	5	7	668	682	1	1	829	472	14	4	359	351	7	9	477	416	2	3	755	859	1	8	668	830
8	3	647	549	6	7	612	456	2	1	942	936	15	4	634	533	8	9	433	471	3	3	2231	2451	2	9	662	821
9	3	348	257	7	7	345	347	3	1	964	855	16	4	340	191	3	10	338	424	4	3	946	1162	4	8	887	1046
10	3	561	556	10	7	427	524	4	1	1399	1497	17	4	363	320	14	10	385	326	5	3	1845	2156	5	8	469	354
11	3	564	645	11	7	343	273	7	1	1479	1814	18	4	1005	906	16	10	553	446	7	3	1946	2098	6	8	727	803
12	3	1133	956	12	7	559	541	8	1	2045	1973	20	4	755	754	1	11	384	334	8	3	841	715	10	8	495	572
13	3	746	815	13	7	415	462	9	1	2719	2800	0	5	379	113	4	11	416	360	9	3	1317	1390	12	8	652	622
14	3	652	676	14	7	692	770	10	1	1596	1588	1	5	1354	1431	1	12	324	298	10	3	1357	1325	17	8	365	330
15	3	856	748	16	7	473	470	11	1	1062	1242	2	5	806	665	10	12	448	486	11	3	920	1109	1	9	363	341
17	3	790	644	0	8	421	532	13	1	301	336	3	5	1922	1140	12	12	476	392	12	3	798	669	2	9	645	838
18	3	1136	1236	1	8	338	357	15	1	703	752	4	5	1674	1669	1	13	346	216	14	3	666	654	3	9	395	368
19	3	871	261	3	8	531	555	16	1	416	401	5	5	451	394	7	13	444	311	15	3	607	489	4	9	964	1087
20	3	400	307	6	8	445	519	17	1	704	808	6	5	717	719	9	13	433	273	17	3	901	865	5	9	565	683
21	3	673	641	7	8	656	609	19	1	415	456	7	5	1196	1052					18	3	937	906	6	9	539	519
0	4	1602	1839	9	8	422	461	6	2	1018	990	8	5	1036	1170	L = -10		19	3	741	607	7	9	813	848		
1	4	536	367	10	8	467	509	1	2	543	651	10	5	298	190	H	K	FC	FC	20	3	552	585	9	9	522	499
2	4	335	234	12	8	459	531	2	2	1206	1417	11	5	467	431	0	8	844	623	21	3	491	481	15	9	352	153
3	4	1052	831	14	8	371	350	3	2	1167	1030	12	5	1379	1314	2	6	690	555	c	4	1405	1505	17	9	501	366
4	4	1687	1584	15	8	463	423	4	2	1143	1148	13	5	1385	1460	4	0	553	298	1	4	897	1009	1	10	358	343
6	4	1692	2056	16	8	346	228	5	2	676	760	14	5	972	953	6	0	1321	1546	3	4	451	238	3	10	987	978
7	4	1801	1960	1	9	374	246	6	2	1006	1144	15	5	989	974	8	0	3747	3949	4	4	1516	1633	5	10	731	689
8	4	764	467	2	9	543	651	7	2	1231	1170	16	5	421	433	10	0	3765	3758	6	4	1477	1522	6	10	473	708
9	4	1662	1848	3	9	405	387	8	2	1233	1352	17	5	455	321	12	1	311	1587	7	4	993	1205	14	10	409	265
11	4	829	961	6	9	367	453	9	2	837	853	6	6	505	512	14	0	882	987	9	4	2095	2089	16	10	444	272
13	4	635	612	7	9	358	217	10	2	1223	1345	1	6	391	420	16	0	1303	1340	10	4	312	485	2	11	323	295
14	4	863	554	8	9	383	269	11	3	878	829	3	6	414	582	18	0	863	864	11	4	295	390	9	11	598	585
15	4	697	667	9	9	362	318	13	2	428	361	4	6	530	447	0	1	1350	1414	13	4	1224	1068	11	11	351	463
16	4	450	276	10	9	388	313	14	2	1215	1253	5	6	375	135	1	1	1397	1365	15	4	602	505	12	11	345	277
5	5	316	391	12	9	756	611	15	2	593	701	6	6	1213	1172	3	1	1302	1183	16	4	380	295	16	11	393	260
1	5	277	490	14	9	733	617	16	2	485	390	7	6	305	10	7	1	384	438	18	4	328	188	7	12	351	326
3	5	409	380	17	9	630	417	17	2	1034	1066	8	6	617	651	8	1	1636	1618	2	5	358	615	8	12	473	395
5	5	787	666	0	10	762	789	19	2	854	870	9	6	456	404	9	1	443	671	7	5	1136	1261	9	12	382	424
6	5	803	884	1	10	513	612	21	2	354	335	13	6	979	928	10	1	2531	2559	9	5	594	592	10	12	521	450
7	5	481	445	3	10	942	929	22	2	462	401	14	6	495	556	11	1	659	847	10	5	428	520</td				

Table 7. (Continued)

L = -1	H	K	FO	FC	2	4	1874	1875	2	9	692	809	6	2	1240	1189	13	6	656	644	11	1	497	587	5	6	326	261
1	0	3265	3796	4	4	4	1483	1865	5	9	1179	1205	8	2	916	1036	14	6	1195	1148	12	1	694	912	6	6	431	292
5	0	2229	1938	6	4	782	1112	7	9	734	697	9	2	1741	1894	16	6	539	526	15	1	621	604	7	6	412	436	
7	0	361	374	6	4	2411	2523	16	9	428	488	10	2	287	359	5	7	568	575	0	2	1274	1281	9	6	894	887	
9	c	1356	1363	7	4	573	434	18	9	348	317	11	2	1329	1270	6	7	466	478	4	2	2198	2112	12	6	602	637	
11	0	1169	1274	8	4	1527	2138	2	10	465	518	15	2	337	219	7	7	440	549	6	2	2052	2066	13	6	516	556	
13	c	507	544	10	4	1024	1233	3	10	435	608	19	2	424	294	9	7	320	366	7	2	1237	1184	14	6	336	152	
15	0	1389	1478	13	4	482	446	4	10	877	914	21	2	442	493	10	7	725	854	8	2	640	697	1	7	1206	1247	
17	0	809	826	14	4	326	435	5	10	403	423	23	2	339	113	12	7	781	802	9	2	1502	1536	3	7	1331	1507	
6	1	1193	1296	15	4	428	458	6	10	633	842	0	3	1817	1903	0	8	425	431	10	2	358	372	4	7	346	413	
1	1	3145	2582	18	4	643	449	8	10	784	826	1	3	1050	1163	1	8	763	900	11	2	680	800	5	7	516	586	
2	1	444	423	20	4	584	623	10	10	613	561	3	3	2576	2558	2	8	676	824	12	2	370	494	6	7	589	471	
3	1	2146	2062	23	4	401	212	16	10	504	317	4	3	545	719	4	9	911	1069	13	2	534	422	8	7	418	308	
4	1	1751	1535	0	5	1520	1740	4	11	397	284	5	3	2494	2686	5	6	670	581	16	2	336	380	13	7	646	658	
5	1	1331	1228	2	5	809	960	8	11	437	432	6	3	511	348	6	8	820	820	17	2	351	206	0	8	606	723	
6	1	740	746	3	5	492	694	0	11	314	246	7	3	2668	2812	7	8	935	797	19	2	372	200	2	8	372	517	
7	1	1153	1273	4	5	393	351	10	11	561	573	8	3	1058	1030	12	8	462	574	20	2	610	625	3	8	853	866	
8	1	1339	1425	5	5	273	133	1	12	507	490	9	3	1835	1937	1	9	564	679	1	3	1018	1088	5	8	1159	1228	
9	1	1860	2132	6	6	714	653	10	12	359	351	10	3	1392	1278	2	9	563	682	2	3	482	369	7	8	701	603	
10	1	1934	1607	7	5	662	685	12	12	359	325	11	3	1307	1264	3	9	531	579	4	3	372	247	8	9	332	354	
11	1	1428	1420	10	5	380	372	7	13	346	93	12	3	346	213	4	9	1022	1328	5	3	1431	1260	5	9	589	612	
12	1	1059	1029	11	5	572	662	9	13	416	233	13	3	542	567	5	9	849	875	6	3	599	566	6	9	597	477	
15	1	582	525	12	5	1071	1051					18	3	630	488	6	9	1045	1041	7	3	1337	1096	7	9	560	558	
17	1	435	507	13	5	862	952	L = -12		20	3	387	448	7	9	966	981	8	3	383	480	8	9	445	566			
19	1	343	426	14	5	1287	1366	H	K	FO	FC	24	3	348	287	8	9	529	543	9	3	615	673	10	9	465	352	
0	2	929	856	15	5	888	888	C	0	2698	2574	0	4	995	1138	9	9	577	473	10	3	274	65	16	9	373	334	
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2	2	838	828	19	5	355	307	4	0	2648	2649	2	4	828	970	6	10	665	801	13	3	312	531	3	10	357	308	
3	2	404	164	9	6	703	712	6	0	517	449	5	4	398	297	8	10	375	353	15	3	316	263	4	10	609	551	
4	2	2684	2700	2	6	401	309	8	0	1788	1857	6	4	1046	963	9	10	373	574	16	3	414	314	6	10	738	676	
5	2	546	342	3	6	476	434	10	0	3043	3235	7	4	359	204	11	10	416	502	18	3	448	373	8	10	684	596	
6	2	2464	2603	4	6	466	563	12	0	1134	1200	8	4	301	36	5	11	319	238	20	3	664	528	10	10	638	521	
7	2	1358	1378	5	6	297	220	16	0	353	372	9	4	532	451	12	11	332	248	0	4	865	885	0	11	389	220	
8	2	813	898	6	6	1005	990	18	0	552	503	10	4	620	728	15	11	372	138	1	4	443	402	10	11	452	503	
9	0	2259	2172	9	6	605	723	22	0	393	64	13	4	603	524	8	12	476	304	2	4	1544	1655	12	11	341	315	
10	1	2107	1744	11	6	822	834	0	1	908	1045	15	4	479	378	5	13	336	143	3	4	898	1034	1	12	352	342	
11	2	849	795	15	6	431	408	1	1	1482	1499	19	4	576	518	4	4	1241	1314									
13	2	336	276	0	7	280	302	2	1	1366	1465	0	5	406	421	L = -13		5	4	1176	1171	L = -14						
14	2	652	793	1	7	1077	1276	3	1	452	476	1	5	584	665	H	K	FO	FC	6	4	513	701	H	K	FO	FC	
16	2	643	750	2	7	307	250	4	1	245	25	2	5	561	693	1	0	1615	1742	7	4	299	466	0	0	3199	3156	
17	2	742	842	3	7	573	706	5	1	799	679	3	5	375	360	3	0	962	741	8	4	985	1137	2	0	2647	2713	
19	2	669	734	4	7	857	778	6	1	906	747	4	5	625	729	5	0	619	463	10	4	430	548	4	0	2253	2335	
0	3	855	1002	5	7	288	235	8	1	913	823	7	5	857	1034	7	5	503	286	14	4	332	478	6	0	1985	1873	
1	3	1975	2152	6	7	565	551	9	1	321	250	8	5	272	195	13	0	532	631	16	4	414	486	8	0	569	422	
2	3	655	903	9	7	568	611	10	1	736	762	10	5	631	634	15	0	1541	1580	0	5	1280	1367	14	0	1268	1441	
3	3	422	328	10	7	422	458	11	1	292	225	11	5	503	415	17	0	1124	1212	2	5	1151	1348	16	0	800	772	
4	3	1377	1618	11	7	1124	1162	12	1	329	148	15	5	352	379	21	0	447	542	5	5	317	125	20	0	451	442	
5	3	1534	1416	13	7	1458	1552	13	1	312	192	20	5	464	404	23	0	375	248	6	5	683	829	0	1	1214	1340	
6	3	1041	1161	15	7	618	741	14	1	1007	1042	0	6	977	911	0	1	830	916	7	5	282	78	1	1	787	901	
7	3	611	598	0	8	812	839	15	1	857	977	1	6	1027	1139	1	1	2972	2862	10	5	403	449	2	1	1426	1602	
8	3	379	484	3	8	1059	1036	16	1	1022	1447	2	6	1102	1249	2	1	727	820	13	5	358	585	5	1	918	919	
9	3	519	638	4	8	308	386	18	1	438	411	3	6	705	713	3	1	1540	1627	14	5	863	845	7	1	556	455	
11	3	1281	1479	5	8	1181	1345	19	1	392	444	4	6	344	193	4	1	1341	1355	15	5	440	464	8	1	539	474	
17	3	322	46	7	8	1055	1015	0	2	1146	1205	5	6	435	446	5	1	935	892	1								

Table 7. (Continued).

0	2	538	563	10	6	744	632	7	2	470	282	12	10	298	138	8	4	683	696	8	1	763	888	10	7	379	247	
1	2	440	548	12	6	576	482	10	2	523	589	11	2	465	569	11	4	645	792	9	1	556	511	11	7	760	640	
2	2	562	612	1	7	936	1093	11	2	455	527	L =-16	12	4	640	710	11	1	826	700	12	7	391	295				
4	2	777	762	2	7	519	669	14	2	351	254	H K F0 FC	13	4	583	678	13	1	918	832	13	7	789	738				
5	2	737	661	5	7	451	331	20	2	433	527	G 0 1035	980	5	337	239	15	1	1019	960	16	7	374	232				
6	2	1142	1232	7	7	544	530	22	2	417	413	2	0	828	809	1	5	670	580	16	1	296	447	1	8	350	353	
7	2	393	526	10	7	747	652	6	3	957	830	4	6	335	448	2	5	575	413	17	1	611	496	2	8	328	479	
8	2	637	653	12	7	941	852	2	3	1352	1256	6	0	878	767	3	5	545	430	C 2	416	246	9	8	343	290		
9	2	538	561	14	7	416	397	4	3	1468	1469	8	0	1171	1009	5	5	365	476	2	2	1150	1163	11	8	424	316	
11	2	787	797	15	7	382	251	5	3	698	725	10	0	918	899	6	5	576	827	3	2	821	821	1	9	565	421	
12	2	674	654	4	8	372	457	6	3	1008	1094	12	0	1212	1084	7	5	877	993	4	2	996	914	3	9	452	308	
14	2	549	702	5	8	562	352	7	3	1458	1557	14	0	1704	1436	8	5	496	687	5	2	1334	1282	5	9	334	178	
15	2	501	559	6	8	561	641	11	3	1082	1140	16	0	1334	1291	9	6	655	610	6	2	265	83	8	9	377	363	
17	2	338	460	7	8	628	624	13	3	500	670	20	0	456	415	10	5	514	546	7	2	1212	1128	10	9	319	156	
18	2	343	376	16	8	352	430	2	4	474	446	22	0	372	215	11	5	640	570	8	2	368	311	13	9	364	235	
2	3	782	847	19	8	506	440	3	4	308	152	0	1	290	337	13	5	640	705	9	2	387	405	2	10	566	511	
2	3	432	491	0	9	332	433	4	4	721	733	1	1	755	679	14	5	385	353	10	2	598	451	4	10	493	509	
3	3	610	676	4	9	602	615	5	4	740	779	2	1	910	998	16	5	363	471	16	3	403	291	8	10	329	265	
4	3	847	836	6	9	692	627	6	4	880	969	4	1	694	712	17	5	386	378	C 3	828	769						
5	3	1181	1164	7	6	379	287	7	4	303	148	5	1	381	328	1	6	337	55	2	3	1236	1108	L =-18				
6	3	926	824	9	9	459	441	8	4	615	506	6	1	716	677	4	6	552	488	4	3	1213	1253	H K F0 FC				
7	3	851	950	11	9	458	270	10	4	326	415	7	1	499	518	5	6	526	395	5	3	677	765	6	0	757	841	
8	3	624	841	5	10	345	217	13	4	366	428	8	1	433	413	6	6	580	546	6	3	672	603	2	6	437	443	
9	3	502	672	6	10	358	480	16	4	604	584	9	1	458	505	8	6	592	458	7	3	852	966	4	0	363	541	
10	3	625	705	9	10	544	544	18	4	614	574	10	1	444	408	9	6	524	468	8	3	387	102	8	0	1040	1020	
11	3	705	659	1	12	435	292	1	5	292	427	11	1	574	472	17	6	1254	1135	9	3	496	569	10	0	1268	1175	
13	3	366	349	5	12	290	94	2	5	359	302	12	1	427	355	12	6	1157	1057	11	3	513	446	12	0	831	724	
15	3	479	356			9	5	573	374	1	2	730	443	14	6	450	339	15	3	691	676	14	0	854	734			
17	3	675	539	L =-15		10	5	694	752	2	2	410	519	17	6	328	201	20	3	343	301	16	0	659	500			
19	3	504	565	H K F0 FC		12	5	898	900	3	2	1046	962	0	7	367	280	2	4	333	362	18	0	331	251			
21	3	429	376	1	0	375	524	20	5	335	179	4	2	780	803	1	7	689	869	4	4	778	801	1	1	404	318	
0	4	288	516	3	0	1269	1340	1	6	1075	1123	5	2	488	379	2	7	695	784	6	4	1300	1317	2	1	675	640	
2	4	1001	1153	7	0	415	493	3	6	725	796	6	2	1071	1203	3	7	374	539	8	4	1346	1373	3	1	606	523	
3	4	367	305	9	0	1067	967	5	6	435	333	7	2	274	325	4	7	304	341	9	4	617	685	4	1	937	1059	
5	4	698	743	11	0	977	941	7	6	729	941	8	2	634	763	8	7	465	447	10	4	680	629	6	1	541	526	
6	4	789	644	13	0	350	481	9	6	825	887	12	2	1681	1137	10	7	527	415	15	4	602	498	7	1	375	410	
7	4	780	854	15	0	1093	1129	10	6	692	694	14	2	922	782	12	7	583	427	16	4	488	430	14	1	594	483	
8	4	526	361	17	0	919	981	11	6	973	943	15	2	577	646	18	7	506	370	18	4	619	619	1	2	708	709	
11	4	475	440	21	0	446	471	12	6	805	746	1	3	961	549	0	8	447	506	6	5	721	758	3	2	726	631	
0	5	366	384	23	0	411	333	13	6	708	632	3	3	450	566	2	8	311	412	2	5	523	539	5	2	525	492	
1	5	354	446	0	1	322	337	14	6	561	612	4	3	799	692	7	8	436	342	3	5	559	498	6	2	581	639	
2	5	612	652	1	1	638	589	17	6	377	403	5	3	994	952	18	8	456	380	7	5	332	256	8	2	382	435	
8	5	719	787	4	1	380	526	3	7	711	689	6	3	1186	1113	2	9	367	370	9	5	550	361	9	2	647	832	
10	5	457	475	6	1	620	713	5	7	561	482	7	3	910	692	5	9	406	306	10	5	597	590	10	2	465	261	
11	5	614	540	8	1	1041	1146	6	7	336	318	8	3	625	522	7	9	347	265	11	5	583	418	12	2	605	593	
12	5	365	372	9	1	411	389	7	7	322	257	9	3	887	836	1	10	330	266	12	5	998	1021	13	2	324	127	
13	5	802	777	10	1	364	400	9	7	439	501	11	3	572	464	7	10	455	220	13	5	444	313	14	2	359	383	
16	5	376	397	11	1	314	290	11	7	431	543	15	3	531	621	6	12	314	160	14	5	529	545	18	2	340	401	
17	5	428	532	12	1	386	294	12	7	357	481	17	3	567	564	1	6	1118	951	1	3	689	552					
0	6	1103	1006	13	1	1092	1077	13	7	374	391	19	3	543	492	L =-17	3	6	827	780	3	3	1340	1286				
1	6	672	667	14	1	483	498	0	8	462	567	21	3	485	421	H K F0 FC	7	6	580	795	5	3	1617	1505				
2	6	962	934	15	1	1051	1078	2	8	430	593	0	4	389	379	1	0	349	214	9	6	522	649	6	3	1165	1037	
3	6	577	1007	16	1	527	480	5	8	319	240	1	4	943	782	3	0	1163	1427	10	6	336	391	7	3	1538	1408	
4	6	654	623	17	1	535	508	17	8	361	292	2	4	449	535	5	0	444	484	12	6	507	588	8	3	670	687	
5	6	718	524	0	2	709	775	1	9	397	377	3	4	1064	1068	0	1	409	302	14	6</td							

Table 7. (Continued)

3	4	891	952	13	1	352	274	10	1	747	572	5	6	581	428	3	4	311	227
5	4	740	657	16	1	327	205	12	1	528	495	6	6	328	252	4	4	497	581
7	4	365	261	18	1	318	222	13	1	291	35	10	6	353	292	6	4	424	591
8	4	499	640	2	2	1007	937	3	2	317	284	1	7	341	309	0	5	352	338
11	4	519	726	3	2	444	504	9	2	447	394	14	7	324	234	9	5	312	137
12	4	512	506	4	2	918	702	12	2	336	87	16	7	362	135	11	7	436	486
13	4	418	574	5	2	720	927	13	2	451	431	6	9	338	235				
15	4	302	67	6	2	563	445	16	2	417	325	10	9	297	139				
17	4	477	416	7	2	912	954	18	2	464	437					L = -24			
0	5	362	372	9	2	452	466	3	3	520	508	L = -22		H	K	FC	FC		
1	5	486	404	10	2	550	254	5	3	695	606	H	K	F0	FC	8	9	500	486
2	5	288	365	12	2	422	199	6	3	397	385	6	0	391	341	10	8	383	302
3	5	499	510	20	3	306	159	7	3	462	399	8	0	619	513	14	6	453	332
5	5	375	352	0	3	454	442	8	3	462	454	10	6	724	555	8	1	322	418
7	5	623	678	2	3	564	594	9	3	620	435	14	0	661	663	2	2	385	414
8	5	480	526	4	3	489	529	1	4	340	279	16	0	331	312	5	2	426	348
10	5	379	333	7	3	723	697	14	4	372	391	3	1	406	346	3	3	528	531
14	5	520	435	9	3	547	533	17	4	507	453	6	1	376	261	4	3	365	322
16	5	454	398	13	3	710	656	18	4	324	42	8	1	828	741	5	3	586	555
17	5	375	194	14	3	517	377	2	5	354	410	9	1	531	554	7	3	612	518
0	6	596	640	16	3	391	305	3	5	400	330	10	1	780	733	1	4	556	455
1	6	483	482	18	3	442	382	4	5	407	307	16	1	375	229	16	4	347	43
2	6	471	577	1	4	344	151	5	5	337	421	3	2	487	304	5	5	380	410
8	6	412	381	5	4	364	374	6	6	517	508	13	2	454	391	7	5	353	344
10	6	721	631	6	4	913	959	1	6	651	556	15	2	442	507	10	6	387	330
11	6	362	370	8	4	999	1025	2	6	612	577	18	2	340	228	12	6	545	401
12	6	735	716	10	4	538	484	3	6	426	344	5	3	339	390	8	7	331	124
14	6	599	452	12	4	333	304	10	6	330	180	12	3	365	175				
1	7	356	458	14	4	324	151	4	7	441	341	17	3	402	286	L = -25			
2	7	581	533	0	5	523	551	6	7	334	279	18	3	369	139	H	K	FC	FC
18	7	393	357	1	5	337	366	8	8	336	91	19	3	455	308	11	8	347	273
0	8	666	684	2	5	773	767	4	9	360	274	1	4	394	374	3	1	381	356
2	8	356	484	3	5	319	280					14	4	449	279	4	1	355	230
13	8	233	396	4	5	423	389	L = -21		4	5	489	486	7	2	346	328		
2	9	368	389	12	5	427	472	H	K	F0	FC	5	5	567	576	13	2	363	24
3	9	519	386	14	5	363	458	7	6	864	789	7	5	430	411	1	3	437	324
4	9	449	476	1	6	516	411	9	0	1105	1060	13	5	360	153	4	4	492	372
5	9	568	479	3	6	769	685	11	0	935	768	2	6	361	244	6	4	442	501
10	9	430	379	6	6	297	171	15	0	408	317	10	6	478	425	12	5	353	194
5	11	360	327	1	7	709	770	0	1	419	521	6	7	462	315	13	5	350	45
				3	7	439	505	2	1	302	138	6	8	392	285	L = -26			
				6	8	433	239	7	1	537	509	L = -23		H	K	FC	FC		
				H	K	F0	FC	12	9	295	38	14	1	411	424				
3	0	855	958	4	10	581	511	1	2	306	190	H	K	FC	FC	12	2	329	132
5	0	345	386	6	10	462	393	8	2	334	413	7	0	499	490	L = -27			
7	6	226	475					11	2	394	179	9	0	915	856	L = -27			
9	0	780	679	L = -20				17	2	370	289	11	0	610	656	H	K	FC	FC
11	0	411	259	H	K	F0	FC	4	3	358	255	1	1	312	290	S	0	482	311
13	0	528	366	0	0	893	1059	5	3	324	226	3	1	330	323	7	0	449	277
15	0	370	227	2	0	491	576	8	3	352	188	9	1	403	275				
0	1	613	746	4	0	790	871	9	3	350	253	11	1	406	257				
1	1	723	729	5	0	391	440	10	3	328	226	13	1	351	358				
2	1	508	397	12	0	328	238	14	3	448	307	15	1	333	316				
3	1	474	638	0	1	603	501	18	3	375	250	3	2	404	305				
4	1	446	342	3	1	474	429	19	3	438	342	11	2	360	239				
5	1	524	693	4	1	451	577	2	4	393	404	0	2	451	365				
8	1	421	405	7	1	453	560	4	4	410	421	2	3	472	495				
10	1	356	282	8	1	731	599	15	5	359	89	4	3	379	339				
11	1	545	518	6	1	476	545	3	6	469	536	6	3	397	295				

Table 8. Final parameters^a for $(\text{NaC}^+)_3\text{Sb}_7^{3-}$

Positional parameters for heavy atoms

	x	y	z
Sb(1)	0.22558(15)	0.18851(22)	0.41768(10)
Sb(2)	0.17610(12)	0.07328(20)	0.47838(10)
Sb(3)	0.32617(13)	0.25736(22)	0.50100(12)
Sb(4)	0.37464(11)	0.09264(20)	0.55983(10)
Sb(5)	0.26285(14)	0.33736(20)	0.56892(13)
Sb(6)	0.27292(12)	0.01810(20)	0.57388(10)
Sb(7)	0.19929(12)	0.18028(21)	0.58058(10)
Na(1)	0.66271(59)	0.28473(89)	0.61846(50)
Na(2)	0.53016(61)	0.3711(10)	0.28429(51)
Na(3)	0.57729(59)	0.8286(11)	0.13623(53)

Anisotropic thermal parameters ($\times 10^3$)^b for heavy atoms

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	5.9(1)	12.7(2)	2.22(5)	3.9(1)	0.36(6)	0.34(9)
Sb(2)	3.27(7)	11.3(2)	3.26(6)	0.4(1)	-0.14(5)	-1.88(9)
Sb(3)	3.91(8)	11.6(2)	4.46(8)	0.3(1)	1.39(6)	2.2(1)
Sb(4)	2.68(6)	10.9(2)	3.64(6)	1.8(1)	0.57(5)	0.7(1)
Sb(5)	4.50(9)	8.5(2)	5.32(9)	0.5(1)	1.15(7)	-1.9(1)
Sb(6)	3.95(8)	10.2(2)	3.05(6)	0.5(1)	0.55(5)	0.92(9)
Sb(7)	3.78(8)	11.3(2)	3.43(6)	1.0(1)	1.57(6)	-0.2(1)
Na(1)	3.8(3)	6.8(8)	2.8(3)	2.0(4)	1.0(2)	0.7(4)
Na(2)	3.5(3)	12(1)	2.8(3)	2.0(5)	1.1(2)	1.0(4)
Na(3)	3.0(3)	13(1)	3.1(3)	-1.6(6)	0.8(2)	0.1(5)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

^bThe anisotropic temperature factors have the general form $\exp(-h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})$.

Table 8. (Continued)

Positional and thermal parameters for the first crypt

	x	y	z	B
N(101)	0.6057(14)	0.0948(22)	0.6186(12)	8.8(8)
C(102)	0.6020(21)	0.0839(34)	0.6771(18)	10.6(13)
C(103)	0.5829(19)	0.1808(32)	0.6954(16)	9.9(11)
O(104)	0.6282(11)	0.2516(17)	0.7031(9)	8.6(6)
C(105)	0.6810(21)	0.2450(34)	0.7536(18)	10.6(12)
C(106)	0.7205(21)	0.3245(35)	0.7619(19)	10.9(13)
O(107)	0.7373(12)	0.3329(20)	0.7122(11)	10.4(7)
C(108)	0.7718(23)	0.4239(39)	0.7184(21)	12.8(15)
C(109)	0.7704(26)	0.4627(41)	0.6716(24)	15.2(16)
N(110)	0.7186(16)	0.4677(24)	0.6220(14)	9.2(8)
C(111)	0.7298(22)	0.4807(35)	0.5721(18)	9.9(13)
C(112)	0.7611(19)	0.3989(33)	0.5577(16)	10.0(11)
O(113)	0.7277(11)	0.3151(20)	0.5559(9)	8.3(6)
C(114)	0.7573(21)	0.2276(36)	0.5483(18)	9.6(12)
C(115)	0.7250(18)	0.1441(28)	0.5582(15)	7.7(10)
O(116)	0.7270(9)	0.1506(15)	0.6150(8)	6.9(5)
C(117)	0.7136(17)	0.0599(27)	0.6351(14)	7.8(9)
C(118)	0.6499(17)	0.0237(28)	0.6100(14)	7.8(9)
C(119)	0.5465(18)	0.0930(28)	0.5779(16)	9.4(10)
C(120)	0.5495(20)	0.1347(34)	0.5232(18)	11.6(12)
O(121)	0.5624(13)	0.2400(21)	0.5323(11)	9.0(7)
C(122)	0.5170(22)	0.2992(36)	0.5446(19)	12.5(14)
C(123)	0.5356(17)	0.4039(28)	0.5468(14)	8.8(9)
O(124)	0.5881(13)	0.4238(21)	0.5892(11)	10.4(7)
C(125)	0.6142(28)	0.5203(44)	0.5952(22)	14.2(16)
C(126)	0.6690(27)	0.5316(38)	0.6289(21)	13.4(15)

Table 8. (Continued) . . .

Positional and thermal parameters for the second crypt

	x	y	z	B
N(201)	0.6393(16)	0.3287(27)	0.3723(14)	10.8(9)
C(202)	0.6877(23)	0.3230(36)	0.3491(19)	12(1)
C(203)	0.6834(27)	0.3905(42)	0.3088(25)	15(2)
O(204)	0.6323(16)	0.3958(25)	0.2572(14)	13.8(9)
O(205)	0.6375(22)	0.3237(35)	0.2169(20)	12(1)
C(206)	0.5836(27)	0.3316(37)	0.1777(21)	13(1)
O(207)	0.5366(21)	0.2890(29)	0.1940(16)	17(1)
C(208)	0.4652(38)	0.2839(55)	0.1526(30)	20(2)
C(209)	0.4262(50)	0.3642(89)	0.1543(43)	28(4)
N(210)	0.4335(29)	0.4466(52)	0.1871(24)	18(2)
C(211)	0.4528(35)	0.5520(62)	0.1852(31)	20(2)
C(212)	0.4652(72)	0.569(11)	0.2380(68)	38(8)
O(213)	0.5142(19)	0.5571(29)	0.2652(18)	16(1)
C(214)	0.5175(22)	0.6048(34)	0.3097(21)	11(1)
C(215)	0.5612(23)	0.5790(38)	0.3566(20)	13(1)
O(216)	0.5505(13)	0.4818(21)	0.3663(11)	10.7(7)
C(217)	0.5906(24)	0.4515(35)	0.4175(20)	13(1)
C(218)	0.6450(23)	0.4133(36)	0.4138(19)	13(1)
C(219)	0.6232(23)	0.2358(39)	0.3994(21)	13(1)
C(220)	0.5872(33)	0.1727(47)	0.3612(27)	18(2)
O(221)	0.5265(15)	0.2052(22)	0.3307(11)	12.0(8)
C(222)	0.4756(29)	0.2090(41)	0.3359(23)	15(2)
C(223)	0.4266(33)	0.2429(56)	0.3189(30)	18(2)
O(224)	0.4168(22)	0.3193(37)	0.2889(22)	20(2)
C(225)	0.3742(36)	0.3351(60)	0.2292(35)	21(3)
C(226)	0.3866(36)	0.4153(58)	0.2034(29)	19(2)

Table 8. (Continued)

 Positional and thermal parameters for the third crypt^c

	x	y	z	B
N(301)	0.5912(19)	0.9531(29)	0.2287(16)	12(1)
C(302)	0.5654(25)	0.9192(40)	0.2671(21)	12(2)
C(303)	0.4978(27)	0.9655(44)	0.2184(22)	14(2)
O(304)	0.4822(16)	0.8642(25)	0.1816(13)	12(1)
C(305)	0.4581(32)	0.9486(49)	0.1420(25)	17(2)
C(306)	0.4244(24)	0.8824(37)	0.1043(20)	11(1)
O(307)	0.4695(17)	0.8624(27)	0.0658(14)	13(1)
C(308)	0.4409(27)	0.7681(42)	0.0576(22)	14(2)
C(309)	0.4797(26)	0.7426(40)	0.0036(23)	13(2)
N(310)	0.5493(19)	0.6942(28)	0.0310(15)	11(1)
C(311)	0.5997(24)	0.7262(36)	0.0157(20)	11(1)
C(312)	0.5872(27)	0.8393(39)	0.0014(22)	13(2)
O(313)	0.6304(18)	0.8426(28)	0.0541(15)	14(1)
C(314)	0.6559(25)	0.9532(39)	0.0603(20)	12(2)
C(315)	0.6097(26)	0.0060(42)	0.0657(21)	13(2)
O(316)	0.5990(18)	0.0174(28)	0.1238(14)	14(1)
C(317)	0.6508(24)	0.0092(38)	0.1780(19)	11(2)
C(318)	0.6294(22)	0.0299(35)	0.2191(18)	10(1)
C(319)	0.6555(33)	0.8977(52)	0.2578(27)	18(2)
C(320)	0.6207(28)	0.7667(45)	0.2542(23)	14(2)
O(321)	0.6721(20)	0.7624(32)	0.2240(17)	16(1)
C(322)	0.6907(31)	0.6851(45)	0.2042(25)	16(2)
C(323)	0.6526(31)	0.6332(46)	0.1660(29)	16(2)
O(324)	0.5958(18)	0.6157(29)	0.1411(15)	14(2)
C(325)	0.5819(26)	0.5787(40)	0.0813(21)	13(2)
C(326)	0.5282(26)	0.6252(40)	0.0589(21)	12(2)

^cEstimated standard deviations in parameters from FBLS⁷⁸
are in parentheses.

Table 9. Interatomic distances and angles^a for the Sb₇³⁻ anion

Distances (Å)						
	Sb(2)	Sb(3)	Sb(4)	Sb(5)	Sb(6)	Sb(7)
Sb(1)	2.711(16)	2.776(43)	4.339(69)	4.190(19)	4.432(24)	4.365(14)
Sb(2)		4.209(12)	4.432(52)	4.434(25)	2.838(46)	2.880(12)
Sb(3)			2.755(15)	2.824(22)	4.159(14)	4.211(34)
Sb(4)				4.313(5)	2.708(8)	4.448(12)
Sb(5)					4.409(4)	2.693(6)
Sb(6)						2.856(5)

Bonded Angles							
Atom 1	Atom 2	Atom 3	Degrees	Atom 1	Atom 2	Atom 3	Degrees
	(Vertex)				(Vertex)		
Sb(1)	Sb(3)	Sb(4)	103.4(8)	Sb(5)	Sb(7)	Sb(2)	105.4(6)
Sb(4)	Sb(3)	Sb(5)	101.3(1)	Sb(5)	Sb(7)	Sb(6)	105.2(2)
Sb(1)	Sb(3)	Sb(5)	96.9(2)	Sb(1)	Sb(2)	Sb(6)	106.0(1)
Sb(2)	Sb(6)	Sb(7)	60.8(3)	Sb(1)	Sb(2)	Sb(7)	102.6(4)
Sb(6)	Sb(7)	Sb(2)	59.3(9)	Sb(4)	Sb(6)	Sb(2)	106.1(7)
Sb(7)	Sb(2)	Sb(6)	59.9(7)	Sb(4)	Sb(6)	Sb(7)	106.1(2)
Sb(3)	Sb(5)	Sb(7)	99.5(5)				
Sb(3)	Sb(1)	Sb(2)	100.2(3)				
Sb(3)	Sb(4)	Sb(6)	99.2(6)				

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

Table 10. Interatomic distances and angles^a for the first
cryptated sodium cation

Bonded Distances			Nonbonded Distances		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (°)
N(101)	C(102)	1.52(5)	N(101)	N(110)	5.76(4)
C(102)	C(103)	1.52(5)	N(101)	O(104)	2.97(4)
C(103)	O(104)	1.40(4)	N(101)	O(116)	2.96(4)
O(104)	C(105)	1.47(5)	N(110)	O(121)	2.90(4)
C(105)	C(106)	1.40(5)	N(110)	O(107)	2.87(4)
C(106)	O(107)	1.44(5)	N(110)	O(113)	2.74(4)
O(107)	C(108)	1.47(5)	N(110)	O(124)	2.95(5)
C(108)	C(109)	1.29(6)	O(104)	O(107)	2.72(4)
C(109)	N(110)	1.44(6)	O(104)	O(113)	5.06(5)
N(110)	C(111)	1.38(5)	O(104)	O(116)	3.94(4)
N(110)	C(126)	1.51(5)	O(104)	O(121)	4.11(5)
C(111)	C(112)	1.45(5)	O(104)	O(124)	3.62(4)
C(112)	O(113)	1.39(4)	O(107)	O(113)	3.91(3)
O(113)	C(114)	1.43(5)	O(107)	O(116)	3.47(3)
C(114)	C(115)	1.44(5)	O(107)	O(121)	5.22(9)
C(115)	O(116)	1.43(4)	O(107)	O(124)	4.06(7)
O(116)	C(117)	1.42(4)	O(113)	O(116)	2.72(3)
C(117)	C(118)	1.50(5)	O(113)	O(121)	3.85(4)
C(118)	N(101)	1.49(4)	O(113)	O(124)	3.91(4)
N(101)	C(119)	1.43(5)	O(116)	O(121)	3.94(6)
C(119)	C(120)	1.52(5)	O(116)	O(124)	4.87(4)
C(120)	O(121)	1.49(5)	O(121)	O(124)	2.88(4)
O(121)	C(122)	1.45(5)	Na(1)	C(102)	3.64(5)
C(122)	C(123)	1.50(5)	Na(1)	C(103)	3.41(5)
C(123)	O(124)	1.37(4)	Na(1)	C(105)	3.36(5)
O(124)	C(125)	1.45(6)	Na(1)	C(106)	3.50(6)
C(125)	C(126)	1.30(6)	Na(1)	C(108)	3.53(7)
			Na(1)	C(109)	3.46(6)
Na(1)	N(101)	2.94(3)	Na(1)	C(111)	3.51(5)
Na(1)	N(110)	2.83(3)	Na(1)	C(112)	3.51(5)
Na(1)	O(104)	2.56(3)	Na(1)	C(114)	3.34(6)
Na(1)	O(107)	2.55(5)	Na(1)	C(115)	3.10(4)
Na(1)	O(113)	2.55(4)	Na(1)	C(117)	3.30(4)
Na(1)	O(116)	2.40(2)	Na(1)	C(118)	3.61(4)
Na(1)	O(121)	2.71(5)	Na(1)	C(119)	3.69(5)
Na(1)	O(124)	2.54(3)	Na(1)	C(120)	3.61(6)
			Na(1)	C(122)	3.32(7)
			Na(1)	C(123)	3.37(5)
			Na(1)	C(125)	3.43(6)
			Na(1)	C(126)	3.41(5)

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

Table 10. (Continued)

Bonded Distances			Nonbonded Distances				
Atom 1	Atom 2	Distance (\AA)	Atom 1	Atom 2	Distance (\AA)		
C(119)	Sb(4)	3.88(4)					
C(120)	Sb(4)	4.49(5)					
C(122)	Sb(3)	4.26(6)					
C(122)	Sb(4)	4.48(5)					
Bonded Angles							
Atom 1	Atom 2	Atom 3	Degrees (Vertex)	Atom 1	Atom 2	Atom 3	Degrees (Vertex)
N(101)	C(102)	C(103)	109(3)	C(123)	O(124)	C(125)	120(4)
C(102)	C(103)	O(104)	112(4)	O(124)	C(125)	C(126)	118(5)
C(103)	O(104)	C(105)	117(3)	C(125)	C(126)	N(110)	119(5)
O(104)	C(105)	C(106)	114(4)	N(101)	Na(1)	N(110)	178.2(10)
C(105)	C(106)	O(107)	106(4)	N(101)	Na(1)	O(104)	65.0(9)
C(106)	O(107)	C(108)	105(3)	N(101)	Na(1)	O(116)	66.4(9)
O(107)	C(108)	C(109)	114(5)	N(101)	Na(1)	O(121)	61.6(9)
C(108)	C(109)	N(110)	126(6)	N(110)	Na(1)	O(107)	64.4(10)
C(109)	N(110)	C(111)	117(4)	N(110)	Na(1)	O(113)	61.0(10)
C(109)	N(110)	C(126)	113(4)	N(110)	Na(1)	O(124)	66.4(11)
C(111)	N(110)	C(126)	114(4)	O(104)	Na(1)	O(107)	64.3(9)
N(110)	C(111)	C(112)	113(4)	O(104)	Na(1)	O(113)	163.1(10)
C(111)	C(112)	O(113)	110(4)	O(104)	Na(1)	O(116)	105.0(10)
C(112)	O(113)	C(114)	115(3)	O(104)	Na(1)	O(121)	102.3(11)
O(113)	C(114)	C(115)	110(4)	O(104)	Na(1)	O(124)	90.6(11)
C(114)	C(115)	O(116)	106(3)	O(107)	Na(1)	O(113)	100.1(10)
C(115)	O(116)	C(117)	111(2)	O(107)	Na(1)	O(116)	89.2(11)
O(116)	C(117)	C(118)	116(3)	O(107)	Na(1)	O(121)	165.4(11)
C(117)	C(118)	N(101)	111(3)	O(107)	Na(1)	O(124)	106.0(13)
C(118)	N(101)	C(102)	110(3)	O(113)	Na(1)	O(116)	66.6(9)
C(118)	N(101)	C(119)	116(3)	O(113)	Na(1)	O(121)	93.8(9)
C(119)	N(101)	C(102)	111(3)	O(113)	Na(1)	O(124)	100.4(10)
N(101)	C(119)	C(120)	110(4)	O(116)	Na(1)	O(121)	100.6(10)
C(119)	C(120)	O(121)	107(3)	O(116)	Na(1)	O(124)	161.9(9)
C(120)	O(121)	C(122)	117(3)	O(121)	Na(1)	O(124)	66.6(11)
O(121)	C(122)	C(123)	109(4)				
C(122)	C(123)	O(124)	113(3)				

Table 11. Interatomic distances and angles^a for the second
cryptated sodium cation

Bonded Distances			Nonbonded Distances		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
N(201)	C(202)	1.43(5)	N(201)	N(210)	5.77(11)
C(202)	C(203)	1.36(6)	N(201)	O(204)	3.02(5)
C(203)	O(204)	1.46(6)	N(201)	O(216)	2.93(5)
O(204)	C(205)	1.46(5)	N(201)	O(221)	3.02(5)
C(205)	C(206)	1.33(6)	N(210)	O(207)	3.20(8)
C(206)	O(207)	1.41(6)	N(210)	O(213)	2.72(9)
O(207)	C(208)	1.66(8)	N(210)	O(224)	3.24(8)
C(208)	C(209)	1.44(11)	O(204)	O(207)	2.73(6)
C(209)	N(210)	1.39(11)	O(204)	O(213)	3.59(5)
N(210)	C(211)	1.53(8)	O(204)	O(216)	4.01(5)
N(210)	C(226)	1.35(8)	O(204)	O(221)	4.40(5)
C(211)	C(212)	1.30(15)	O(204)	O(224)	5.43(6)
C(212)	O(213)	1.14(15)	O(207)	O(213)	4.22(6)
O(213)	C(214)	1.29(5)	O(207)	O(216)	5.04(5)
C(214)	C(215)	1.34(6)	O(207)	O(221)	3.73(5)
C(215)	O(216)	1.40(5)	O(207)	O(224)	4.25(8)
O(216)	C(217)	1.40(5)	O(213)	O(216)	2.64(5)
C(217)	C(218)	1.40(6)	O(213)	O(221)	5.11(5)
C(218)	N(201)	1.55(5)	O(213)	O(224)	4.14(6)
N(201)	C(219)	1.55(5)	O(216)	O(221)	3.92(4)
C(219)	C(220)	1.37(7)	O(216)	O(224)	2.83(7)
C(220)	O(221)	1.45(7)	O(221)	O(224)	2.90(6)
O(221)	C(222)	1.52(6)			
C(222)	C(223)	1.31(8)	Na(2)	C(202)	3.56(6)
C(223)	O(224)	1.28(7)	Na(2)	C(203)	3.42(6)
O(224)	C(225)	1.54(8)	Na(2)	C(205)	3.50(6)
C(225)	C(226)	1.36(9)	Na(2)	C(206)	3.36(6)
			Na(2)	C(208)	3.42(8)
Na(2)	N(201)	2.85(6)	Na(2)	C(209)	3.42(12)
Na(2)	N(210)	2.95(7)	Na(2)	C(211)	3.59(8)
Na(2)	O(204)	2.69(4)	Na(2)	C(212)	3.16(16)
Na(2)	O(207)	2.60(4)	Na(2)	C(214)	3.32(5)
Na(2)	O(213)	2.61(4)	Na(2)	C(215)	3.34(5)
Na(2)	O(216)	2.50(3)	Na(2)	C(217)	3.40(6)
Na(2)	O(221)	2.59(3)	Na(2)	C(218)	3.55(8)
Na(2)	O(224)	2.78(5)	Na(2)	C(219)	3.56(7)

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

Table 11. (Continued) . . .

Bonded Distances			Nonbonded Distances				
Atom 1	Atom 2	Distance (\AA)	Atom 1	Atom 2	Distance (\AA)		
			Na(2)	C(220)	3.38(7)		
			Na(2)	C(222)	3.38(6)		
			Na(2)	C(223)	3.33(7)		
			Na(2)	C(225)	3.50(9)		
			Na(2)	C(226)	3.38(9)		
Bonded Angles							
Atom 1	Atom 2	Atom 3	Degrees (Vertex)	Atom 1	Atom 2	Atom 3	Degrees (Vertex)
N(201)	C(202)	C(203)	113(5)	C(223)	O(224)	C(225)	130(6)
C(202)	C(203)	O(204)	123(5)	O(224)	C(225)	C(226)	115(7)
C(203)	O(204)	C(205)	112(4)	C(225)	C(226)	N(210)	136(8)
O(204)	C(205)	C(206)	101(4)				
C(205)	C(206)	O(207)	112(5)	N(201)	Na(2)	N(210)	168(2)
C(206)	O(207)	C(208)	123(5)	N(201)	Na(2)	O(204)	66(1)
O(207)	C(208)	C(209)	118(7)	N(201)	Na(2)	O(216)	66(1)
C(208)	C(209)	N(210)	134(10)	N(201)	Na(2)	O(221)	67(1)
C(209)	N(210)	C(211)	138(8)	N(210)	Na(2)	O(207)	70(2)
C(209)	N(210)	C(226)	88(7)	N(210)	Na(2)	O(213)	58(2)
C(211)	N(210)	C(226)	126(7)	N(210)	Na(2)	O(224)	69(2)
N(210)	C(211)	C(212)	96(9)	O(204)	Na(2)	O(207)	62(2)
C(211)	C(212)	O(213)	116(15)	O(204)	Na(2)	O(213)	85(1)
C(212)	O(213)	C(214)	103(10)	O(204)	Na(2)	O(216)	101(1)
O(213)	C(214)	C(215)	117(5)	O(204)	Na(2)	O(221)	113(1)
C(214)	C(215)	O(216)	106(4)	O(204)	Na(2)	O(224)	166(1)
C(215)	O(216)	C(217)	110(4)	O(207)	Na(2)	O(213)	108(1)
O(216)	C(217)	C(218)	113(4)	O(207)	Na(2)	O(216)	162(1)
C(217)	C(218)	N(201)	116(4)	O(207)	Na(2)	O(221)	92(1)
C(218)	N(201)	C(202)	114(4)	O(207)	Na(2)	O(224)	104(2)
C(218)	N(201)	C(219)	107(3)	O(213)	Na(2)	O(216)	62(1)
C(219)	N(201)	C(202)	118(4)	O(213)	Na(2)	O(221)	158(1)
N(201)	C(219)	C(220)	113(5)	O(213)	Na(2)	O(224)	100(1)
C(219)	C(220)	O(221)	117(6)	O(216)	Na(2)	O(221)	101(1)
C(220)	O(221)	C(222)	123(4)	O(216)	Na(2)	O(224)	93(2)
O(221)	C(222)	C(223)	109(5)	O(221)	Na(2)	O(224)	65(1)
C(222)	C(223)	O(224)	132(8)				

Table 12. Interatomic distances and angles^a for the third
cryptated sodium cation

Bonded Distances		Nonbonded Distances			
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
N(301)	C(302)	1.38(8)	N(301)	N(310)	5.98(7)
C(302)	C(303)	1.78(8)	N(301)	O(304)	2.73(7)
C(303)	O(304)	1.65(7)	N(301)	O(116)	2.86(7)
O(304)	C(305)	1.52(8)	N(301)	O(121)	3.26(7)
C(305)	C(306)	1.37(9)	N(310)	O(307)	3.26(6)
C(306)	O(307)	1.67(7)	N(310)	O(313)	2.72(6)
O(307)	C(308)	1.45(7)	N(310)	O(324)	2.87(6)
C(308)	C(309)	1.90(9)	O(304)	O(307)	2.86(5)
C(309)	N(310)	1.68(7)	O(304)	O(313)	5.44(5)
N(310)	C(311)	1.42(7)	O(304)	O(316)	4.07(5)
N(310)	C(326)	1.37(7)	O(304)	O(321)	4.43(6)
C(311)	C(312)	1.61(8)	O(304)	O(324)	4.64(5)
C(312)	O(313)	1.39(7)	O(307)	O(313)	3.86(6)
O(313)	C(314)	1.63(7)	O(307)	O(316)	3.61(6)
C(314)	C(315)	1.34(8)	O(307)	O(321)	5.31(6)
C(315)	O(316)	1.58(7)	O(307)	O(324)	4.50(6)
O(316)	C(317)	1.52(7)	O(313)	O(316)	3.21(6)
C(317)	C(318)	1.32(8)	O(313)	O(321)	4.25(6)
C(318)	N(301)	1.45(8)	O(313)	O(324)	4.05(6)
N(301)	C(319)	1.63(9)	O(316)	O(321)	4.36(6)
C(319)	C(320)	1.97(10)	O(316)	O(324)	5.56(6)
C(320)	O(321)	1.61(8)	O(321)	O(324)	3.05(6)
O(321)	C(322)	1.31(8)			
C(322)	C(323)	1.30(9)	Na(3)	C(302)	3.63(6)
C(323)	O(324)	1.29(8)	Na(3)	C(303)	3.71(6)
O(324)	C(325)	1.53(7)	Na(3)	C(305)	3.27(6)
C(325)	C(326)	1.36(8)	Na(3)	C(306)	3.47(6)
Na(3)	N(301)	2.84(6)	Na(3)	C(308)	3.27(6)
Na(3)	N(310)	3.14(5)	Na(3)	C(309)	3.61(6)
Na(3)	O(304)	2.84(4)	Na(3)	C(311)	3.56(6)
Na(3)	O(307)	2.62(4)	Na(3)	C(312)	3.51(6)
Na(3)	O(313)	2.75(4)	Na(3)	C(314)	3.27(6)
Na(3)	O(316)	2.70(4)	Na(3)	C(315)	3.27(6)
Na(3)	O(321)	2.74(5)	Na(3)	C(317)	3.02(6)
Na(3)	O(324)	2.96(4)	Na(3)	C(318)	3.46(6)
			Na(3)	C(319)	3.19(7)

^aEstimated standard deviations from FBOND⁷⁸ are in parentheses.

Table 12... (Continued)

Bonded Distances			Nonbonded Distances		
Atom 1	Atom 2	Distance (\AA)	Atom 1	Atom 2	Distance (\AA)
	Na(3)	C(320)	2.96(7)		
	Na(3)	C(322)	3.31(7)		
	Na(3)	C(323)	3.17(7)		
	Na(3)	C(325)	3.73(6)		
	Na(3)	C(326)	3.40(6)		
Bonded Angles					
Atom 1	Atom 2 (Vertex)	Atom 3	Degrees		
N(301)	C(302)	C(303)	83(4)		
C(302)	C(303)	O(304)	94(4)		
C(303)	O(304)	C(305)	72(4)		
O(304)	C(305)	C(306)	88(5)		
C(305)	C(306)	O(307)	101(4)		
C(306)	O(307)	C(308)	83(4)		
O(307)	C(308)	C(309)	88(4)		
C(308)	C(309)	N(310)	113(4)		
C(309)	N(310)	C(311)	122(4)		
C(309)	N(310)	C(326)	92(4)		
C(311)	N(310)	C(326)	145(5)		
N(310)	C(311)	C(312)	105(4)		
C(311)	C(312)	O(313)	78(4)		
C(312)	O(313)	C(314)	105(4)		
O(313)	C(314)	C(315)	104(5)		
C(314)	C(315)	O(316)	121(5)		
C(315)	O(316)	C(317)	121(4)		
O(316)	C(317)	C(318)	108(5)		
C(317)	C(318)	N(301)	112(5)		
C(318)	N(301)	C(302)	142(5)		
C(318)	N(301)	C(319)	84(4)		
C(319)	N(301)	C(302)	94(5)		
N(301)	C(319)	C(320)	96(5)		
C(319)	C(320)	O(321)	73(5)		
C(320)	O(321)	O(322)	127(5)		
O(321)	C(322)	C(323)	120(6)		
C(322)	C(323)	O(324)	145(7)		
C(323)	O(324)	C(325)	114(5)		
O(324)	C(325)	C(326)	98(5)		
C(325)	C(326)	N(310)	96(5)		

final least squares cycle. Interatomic distances and angles for the Sb_7^{3-} anion are given in Table 9 while distances and angles for the first and second crypts are given in Table 10 and 11, respectively. The program FBOND⁷⁸ was used to obtain bond distances and angles for the third crypt, and these are listed in Table 12.

Discussion

The packing of three cryptated sodium cations per Sb_7^{3-} cluster anion is shown in a projection of the unit cell on the (010) plane in Figure 3.¹ For clarity the cryptated sodium cations are represented simply as a N-Na-N linkage, and the three independent cryptated cations are identified by numerals.

The anion

The Sb_7^{3-} anion is not only the first well-characterized homopolyatomic anion for a metallic element, but it is also apparently one of only a few rigorously established examples of a seven atom polyhedron.⁶ The geometry of the anion is shown in Figure 4. The seven antimony atoms are clustered in an end-capped trigonal prism having approximate C_{3v} symmetry.

¹The projection of the unit cell on the (010) plane and plots of the Sb_7^{3-} anion and cryptated sodium cations that follow were plotted using the thermal ellipsoid plotting program ORTEP.⁶⁴

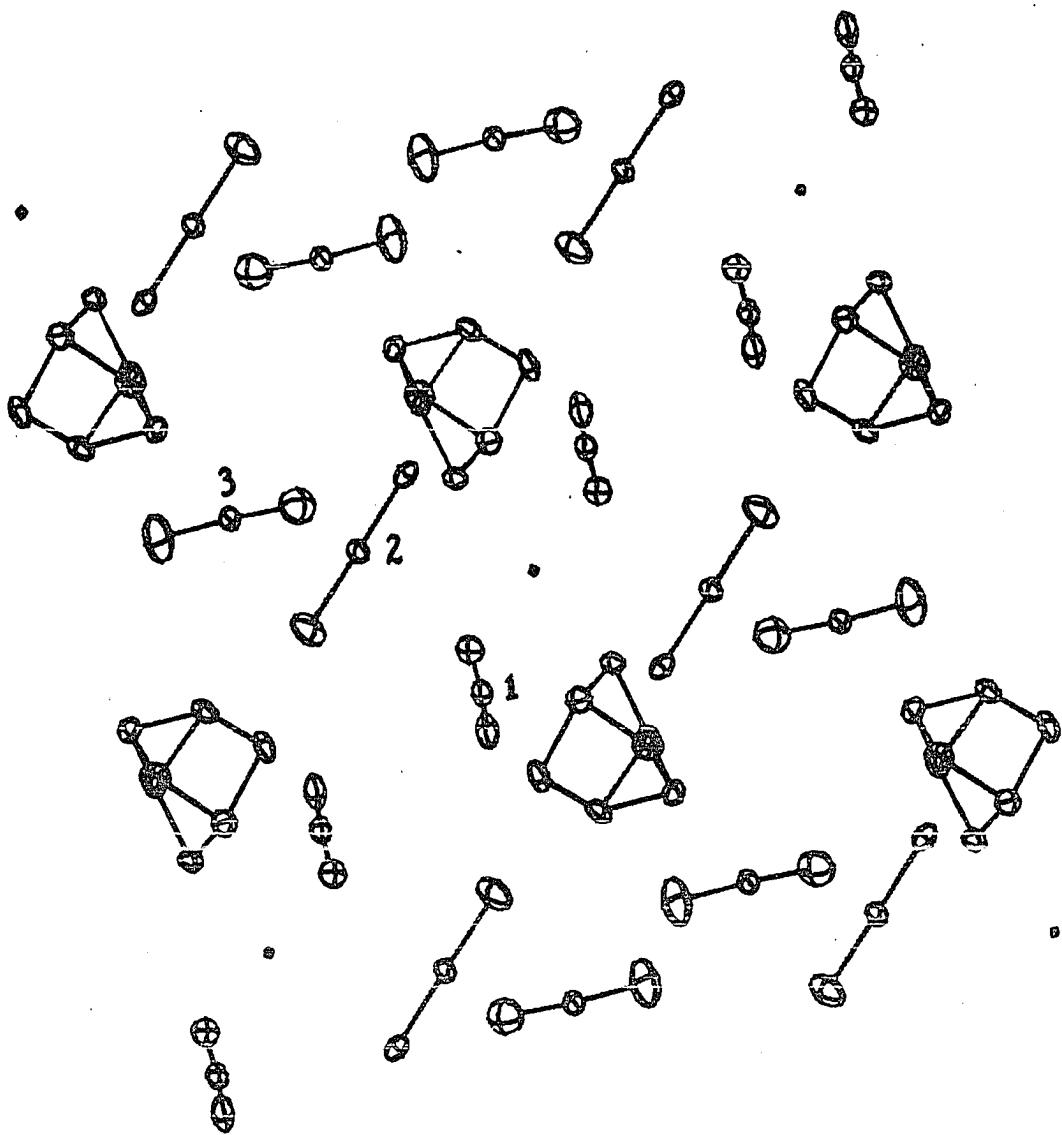


Figure 3. Projection of the structure of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ on the (010) plane.

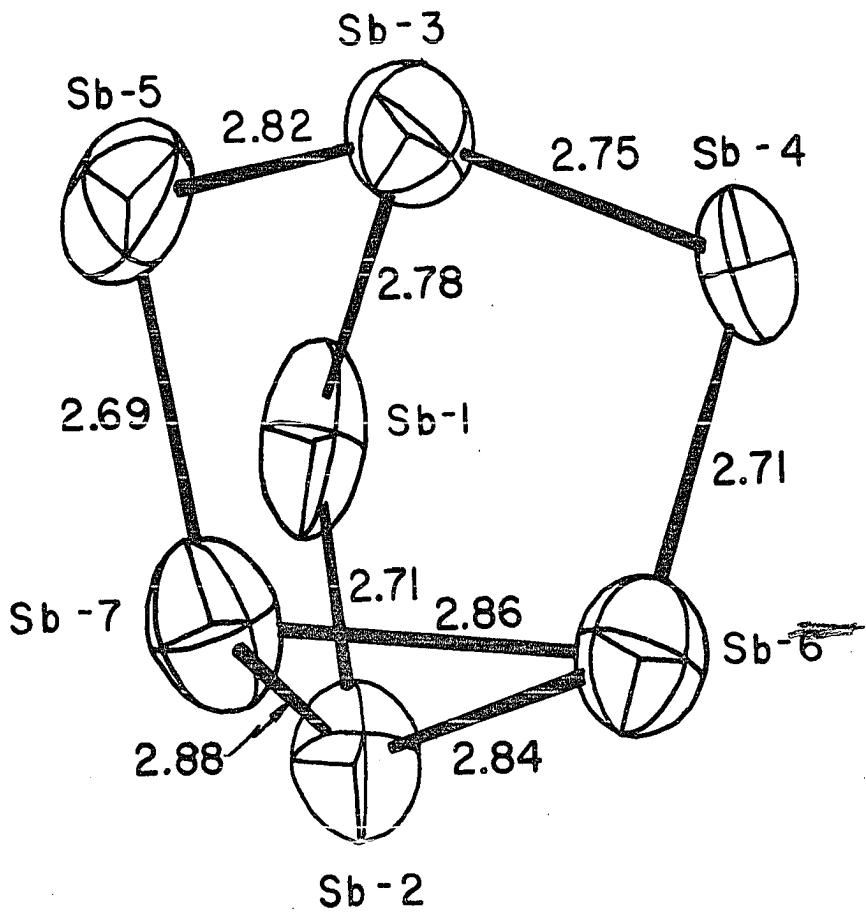


Figure 4. Geometry of the Sb_7^{3-} anion in $(\text{NaC}^+)_3\text{Sb}_7^{3-}$.

Least squares planes have been calculated¹ for the three four-atom faces: 1,2,6,4; 1,2,7,5; and 5,7,6,4. The perpendicular distance of each of the four atoms from the respective plane is given in Table 13. The angle between the normals to the planes determined by atoms 4,5,1 and 6,7,2 is 0.5(7)°.⁶⁵

Table 13. Deviations from least squares planes

Atom Distance, Å	Atom Distance, Å	Atom Distance, Å			
Sb(4)	0.0042	Sb(1)	-0.0189	Sb(1)	0.0287
Sb(5)	-0.0042	Sb(2)	0.0276	Sb(2)	-0.0439
Sb(6)	-0.0063	Sb(5)	0.0193	Sb(4)	-0.0288
Sb(7)	0.0063	Sb(7)	-0.0280	Sb(6)	0.0440

A few years ago Muetterties and Wright reviewed the literature concerning molecular polyhedra of high coordination number.⁸⁰ Important polyhedra for the seven-atom family included the capped octahedron (C_{3v}), the pentagonal bipyramid (D_{5h}) and the face-capped trigonal prism (C_{2v}). A fourth basic geometry for seven-coordination which has been rigorously

¹ Least squares planes were calculated using the local program LSP2 written by Wayne Rohrbaugh.

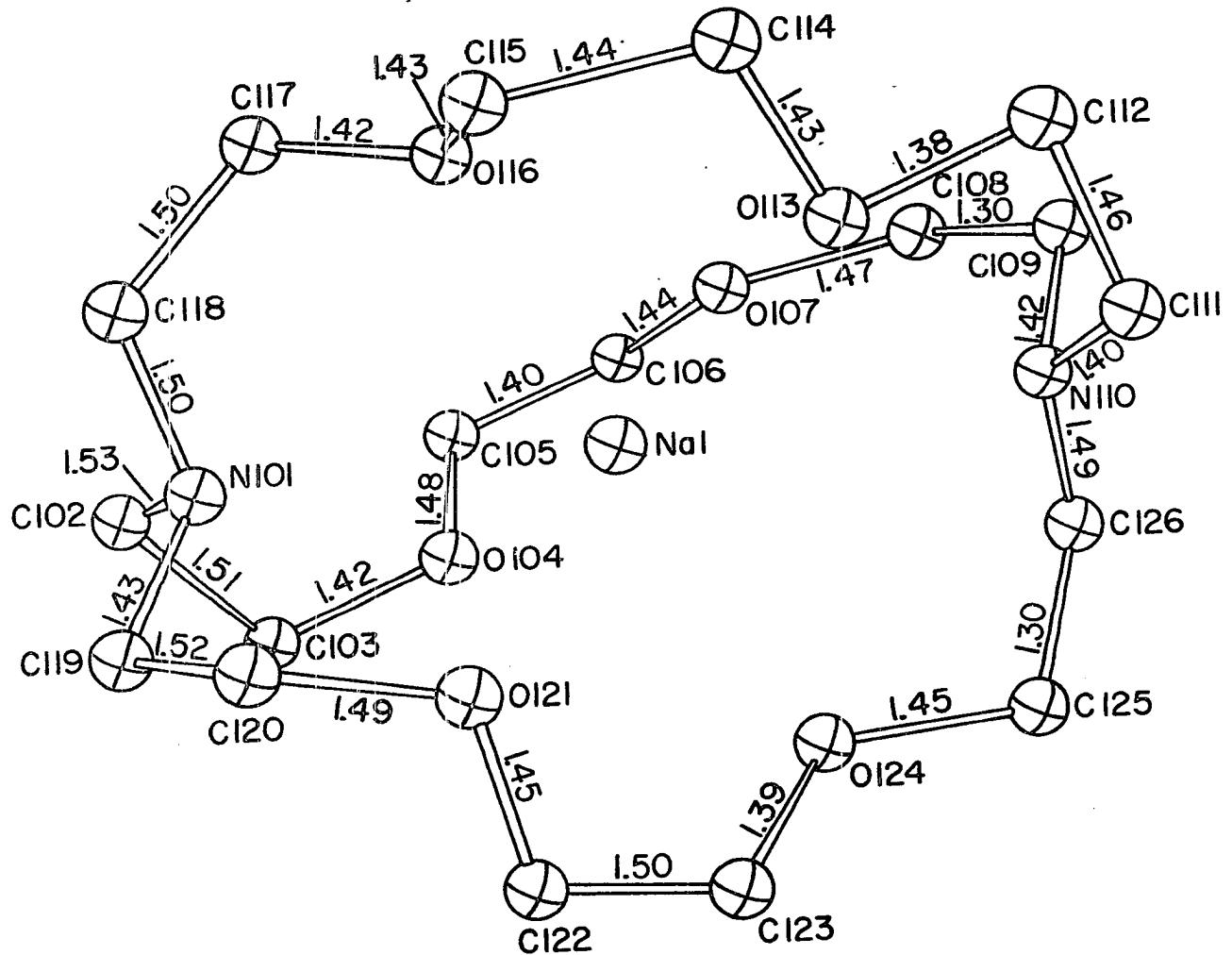
established for complexes, metal clusters and polymeric oxides is the tetragonal base-trigonal base (C_s) polyhedron. It is important to note that these polyhedra have been proposed for ML_7 complexes rather than for a homopolyatomic noncentered cluster as is under consideration here. The C_{3v} , D_{5h} and C_{2v} idealized polyhedra represent limiting symmetry forms as opposed to energetically favored or experimentally established geometries. Conformational interconversions require only slight bending modes, and the energy differences between these idealized geometries should be small with respect to intermolecular forces generated by ordering or by solvation phenomena in the solid, liquid or solution states.⁸¹ Gillespie, among others, has evaluated the relative stabilities of the MX_7 models simply by considering repulsive forces generated from interactions of like ligands constrained to a spherical surface.⁸² The analysis has limited predictive value, however, as the energy differences are very small, attractive forces are ignored and calculations are limited to spherical models.

Recently Muetterties and Guggenberger have emphasized that there is a paucity of available structural data for the seven atom family.⁸³ While there are no good observed C_{3v} -type structures, in $Rb_5Zr_4F_{21}$ there are two independent ZrF_7 polyhedra with the same structure which is midway between the C_{3v} and D_{5h} geometries.⁸⁴ Among several complexes which

have been reported which are close to the pentagonal bi-pyramidal structure are ZrF_7^{3-} ⁸⁵, ReF_7^{86} , IF_7^{87} and $V(CN)_7^{4-}$ ⁸⁸. Two compounds $Na_5Zr_2F_{13}^{89}$ and $K_2NbF_7^{90}$ have been reported which adopt the C_{2v} structure. The structure found for the Sb_7^{3-} anion does not approach any of these idealized polyhedra. It is similar, however, to the structure of P_4S_3 . Here phosphorus atoms form a tetrahedron and sulfur atoms bridge along three adjacent edges of the tetrahedron.⁸ If outer shell p electrons are considered, the two clusters are isoelectronic. Using a Lewis electron-pair scheme one has a cluster with nine electron-pair bonds and a lone pair on each bridging atom.

The cations

For each of the three independent cryptated cations the sodium ion occupies the central cavity of the macrobicycle. The coordination polyhedron about sodium is bicapped trigonal antiprismatic. The geometry of the first and second cryptated sodium cations is illustrated in Figures 5 and 6, respectively. The bond distances indicated in the figures were calculated prior to the final lattice constant refinement. The numbering system for the third crypt which is not illustrated parallels that of the other two. Moras, Metz and Weiss noted that as the size of the alkali cation decreases from cesium to sodium, the oxygen coordination changes from approximately trigonal prismatic in the case



8

Figure 5. Geometry of the first cryptated sodium cation in $(NaC^+)_3Sb_7^{3-}$.

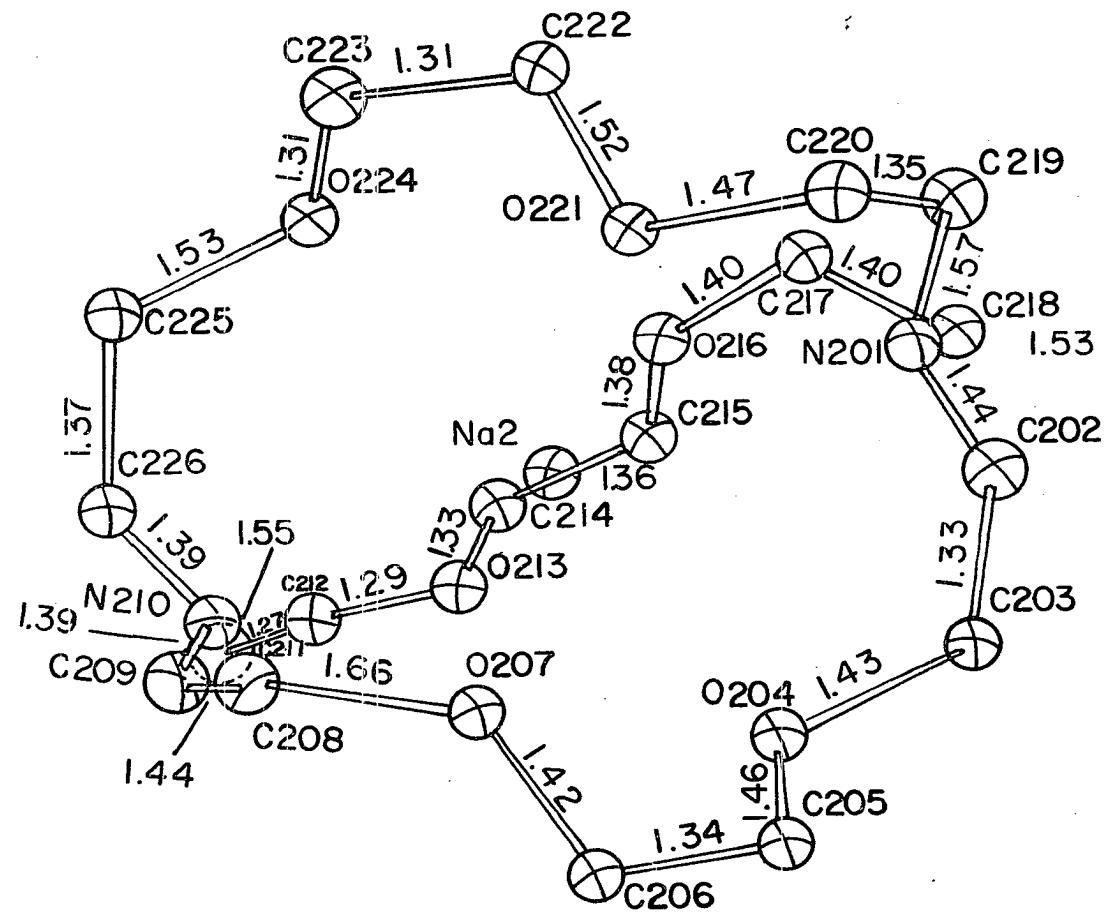


Figure 6. Geometry of the second cryptated sodium cation in $(NaC^+)_3Sb_7^{3-}$.

of CsC^+I^- and RbC^+I^- ⁹¹ and KC^+I^- ⁹² to very nearly trigonal antiprismatic in the case of NaC^+I^- .⁴² The conformational flexibility of 2,2,2-crypt was also noted by Dye *et al.* who likewise found trigonal antiprismatic coordination about sodium in NaC^+Na^- ³⁸ and confirmed the ability of the strands to twist. While free 2,2,2-crypt exists in solution as an equilibrium mixture of three conformations having the bridgehead nitrogens either out-out, in-out, or in-in,⁹³ all crystal structures so far determined for cryptated metal ions logically have contained crypt in the in-in conformation.⁴¹ The N(101)-N(110) distance of 5.76 Å found here compares with 6.87 Å in free crypt.⁹⁴

A convenient way to consider the atom placements in the present structure is by comparison with the known structures of NaC^+Na^- ³⁸ and NaC^+I^- .⁴² The former compound crystallizes in the space group R32 while the latter one crystallizes in the space group P3lc. Although P3lc does not have the two-fold rotation axes of R32, both space groups have three-fold symmetry. Interatomic distances and angles found for the two compounds are compared with averages for the first crypt in Table 14.

The refinement reported here is more satisfactory for the first crypt than for the other two. That of the second crypt is reasonably satisfactory with the exception of the atoms near the N(210) bridgehead. While the refinement of the third crypt is much less satisfactory than for the other

Table 14. Interatomic distances and angles for cryptated sodium cations

Bonded Distances (\AA)	NaC^+Na^- ^a	NaC^+I^- ^b	Crypt 1 ^b
Na-N	2.72(1)	2.75(2)	2.88(8)
Na-O	2.57(1)	2.58(2)	2.55(10)
N-Cl	1.48(2)	1.47(2)	1.46(5)
Cl-C2	1.29(2)	1.44(3)	1.43(11)
C2-O	1.41(1)	1.44(2)	1.44(4)
O-C3	1.40(2)	1.40(5)	1.43(3)
C3-C3(2)	1.31(3)	1.40(4)	1.45(5)
 Nonbonded Distances (\AA)			
Na-Cl	3.45(2)	3.53(2)	3.55(11)
Na-C2	3.46(2)	3.46(2)	3.46(11)
Na-C3	3.34(3)	3.39(2)	3.33(13)
O-O(2)	2.86(2)	2.79(2)	2.77(9)
O-O(3)	4.09(2)	4.07(2)	3.98(9)
O-O(3 ¹ 2)	5.13(2)	5.12(2)	5.05(17)
O-O(3 ² 2)	3.38(2)	3.53(2)	3.65(19)
N-N(2)	5.44(2)	5.50(2)	5.76
 Angles (deg)			
Na-N-Cl	107(1)	110(1)	105(4)
Cl-N-Cl(3)	112(1)	109(1)	113(3)
N-Cl-C2	128(1)	113(2)	115(7)
Cl-C2-O	120(1)	117(3)	113(4)
C2-O-C3	107(1)	100(2)	114(5)
O-C3-C3(2)	121(2)	116(3)	110(3)
O-Na-O(2)	67.6(3)	65.7(4)	66(1)
O-Na-O(3)	105.4(3)	104.4(4)	102(2)
O-Na-O(3 ¹ 2)	171.2(3)	167.0(4)	163(2)
O-Na-O(3 ² 2)	82.0(3)	86.6(4)	91(2)

^aEstimated standard deviation of the least significant digit is given in parentheses.

^bEstimated standard deviation of the average of distances from Table 10 is given in parentheses.

two, inspection of the Na-N, Na-O and Na-C distances in Table 12 assures that the ligand complexing Na(3) is indeed 2,2,2-crypt. The specter of disorder at the bridgeheads N(210), N(301) and N(310) in this structure determination was indicated by multiple carbon positions in the difference maps phased on the basis of only the heavy atom positions. Block least squares refinement of judiciously chosen positions for the atoms of the second and third crypts followed by refinement of the positions and isotropic thermal parameters resulted in considerably larger thermal parameters than obtained in the case of the first crypt. Stout and Jensen have discussed the difficulties arising from disorder which is limited to a given portion of a molecule.⁹⁵ They suggest that this type of disorder is indicated by abnormally high thermal parameters for whole atoms located at sites having partial occupancy. The introduction of fractional atom positions for carbon atoms surrounding the N(210) bridgehead of the second crypt and for C(305), C(308), C(309), C(319), C(320), O(321), C(322) and C(323) in the third crypt did result in smaller converged isotropic thermal parameters for those atoms but did not provide a statistically significant⁶² improvement in the weighted agreement factor.

It may be noted that in the block least squares refinement of the second crypt more reasonable distances and angles were found than with the full matrix one. For the former

refinement estimated standard deviations for the distances between 0.06 and 0.08 \AA and for the angles 3.7 and 5.2° were obtained. Apparently to the extent that the block diagonal approach is a rougher approximation than the full-matrix one, errors are distributed over the macrobicycle as a whole. In view of this experience with the second crypt it seemed appropriate to report the block least squares refinement for the third crypt rather than carry out a full-matrix refinement of dubious value. Some consolation is derived from the fact that Dye et al.³⁸ observed abnormally high thermal parameters for carbon, nitrogen and oxygen atoms of 2,2,2-crypt in NaC^+Na^- plus unusually short C-C distances of 1.29 and 1.31 \AA and bond angles at carbon of 128, 120 and 122°. They noted that artificial shortening of interatomic distances and opening of bond angles often occur in structures with high thermal parameters. Among the factors presumably contributing to the difficulties experienced in the refinement reported here is the fact that a thirty per cent decay in the intensities of the standards occurred during data collection. Dye et al. reported observing thermal decomposition during data collection for NaC^+Na^- .³⁸ However, final atomic parameters obtained from data they collected from a second crystal agreed within 3σ of those determined from the original data. In view of the fact that the goniometer stage conducts heat from the motors driving the four circles of the

diffractometer used here, the $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ crystal may have suffered some thermal decomposition during data collection. The effect of instrumental intemperance⁶³ at the time of data collection is unknown. All of these problems and details are, of course, less significant and interesting than the anion discovered.

Conclusion

The solution of the crystal structure of (cryptated sodium) heptantimonide(-3) provides the first example of a stable solid containing a well-characterized homopolyatomic cluster anion for a metallic element. Only recently Corbett indicated that there is no evidence for solid compounds containing Sb_7^{3-} .⁶ The demonstrated success of this synthetic approach as well as the preliminary results of Kummer and Diehl who achieved the isolation of Sn_9^{4-} in salts with sodium complexed with ethylenediamine³⁶ suggests the desirability of further synthetic effort in this area.

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