

1975

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

Douglas Guy Adolphson
Iowa State University

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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

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Major: Inorganic Chemistry

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Ames, Iowa

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 $450\text{--}550^\circ$ with a large area of hafnium foil at $610\text{--}650^\circ$ 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_2 , 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_2 .¹³ A report of the synthesis of ZrCl_2 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 Bi_9^{5+} associated with the large complex anions $[BiCl_5]^{2-}$ and $[Bi_2Cl_8]^{2-}$ in the ratio 2:4:1. When the reduction is carried out in the aluminum chloride solvent system, two compounds $Bi_5^{3+}(AlCl_4^-)_3$ and $(Bi^+AlCl_4^-)_n$ crystallize following reduction of the composition $BiCl_3 \cdot AlCl_3$ 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 $Bi_5^{3+}(AlBr_4^-)_3$ 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

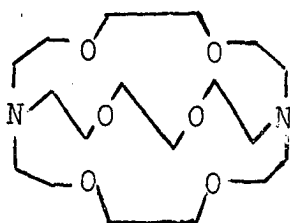
Table 1. Zintl phases

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 $\text{BiCl}_{1.167}$.⁶ 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 $\text{Na}_4\text{Sn}_9 \cdot 6-8$ 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 $\text{Bi-BiBr}_3\text{-AlBr}_3$ 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 ZrCl 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 3.42Å. 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 electropolished 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° 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 3.42Å 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 $a=9.19$, $b=3.42$, $c=5.92\text{Å}$ and $\beta=103^\circ$. Unfortunately, by the time that priority for the diffractometer could be established, neither crystal diffracted

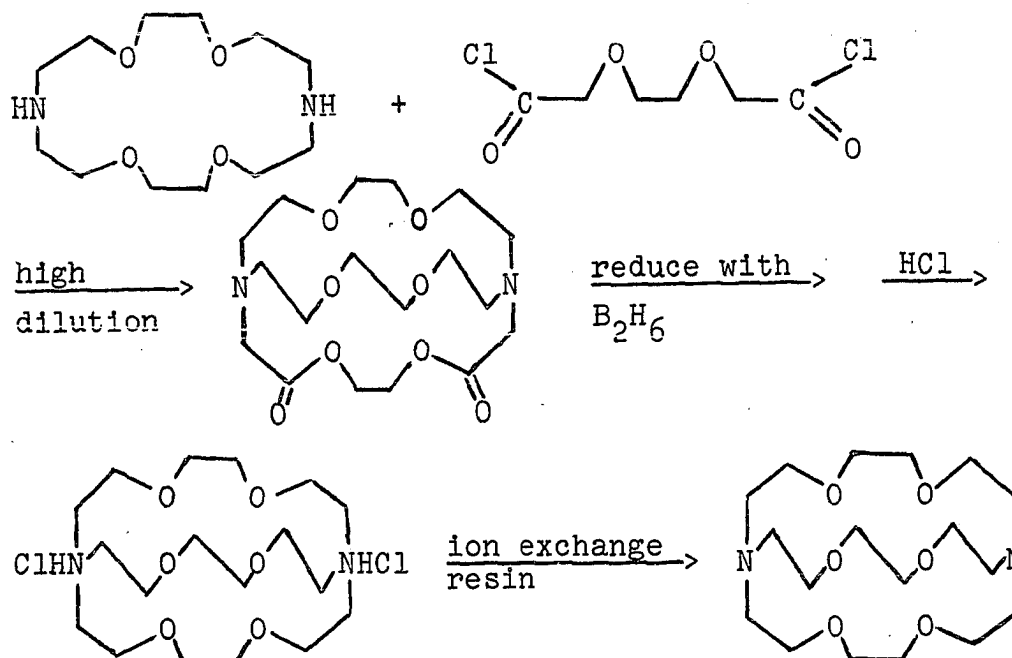
X-radiation. Since a search of the reaction product from which these two crystals had originally been obtained failed to produce a suitable crystal, the reaction was repeated using the same conditions. This reaction was apparently defeated by power failures during both the equilibration and cooling periods. 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 Pedersen³⁹ 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) or silicone lubricant ($[\text{NaC}^+]_3\text{Sb}_7^{3-}$) 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 $hl\bar{l}$, the second level the $h2\bar{l}$, 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 $Ok\bar{l}$ 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)°.

$(NaC^+)_3Sb_7^{3-}$ 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 $(NaC^+)_3Sb_7^{3-}$ 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

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

where all terms are as defined above.⁵⁷ In the case of ZrCl₂ 203 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 ZrCl₂ the condition $h+k=2n$ for all reflections $hk\ell$ 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 $hk\ell$ reflections. The condition $k=2n$ found for $0k0$ reflections requires a 2-fold screw axis and the condition $h+l=2n$ for $h0\ell$ 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 $|F(hkl)|^2$. The structure factor $F(hkl)$ represents the resultant amplitude of the waves scattered in the direction of the reflection hkl by the j atoms in the unit cell:

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

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:

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + lz)].$$

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

$$R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

and

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

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 isotropic 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($\times 10^3$)
	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 $\exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})$.

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 indeterminate 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 = 4				L = 9				L = -4				L = -8			
H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
2	0	60	71	3	3	335	348	0	0	149	143	0	0	627	553	0	0	181	167
4	0	583	606	0	0	667	553	2	0	202	214	4	0	453	501	2	0	205	202
6	0	111	103	2	0	267	304	1	1	98	101	6	0	97	101	4	0	209	197
1	1	237	230	4	0	338	315	0	2	146	130	1	1	334	359	1	1	171	191
3	1	257	357	1	1	238	372	L = 10				3	1	211	200	3	1	209	198
5	1	153	140	3	1	294	255	H	K	FO	FC	5	1	180	185	5	1	194	171
0	2	1136	890	5	1	176	172	0	0	123	117	0	2	484	454	0	2	138	147
4	2	486	505	0	2	471	452	L = -1				2	2	213	200	2	2	171	181
6	2	75	94	2	2	218	227	H	K	FO	FC	4	2	396	433	4	2	168	177
1	3	170	161	4	2	264	280	2	0	237	229	6	2	83	92	L = -9			
3	3	179	166	1	3	138	159	4	0	177	206	1	3	226	217	H	K	FO	FC
0	4	570	459	3	3	202	203	6	0	156	155	3	3	121	129	0	0	158	143
L = 1				L = 5				L = -2				L = -5				L = -10			
H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
0	0	353	316	0	0	381	382	0	0	238	232	0	0	363	382	0	0	131	117
2	0	209	206	2	0	224	232	2	0	834	804	2	0	243	358	4	0	173	158
4	0	221	235	4	0	221	215	6	0	460	454	4	0	222	231	1	1	147	158
6	0	135	128	1	1	357	384	0	2	211	206	6	0	115	117	3	1	137	136
1	1	812	817	3	1	218	226	1	1	271	266	1	1	274	301	0	2	138	130
3	1	174	168	5	1	200	196	3	3	492	493	3	1	494	432	2	2	192	195
5	1	428	439	0	2	269	254	0	4	199	151	5	1	154	162	L = -7			
0	2	342	363	2	2	169	198	L = -3				0	2	272	255	H	K	FO	FC
2	2	180	175	4	2	189	194	H	K	FO	FC	2	2	194	177	0	0	295	275
4	2	207	201	1	3	266	283	0	0	234	217	4	2	203	202	2	0	388	369
1	3	536	528	L = 6				2	0	292	284	1	3	189	201	4	0	194	211
3	3	102	112	H	K	FO	FC	6	0	159	166	3	3	309	334	6	0	257	301
0	4	177	181	0	0	313	275	1	1	271	266	0	2	233	228	1	1	220	225
L = 2				2	0	228	254	3	1	271	349	2	2	321	307	3	1	272	240
H	K	FO	FC	4	0	208	186	5	1	155	151	4	2	176	188	5	1	137	140
0	0	258	232	1	1	241	247	0	2	200	169	0	2	272	255	0	2	233	228
2	0	695	658	3	1	228	216	4	2	585	619	2	2	321	307	2	2	321	307
4	0	210	197	0	2	228	227	4	2	63	42	4	2	176	188	4	2	176	188
6	0	351	329	2	2	181	222	6	2	407	412	1	3	165	171	6	0	257	301
1	1	291	292	1	3	177	196	1	3	162	147	3	3	179	192	1	1	220	225
3	1	211	209	L = 7				3	3	152	162	5	1	137	140	3	1	272	240
5	1	221	211	H	K	FO	FC	0	4	115	105	0	2	233	228	5	1	137	140
0	2	184	168	0	0	296	244	L = -7				0	2	233	228	0	2	233	228
2	2	502	534	2	0	177	196	H	K	FO	FC	2	2	321	307	2	2	321	307
4	2	164	172	4	0	227	208	0	0	234	217	4	2	176	188	4	2	176	188
1	3	223	206	1	1	210	211	2	0	292	284	1	3	165	171	1	3	165	171
3	3	147	138	3	1	163	151	4	0	159	166	3	3	179	192	3	3	179	192
0	4	115	108	0	2	243	212	6	0	144	148	L = -6				2	2	321	307
L = 3				2	2	157	177	1	1	748	655	H	K	FO	FC	2	2	321	307
H	K	FO	FC	3	1	163	151	3	1	169	164	0	0	277	244	2	0	251	237
0	0	247	217	0	2	243	212	5	1	485	481	4	0	184	177	4	0	184	177
2	0	314	363	2	2	157	177	0	2	199	212	6	0	187	171	6	0	187	171
4	0	190	182	L = 8				2	2	241	235	1	1	213	246	1	1	213	246
6	0	211	192	H	K	FO	FC	4	2	137	140	3	1	226	215	3	1	226	215
1	1	261	261	0	0	206	167	6	2	133	133	5	1	255	249	5	1	255	249
3	1	506	450	2	0	147	163	1	3	478	460	0	2	218	213	0	2	218	213
5	1	185	193	1	1	231	229	3	3	66	111	2	2	207	208	2	2	207	208
0	2	191	208	3	1	135	132	L = -6				4	2	159	157	4	2	159	157
2	2	230	252	0	2	158	147	H	K	FO	FC	1	3	161	194	1	3	161	194
4	2	147	157	2	2	120	148	0	0	277	244	L = -5				2	2	207	208

^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

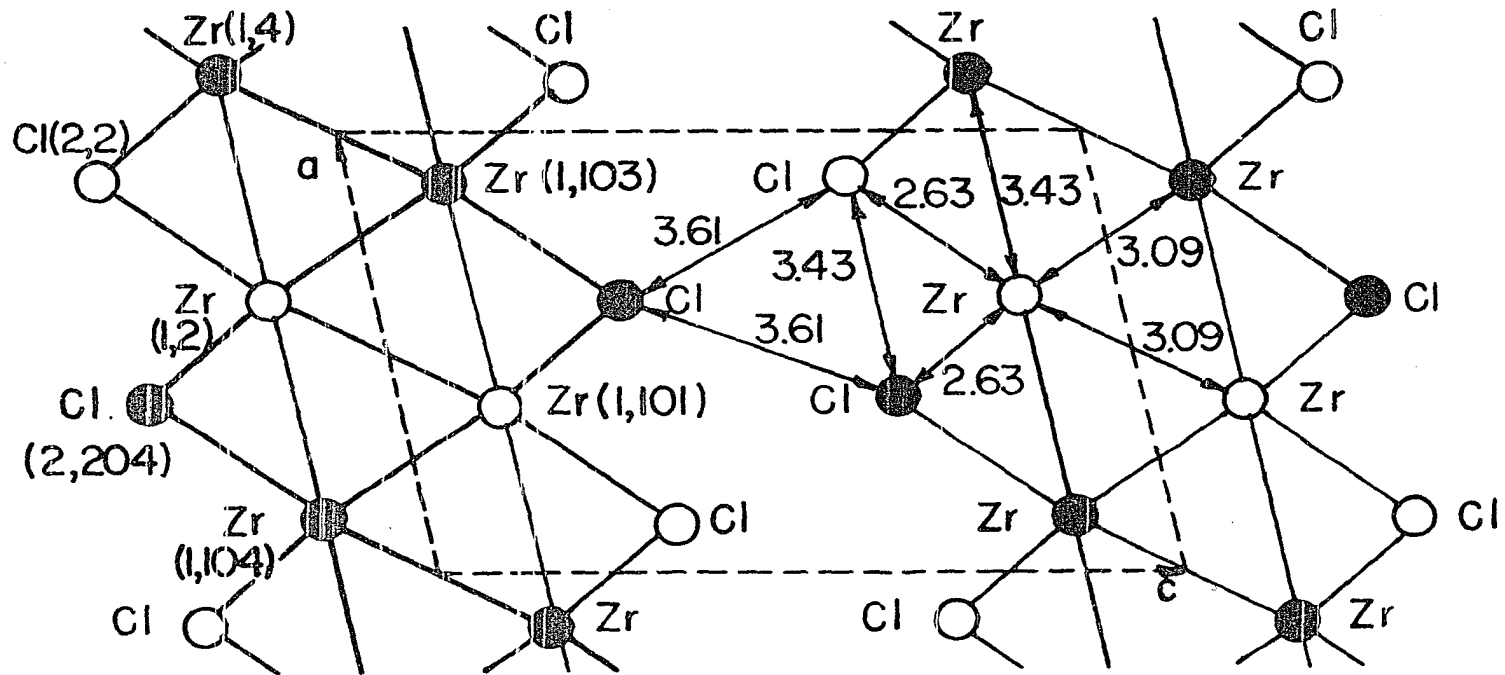
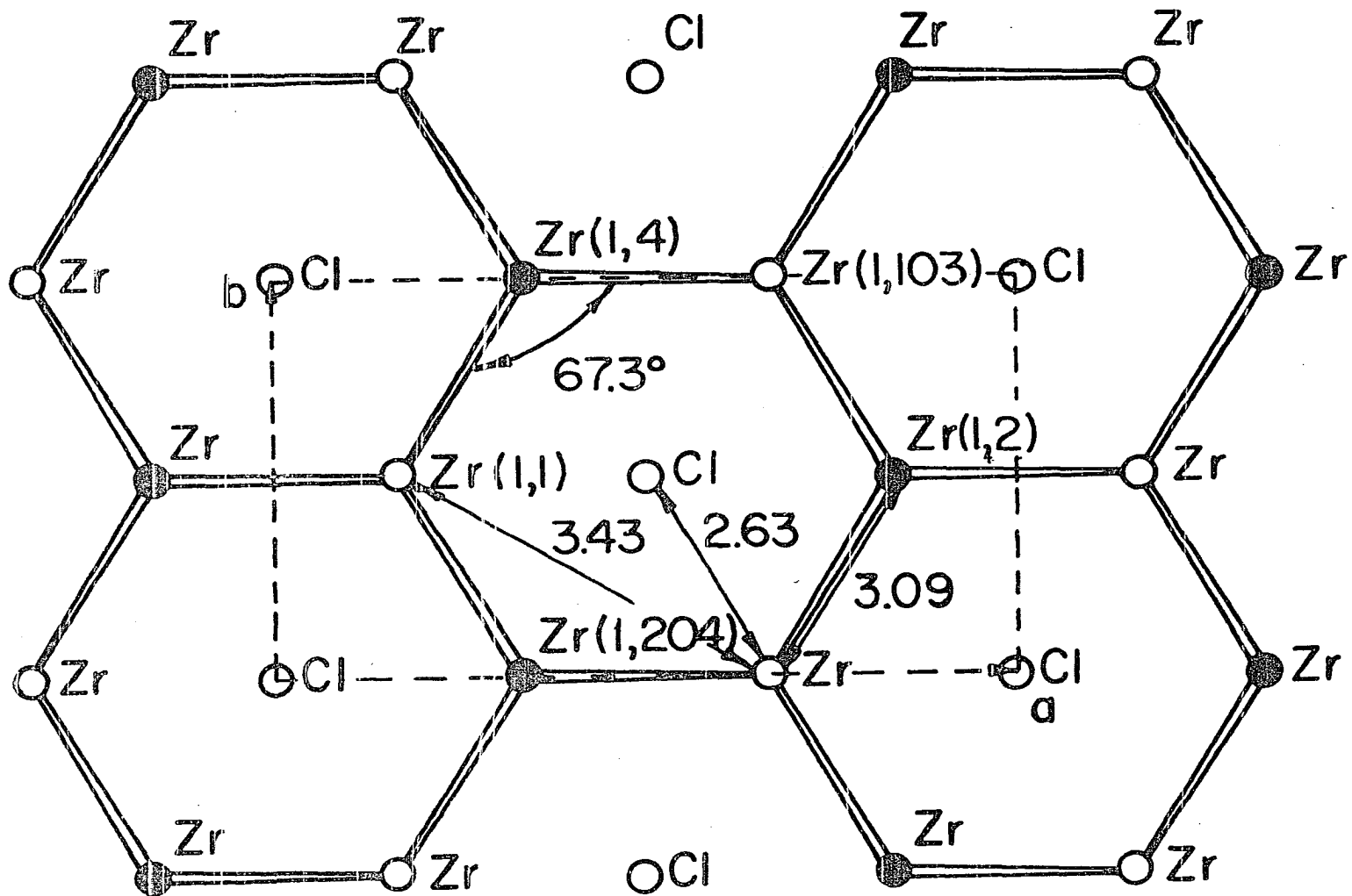


Figure 1. Projection of the structure of $ZrCl$ on the (010) plane. Atoms at $y=0.0$ are represented by open circles while those at $y=0.5$ are shaded.

Figure 2. Projection of the structure of ZrCl_2 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			
	Å	Atom 1	Atom 2 (Vertex)	Atom 3	Degrees
Intralayer Zr-Zr	3.419(3)	Zr(1,1)	Zr(1,4)	Zr(1,103)	67.30(15)
	3.428(3)				
Cl-Cl	3.419(3)	Zr(1,204)	Zr(1,4)	Zr(1,2)	60.09(3)
	3.428(3)	Zr(1,4)	Zr(1,2)	Zr(1,104)	120.18(7)
		Zr(1,4)	Zr(1,2)	Zr(1,101)	124(4)
		Zr(1,4)	Zr(1,2)	Zr(1,103)	56(4)
Interlayer Zr-Zr	3.09(14)	Zr(1,101)	Zr(1,2)	Zr(1,103)	67.30(15)
	3.09(14)	Zr(1,104)	Zr(1,2)	Zr(1,103)	90(5)
		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)
		Cl(2,2)	Zr(1,2)	Zr(1,103)	105(1)
Zr-Cl	2.63(13)	Cl(2,2)	Zr(1,2)	Zr(1,4)	49(3)
	2.63(11)	Cl(2,2)	Zr(1,2)	Cl(2,104)	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 $GdCl_3$ and Gd_2Cl_3 .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 $ZrCl_4$ ⁶⁶ and a zirconium-chlorine distance of 2.44 Å in Rb_2ZrCl_6 .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 $\sum N_i n_i$ 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 Hf₂S by Franzen and Graham.⁶⁹ In Hf₂S 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 $\text{ZrClH}_{0.5}$.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 $U(hk\ell)$ is 1. For N equal atoms in a centrosymmetric unit cell the average value of $|U(hk\ell)|^2$ 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 $e^{-}/\text{\AA}^3$, respectively, in the vicinity of Sb(5) and one ripple of less than 3 $e^{-}/\text{\AA}^3$ near Sb(6). This is not unreasonable since scattering factors for Sb^0 were used. Otherwise, the map showed only a randomly fluctuating background of $\leq \pm 1 e^{-}/\text{\AA}^3$. 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 Sb_7^{3-} 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 = 0				L = 1				L = 2			
H	K	FC	FD	H	K	FC	FD	H	K	FD	FC
4	C	1537	1436	1	4	1530	1054	1	8	783	665
6	0	1349	1369	2	4	1383	1221	2	8	1072	1118
8	0	459	384	3	4	375	362	4	8	459	528
10	0	638	401	4	4	567	561	5	8	361	471
14	0	757	752	5	4	1128	993	6	8	893	749
16	0	582	393	6	4	666	560	7	8	451	291
18	0	456	497	7	4	1120	952	8	8	1089	1084
20	0	1053	1189	8	4	1315	1424	9	8	422	381
22	0	334	374	9	4	515	483	10	8	367	303
24	0	332	147	10	4	1325	1131	11	8	381	198
1	1	761	689	11	4	1089	1005	12	8	396	300
3	1	244	437	12	4	949	816	13	8	542	513
4	1	577	602	13	4	1006	924	14	8	381	447
5	1	957	1295	14	4	661	531	15	8	782	724
6	1	2958	3033	15	4	377	430	16	8	964	887
7	1	3917	3476	16	4	384	531	17	8	1764	1741
8	1	687	816	17	4	527	576	18	8	717	687
9	1	829	664	18	4	582	613	19	8	1546	1518
10	1	2356	2260	19	4	741	733	20	8	834	754
11	1	1124	887	20	4	1308	1681	21	8	478	438
12	1	2001	1914	21	4	1617	1602	22	8	3866	3815
13	1	493	395	22	4	424	461	23	8	3158	3083
14	1	512	525	23	4	1191	1193	24	8	1762	1717
15	1	661	679	24	4	287	318	25	8	4079	3859
16	1	716	727	25	4	1569	1367	26	8	625	564
C	2	2353	2361	26	4	515	502	27	8	2702	2544
1	2	4563	4376	27	4	924	1090	28	8	839	874
2	2	1472	1416	28	4	527	468	29	8	811	988
3	2	1515	1091	29	4	443	286	30	8	945	843
4	2	1542	1361	30	4	625	567	31	8	781	775
5	2	2990	2840	31	4	415	358	32	8	375	309
6	2	775	792	32	4	478	647	33	8	803	559
7	2	1415	1216	33	4	2471	2328	34	8	1715	1450
8	2	1223	1363	34	4	2505	2584	35	8	306	397
9	2	864	731	35	4	2361	2226	36	8	265	212
10	2	1707	1367	36	4	4217	4094	37	8	1478	1415
11	2	867	668	37	4	1410	1464	38	8	502	361
12	2	787	815	38	4	3507	3752	39	8	1110	972
13	2	254	372	39	4	754	723	40	8	1411	1238
14	2	367	269	40	4	349	220	41	8	432	365
15	2	439	357	41	4	414	353	42	8	1584	1550
16	2	1397	1372	42	4	1080	1045	43	8	370	256
17	2	656	589	43	4	655	409	44	8	600	703
18	2	4022	4009	44	4	655	760	45	8	510	455
19	2	1475	1511	45	4	427	426	46	8	527	469
20	2	4566	4213	46	4	368	518	47	8	979	827
21	2	1519	1339	47	4	1497	1491	48	8	3092	2895
22	2	2396	2580	48	4	1016	1002	49	8	2607	2286
23	2	2048	1937	49	4	1811	1749	50	8	1281	1162
24	2	2471	2601	50	4	1294	1206	51	8	2907	2816
25	2	3673	3436	51	4	373	228	52	8	1868	1881
26	2	1838	1786	52	4	543	563	53	8	800	976
27	2	1748	1570	53	4	654	663	54	8	3938	4047
28	2	953	1016	54	4	726	617	55	8	1869	1757
29	2	725	804	55	4	754	645	56	8	3306	3116
30	2	453	616	56	4	531	493	57	8	995	1037
31	2	775	772	57	4	728	671	58	8	1110	1149
				58	4	684	709	59	8	342	405
				59	4	959	1142	60	8	1680	1666
				60	8	959	1142				

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Table 7. (Continued)

Table with multiple columns containing numerical data. The table is organized into sections by L values (L=10, L=9, L=12, L=11) and includes headers for H, K, FC, and FC. The data consists of rows of numbers, with some rows corresponding to specific L values.

Table 7. (Continued)

L = -11				L = -12				L = -13				L = -14			
H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
1	0	3255	3796	2	4	1874	1379	2	9	692	809	6	2	1240	1189
5	0	2229	1938	3	4	1347	1509	3	9	898	851	7	2	919	1036
7	0	361	374	4	4	1423	1965	5	9	1179	1205	8	2	435	395
9	0	1356	1363	5	4	782	1712	7	9	734	697	9	2	1741	1894
11	0	1109	1274	6	4	2411	2523	16	9	428	458	10	2	287	359
13	0	507	544	7	4	570	434	18	9	348	310	11	2	1329	1270
15	0	1389	1478	8	4	1507	2138	2	10	466	518	15	2	337	219
17	0	809	826	9	4	1024	1233	3	10	435	608	19	2	404	204
0	1	1193	1296	10	4	482	446	4	10	877	914	21	2	442	493
1	1	3145	2580	11	4	428	450	5	10	403	423	23	2	309	113
2	1	444	423	12	4	643	449	6	10	633	842	0	3	1817	1903
3	1	2146	2062	13	4	884	623	7	10	784	826	1	3	1050	1163
4	1	1751	1535	14	4	407	212	8	10	613	561	2	3	2576	2558
5	1	1331	1228	15	4	1520	1740	9	11	504	317	3	3	545	719
6	1	740	746	16	4	809	960	10	11	397	284	4	3	2494	2686
7	1	1153	1273	17	4	437	432	11	11	437	432	5	3	511	348
8	1	1339	1425	18	4	492	694	12	11	314	246	6	3	2668	2812
9	1	1860	2153	19	4	539	351	13	11	561	573	7	3	1058	1030
10	1	1934	1807	20	4	573	133	14	12	507	490	8	3	1835	1930
11	1	1428	1420	21	4	714	653	15	12	359	351	9	3	1392	1278
12	1	1059	1029	22	4	562	685	16	12	359	325	10	3	1307	1264
13	1	582	525	23	4	300	372	17	13	346	93	11	3	346	213
14	1	435	507	24	4	572	662	18	13	416	233	12	3	542	560
15	1	343	426	25	4	1071	1751	19	13	530	488	13	3	530	488
16	2	929	856	26	4	882	952	20	13	387	448	14	3	966	981
17	2	1062	1152	27	4	1287	1360	21	13	348	287	15	3	529	543
18	2	838	823	28	4	988	888	22	13	495	1138	16	3	577	473
19	2	404	164	29	4	380	496	23	13	674	821	17	3	364	396
0	2	2684	2700	30	4	2648	2649	24	13	828	970	18	3	605	801
1	2	546	342	31	4	517	449	25	13	398	297	19	3	357	353
2	2	2464	2603	32	4	1788	1857	26	13	406	963	20	3	373	574
3	2	1358	1378	33	4	3043	3235	27	13	359	264	21	3	416	502
4	2	813	890	34	4	1134	1200	28	13	301	36	22	3	319	238
5	2	2259	2172	35	4	353	372	29	13	532	451	23	3	332	248
6	2	1507	1744	36	4	552	503	30	13	600	728	24	3	372	138
7	2	849	795	37	4	393	64	31	13	460	524	25	3	406	304
8	2	336	276	38	4	908	1045	32	13	479	378	26	3	336	143
9	2	852	793	39	4	1482	1499	33	13	576	518	27	3	1241	1314
10	2	643	750	40	4	1366	1465	34	13	406	421	28	3	1176	1171
11	2	742	842	41	4	452	476	35	13	584	665	29	3	513	701
12	2	669	734	42	4	245	25	36	13	561	693	30	3	299	466
13	2	855	1002	43	4	799	679	37	13	375	360	31	3	962	741
14	3	1975	2152	44	4	906	747	38	13	625	729	32	3	619	463
15	3	655	903	45	4	913	823	39	13	857	1034	33	3	502	286
16	3	422	328	46	4	321	250	40	13	527	195	34	3	532	631
17	3	1377	1618	47	4	736	762	41	13	631	634	35	3	1541	1580
18	3	1534	1416	48	4	252	225	42	13	503	415	36	3	1124	1212
19	3	1041	1161	49	4	329	148	43	13	352	379	37	3	447	542
0	3	511	568	50	4	312	192	44	13	464	404	38	3	375	248
1	3	379	484	51	4	1007	1042	45	13	977	911	39	3	830	916
2	3	519	638	52	4	857	977	46	13	61027	1139	40	3	2972	2862
3	3	1281	1479	53	4	1422	1447	47	13	1102	1240	41	3	727	820
4	3	322	46	54	4	638	411	48	13	705	713	42	3	1540	1627
5	3	475	427	55	4	392	444	49	13	344	193	43	3	1341	1355
6	3	498	444	56	4	1146	1205	50	13	435	446	44	3	935	892
7	3	551	450	57	4	769	941	51	13	412	371	45	3	1266	1332
8	4	1859	1938	58	4	902	961	52	13	325	196	46	3	552	483
				59	4	1179	1288	53	13	448	514	47	3	1034	988
				60	4	1271	1278	54	13	907	999	48	3	1107	1166

Table 8. Final parameters^a for (NaC⁺)₃Sb₇³⁻

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 (x10³)^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 $\exp(-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

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

Atom 1 Atom 2 Distance (Å)

Nonbonded Distances

Atom 1 Atom 2 Distance (Å)

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)

N(201)	C(202)	C(203)	113(5)
C(202)	C(203)	O(204)	123(5)
C(203)	O(204)	C(205)	112(4)
O(204)	C(205)	C(206)	101(4)
C(205)	C(206)	O(207)	112(5)
C(206)	O(207)	C(208)	123(5)
O(207)	C(208)	C(209)	118(7)
C(208)	C(209)	N(210)	134(10)
C(209)	N(210)	C(211)	138(8)
C(209)	N(210)	C(226)	88(7)
C(211)	N(210)	C(226)	126(7)
N(210)	C(211)	C(212)	96(9)
C(211)	C(212)	O(213)	116(15)
C(212)	O(213)	C(214)	103(10)
O(213)	C(214)	C(215)	117(5)
C(214)	C(215)	O(216)	106(4)
C(215)	O(216)	C(217)	110(4)
O(216)	C(217)	C(218)	113(4)
C(217)	C(218)	N(201)	116(4)
C(218)	N(201)	C(202)	114(4)
C(218)	N(201)	C(219)	107(3)
C(219)	N(201)	C(202)	118(4)
N(201)	C(219)	C(220)	113(5)
C(219)	C(220)	O(221)	117(6)
C(220)	O(221)	C(222)	123(4)
O(221)	C(222)	C(223)	109(5)
C(222)	C(223)	O(224)	132(8)

Atom 1 Atom 2 Atom 3 Degrees
(Vertex)

C(223)	O(224)	C(225)	130(6)
O(224)	C(225)	C(226)	115(7)
C(225)	C(226)	N(210)	136(8)
N(201)	Na(2)	N(210)	168(2)
N(201)	Na(2)	O(204)	66(1)
N(201)	Na(2)	O(216)	66(1)
N(201)	Na(2)	O(221)	67(1)
N(210)	Na(2)	O(207)	70(2)
N(210)	Na(2)	O(213)	58(2)
N(210)	Na(2)	O(224)	69(2)
O(204)	Na(2)	O(207)	62(2)
O(204)	Na(2)	O(213)	85(1)
O(204)	Na(2)	O(216)	101(1)
O(204)	Na(2)	O(221)	113(1)
O(204)	Na(2)	O(224)	166(1)
O(207)	Na(2)	O(213)	108(1)
O(207)	Na(2)	O(216)	162(1)
O(207)	Na(2)	O(221)	92(1)
O(207)	Na(2)	O(224)	104(2)
O(213)	Na(2)	O(216)	62(1)
O(213)	Na(2)	O(221)	158(1)
O(213)	Na(2)	O(224)	100(1)
O(216)	Na(2)	O(221)	101(1)
O(216)	Na(2)	O(224)	93(2)
O(221)	Na(2)	O(224)	65(1)

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)
C(311)	C(326)	1.37(7)	O(304)	O(321)	4.43(6)
C(312)	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)	Na(3)	C(302)	3.63(6)
C(322)	C(323)	1.30(9)	Na(3)	C(303)	3.71(6)
C(323)	O(324)	1.29(8)	Na(3)	C(305)	3.27(6)
O(324)	C(325)	1.53(7)	Na(3)	C(306)	3.47(6)
C(325)	C(326)	1.36(8)	Na(3)	C(308)	3.27(6)
Na(3)	N(301)	2.84(6)	Na(3)	C(309)	3.61(6)
Na(3)	N(310)	3.14(5)	Na(3)	C(311)	3.56(6)
Na(3)	O(304)	2.84(4)	Na(3)	C(312)	3.51(6)
Na(3)	O(307)	2.62(4)	Na(3)	C(314)	3.51(6)
Na(3)	O(313)	2.76(4)	Na(3)	C(315)	3.27(6)
Na(3)	O(316)	2.70(4)	Na(3)	C(317)	3.02(6)
Na(3)	O(321)	2.74(5)	Na(3)	C(318)	3.46(6)
Na(3)	O(324)	2.96(4)	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 (Å)	Atom 1	Atom 2	Distance (Å)
			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

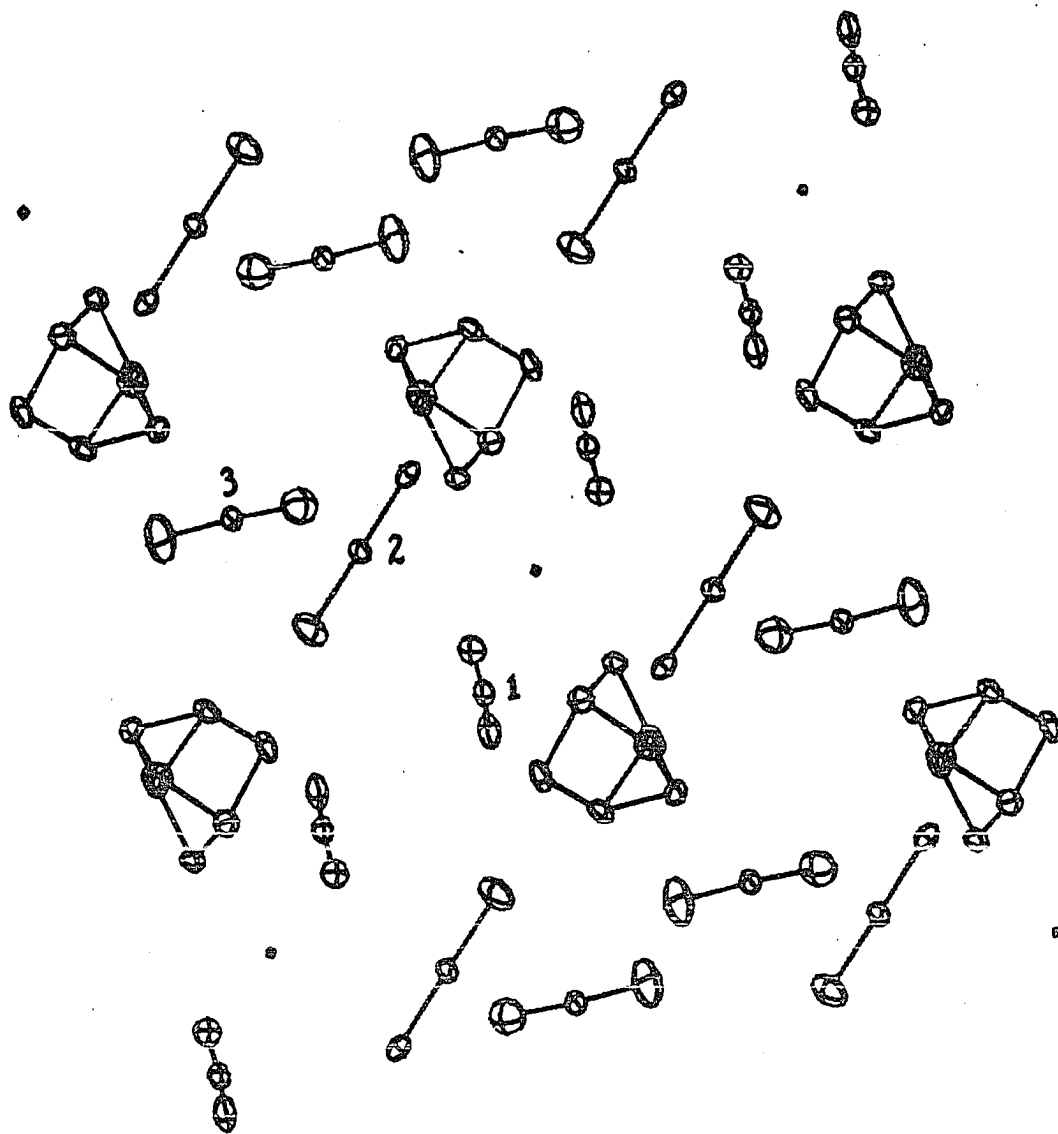


Figure 3. Projection of the structure of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ on the (010) plane.

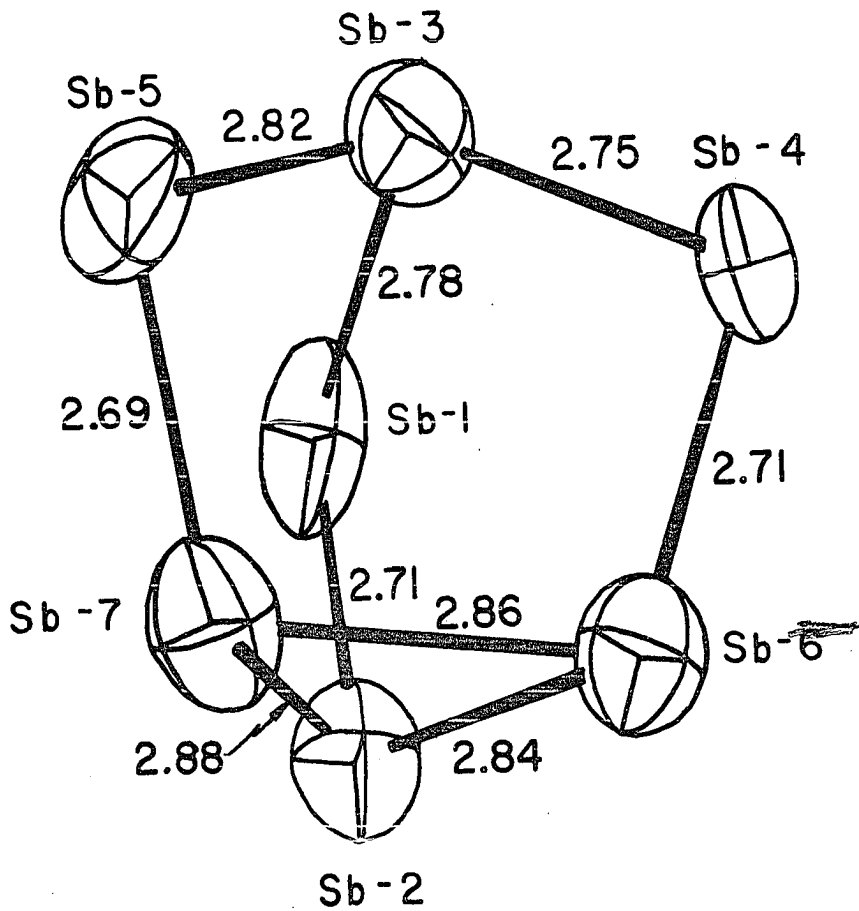


Figure 4. Geometry of the Sb_7^{3-} anion in $(\text{NaC}^+)_3\text{Sb}_7^{3-}$.

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 $0.5(7)^\circ$.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

¹Least 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 bipyramidal 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

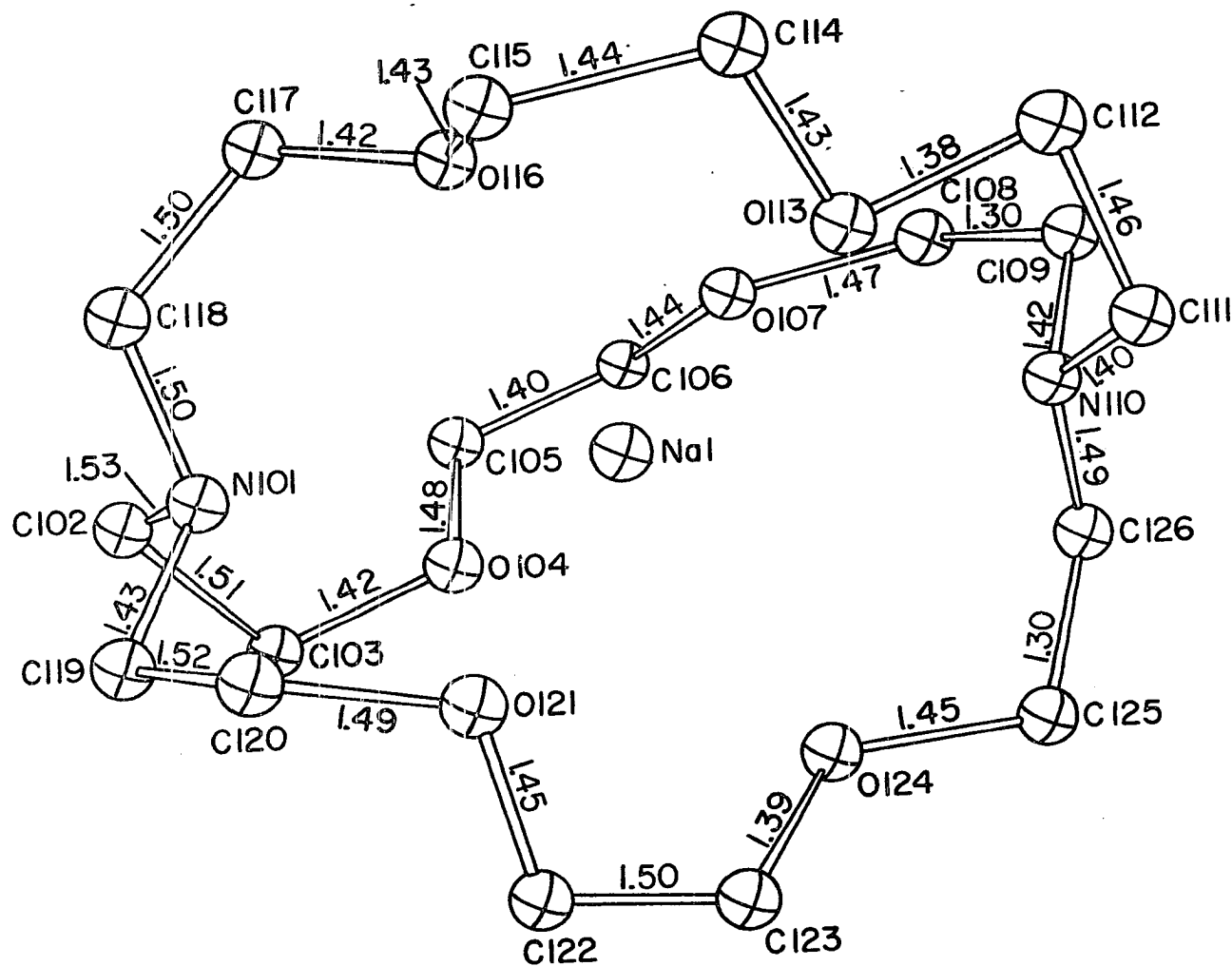


Figure 5. Geometry of the first cryptated sodium cation in $(\text{NaC}^+)_3\text{Sb}_7^{3-}$.

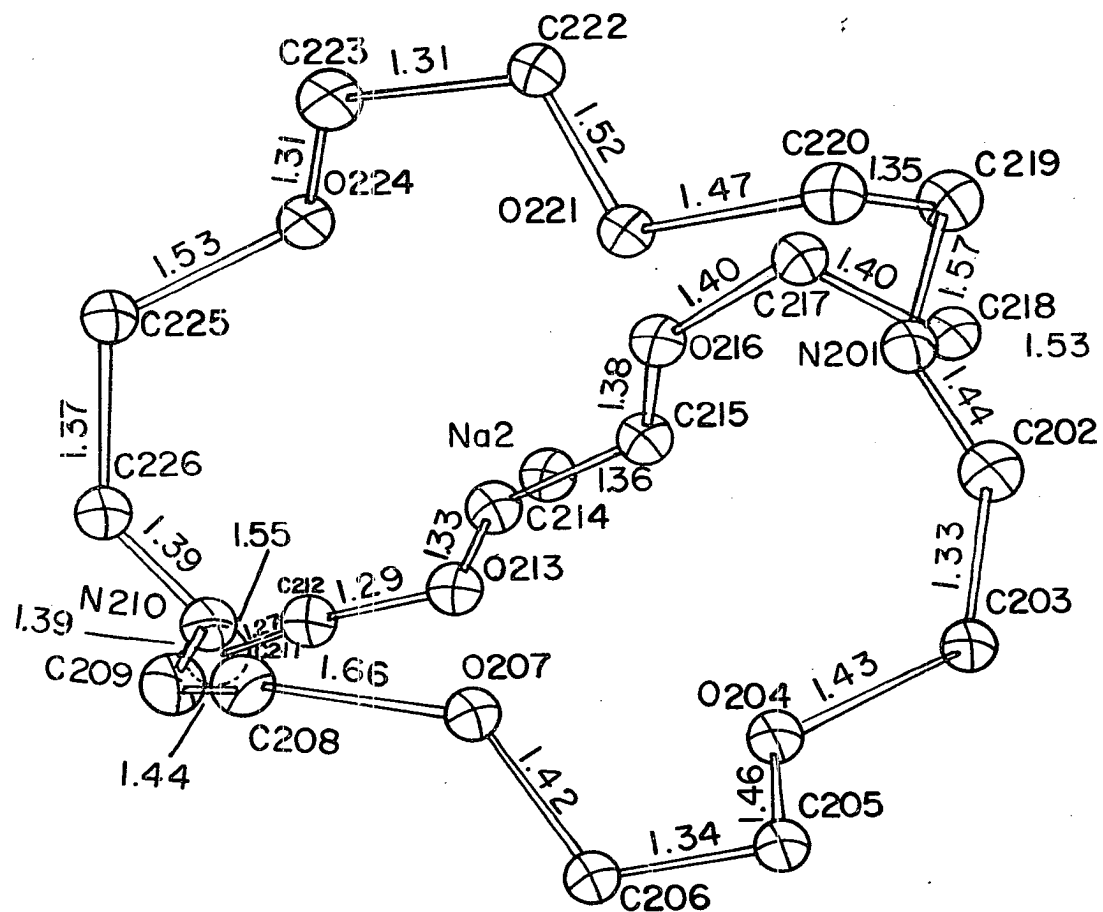


Figure 6. Geometry of the second cryptated sodium cation in $(\text{NaC}^+)_3\text{Sb}_7^{3-}$.

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 5.76Å found here compares with 6.87Å 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 P31c. Although P31c 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 (Å)	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-C1	1.48(2)	1.47(2)	1.46(5)
C1-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 (Å)			
Na-C1	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-C1	107(1)	110(1)	105(4)
C1-N-C1(3)	112(1)	109(1)	113(3)
N-C1-C2	128(1)	113(2)	115(7)
C1-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 0.08Å 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 1.31Å 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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