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The crystal structures of compounds involving metal-metal bonding: I. Gd_8Cl_{12} II. $Te_4(AlCl_4)_2$

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THE CRYSTAL STRUCTURES OF COMPOUNDS INVOLVING
METAL-METAL BONDING. I. $\text{Gd}_8\text{Cl}_{12}$ II. $\text{Te}_4(\text{AlCl}_4)_2$

by

Donald Arthur Lokken

A Dissertation Submitted to the
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1970

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INTRODUCTION

Much attention has recently been focused on metal-metal bonding and other phenomena associated with metals in lower than normal oxidation states. Rewards of these researches have included the discovery of many new and interesting "cluster compounds", as reviewed, for example, by Schäfer and Schnering (1), and Cotton (2). It has also led to the postulation of new types of bonding, e.g. the three-center bonds of the boron hydrides (3) and the delta bond of $\text{Re}_2\text{Cl}_8^{2-}$ (4), as well as examples of apparent delocalization of electrons over polynuclear ions. One case of the latter phenomenon is described by Corbett and Rundle (5) for the Bi_9^{5+} cation.

X-ray diffraction was the only structural technique which yielded unambiguous results in nearly all of these studies, and was the method chosen to resolve the problems encountered in this research.

A few years ago a compound that was thought to be bismuth monochloride was found, by X-ray studies, to be $\text{Bi}_{12}\text{Cl}_{14}$. It contained the homopolyatomic cation Bi_9^{5+} , apparently being stabilized by the large complex anions, $[\text{BiCl}_5]^{2-}$ and $[\text{Bi}_2\text{Cl}_8]^{2-}$ (6). The existence of this cation was rationalized by a molecular orbital treatment of its bonding (5) in which the 22 bismuth p-electrons are contained in eleven bonding

molecular orbitals.

More recent studies have shown that other polybismuth cations exist in the AlCl_4 -system. Bjerrum, Boston and Smith (7, 8) identified the cations Bi_5^{3+} and Bi_8^{2+} from spectral studies of the equilibria of various ratios of BiCl_3 to bismuth metal in molten NaAlCl_4 or the eutectic mixtures of AlCl_3 - NaCl or ZnCl_2 - KCl . Corbett (9) worked out the phase diagram for the pseudo-binary system, $\text{Bi-BiCl}_3\text{-AlCl}_3$, and isolated solid compounds corresponding to $\text{Bi}_5(\text{AlCl}_4)_3$ and $[\text{Bi}_4(\text{AlCl}_4)]_n$. He then assumed $n=2$ in the latter compound, since mull and reflectance spectra agreed quite well with the solution spectrum reported for Bi_8^{2+} (8), and did a series of LCAO-MO calculations, including overlap, for a variety of configurations. These calculations led to unambiguous predictions of trigonal bipyramidal (D_{3h}) geometry for Bi_5^{3+} and square-anti-prismatic (D_{4d}) geometry for Bi_8^{2+} (9).

The first studies reported here were undertaken to determine the nature of these unusual compounds. The chance to test the ability of relatively straight-forward MO theory to predict geometry of unknown species was considered to be an added bonus.

This was not the first attempt to solve crystal structures in this system. Levy, et al. (10, 11) reported radial distribution analyses of the X-ray scattering by

liquid and powdered samples of a compound thought to be $(\text{BiAlCl}_4)_n$ (10). They also reported powder pattern data and the space group of a single crystal. All results indicated, or were consistent with, the presence of triangular bismuth units, implying the presence of the Bi_3^{3+} cation. Corbett has suggested that such an ion does not have a reasonable bonding scheme (9). The trimeric units are consistent with the proposed trigonal bipyramidal structure of the Bi_5^{3+} ion which contains seven such triangles. The powder data reported by Levy, et al. agree quite well with those of $\text{Bi}_5(\text{AlCl}_4)_3$, but nothing resembling their rhombohedral (R3c) unit cell has been found in this study.

Although no structures were solved in the bismuth system and no cation geometries were confirmed, results of the crystal growth experiments, as well as speculation on the nature of the twinning problem encountered, will be reported in Chapter 3.

While the bismuth structural studies were underway the author was helping D. A. Adolphson learn crystallography and grow crystals of the strange compound reported to be $\text{GdCl}_{1.6}$ (12). Magnetic studies (13) showed essentially nothing beyond the $4f^7$ core of Gd^{3+} , leading to speculation of metal-metal bonding. Adolphson's induction into the Army resulted in the author's inheritance of the crystals that had been grown. The determination of the crystal

structure of $\text{Gd}_8\text{Cl}_{12}$ will be reported in Chapter 4 of this thesis.

Simultaneous studies were also taking place on the crystalline phases present in the $\text{Te}-\text{TeCl}_4-\text{AlCl}_3$ system on which Prince¹ was determining the phase diagram. The author ran preliminary single crystal studies on four compounds of undetermined structure, finally choosing the phase corresponding to " $\text{Te}_2(\text{AlCl}_4)$ " for structure studies. The crystal and molecular structures of $\text{Te}_4(\text{AlCl}_4)_2$ will be reported in Chapter 5.

¹D. J. Prince, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1968.

EXPERIMENTAL PROCEDURE

Preparation and Handling of Compounds

Preparation of Gd_8Cl_{12}

In the original report of the existence of " $GdCl_{1.6}$ ", Mee and Corbett (12) stated that they were able to obtain large crystals by equilibration of $GdCl_3$ (m.p. $\approx 605^\circ$) with excess metal at about 650° and then slowly raising the sample, sealed in a tantalum container inside an evacuated silica tube, through a temperature gradient from about 650° at the bottom to about 600° at the top, over a period of several days. In the present study this method produced only crystalline powder. Finally the technique of growing crystals by allowing the trihalide vapor to react with the gadolinium metal was employed. A $1/4$ " x $1/2$ " thermocouple well was welded into a $3/8$ " x 2" tantalum tube which had been cleaned by induction heating under vacuum. The tube was loaded with 0.33 g. $GdCl_3$ and 1.85 g. Gd (4 chunks) in an argon-filled glove box, crimped, and welded shut under argon atmosphere. This tube was placed in a fused silica container, with an internal chromel-alumel thermocouple, evacuated and heated at 610° ¹ (between the peritectic and the eutectic of the system) for nine days. It was then cooled slowly and

¹All temperatures are in degrees Celsius unless otherwise noted.

opened in an argon-filled glove box.¹ Several large (0.2 x 0.8 mm) black crystals were obtained imbedded in a matrix on the gadolinium metal. Most of these were frayed on the ends showing the hair-like structure which had thwarted previous X-ray crystallographic attempts. Efforts to cut these "pillars" into workable lengths all led to "hairs". These seemed quite strong and flexible but any attempts to cut them laterally with a scalpel yielded progressively finer hairs. Finally six or eight of the remaining chunks were mounted in Lindemann glass capillaries where one of them appeared barely adequate for diffraction studies, while the others all gave double or multiple diffraction spots. The size of the crystal was determined by viewing it through a Bausch and Lomb "Stereozoom" microscope equipped with a calibrated scale in one eyepiece. It appeared to be a nearly pentagonal needle about 0.07 mm across by 0.495 mm long when viewed at 60 x magnification.

The density of the phase was determined to be $5.14 \pm .3 \text{ gm cm}^{-3}$ by micropycnometric methods using a 1 cm^3 pycnometer with chloroform (dried over CaH_2) and 36 mg of "bundles" of crystals from the above reaction. Since only this small amount of "clean" material was available, it was

¹D. A. Adolphson, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1968.

dried and reused in the pycnometry to average out some of the random error. The determined density corresponds fairly well with the theoretical, $\rho=5.23$, obtained once the structure was determined.

Since there might be some doubt about the presumed stoichiometry (Cl/Gd=1.6), both emission spectroscopic and electron microprobe analyses were performed on small samples of crystal clusters. The emission spectroscopy eliminated the possible presence of other heavy metals¹ while the electron microprobe analyses² eliminated extraneous elements heavier than chlorine (most of the rare earth metals were observed at the 100 ppm level by fluorescence) and (although at lower sensitivities), were unable to find oxygen or nitrogen. It was concluded from these analyses that the compound was truly a pure, reduced gadolinium chloride.

There were also some clear-white and light red colored needles scattered throughout the system (in and on the matrix). These were very small (ca. 0.02 mm diameter) but a few of each were eventually mounted in capillaries, aligned and photographed. They appeared to be the same compound, apparently with a monoclinic unit cell with $a^{\circ}=7.5\text{\AA}$, $b^{\circ}=10.7\text{\AA}$,

¹E. Dekalb, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1969.

²F. Laabs, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1969.

$c^\circ=8.1\text{\AA}$ and $\beta=103.4^\circ$. This does not correspond directly to any of the three known crystallographic forms of rare-earth metal trichloride (14, 15, 16, 17) but is possibly related to the structure observed for those metals heavier than terbium (e.g., DyCl_3 is monoclinic with $a^\circ=6.91\text{\AA}$, $b^\circ=11.97\text{\AA}$, $c^\circ=6.40\text{\AA}$ and $\beta=101.2^\circ$) (16). The nature of these crystals is therefore not established, they may be a new form of GdCl_3 or some more-reduced chloride or oxychloride. The two colors could result from the presence of f-centers in the red crystals.

Preparation of $\text{Te}_4(\text{AlCl}_4)_2$

The author did preliminary crystallographic studies on phases of the $\text{Te}-\text{TeCl}_4-\text{AlCl}_3$ system in conjunction with the phase diagram and synthetic work already underway.¹ Long needle-like white crystals of the $\text{TeCl}_4-\text{AlCl}_3$ adduct, which spectral evidence indicates can be formulated $(\text{TeCl}_3^+)(\text{AlCl}_4^-)$ ¹ appeared to have an orthorhombic unit cell $13.0\text{\AA} \times 12.6\text{\AA} \times 6.6\text{\AA}$. Two compounds with effective degree of reduction corresponding to " Te_3^+ " were also considered. They both crystallize in hexagonal space groups, one either $P6/m\text{cc}$ or $P6\text{cc}$ with $a^\circ=9.6\text{\AA}$ and $c^\circ=12.8\text{\AA}$, and the other

¹D. J. Prince, Ames Laboratory of the United States Atomic Energy Commission, Iowa State University, Ames, Iowa. Private communication. 1969.

being much larger with $a^\circ=10.1\text{\AA}$ and $c^\circ=24.8\text{\AA}$. Neither diffracted very well, producing blurred spots which decreased in intensity very rapidly with increasing θ , being essentially gone by $\theta=40^\circ$ with $\text{CuK}\alpha$ radiation. It was later determined¹ that the compound with the larger unit cell was a double salt of the " Te_3^+ " species with NaAlCl_4 . The final compound to be studied had a state of reduction corresponding to " Te_2^+ " and was thought to be the ion observed spectrally in molten NaAlCl_4 by Bjerrum and Smith (20) and in fluorosulfuric acid by Gillespie *et al.* (21). They characterized it as Te_4^{2+} analogous to the Se_4^{2+} ion which Gillespie and co-workers had previously reported (22) and predicted to be square-planar from spectroscopic studies and incomplete X-ray diffraction data supplemented by a bonding discussion applying the "closed-shell criterion" (23). In a more comprehensive discussion of bonding in this and similar metal-metal bonded clusters, Corbett (24) arrived at the same prediction.

The compound $\text{Te}_4(\text{AlCl}_4)_2$ is readily prepared by adding the stoichiometric amounts of Te, TeCl_4 and AlCl_3 to a fused silica container in a glove box under inert atmosphere, partially evacuating the tube, sealing it off and heating it

¹D. J. Prince, Ames Laboratory of the United States Atomic Energy Commission, Iowa State University, Ames, Iowa. Private communication. 1969.

for a few hours at a temperature above the melting point of the compound ($\approx 225^\circ$), and then slowly cooling it. Crystals obtained in this way are usually grown together. A better way of growing isolated crystals involves recrystallization from molten NaAlCl_4 . Many isolated crystals too large for X-ray studies are formed in this fashion while smaller ones are more difficult to obtain. In the preliminary X-ray studies one single crystal was found which yielded unit cell constants and space group information but crystals of this compound also diffracted X-rays poorly. Not enough (or strong enough) reflections were found to accomplish a structure determination. Only two more single crystals were obtained from the approximately one hundred crystals considered. One of these was used in the structure determination reported in Chapter 5.

The density of the phase was determined to be 3.04 gm cm^{-3} by weighing and measuring a cast rod. A later repeat of the same thing on another sample¹ gave $\rho=3.05 \text{ gm cm}^{-3}$. These values are known to be slightly low because the rods developed small cracks from shrinkage during cooling. The value, $\rho=3.04$, corresponds to 3.82 molecules of $\text{Te}_4(\text{AlCl}_4)_2$ per unit cell. This is near enough to 4.0 for the difference to be accounted for by the above-mentioned error.

¹D. J. Prince, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1969.

Micropycnometric measurements on samples recrystallized from molten NaAlCl_4 yielded densities of 2.6 and 2.7 gm cm^{-3} , but the crystals used were known to have some NaAlCl_4 ($\rho=2.0$) on them.

Mounting of crystals

The crystals, once grown, were taken into a specially built glove box (23) with a Plexiglas top and a small plate glass window with a work shelf five inches below it. This arrangement permits one to sort and mount the very reactive crystals under inert (argon) atmosphere while observing them through a long focal length microscope. A Bausch & Lomb "Stereozoom" with 0.5 x objective lens and 10 x eyepieces containing a scale calibrated in tenths of millimeters was used. The samples were carefully broken up using a sharp-pointed scalpel or a tungsten wire, since grinding shattered them too badly and coated all fragments with powder. If a single large crystal was found it was removed from the matrix and placed in a small pool of vacuum-melted petroleum jelly (in order to keep the chips from flying) and then cut to the proper size (ca. 0.1 mm cubed) with a scalpel. The desired crystal was then picked up on the end of a thin glass stalk (ca. 0.2 mm diameter) tipped with petroleum jelly and gently inserted into a 0.3 mm i.d. Lindemann (LiBeBO_3) glass capillary. The stalk was then twisted to lightly coat the inside wall

of the capillary with petroleum jelly and deposit the crystal in it. The capillary was then sealed off on a resistance heated wire contained in the glove box. Throughout this delicate operation the very fragile capillary was held in a short piece of 2 mm i.d. Pyrex tubing which enclosed and protected all of the capillary except the funnel-shaped open end. When enough crystals had been mounted and sealed-off the dry-box was opened and the capillaries were shortened to the correct length (ca. 1 cm) with a fine-tipped gas-oxygen flame. This shortened capillary containing the crystal was then held in a 7 mm long by 3 mm o.d. piece of metal tubing, either by modeling clay for preliminary studies or Apiezon W for data taking. This metal tube was then placed in a goniometer head and kept there for all camera and diffractometer work.

X-Ray Diffraction Techniques

Basic diffraction theory

When X-rays fall on any matter with an ordered distribution of electron density with a period of the same order of magnitude as the X-ray wavelength, they are diffracted. In the case of a monocrystal these diffraction maxima are sharp and can be observed as small spots on a film or measured directly by a scintillation counter. These spots yield all of the information necessary to determine the structure of

most crystalline compounds. Their spacing gives the interplanar spacings, d_{hkl} , according to the Bragg relationship, $\lambda = 2d_{hkl} \sin \theta$, in which λ is the wavelength of the radiation and 2θ is the angle between the extended incident beam and the diffracted beam. Their relative intensities yield the actual positions and effective atomic numbers (again relative) of each atom.

Camera techniques

Prior to the collection of intensity data in the studies described here, oscillation photographs were taken on a Weissenberg camera, as described by Buerger (24), in order to align the crystal so that one axis (called the spindle-axis) was normal to the X-ray beam. Several levels of equi-inclination Weissenberg photographs were then taken. This technique involves the use of a shield with a slit in it to allow only one pre-chosen "level" of diffraction maxima (as defined by a straight line on an oscillation photograph) to pass through to the film. These levels correspond to cones of spots diffracted all around the spindle axis. If the spindle axis is the c-axis, for instance, then the "zero-level Weissenberg" will contain all of the $hk0$ reflections while the second-level Weissenberg will contain all of the $hk2$ reflections. The Weissenberg method involves translating the camera back and forth as the crystal oscillates. This

spreads the spots out over the film in a series of arcs or "pinacoids" from which the Miller indices, h , k and l , of each reflection can be readily determined. From these photographs one is able to determine the "extinctions" (positions of systematic zero intensity), and from them, determine the space group. If one needs to know the extinctions along the spindle axis it is necessary to either realign the crystal about another axis for Weissenberg photographs or else photograph it as aligned, using a precession camera (25) which gives an undistorted reproduction of the reciprocal lattice.

Space group determination

The non-extinction conditions for Gd_8Cl_{12} were found to be $(h+k=2n+1)$ which indicates space groups $C2/m$, $C2$, or Cm with the choice among these uncertain without further information. The data seemed to show considerable "profile" (large intensities right next to small ones) indicative of centric space groups¹, so the group $C2/m$ (#12) was chosen for initial consideration. (The space group was subsequently determined to be the acentric Cm (#8)).

In the case of $Te_4(AlCl_4)_2$ the non-extinction conditions $(hk0, h=2n; 0k1, k=2n; h0l, l=2n)$ lead immediately to the unique space group, $Pbca$ (#61).

¹R. K. McMullen, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1969.

Data collection

Once the space group has been determined, intensity data are collected for all of the reflections within one asymmetric unit of reciprocal space for increasing values of theta (until either one has sufficient data to determine the structure or else reflections are so weak as to be indeterminate). This can be done by estimating relative intensities of spots on film, or better, by a scintillation counter on a device known as a diffractometer. In the present study, the data were collected on an automated diffractometer, i.e., one in which a computer controls the diffractometer, via an interface, instructing it to record intensities for positions calculated from a few pieces of input data with little operator interference. The device used here is a Hilger-Watts four circle diffractometer coupled to an SDS 910/1401 computer set up by Dahm, Benson, Nimrod, Fitzwater and Jacobson (26). Routines are programmed for finding maximum intensities of three known peaks and calculating their diffracting positions, which serve to locate all other potential diffraction maxima. Programs can also be called for moving the four space coordinates (defining the orientation of the crystal and the counter), for scanning the diffraction maxima and background, and for periodically rechecking the standard peaks and retuning if necessary. For both of the structure determinations described here

Zr-filtered MoK α radiation was used.

Gd₈Cl₁₂ For the Gd₈Cl₁₂ crystal integrated intensity data were collected. This was done by using a θ -2 θ scan technique with 0.01° θ and 0.4 sec per step. The peak width increases with θ so the number of steps is chosen to be (30 + 1 per degree θ) with a one-half time reading for background at each side of the peak. For example, for a peak at $\theta=30^\circ$, 120 steps would be read at 0.01° spacings and a 1/2 reading would be made at start and finish to determine the background. The total background is then subtracted from the total scan counts to give the integrated intensity. A periodic count was made on the three standard peaks to check for electronic, mechanical, or crystal instability. No significant instability was detected, although the instrument did retune occasionally for maximum precision.

One asymmetric unit of a monoclinic structure includes two octants. For this study, two asymmetric units of data were collected (HKL+ $\bar{H}\bar{K}L$ and $H\bar{K}L+\bar{H}K\bar{L}$) for $0 < \theta \leq 35^\circ$ with MoK α radiation, resulting in about 2800 reflections. The crystal was quite large and diffracted well, giving "observed" intensities for more than 95% of these positions.

Te₄(AlCl₄)₂ The data for the Te₄(AlCl₄)₂ structure determination were recorded similarly, only instead of scanning the peak in steps, a ten second stationary count

was made on the maximum while background readings were taken as before. About 100 reflections were also recorded by the "integrated intensity" scanning method in order to calibrate the peak height data at different values of θ . This time data were taken for $0 < \theta \leq 30^\circ$. Only a small percentage of the positions yielded observed intensities beyond $\theta = 20^\circ$ to 25° . The relationship between the two sets of data was linear ($I_{\text{integ.}} = 0.9 I_{\text{peak ht.}}$) out to $\theta \approx 20^\circ$ where the broadening of the maxima caused a relative increase in the integrated intensities. A correction was worked out but not applied to the final data since most were in the region $0 < \theta < 20^\circ$.

PRELIMINARY STUDIES OF
 $\text{Bi}_5(\text{AlCl}_4)_3$ AND Bi_4AlCl_4
Results of Crystal Growth and
Diffraction Studies

When the crystal search was first begun on this system the phases had not yet been resolved. The samples were quite reactive with air so all handling had to be done in a glove box under argon atmosphere. The high X-ray absorption by the bismuth in the system necessitated the use of quite small crystals (less than 100μ cubed) for diffraction studies. In order to properly see and mount such small crystals it was necessary to use a microscope. This proved to be incompatible with the available glove box so argon-flushed polyethylene glove bags were tried with the microscope inside.

The crystals that were mounted in this fashion never gave satisfactory diffraction patterns. They either were amorphous or else gave powder patterns. Since the powder patterns of the phases were not known it was impossible to tell whether the "crystals" were indeed polycrystalline (or worse) or if they were reacting with the atmosphere of the glove bag to form a polycrystalline oxy-salt. At this stage a glove box designed for the use of a microscope was located (23). It proved to be quite adequate and the crystal search was continued. Most of the first "crystals" were indeed

amorphous. The system has a penchant for glass formation and many of the black, shiny faces observed revealed, on higher magnification, the concoidal fracture associated with obsidian.

The phases were eventually sorted out (9) and two crystallographically distinct compounds became evident. One, which separated from the melt in shale-like leaves (coated with melt), turned out to be the most reduced phase $(\text{Bi}_4^+)_{\text{n}}$. Chips of these were mounted, although they never looked very good, and oscillation and Weissenberg photographs were taken. The spots on the film were always doubled or of higher multiplicity but the unit cell seemed to be orthorhombic with dimensions $18.0\text{\AA} \times 15.5\text{\AA} \times 13.1\text{\AA}$.

The other phase, which corresponds to $\text{Bi}_5(\text{AlCl}_4)_3$, showed more promise. Some crystals were obtained that were nearly perfect cubes and at times the oscillation photographs seemed to be fine. Weissenberg photographs, however, showed doubling of some or all of the spots. The system looked so promising that it was assumed that finding a suitable crystal was only a matter of time. Some two years and 2000 crystals later the project was abandoned. Crystals had been grown directly from the reduced melts by slowly cooling it. They had been formed by recrystallization from various molten salt solvents (NaAlCl_4 , KAlCl_4 , NaCl-AlCl_3 eutectic and KCl-AlCl_3 eutectic). They had even been grown

by a chemical transport reaction in a temperature gradient. The last method produced only a few good crystals, but externally, some of them appeared flawless. The reaction seems to involve the disproportionation of $\text{Bi}_5(\text{AlCl}_4)_3$ (l) to $\text{BiAlCl}_4(\text{g})$ and bismuth metal in the "hot" end ($300^\circ\text{-}400^\circ$). This $\text{BiAlCl}_4(\text{g})$ apparently migrates to the "cold" end ($100^\circ\text{-}300^\circ$) where it disproportionates to $\text{Bi}_5(\text{AlCl}_4)_3$ (liquid or solid, depending upon temperature) plus BiCl_3 and AlCl_3 .

The best of these crystals still gave doubled spots. The "pseudo-symmetry" of the system is face-centered-orthorhombic (nearly cubic) showing extinctions unless h , k and l are all odd or all even. The dimensions were found to be approximately $a^\circ=b^\circ=16.8\text{\AA}$ and $c^\circ=17.2\text{\AA}$. This gives a unit cell of 4866\AA^3 which, along with the density of 4.10 gm cm^{-3} (determined from cast rods), implies $7.75 (\approx 8)$ $\text{Bi}_5(\text{AlCl}_4)_3$ entities per unit cell.

Discussion

One interpretation of the problem invokes the twinning of a monoclinic system to give a pseudo-orthorhombic unit cell. Examples of this phenomenon have recently been presented and discussed by Dunitz (27). In some of the simpler cases the structures have been solved.

In the present example it was decided that, not only was there a variation of about 1° (from 90°) in some of the angles, but that the axial lengths seemed to change as well. That is, a given point of the reciprocal lattice (as photographed) might be doubled in one direction by the 89° - 91° angle splitting and both of the spots there might be doubled in another direction corresponding to two axial lengths; one slightly more than 16.8\AA and the other nearly 17.2\AA .

Apparently the "true" unit cell of $\text{Bi}_5(\text{AlCl}_4)_3$ is of monoclinic or lower symmetry. All three axes seem to be nearly equivalent and the energy required to twin and grow in a slightly less desirable direction is more than compensated for by the large supercooling inherent in the system. The result is a crystal with the observed face-centered orthorhombic pseudosymmetry.

Perhaps one explanation of what is going on is that given by Cullity (28). He refers to the twinning common to FCC metals which he describes as leaving the two parts related by a 180° rotation about a twin axis of the form $\langle 111 \rangle$, or equivalently, by reflection across the $\{111\}$ plane normal to the twin axis. The crystal may then grow in this new orientation or revert back to the original, leaving a twin band which can be symbolized by the sequence

ABCABC

BACBAC

ABCABC

parent
crystaltwin
bandparent
crystal

This type of twinning, repeated many times, might lead to the type of diffraction pattern observed for $\text{Bi}_5(\text{AlCl}_4)_3$. These problems make a meaningful structure solution unlikely except in the improbable event that a "perfect" crystal might someday be obtained at near equilibrium conditions. The best hope for determining the geometry of the Bi_5^{3+} unit by X-ray diffraction probably lies in the ZnCl_4^{2-} system where its spectrum was seen in the melt by G. P. Smith (7). Chances are that it would crystallize in some other (and hopefully less symmetric) space group and also that the dinegative anion might hold the system together more strongly (electrostatically) and hence lead to less thermal motion and better X-ray diffraction.

THE CRYSTAL STRUCTURE OF $\text{Gd}_8\text{Cl}_{12}$

Data Reduction

Absorption correction

Once the data are collected the next steps are collectively called "data reduction". The first item is correction of the raw intensities for preferential absorption of the incident and diffracted beams in some directions, caused by the irregular shape of the crystal. In the studies reported here, this was done by the program ABCOR¹ (29), which calculates a transmission factor, A, given by

$$A = \int \left(\frac{1}{V}\right) \exp[-\mu(r_\alpha + r_\beta)] dV,$$

where the integration is over the volume of the crystal, V, and where μ is the linear absorption coefficient, r_α the path length along the primary beam direction, and r_β that along the diffracted beam direction.

For $\text{Gd}_8\text{Cl}_{12}$ the linear absorption coefficient, μ , was calculated to be 256.5 cm^{-1} from the mass absorption coefficients, μ/ρ , tabulated by Cullity (28) and the experimental density ($\rho=5.1 \text{ gm cm}^{-3}$). Values for A were calculated in the range ($0.146 < A < 0.243$).

The ABCOR program reads h, k and l in "2A4" format

¹Crystallographic computer programs used for this and subsequent steps are listed in Table 1.

Table 1. Computer programs obtained from outside sources

Program name	Language	Description	Authors	Reference
ABCOR	Fortran	Absorption correction for polyhedra	W. R. Busing and H. A. Levy	29
ALF	PL/I	General Fourier synthesis	J. Rodgers and R. A. Jacobson	30
LCR-2	Fortran	Lattice constant least-squares refinement	D. E. Williams	31
ORFLS	Fortran	Oak Ridge cryst. least squares procedure	W. R. Busing, K. O. Martin, and H. A. Levy	32
ORFFE	Fortran	Oak Ridge cryst. function and error program	W. R. Busing, K. O. Martin and H. A. Levy	33
TABLE	Fortran	Structure factor tabulation	M. L. Hackert ^a	

^aHackert, M. L., Department of Chemistry, Iowa State University, Ames, Iowa. Private communication. 1969.

whereas they had been punched in "3I3". This results in a missing minus sign for any negative "h" of magnitude greater than nine. An intermediate program titled "PACH" was written to rectify this.

Data workup

A data workup program was written and used. It divides each integrated intensity by its transmission factor, A, and also by a Lorentz and polarization factor (30) given by

$$L_p = \frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$$

for the 2θ scan employed here. The square root of these corrected intensities is proportional to the absolute value of the structure factor.

Structure factors

The structure factor, F_{hkl} , is the resultant of j waves scattered in the direction of the reflection hkl by the j atoms in the unit cell. Each wave has an amplitude proportional to f_j , the scattering factor of the atom, and a phase δ with respect to the wave scattered by hypothetical electrons at the origin of the cell. The structure factor in exponential form is

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

The electron density is then the Fourier transform of the structure factors¹ and is given by

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx + ky + lz)}$$

Lattice constants

The unit cell parameters and their standard deviations were obtained by a least-squares fit (33) to the 2 θ angles of twelve independent reflections, whose centers were determined by left-right, top-bottom beam splitting on a Hilger-Watts four circle diffractometer (26) using MoK α radiation ($\lambda=0.71069\text{\AA}$). Any error in the instrumental zero was eliminated by centering the reflection at both +2 θ and -2 θ . The final values with estimated standard deviations in parentheses are: $a^\circ=15.2369(42)\text{\AA}$, $b^\circ=3.8963(11)\text{\AA}$, $c^\circ=10.1793(29)\text{\AA}$, $\alpha=\gamma=90.000^\circ$, and $\beta=117.662(29)^\circ$.

Structure Determination

Solving the structure

Once the magnitudes of the structure factors are known

¹The derivation and more complete discussion of these relationships can be found in any standard crystallographic text such as Stout and Jensen (34) or Buerger (35).

some method is usually sought to determine their signs (or phases) with which a Fourier map can be generated to locate actual atomic positions. The approach used here is that of Patterson (36). He pointed out that a Fourier calculation could be carried out using the phaseless quantities $|F|^2$ as the coefficients. This results in a map having maxima corresponding to all interatomic vectors with magnitudes proportional to the products of the atomic numbers of the two atoms involved. The Patterson function can be expressed as

$$P(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx+ky+lz)$$

The structure factors from the data workup were used to generate a three-dimensional Patterson¹ map. All 1378 reflections of the HKL + $\bar{H}KL$ data set were used.

The Patterson map seemed to be quite straightforward. All of the vectors lay on the $y=0$ and $y=\frac{1}{2}$ sections indicating a two-dimensional layer structure. However the spectre of "partial occupancy" or some such disorder hung overhead.

Interpretation of the Patterson map on the bases of of the centric (C2/m) space group yielded one two-fold and

¹The Patterson map and all other Fourier maps were generated by the program ALF by Rodgers and Jacobson (30).

two four-fold metal positions. A few cycles of least-squares refinement¹ led to a residual index², $R=0.24$, using the 300 strongest reflections. The unit cell was really too small to accommodate all of these metals, so the two four-fold positions were tried at one-half occupancy (as one might find for a disordered structure). This lowered the R-factor to 0.22 but a subsequent Fourier map was still ambiguous as to proper chlorine positions. Using the 1378 reflections of the complete HKL + $\bar{H}KL$ data-set resulted in $R=0.34$ but did not help locate the chlorines.

At this point it was decided to revert to one of the acentric space groups (C2 or Cm). Since Patterson peaks occur only at $y=0$ and $y=\frac{1}{2}$, the group C2 would be the same as C2/m. This left only Cm to be considered. After some manipulation of possible metal and chlorine positions, four two-fold gadoliniums and six two-fold chlorines were put into the unit cell. Three cycles of least squares refinement gave an unweighted R-factor of 0.090 and a

¹A full-matrix least-squares refinement was carried out using ORFLS (32) modified to correct for both real and imaginary parts of anomalous dispersion. The scattering factors used are those of Hansen, et al. (37) with correction for anomalous dispersion (38).

²The residual indices are defined by:

$$\begin{array}{ll} \text{unweighted} & R = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|} \\ \text{weighted} & R_w = \left[\frac{\sum_w (|F_o| - |F_c|)^2}{\sum_w |F_o|^2} \right]^{\frac{1}{2}}. \end{array}$$

difference Fourier map with very little residual electron density.

Refinement

The absorption correction (29) was repeated, using more accurate crystal dimensions and a new linear absorption coefficient calculated from the newly determined stoichiometry. Since most of the reflections were large and counter statistics should not contribute significantly to their reliability, a weight of 1.0 was used for all reflections. Several cycles of least squares refinement with anisotropic thermal parameters led to $R=0.053$ and $R_w=0.065$ (using the entire HKL + $\bar{H}KL$ dataset (1378 reflections)). Sorting out the 47 "unobserved" reflections ($F_{obs} < 3\sigma_F$) resulted in $R=0.073$ and $R_w=0.083$ for isotropic refinement, and $R=0.052$ and $R_w=0.065$ for anisotropic refinement on the 1331 observed reflections.

The atomic positions and thermal parameters of the isotropic and anisotropic refinements are tabulated in Tables 2 and 3. The observed and calculated structure factors are listed in Table 4. A projection of the structure down the unique b-axis, from which atoms listed in the tables may be located, is shown in Figure 1. A perspective drawing of the metal chain is to be found in Figure 2.

Table 2. Final positions and temperature factors^a from isotropic refinement of Gd₈Cl₁₂

Atom	x	y ^b	z	B
Gd 1 ^c	0.0	0.0	0.0	0.78(5)
Gd 2	0.2737(3)	0.0	0.7568(4)	0.72(5)
Gd 3	0.5463(3)	0.0	0.3417(4)	0.64(5)
Gd 4	0.8207(1)	0.0	0.1029(2)	0.60(4)
Cl 5	0.1786(16)	0.0	0.9336(22)	1.41(28)
Cl 6	0.0712(12)	0.0	0.5642(17)	0.70(20)
Cl 7	0.4582(14)	0.0	0.7794(20)	1.15(26)
Cl 8	0.3590(13)	0.0	0.3169(18)	0.80(22)
Cl 9	0.7532(15)	0.0	0.5390(23)	1.42(28)
Cl 10	0.6405(12)	0.0	0.1682(16)	0.53(18)

^aErrors in least significant digits from ORFLS (34) are in parentheses.

^bFixed by symmetry of cell.

^cGd 1 chosen to define the origin.

Table 3. Final positions and anisotropic thermal parameters^a for Gd₈Cl₁₂

Atom	x	y ^b	z	β_{11} ^c	β_{22}	β_{33}	β_{13}
Gd 1 ^d	0.0	0.0	0.0	6(1)	55(11)	38(3)	4(1)
Gd 2	0.2738(2)	0.0	0.7575(4)	6(1)	80(11)	30(3)	4(1)
Gd 3	0.5463(2)	0.0	0.3426(3)	6(1)	122(12)	20(2)	1(1)
Gd 4	0.8208(11)	0.0	0.1029(2)	7(1)	154(13)	15(2)	2(1)
Cl 5	0.1784(11)	0.0	0.9336(18)	8(5)	466(98)	34(13)	2(7)
Cl 6	0.0721(10)	0.0	0.5658(16)	6(4)	105(52)	56(13)	14(6)
Cl 7	0.4605(10)	0.0	0.7828(13)	9(5)	74(49)	11(8)	5(5)
Cl 8	0.3610(12)	0.0	0.3181(20)	7(5)	388(96)	69(17)	11(8)
Cl 9	0.7546(11)	0.0	0.5409(14)	11(6)	335(81)	16(10)	-4(6)
Cl 10	0.6403(9)	0.0	0.1684(14)	5(5)	35(41)	31(11)	8(6)

^aErrors in least significant digits from ORFLS (34) are in parentheses.

^bFixed by symmetry of cell.

^c β 's have been multiplied $\times 10^4$, $\beta_{12} = \beta_{23} = 0$.

^dGd 1 chosen to define origin.

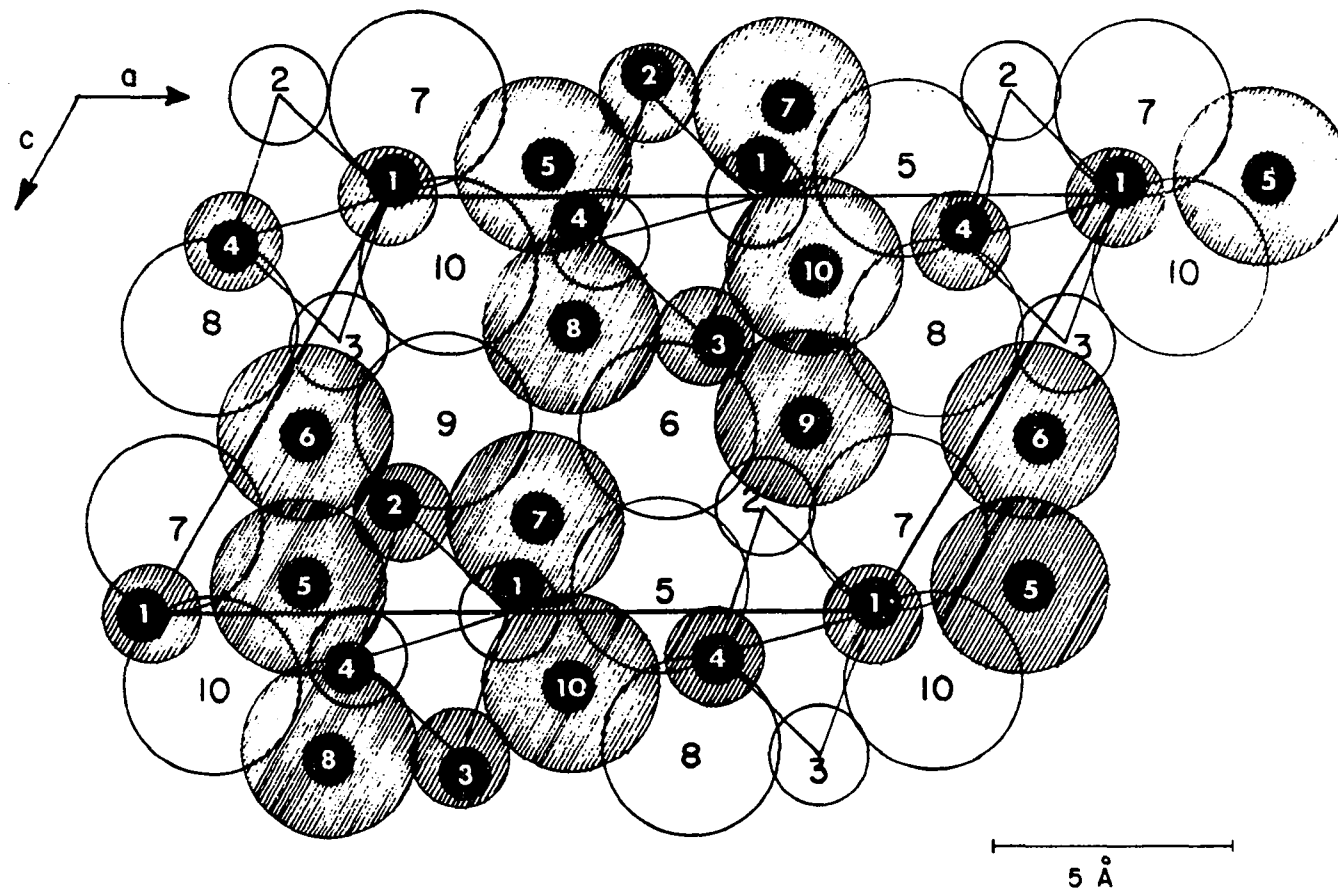


Figure 1. Projection of the structure of Gd_8Cl_{12} on the (010) plane

Atoms at $y=0.5$ are represented by open circles while those at $y=0.0$ are shaded. The numbers on the atoms correspond to Tables 2 and 3. Atomic boundaries are drawn using ionic radii ($Cl^- = 1.81\text{\AA}$, $Gd^{3+} = 1.02\text{\AA}$).

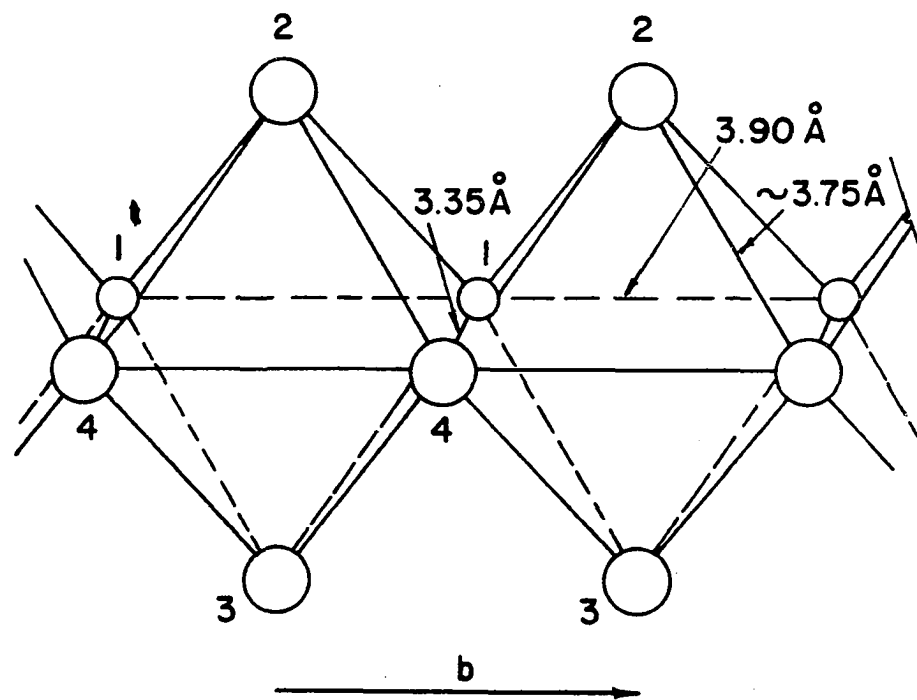


Figure 2. Perspective representation of a section of the metal chain in Gd_8Cl_{12}

The circles represent gadolinium atoms with the numbers corresponding to Tables 2, 3 and 4 and to Figure 1.

Table 4. Observed and calculated structure factors^a for Gd₈Cl₁₂

Table with multiple columns containing numerical data for structure factors. The table is organized into several sections, likely corresponding to different Miller indices (hkl) or symmetry-equivalent reflections. Each section contains observed (O) and calculated (C) values for various reflections. The data is presented in a grid-like format with rows and columns of numbers.

^aStructure factors have been multiplied x 10.

Improving the refinement A few of the axial reflections (e.g., $hkl=200, 400, 600, 800$) are observed to be quite a bit larger than F_{calc} (Table 4). This can probably be explained by a phenomenon observed earlier. While scanning out the y-axis, it was noticed that a broad peak was observed for the symmetry extinct 010 reflection. Upon considering its size and shape, it was concluded that it was a cutoff on white radiation peak (Zr-filtered Mo radiation has a profile showing a peak at one half the wave length of $MoK\alpha$). This can be expected to incorrectly elevate the observed intensities of reflections from any plane with twice the d-spacing of a very strongly diffracting plane.

Elimination or correction of these reflections and the adoption of a weighting scheme might lower both the R-factor and the standard deviations by a small amount but this does not seem worthwhile at this time.

A difference electron density map (30) showed that all atoms had been properly accounted for. The greatest profile on the map amounted to less than $\pm 1.5 e^{-}/\text{\AA}^3$.

Interatomic distances and angles

Interatomic distances and angles were computed using ORFFE, the function and error program of Busing et al. (33).

The estimated standard deviations were obtained from the variance - covariance matrix of the final least-squares cycle. These are all tabulated from isotropic refinement in Table 5 and from anisotropic refinement in Table 6. The atoms at $y=0.5$ are marked by asterisks and correspond to the unshaded circles in Figure 1 (which is a projection of the entire structure down $[010]$).

Discussion

The enigmatic compound Gd_8Cl_{12} is not fully understood even now that its structure is known. The question, "Why does it exist at all?", is still unanswered. It appears to owe its existence to the energy gained by metal-metal bond formation. The structure seems to consist of strongly bonded gadolinium "dimers" (atoms 1 and 4 in both Figures 1 and 2) held together by more weakly bonded "bridging" gadoliniums (atoms 2 and 3) to give infinite chains. The short distance is 3.349\AA (compared with 3.573\AA and 3.636\AA in hexagonal close-packed gadolinium metal) (39) while the bridging distance varies from 3.71\AA to 3.78\AA and the distance between equivalent atoms in the b-direction is 3.896\AA .

All of these distances are probably short enough for some orbital overlap but whether the longer ones can be considered metal-metal bonds or not is questionable. It has

Table 5. Interatomic distances and angles^a from isotropic refinement of Gd₈Cl₁₂

Interatomic Distances			Interatomic Angles			
Reference Atom	Neighbor Atom	° A	Atom 1	Atom 2 (Vertex)	Atom 3	Degrees
Gd 1	Gd 4	3.349(2)	Gd 1	Gd 2*	Gd 4	52.89(5)
	Gd 2*	3.726(4)	Gd 1	Gd 3*	Gd 4	53.30(5)
	Gd 3*	3.757(3)	Gd 2	Gd 4*	Gd 3	93.26(7)
Gd 4	Gd 2*	3.792(3)	Gd 2	Gd 1*	Gd 3	93.56(7)
	Gd 3*	3.709(4)	Gd 1	Gd 2	Gd 1*	63.04(7)
Gd 2	Gd 3	5.453(3)	Gd 1	Gd 3	Gd 1*	62.47(6)
	Gd 3*	4.479(5)	Gd 4	Gd 2	Gd 4*	61.83(6)
Gd 1	Cl 5	3.09(2)	Gd 4	Gd 3	Gd 4*	63.36(7)
	Cl 7*	2.81(1)	Cl 7	Gd 1	Cl 7*	87.6(5)
	Cl 10*	2.81(1)	Cl 10	Gd 1	Cl 10*	87.7(4)
Gd 4	Cl 10	3.11(2)	Cl 9	Gd 2	Cl 9*	86.0(6)
	Cl 5*	2.83(1)	Cl 5	Gd 1	Cl 10*	68.6(4)
	Cl 8*	2.78(1)	Cl 7*	Gd 1	Cl 10*	80.3(4)
Gd 2	Cl 7	2.71(2)	Cl 6	Gd 2	Cl 9*	76.6(4)
	Cl 5	2.79(2)				
	Cl 6	2.79(2)				
	Cl 9*	2.86(2)				
Gd 3	Cl 8	2.75(2)	<u>Dihedral Interplanar Angle</u>			
	Cl 10	2.74(2)	Atoms of Plane 1	Atoms of Plane 2	Degrees	
	Cl 9	2.84(2)	Gd 1	Gd 2		
	Cl 6*	2.88(1)	Gd 4	Gd 3	91.33(5)	
Cl 10	Cl 9	3.34(2)	Gd 1*	Gd 2*		
	Cl 8*	3.53(2)				
	Cl 5*	3.335(9)				
Cl 7	Cl 5*	3.55(2)				
	Cl 9*	3.53(2)				
Cl 6	Cl 8*	3.61(2)				
	Cl 9*	3.50(1)				

^aEstimated standard deviations from ORFFE (35) are in parentheses.

* Indicates atom at $y = 0.5$.

Table 6. Interatomic distances and angles^a from anisotropic refinement of Gd₈Cl₁₂

Interatomic Distances			Interatomic Angles			
Reference Atom	Neighbor Atom	$\overset{\circ}{\text{A}}$	Atom 1	Atom 2 (Vertex)	Atom 3	Degrees
Gd 1	Gd 4	3.349(1)	Gd 1	Gd 2*	Gd 4	52.96(4)
	Gd 2*	3.725(3)	Gd 1	Gd 3*	Gd 4	53.22(4)
	Gd 3*	3.764(3)	Gd 2	Gd 4*	Gd 3	93.35(6)
Gd 4	Gd 2*	3.785(3)	Gd 2	Gd 1*	Gd 3	93.49(6)
	Gd 3*	3.711(3)	Gd 1	Gd 2	Gd 1*	63.07(6)
Gd 2	Gd 3	5.454(3)	Gd 1	Gd 3	Gd 1*	62.34(6)
	Gd 3*	4.479(5)	Gd 4	Gd 2	Gd 4*	61.95(5)
Gd 1	Cl 5	3.09(2)	Gd 4	Gd 3	Gd 4*	63.32(7)
	Cl 7*	2.794(8)	Cl 7	Gd 1	Cl 7*	88.4(3)
	Cl 10*	2.811(9)	Cl 10	Gd 1	Cl 10*	87.7(4)
Gd 4	Cl 10	3.12(1)	Cl 9	Gd 2	Cl 9*	86.1(4)
	Cl 5*	2.83(1)	Cl 5	Gd 1	Cl 10*	68.7(3)
	Cl 8*	2.78(1)	Cl 7	Gd 1	Cl 10*	79.8(3)
Gd 2	Cl 7	2.74(1)	Cl 6	Gd 2	Cl 9*	76.9(3)
	Cl 5	2.78(2)				
	Cl 6	2.77(1)				
	Cl 9*	2.85(1)				
Gd 3	Cl 8	2.72(2)				
	Cl 10	2.75(1)				
	Cl 9	2.86(1)				
	Cl 6*	2.88(1)				
Cl 10	Cl 9	3.36(2)	Gd 1	Gd 2		
	Cl 8*	3.56(2)	Gd 4	Gd 3	91.33(4)	
	Cl 5*	3.337(7)	Gd 1*	Gd 2*		
Cl 7	Cl 5*	3.53(2)				
	Cl 9*	3.54(2)				
Cl 6	Cl 8*	3.60(2)				
	Cl 9*	3.50(1)				

Dihedral Interplanar Angle		
Atoms of Plane 1	Atoms of Plane 2	Degrees
Gd 1	Gd 2	
Gd 4	Gd 3	91.33(4)
Gd 1*	Gd 2*	

^aEstimated standard deviations from ORFFE (35) are in parentheses.

* Indicates atom at $y = 0.5$.

been pointed out¹ that there is a plethora of orbitals, unlimited by symmetry consideration, available for bonding between the metals.

One measure of the degree of bond formation is given by Pauling (39). Using his bond-order equation

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

where n is the bond order and $D(1)$ is twice the "single-bond radius" (3.246\AA for gadolinium) (39), one obtains bond orders of 0.67 for the "dimers" and 0.15 for the bridging metals, (metallic gadolinium spreads three electrons over 12 bonds for $n=0.25$).

Some of these chlorines approach the gadoliniums even closer (2.71\AA) than they approach the Gd^{3+} ions in Gd Cl_3 (closest approach = 2.82\AA) (14), although a direct comparison cannot be made since the latter has a higher coordination number of chlorines.

The chlorine-chlorine approach is also very close in some cases (3.34\AA as compared with 3.62\AA for the sum of the usual ionic radii (39)), but this phenomenon is also observed in the trichloride (14). It is therefore uncertain to what extent these relatively short Gd-Cl and Cl-Cl distances correspond to participation by the chlorines

¹J. D. Corbett, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1969.

in covalent bonding. If one considers the chlorines as primarily ionic, they are situated at about where they would be expected; filling the holes in the metallic structure and nestling as near as possible to the more positively charged metals.

The structure does account for most of the unusual properties of the system. The extreme crystal strength in the b-direction is probably attributable to the metal-metal bonded chains. These could also allow electron spin pairing, accounting for the low magnetic susceptibility (13). The lack of metallic conductance along the needle axis (b-direction) found by Mee and Corbett (12) is neither justified nor refuted. For one thing, their crude measuring technique might have failed to properly contact the ends of the metal chains (since the crystals easily fray). It is possible that the bridging metal bonds might be too long to allow sufficient overlap for conduction-band formation or that any bands formed are filled. This latter possibility is not very likely because, as mentioned before, there seem to be a great number of atomic orbitals which could be used for direct sigma-type bonding.

The reason for the unusual stoichiometry of Gd_8Cl_{12} is still a mystery. One does not encounter many "sesquichlorides" in the literature!

Strange as this compound is, similar compounds seem to

exist among the scandium halides where McCollum and Corbett (40) have found $\text{ScCl}_{1.5}$ and $\text{ScBr}_{1.5}$. Single crystals of these compounds have not been obtained but the same fibrous crystal habit common to $\text{Gd}_8\text{Cl}_{12}$ is observed.

THE CRYSTAL STRUCTURE OF $\text{Te}_4(\text{AlCl}_4)_2$

Data Reduction

Data collection

The data collection for $\text{Te}_4(\text{AlCl}_4)_2$ proceeded parallel to that described for $\text{Gd}_8\text{Cl}_{12}$.¹ In all, 2616 independent reflections were recorded in one octant (HKL) for $0 < \theta \leq 30^\circ$. Although these were peak height data, equivalent peaks measured by the scanning procedure indicated a linear relationship between the two for the region containing most of the significant reflections.

Absorption correction

Absorption corrections were made using ABCOR (29) with $\mu = 83.04 \text{ cm}^{-1}$, calculated from Cullity's (28) mass absorption coefficients and the theoretical density (3.2 gm cm^{-3}) expected for four $\text{Te}_4(\text{AlCl}_4)_2$ entities per unit cell. Since the linear absorption coefficient is quite small, the irregular crystal was merely approximated by the nearest rectangular plate ($50 \times 160 \times 200 \mu$). Transmission factors were in the range ($0.284 \leq A \leq 0.660$).

Data workup

Lorentz and polarization corrections were applied as before¹. This time however, the standard deviations, σ_I and

¹cf. Chapter 4, "The Crystal Structure of $\text{Gd}_8\text{Cl}_{12}$ ", this text.

σ_F are more significant. This crystal was quite small and diffracted poorly so counter statistics are a significant source of error in the intensities and hence in the structure factors. For this reason the σ_F values were used not only as the criterion for whether or not a weak reading was an "observed" peak, but also as the basis of a weighting scheme in the least-squares refinement, reflecting the reliability of each reflection. In the data-workup, the standard deviation in intensity measurements was computed as

$$\sigma_I = [I_{\text{back}} + I_{\text{tot}} + (\Delta I_{\text{back}} \times I_{\text{back}}) + (\Delta I_{\text{tot}} \times I_{\text{tot}})]^{\frac{1}{2}}$$

The standard deviation in the structure factor was then taken as

$$\sigma_F = \left[\frac{I_{\text{integ}} + \sigma_I}{L_p \times A} \right]^{\frac{1}{2}} - F_{\text{obs}}$$

where

$$F_{\text{obs}} = [I_{\text{integ}} / L_p \times A]^{\frac{1}{2}}$$

If one considers $3\sigma_F$ to be the threshold level for F_{obs} , then a total of 1532 of the 2616 reflections were definitely observed.

Lattice constants

The unit cell parameters were determined from the

orientation matrices computed while aligning¹ the crystal on the Hilger-Watts four circle diffractometer. The symmetry of the cell (orthorhombic space group Pbc_a (#61)) requires that $\alpha=\beta=\gamma=90.000^\circ$. Therefore the axial lengths calculated from the matrices giving $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ nearest to zero should be most nearly correct. The errors in parentheses were computed from the deviations among the parameters for different "tunings" by the automated unit. Final values are; $\underline{a}=10.740(5)\text{\AA}$, $\underline{b}=14.128(6)\text{\AA}$, $\underline{c}=11.834(5)\text{\AA}$, and $\alpha=\beta=\gamma=90.000^\circ$.

Structure Determination

Solving the structure

A Patterson map (30) was generated from all 2616 pieces of data (including "unobserved").

Harker sections One of the better ways of extracting useful structural information from a Patterson map is that described by Harker (41). He pointed out that particularly high concentrations of vector points occur on the Patterson because vectors between corresponding atoms related by symmetry elements have one or two constant coordinates.

In the space group Pbc_a considered here, the a-glide mirrored in the c-direction should introduce peaks at

¹The reflections used for alignment were hkl=060, 006 and 800.

$(1/2, 0, w)$, the b-glide mirrored in the a-direction, $(u, 1/2, 0)$, and the c-glide mirrored in the b-direction, $(0, v, 1/2)$. The relative heights of the largest "Harker" peaks found on the Patterson map, followed by their coordinates, are: 204($1/2, 0, .234$), 171($1/2, 0, .371$), 349($0, .335, 1/2$), 252($.28, 1/2, 0$) and 419($1/2, 1/2, 0$).

The first two of these give potential z-coordinates of .367, .133, .436 and .064. Only two y-coordinates are found; $y=.418$ and $.082$. The 252 peak yields $x=.391$ and $.109$, while the exceptionally large 419 peak seems to indicate $x=0$ or 0.5 .

There should be at least two independent telluriums in the unit cell since the density and stoichiometry require sixteen tellurium atoms and the highest multiplicity of any position is eight-fold. The fact that only one set of y-coordinates was found was very puzzling until it was observed that two of the stronger non-Harker peaks (104 and 109) had $y=.336$ which is the difference between the two y-components found from the Harker peak at 349. This indicates that both asymmetric tellurium atoms have approximately the same y-components and also explains the large size of the 349 peak. The 419 peak is also apparently doubled from what would have been expected by the x coordinates being (accidentally) very nearly zero and one-half.

The problem of which combinations of the four x-, two y-, and four z-components to use was solved by comparing the larger non-Harker peaks assuming that they arise from interset vectors. The proper combinations located the tellurium atoms in eight-fold general positions. The coordinates of those in the first octant are (0, .082, .367) and (.391, .418, .436).

Using these positions for two cycles of least-squares refinement¹ resulted in an R-factor of 0.50. Despite this unexpectedly high value, a Fourier map revealed a nearly square planar cluster of tellurium atoms about the center of symmetry at (1/2, 1/2, 1/2) with the reasonable bond distances $\approx 2.7\text{\AA}$. There were additional peaks on the map which could be interpreted as one eight-fold set of aluminum atoms surrounded tetrahedrally by four eight-fold sets of chlorines. A few cycles of "least-squares" brought the R-factor down to 0.25. Refinement with anisotropic temperature factors improved this only slightly (to 0.22), before some of the temperature factors went "non-positive definite".

¹A full-matrix least-squares refinement was carried out using ORFLS (32) modified to correct for both real and imaginary parts of anomalous dispersion. The scattering factors used are those of Hansen, et al. (37) with correction for anomalous dispersion (38).

Refinement

The author, while cursing the poor quality of the crystal and of the peak height data made a thorough comparison of the observed and calculated structure factors. This led to the discovery of certain trends in the mis-match which pointed directly to the absorption correction. An error of 90° (in the direction the axis was "pointing" while diffracting) was found. Correction of this, followed by least-squares refinement, resulted in $R=0.186$ and $R_w^1=0.116$ for the entire set of intensity data (2616 reflections). Allowing the thermal parameters to vary anisotropically resulted in $R=0.114$ and $R_w=0.088$.

It was next observed that the greatest part of the misfit was caused by the 020 reflection ($F_{\text{obs}} = 24$, $F_{\text{calc}} = 292$). A precession photograph was taken to check this. The 020 reflection was one of the strongest on the film. Apparently some error (perhaps mechanical) had been encountered while measuring it on the diffractometer. A few cycles of anisotropic least-squares refinement without the 020 reflection led to $R=0.104$ and $R_w=0.039$.

If one considers $F_{\text{obs}} > 3\sigma_F$ as the threshold for "observed" reflections, only 1531 of the 2615 reflections

¹The weighting scheme uses $w=1/\sigma_F$, thereby basing the reliability of an intensity reading on counter statistics. This is especially justified in this case since so many reflections are very weak.

remain. Least-squares refinement using these reflections and isotropic temperature factors gives $R=0.151$ and $R_w=0.084$. The use of anisotropic thermal parameters improves this to $R=0.076$ and $R_w=0.037$.

Atomic coordinates and temperature factors from the final isotropic refinement are given in Table 7 while those from the anisotropic refinement are in Table 8. A projection of the structure onto the (001) plane is shown in Figure 3. The parallelograms represent the Te_4^{2+} units with the heavily lined boundaries facing the viewer. The aluminum atoms are indicated by '+' and the chlorine atoms by spots. Tetrahedra marked with dashed lines have the apex directed away from the viewer. The shaded tellurium clusters have their centers at $y=0.500$ while the shaded tetrahedra are centered at $y=0.416$ and $y=0.584$. The unshaded Te_4^{2+} clusters are at $y=0.00$ and the AlCl_4^- tetrahedra at $y=0.084$ and -0.084 . The positions of the apical chlorine atoms (Cl 1) in the projection indicate the "tilt" of the tetrahedra with respect to the (001) plane.

Final observed and calculated structure factors are listed in Table 9.

Table 7. Final positions and temperature factors^a from isotropic refinement^b of $\text{Te}_4(\text{AlCl}_4)_2$

Atom	x	y	z	B
Te 1	0.0109 (2)	0.0740 (1)	0.3682 (2)	4.88 (5)
Te 2	0.3924 (2)	0.4100 (1)	0.4341 (2)	5.14 (5)
Al 1	0.3882 (9)	0.3586 (6)	0.0841 (7)	4.4 (2)
Cl 1	0.3835 (10)	0.1222 (7)	0.4100 (8)	8.4 (3)
Cl 2	0.0694 (10)	0.3306 (7)	0.3553 (7)	7.7 (2)
Cl 3	0.3129 (8)	0.4787 (5)	0.1715 (6)	5.4 (2)
Cl 4	0.2761 (8)	0.2402 (6)	0.1262 (7)	6.8 (2)

^aErrors in the least significant digits from ORFLS (34) are in parentheses.

^bIn the final cycle, each variable shifted no more than 0.03 times the error associated with it.

Table 8. Final positional and anisotropic thermal parameters^{a,b} for Te₄(AlCl₄)₂

Atom	x	y	z	β_{11}^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te 1	0.0106(1)	0.0742(1)	0.3681(1)	151(1)	61(1)	70(1)	15(1)	1(1)	8(1)
Te 2	0.3926(1)	0.4098(1)	0.4342(1)	151(1)	62(1)	78(1)	-26(1)	-6(1)	-1(1)
Al 1	0.3883(4)	0.3584(3)	0.0840(3)	123(6)	55(2)	65(3)	2(3)	-8(4)	-2(2)
Cl 1	0.3834(5)	0.1227(3)	0.4102(3)	246(8)	153(4)	64(3)	-16(5)	7(4)	-16(3)
Cl 2	0.0696(4)	0.3306(3)	0.3544(4)	123(5)	104(3)	167(5)	28(4)	27(4)	17(3)
Cl 3	0.3131(4)	0.4786(2)	0.1714(3)	151(6)	60(2)	100(3)	21(3)	-19(3)	-14(2)
Cl 4	0.2756(4)	0.2398(3)	0.2157(3)	151(6)	64(2)	156(4)	-4(3)	45(4)	-9(3)

^aErrors in the least significant digits from ORFLS (34) are in parentheses.

^bIn the final cycle, each variable shifted no more than 0.01 times the error associated with it.

^c β 's have been multiplied $\times 10^4$.

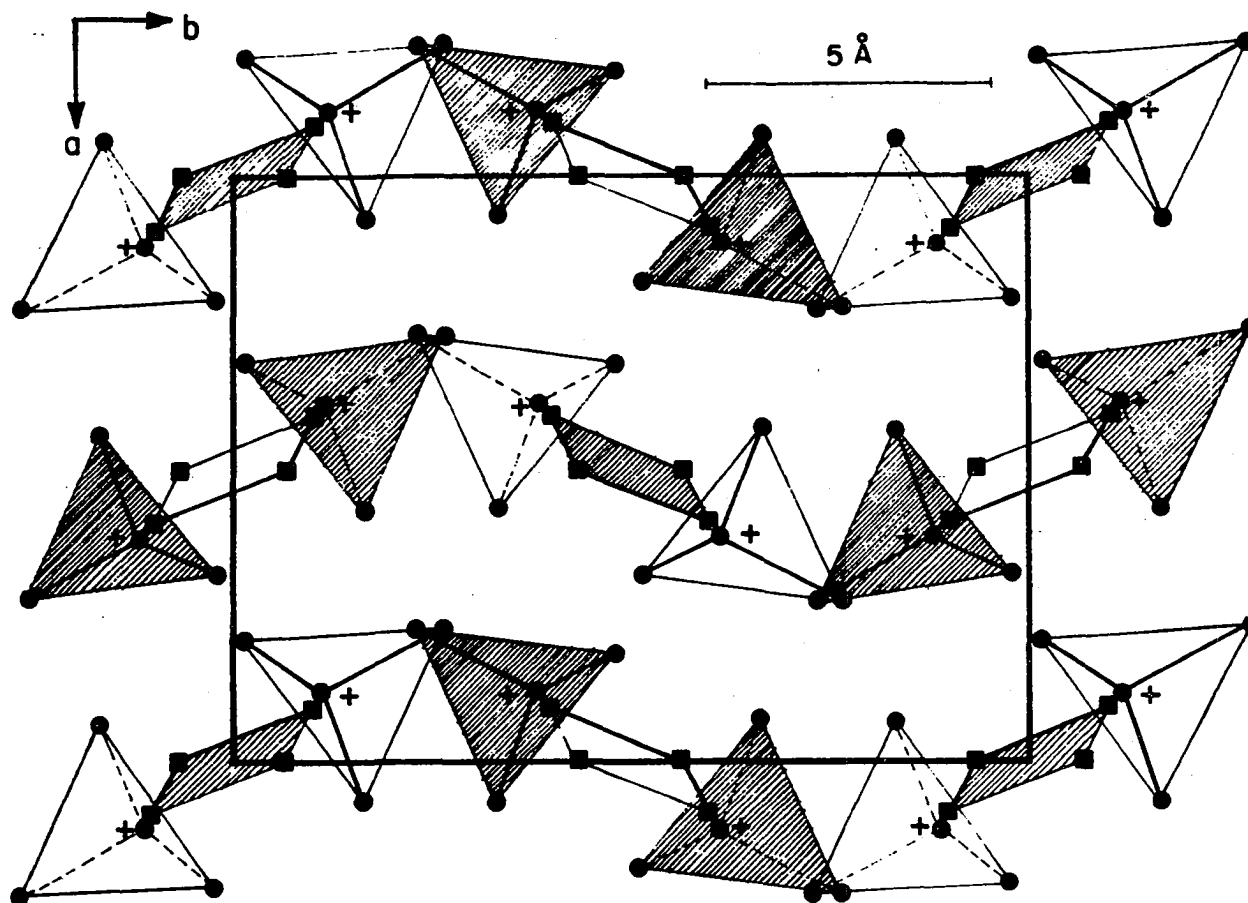


Figure 3. Projection of the structure of $\text{Te}_4(\text{AlCl}_4)_2$ on the (001) plane

The shaded figures are centered at $y=0.50 + .084$. The parallelograms represent the Te_4^{2+} units while the projected tetrahedra represent AlCl_4^- . The aluminum positions are noted by '+'.

Table 9. Observed and calculated structure factors^a for Te₄(AlCl₄)₂

Table with multiple columns containing numerical data for structure factors. The table is organized into several sections, each with its own header (e.g., h k l, h k l, h k l). The data includes observed values and calculated values for various reflections. The table is very dense and spans most of the page.

^aStructure factors have been multiplied x 10.

Interatomic distances and angles

Interatomic distances and angles were computed using ORFFE, the function and error program of Busing, et al.

(33). The estimated standard deviations were obtained from the variance-covariance matrix of the final least-squares cycle.

The values are tabulated from isotropic refinement in Table 10 and from anisotropic refinement in Table 11. The designations Te 1a and Te 2a indicate the atoms labeled Te 1 and Te 2 in Tables 7 and 8, while the 'b' designation refers to their counterparts in the same cluster related by the center of symmetry.

Discussion

At the time this study was undertaken, no crystal structure had determined for any compound of a reduced group VI A element. Gillespie and co-workers (21) had some idea of the shape of Se_4^{2+} from limited X-ray diffraction data supplemented by spectroscopic studies, but no crystal structure had been solved.

Concurrent with the study described here, McMullan Prince and Corbett (42) determined the structure of another group VI A homopolyatomic cation, Se_8^{2+} , in the tetrachloroaluminate system. It has a double ring structure

Table 10. Selected interatomic distances and angles from isotropic refinement^a of $\text{Te}_4(\text{AlCl}_4)_2$

Cation Distances			Cation Angles			
Reference Atom	Neighbor Atom	° Å	Atom 1	Atom 2 (Vertex)	Atom 3	Degrees
Te 1a	Te 2a	2.675(3)	Te 1a	Te 2a	Te 1b	89.83(9)
Te 1a	Te 2b	2.655(3)	Te 2a	Te 1b	Te 2b	90.17(9)
Te 1a	Te 1b	3.763(4)	Te 1b	Te 2b	Te 1a	89.83(9)
Te 1b	Te 2b	2.675(3)	Te 2b	Te 1a	Te 2b	90.16(9)
Te 1b	Te 2a	2.655(3)				
Te 2a	Te 2b	3.774(4)				

Anion Distances			Anion Angles			
Atom 1	Atom 2	° Å	Atom 1	Atom 2 (Vertex)	Atom 3	Degrees
Al	Cl 1	2.08(1)	Cl 1	Al	Cl 2	112.5(6)
Al	Cl 2	2.11(1)	Cl 1	Al	Cl 3	111.5(5)
Al	Cl 3	2.14(1)	Cl 1	Al	Cl 4	108.8(5)
Al	Cl 4	2.12(1)	Cl 2	Al	Cl 4	107.2(5)
			Cl 2	Al	Cl 3	109.3(5)
			Cl 3	Al	Cl 4	107.2(5)

^aNumbers in parentheses are estimated standard deviations from ORFFE (33) for the least significant digits.

Table 11. Selected interatomic distances and angles from anisotropic refinement^a of $\text{Te}_4(\text{AlCl}_4)_2$

Cation Distances			Cation Angles			
Atom 1	Atom 2	Å	Atom 1	Atom 2	Atom 3	Degrees
Te 1a	Te 2a	2.673(1)	Te 1a	Te 2a	Te 1b	89.94(4)
Te 1a	Te 2b	2.660(1)	Te 2a	Te 1b	Te 2b	90.06(4)
Te 1a	Te 1b	3.769(2)	Te 1b	Te 2b	Te 1a	89.94(4)
Te 1b	Te 2b	2.673(1)	Te 2b	Te 1a	Te 2b	90.06(4)
Te 1b	Te 2a	2.660(1)				
Te 2a	Te 2b	3.773(2)				

Anion Distances			Anion Angles			
Atom 1	Atom 2	Å	Atom 1	Atom 2	Atom 3	Degrees
Al	Cl 1	2.077(5)	Cl 1	Al	Cl 2	112.9(3)
Al	Cl 2	2.117(6)	Cl 1	Al	Cl 3	111.6(2)
Al	Cl 3	2.145(5)	Cl 1	Al	Cl 4	108.5(2)
Al	Cl 4	2.124(5)	Cl 2	Al	Cl 4	107.4(2)
			Cl 2	Al	Cl 3	109.1(2)
			Cl 3	Al	Cl 4	107.2(2)

^aNumbers in parentheses are estimated standard deviations from ORFFE (33) for the least significant digits.

resembling that of bicyclo [3.3.0] octane.

The compound $\text{Te}_4(\text{AlCl}_4)_2$ is made up of square-planar Te_4^{2+} units as predicted in a qualitative consideration of possible bonding orbitals by Gillespie (21) and by the more quantitative approach of Corbett (22), where the ordering of energy levels is such as to accommodate the 14 p-electrons of Po_4^{2+} in bonding molecular orbitals. Direct analogy predicts the isoelectronic Te_4^{2+} to have D_{4h} symmetry also. The very slight deviations from a perfect square reported in Table 11, if significant, are probably caused by the non-cubic electrostatic field surrounding the ion. This was also observed by Prince¹, in i.r. spectra where two bands corresponding to Te-Te stretches were found (prominent band at 133 cm^{-1} with a shoulder at 124 cm^{-1}). The AlCl_4^- ions seem to be only slightly distorted from the perfect tetrahedra expected for isolated ions. By looking at the shaded Te_4^{2+} parallelogram in the center of Figure 3, one can see that it is "sandwiched" between the parallel faces of the shaded AlCl_4^- tetrahedra located at its upper right and lower left. The crystal structure of $\text{Te}_4(\text{AlCl}_4)_2$, therefore, seems to be dictated by the most efficient means of packing these relatively independent ions. The only really unusual aspect of the

¹D. J. Prince, Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa. Private communication. 1969.

structure is the Te_4^{2+} cation. In addition to having a stable electronic configuration, as just described, it probably also owes its existence to the stabilizing effect of the large, acidic AlCl_4^- anion which seems to nurture many of these homopolyatomic cations (9, 42, 43).

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