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Crystal Structure of Zirconium Monochloride. A Novel Phase Containing Metal–Metal Bonded Sheets

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Received January 7, 1976

AIC600022

Monocrystals of ZrCl were obtained by the reaction of $ZrCl_4(g)$ with a large excess of electropolished Zr in a sealed tantalum tube under a 600–800 °C gradient for 24 days. Integrated diffraction data were secured on an automated diffractometer using Mo Kα radiation. Systematic absences among 203 observed reflections together with tuned diffraction data established a C-centered monoclinic cell with $a = 5.943$ (6), $b = 3.419$ (3), $c = 9.087$ (18) Å, $\beta = 102.5$ (1)°, $Z = 4$. The structure was solved by standard Patterson and Fourier techniques to a conventional residual of 0.080 and $R_w = 0.087$. The structure contains homoatomic layers sequenced Cl–Zr–Zr–Cl so as to generate four-layer sheets, the layers and sheets being geometrically close to cubic close packed along [001]. The result is found to be within experimental error of a higher symmetry trigonal cell ($Z = 6$) with the rhombohedral space group $R\bar{3}m$. The diffraction data were therefore converted, averaged, and refined utilizing 85 independent reflections, half as many positional parameters, and $a = 3.424$ (2), $c = 26.57$ (4) Å to give $R = 0.071$ and $R_w = 0.087$. Distances are not statistically distinguishable in the two refinements; although the rhombohedral description is formally preferred, the *real* symmetry probably depends appreciably on the crystalline perfection in the [001] direction. Each zirconium atom has three neighbors in the adjacent sheet at 3.09 Å (Pauling bond order of 0.5), six more in the same sheet at 3.42 Å, and three chlorine atoms on the other side at 2.63 Å. Weak chlorine–chlorine interactions between sheets at 3.61 Å contrast with the strong metal–metal binding within the sheets; the former are presumably responsible for the graphitic properties and anisotropic conduction of the compound.

Introduction

Many of the earlier reports of trihalide[1–3] and dihalide phases[4–6] of zirconium and hafnium have pertained to products of uncertain purity owing to nonequilibrium reaction conditions, the use of powdered metal as the reducing agent, or contamination from side reactions with the silica containers. However, a recent study of the lower chlorides of zirconium and hafnium[7] demonstrated that the use of the respective metal foil or sheet as the reductant and sealed tantalum tubing as an inert container allows ready access to a number of uncontaminated products by reduction of the tetrachlorides at 600–800 °C. The most unusual products are the highly conducting monochlorides which are obtained either directly when a sufficient excess of foil is used or after a second equilibration with metal if the surface becomes blocked in the first reaction. Hafnium gives a slower reaction and a smaller yield, and the two monochlorides are evidently isostructural.[7] The novelty of the monochloride stoichiometry together with its metallic character prompted the present study. A parallel study on the synthesis of ZrCl by Troyanov and Tsirel'nikov[8] yielded a similar result judging from the powder pattern. However, a subsequent crystal structure determination for ZrCl reported by Troyanov[9] is poorly refined ($R = 0.29$) and yields very unrealistic interatomic distances.

Experimental Section

Synthesis. The zirconium strips used had been cold-rolled to a 15–20 mil sheet from reactor-grade crystal bar zirconium which contained less than 0.05% hafnium. The tetrachloride was prepared by treating the metal with electronic grade HCl (Precision Gas Products) as the temperature was raised from 300 to 500 °C. The $ZrCl_4$ was purified by vacuum sublimation through a coarse frit.

The usual[7] preparation of ZrCl by reaction of $ZrCl_4$ with the metal in a closed tantalum container at 600–650 °C results in polycrystalline product. Adequate single crystals were obtained after a great many variations of the conditions from a preparation in which two electropolished zirconium strips about 1 cm by 8 cm were reacted with 0.05 g of zirconium tetrachloride in a sealed tantalum container in a 600–800 °C gradient for 24 days, after which the sample was cooled at a rate of 1.25°/h for 7 days and then quenched to room temperature. Evidently the initial reaction occurs at the hot end of the metal, thereby greatly lowering the $ZrCl_4$ activity; this product then slowly decomposes to yield a well crystallized material on the foil at a somewhat cooler point.

The reaction product was examined in a specially designed inert atmosphere box constructed with a nearly horizontal window to facilitate the use of a stereo microscope with a 7 in. focal length. The shiny black platelets of ZrCl clinging to the central portion of the metal strips were removed and sorted with a scalpel. Candidates for mounting were picked up on the end of a thin glass stalk tipped with Vaseline and inserted into 0.2 mm i.d. Lindemann glass capillaries which were in turn sealed with a resistance wire within the box. The initial screening used conventional oscillation and Weissenberg film methods since the location of an adequate monocrystal free of streaking or the more common multiple spots required X-ray examination of over 200 candidates. The crystal selected was a highly reflective black platelet measuring 0.14 × 0.11 × 0.02 mm which gave relatively sharp spots with only a hint of streaking.

Data Collection and Reduction. X-ray data were taken with an automated four-circle diffractometer designed and built in the Ames Laboratory.[10] The upper full circle (STOE) is equipped with encoders and drive motors, while the design of the base allows the encoders to be directly connected to the main $\theta = \omega$ and 2θ shafts using solid and hollow shaft encoders, respectively. The diffractometer is equipped with a scintillation counter and is interfaced with a PDP-15 computer in a real-time mode.

The data set was recorded on the basis of a monoclinic unit cell with $a = 5.95$, $b = 3.43$, $c = 9.09$ Å, and $\beta = 102.43°$ obtained for an initial orientation.[11] This compares well (except for a trivial axis interchange) with lattice constants $a = 9.19$, $b = 3.42$, $c = 5.92$ Å, and $\beta = 103°$ estimated from previous film work with other crystals which proved to be unsuitable for a complete structure determination. An ω scan mode was employed for data collection. The data were collected at ambient temperature (~30 °C) within a 2θ sphere of 0.596 Å using Mo Kα radiation (λ 0.709 54 Å) monochromatized with a graphite crystal at a takeoff angle of 4.5°. During data collection the intensities of three standard peaks were monitored every 50 reflections to check for instrument and crystal stability; no decrease in the intensities was observed. A total of 230 integrated intensities were obtained from 416 reflections checked in the two octants HKL and $HK\bar{L}$. Final unit cell parameters (and their estimated deviations), $a = 5.943$ (6), $b = 3.419$ (3), $c = 9.087$ (18) Å, and $\beta = 102.5$ (1)°, were obtained by a least-squares fit[12] to twice the ω values of 16 independent reflections, the centers of which were determined by left–right, top–bottom beam splitting on the same crystal as aligned on the diffractometer.

The observed intensities were corrected for Lorentz and polarization effects[13] and the standard deviations were calculated as previously described.[14] The 203 reflections with $I > 3\sigma(I)$ were used in subsequent calculations. An absorption coefficient was calculated for each reflection using a linear absorption coefficient[15] of 66 cm^{-1} and a program[16] which considers the contribution to the diffracted intensity

Table I. Final Cell, Refinement, and Atom Parameters for ZrCl

Monoclinic, Space Group $C2$
$a = 5.943\ (6), b = 3.419\ (3), c = 9.087\ (18)$ Å, $\beta = 102.5\ (1), Z = 4$
$R = 0.080, R_w = 0.087$, 203 reflections

Trigonal, Space Group $R\bar{3}m$
$a = 3.424\ (2), c = 26.57\ (4)$ Å, $Z = 6$
(Rhombohedral $a = 9.074\ (13), \alpha = 21.75\ (4)°, Z = 2$)
$R = 0.071, R_w = 0.087$, 85 reflections

	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{13}
			Monoclinic				
Zr	0.3779 (2)	0	0.134 1 (2)	31 (7)	3 (22)	63 (3)	11 (3)
Cl	0.1098 (7)	0	0.329 6 (6)	43 (13)	21 (38)	67 (5)	17 (6)
			Trigonal				
Zr	0	0	0.122 05 (10)	118 (52)	118 (52)	7.2 (5)	0
Cl	0	0	0.390 1 (3)	177 (80)	177 (80)	7.3 (8)	0

[a] The general thermal parameter expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Values listed are $\beta \times 10^4$.

from a tetrahedron in which the path length of the rays is a linear function of the coordinates of the diffracting element. Data sets which had been uncorrected and corrected for absorption were both employed in parallel refinements.

Structure Determination and Refinement. All calculations were carried out at the Iowa State University Computation Center. Atomic scattering factors used were those of Hanson et al.[17] with corrections for both real and imaginary parts of anomalous dispersion.[15] The reflections were originally weighted by σ_F^{-2} to account for the reliability of each measurement. During the course of the refinement the following programs were used: TALABS[16] for absorption correction, ALFF[18] for Fourier summation, ORFLS[19] for least-squares refinement, OMEGA[20] for new weights, ORFFE[21] for structure parameters and estimation of errors, and ORTEP[22] for figure illustrations.

The sole systematic condition noted on inspection of the reflection data was $h + k = 2n$ for all reflections hkl. This condition requires the cell to be C centered and limits the space group choice to $C2$ (No. 5), Cm (No. 8), and $C2/m$ (No. 12). The three-dimensional Patterson map contained four strong peaks of equal intensity at $u, v, w = {}^3/_4, 0, {}^1/_4; {}^1/_4, {}^1/_2, {}^1/_4; {}^1/_4, 0, {}^3/_4$, and ${}^3/_4, {}^1/_2, {}^3/_4$. Inspection of the interatomic vectors expected from atoms in general positions in the three possible space groups prompted the immediate choice of the accentric $C2$. After assignment of the position of the Zr atom to ca. ${}^3/_8, 0, {}^1/_8$, with $y \equiv 0$ to fix the origin, three cycles of full-matrix least-squares refinement on the two positional parameters resulted in an unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.384. The chlorine position was located from an electron density Fourier map, and five cycles of refinement on the x and z coordinates of both atoms resulted in convergence with $R = 0.146$. Subsequent refinement of the isotropic temperature factors as well converged after two cycles to give residuals R and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.120 and 0.150, respectively. Variation of the zirconium occupancy factor as a test indicated a negligible difference from unity, and a difference Fourier synthesis calculated at this point was flat to ±2 electrons/Å, indicating there were no misplaced atoms. Refinement using the absorption-corrected data set resulted in converged parameters with the same value of R_w. Variation of the y parameter for chlorine at this point had no effect on the residuals; since the resultant datum was not statistically different from zero it was held at this value.

Conversion of the isotropic temperature factors to anisotropic factors led to the result that β_{22} for both atoms could not be varied without becoming negative. Refinement using the original reduced data set while damping the shifts in β_{22} resulted in converged parameters with discrepancy factors R and R_w of 0.081 and 0.109, and refinement using intensities corrected for absorption proceeded similarly and converged with $R = 0.081$ and $R_w = 0.111$ when the shifts in β_{22} were again damped. At least a partial explanation for the problems encountered in this refinement was provided by the discovery of a statistical error in the program which controlled the data-taking procedure, namely the handling of the larger reflections which are counted for a shorter period of time than the smaller ones and rescaled. While the quantitative effect of this problem is difficult to assess, it seemed appropriate to reweight the data set in ten groups sorted according to F_o since the counting statistics for the larger reflections were in question. After this step all positional and thermal parameters (including β_{22} and y for Cl) converged after two cycles giving final residual indices R and R_w of 0.080 and 0.087, respectively. The positional parameters for both zirconium and chlorine were within one standard deviation of those obtained using the original weighting scheme, but the errors in these parameters are smaller, as expected. The final observed and calculated structure factors are available as supplementary material.

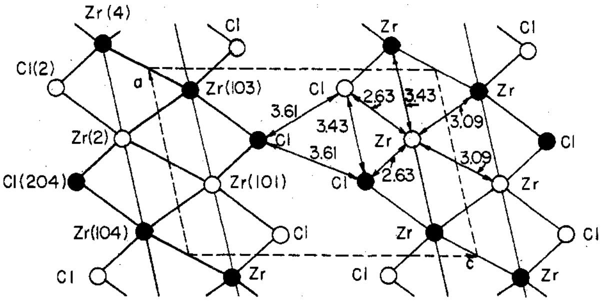

Figure 1. Projection of the structure of ZrCl on the monoclinic (010) plane. Open circles correspond to atoms with $y = 0$; filled circles, $y = 0.5$.

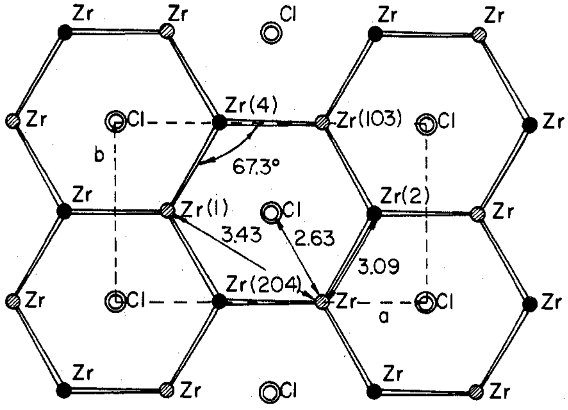

Figure 2. Projection of one sheet of the ZrCl structure on the (001) plane. The solid and shaded circles differentiate between atoms in the two metal layers. The distances, angle, and atom identifications refer to the monoclinic cell.

Structure Description

An Alternate Space Group. The final positional and thermal parameters deduced for ZrCl in the monoclinic space group $C2$ are listed in Table I, while their result is depicted in Figures 1 and 2, the (010) and (001) projections. The chemical aspects of these will be considered after some geometric (space group) factors are settled.

The projection in Figure 1 reveals a remarkable structure, namely sheets composed of four homoatomic layers in the sequence Cl–Zr–Zr–Cl. The geometry of the interlayer (and

Table II. Interatomic Distances and Angles[a] in ZrCl Based on Final Results with Both Crystal Symmetries

Interatomic distances, Å			Interatomic angles,[b] deg				
	Monoclinic	Trigonal	Atom 1	Atom 2 (vertex)	Atom 3	Monoclinic	Trigonal
	Intralayer						
Zr–Zr	3.419 (3)	3.424 (2)					
	3.428 (3)		Zr(1)	Zr(4)	Zr(103)	67.3 (1)	67.4 (1)
			Zr(204)	Zr(4)	Zr(2)	60.09 (3)	60.00
Cl–Cl	3.419 (3)	3.424 (2)	Zr(4)	Zr(2)	Zr(104)	120.18 (7)	120.00
	3.428 (3)		Zr(4)	Zr(2)	Zr(103)	56.4 (1)	56.32 (6)
	Interlayer		Cl(2)	Zr(2)	Zr(103)	105.4 (1)	105.4 (1)
Zr–Zr	3.093 (5)	3.087 (5)	Cl(2)	Zr(2)	Zr(4)	49.3 (1)	49.4 (1)
	3.094 (6)		Cl(2)	Zr(2)	Cl(104)	81.3 (2)	81.2 (2)
Cl–Cl	3.613 (10)	3.607 (14)	Zr(2)	Cl(2)	Zr(4)	81.3 (2)	81.2 (2)
	3.611 (11)						
Zr–Cl	2.630 (5)	2.629 (6)					
	2.631 (6)						

[a] Estimated standard deviations from ORFFE[21] in parentheses include uncertainties in cell dimensions. [b] Atom reference numbers correspond to those shown in Figures 1 and 2; the symmetry operation sequence used is $x, y, z; \bar{x}, y, \bar{z}; \frac{1}{2}+x, \frac{1}{2}+y, z; \frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$.

intersheet) packing is substantially cubic close packed if the difference in kinds of atoms is neglected, a fact emphasized by the (001) projection of one sheet in Figure 2. The angles and distances in this projection deviate from ideal 60° and equality respectively by <0.2° and ≤0.01 Å, which are likely within experimental error, and correspondingly the *a* axis is $\sim(3)^{1/2}b$. These circumstances raise the question as to whether a higher symmetry hexagonal unit cell would describe the structure as well or better. The thought is further supported by the observation that the packing in the [001] direction repeats in exactly three cells to within the 0.12° uncertainty in β, so that c (new) = $3d_{001}$(monoclinic). In detail, the monoclinic cell results are found to closely fit the trigonal equivalent of the rhombohedral space group $R\bar{3}m$, with the atoms in 6*c* positions at 0, 0, $\pm z$ with $z(\mathrm{Zr}) = 0.122$, $z(\mathrm{Cl}) = 0.390$, and $a = 3.42$ Å, $c = 26.6$ Å, $Z = 6$ calculated directly from the monoclinic results.

The correctness of the higher symmetry structure was assessed by a comparable refinement. Indices in the monoclinic reduced data set were converted to the trigonal equivalents and redundant data averaged by FDATA[23] to yield 85 net reflections with very acceptable statistics. Isotropic refinement gave almost no shifts of the input positions, and conversion to anisotropic thermal parameters gave convergence at $R = 0.072$ and $R_w = 0.103$, less than at the equivalent stage of the monoclinic refinement. The stronger reflections were again observed to have larger values of $w\|F_o| - |F_c\|$ so the data set was reweighted as before in five overlapping groups, yielding final values of $R = 0.071$, $R_w = 0.087$.

The preferred space group seems to clearly be rhombohedral based on the close similarity of what should be equivalent reflections, and a refinement to the same value of R_w in the higher symmetry with about half as many variables. The final atom parameters and interatomic distances and angles are compared in Tables I and II. Equivalent distances are not statistically distinguishable in the two refinements. Least-squares refinement of ten independent tuned reflections yielded trigonal cell constants $a = 3.424$ (2) and $c = 26.57$ (4) Å (rhombohedral $a = 9.074$ (13), $\alpha = 21.75$ (4)°).

Some retrospection regarding the circuitous route to this conclusion is appropriate. The difficulty in locating a good crystal for this study required that over 200 samples were examined by oscillation and some by Weissenberg film techniques, and yet in no case was any hint of other than monoclinic symmetry noted, including via diffractometer orientation procedures. The preferred orientation of the flat plates with (001) normal to the capillary axis may be responsible for much of this. In retrospect only the appreciable disparity between β_{11} and β_{22} for zirconium (Table I) and the initial trouble with β_{22} in the monoclinic refinement could have hinted at any anomalous coupling associated with refinement in too low a symmetry. Multiple spotting and streaking are the most common imperfections observed on films, presumably associated with intersheet cleavage or disorder. Thus *real* crystals with small deviations of this sort may be better described by the shorter intersheet repeat of the monoclinic cell.

Discussion

The four layer sheet structure of ZrCl is without precedent. Each zirconium has three metal neighbors in the next layer at 3.09 Å, six metal neighbors in the same layer at 3.42 Å, and three chlorine neighbors in the opposite layer at 2.63 Å. Intralayer Cl–Cl distances are 3.42 Å while interlayer Cl–Cl distances are 3.61 Å, representing very appropriate distances between chlorine atoms bound to common zirconium atoms and for interactions between weakly bound sheets, respectively. The zirconium–chlorine distances of 2.63 Å compare with 2.50, 2.66, and 2.31 Å in $ZrCl_4$[24] and 2.44 Å in Rb_2ZrCl_6,[25] rather different environments involving chlorine about six-coordinate zirconium(IV). The strong metal–metal bonding implied by the short distance between zirconium layers is the most significant bonding feature of this structure. Each zirconium atom has three neighbors in the other layer at 3.09 Å, which compares with 3.19 Å found in the 12-coordinate metal. The familiar Pauling bond order equation[26] predicts an approximate bond order of 0.5 for each of the three 3.09 Å distances and 0.1 for each of the six longer intralayer separations at 3.42 Å.

The physical properties of ZrCl are implicit in the alternating bilayer structure found for the compound. The phase occurs as shiny black platelets, the broad faces of which are parallel to the (001) planes. While there are strong interactions between Zr–Zr planes and Zr–Cl planes, the Cl–Cl interplanar (intersheet) distances of 3.61 Å indicate only weak van der Waals interactions, consistent with the graphitic character of the compound and its propensity toward polycrystallinity. Since the basic unit is a sheet composed of four tightly bound layers the usual description of the layering geometry ···|abca|bcab|cabc|··· is better conveyed by a notation describing sheet configurations, ··ABCABC··. Recently ZrBr has been prepared in this laboratory and shown from powder diffraction data to possess the alternate intersheet packing ACB···.[27] The interlayer coordination about halogen is thus antiprismatic (three metal and three halogen) in ZrCl but prismatic in ZrBr. The two-dimensional metallic character implied by the present structural result and previous semiquantitative resistance measurements[7] have recently been confirmed by XPS studies of the valence region.[27] Also, Troyanov[9] has reported that the electrical conductivity of single crystal platelets of ZrCl has been found (by an unspecified method) to be about 1.5×10^{-3} ohm^{-1} cm^{-1} normal to the plate and 55 ohm^{-1} cm^{-1} within the plate.

During the course of the present investigation a structure for ZrCl was reported by Troyanov.[9] In an earlier report of the preparation of ZrCl and its powder pattern, Troyanov and Tsirel'nikov[8] had indexed the powder pattern on the basis of a rhombohedral cell with $a = 9.12$ Å, $\alpha = 21.62°$, and $Z = 2$, corresponding to the trigonal cell $a = 3.41$ Å, $c = 26.66$ Å, $Z = 6$, as found here. The reported structure was solved using film data, and the poor refinement ($R = 0.29$) was attributed to difficulties in measuring the 60 $h0l$ intensities used. Few details are provided regarding procedures and methods. Nonetheless the space group and the basic ordering of the layers were correctly deduced, although this was quite obscured by thoroughly unreasonable interlayer distances reported, viz., 2.87 Å for Zr–Zr, 2.81 Å for Cl–Cl, and 3.10 Å for Zr–Cl vs. 3.09, 3.61, and 2.63 Å, respectively, determined in the present work.

Finally a significant correspondence in metal–metal bonding is to be noted between that found here for ZrCl (and implied for HfCl according to powder data[7,28]) and that reported by Franzen and Graham[29] for Hf_2S. Generally structural similarities in metal–metal bonding between reduced transition metal chlorides and sulfides have been exceedingly small, but in this case similar double metal layers can be discerned. Indeed, the coordination polyhedra about the metal, the relative metal–metal distances, and calculated bond orders about Hf in Hf_2S are remarkably similar to those about Zr in ZrCl. However, the smaller fraction of nonmetal in the isoelectronic sulfide places only a single bridging layer of sulfur between the double metal layers, thereby greatly reducing the structural and presumably the electrical anisotropy. In contrast there seems to be no clear relationship between the structures of ZrCl and the isoelectronic NbO.

Registry No. ZrCl, 14989-34-5; $ZrCl_4$, 10026-11-6; zirconium, 7440-67-7.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes for ZrCl (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) E. M. Larsen and J. J. Leddy, *J. Am. Chem. Soc.*, **78**, 5983 (1956).
(2) B. Swaroop and S. N. Flengas, *Can. J. Chem.*, **42**, 1495 (1964).
(3) S. I. Troyanov, V. I. Tsirel'nikov, and L. N. Komissarova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tckhnol.*, **12**, 851 (1969).
(4) F. R. Sale and R. A. J. Shelton, *J. Less-Common Met.*, **9**, 60 (1965).
(5) D. B. Copley and R. A. J. Shelton, *J. Less-Common Met.*, **20**, 359 (1970).
(6) B. Swaroop and S. N. Flengas, *Can. J. Chem.*, **43**, 2115 (1965).
(7) A. W. Struss and J. D. Corbett, *Inorg. Chem.*, **9**, 1373 (1970).
(8) S. I. Troyanov and V. I. Tsirel'nikov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **15**, 1762 (1970).
(9) S. I. Troyanov, *Vestn. Mosk. Univ., Khim.*, **28**, 369 (1973).
(10) D. R. Schroeder and R. A. Jacobson, *Inorg. Chem.*, **12**, 210 (1973).
(11) R. A. Jacobson, "An Algorithm for Automated Indexing and Bravais Lattice Selection, The Programs BLIND and ALICE", USAEC Report IS-3469, Ames Laboratory, Iowa State University, Ames, Iowa, 1974.
(12) D. E. Williams, "LCR2, A Fortran Lattice Constant Refinement Program", USAEC Report IS-1052, Ames Laboratory, Iowa State University, Ames, Iowa, 1964.
(13) J. Rodgers and R. A. Jacobson, USAEC Report IS-2155, Ames Laboratory, Iowa State University, Ames, Iowa, 1967.
(14) S. A. Lawton and R. A. Jacobson, *Inorg. Chem.*, **7**, 2124 (1968).
(15) "International Tables for X-ray Crystallography", Vol. III, 2d ed, Kynoch Press, Birmingham, England, 1962.
(16) J. D. Scott, Queen's University, Kingston, Ontario, private communication, 1971.
(17) H. P. Hanson, F. Herman, J. D. Lea, and S. Skilman, *Acta Crystallogr.*, **18**, 502 (1965).
(18) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, USAEC Report IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.
(19) W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(20) C. R. Hubbard, Ames Laboratory, private communication, 1971.
(21) W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
(22) C. K. Johnson, USAEC Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(23) F. Takusagawa and R. A. Jacobson, private communication, 1975. There were six reflections for which any component deviated from the overall average by between 14 and 24%.
(24) B. Krebs, *Z. Anorg. Allg. Chem.*, **378**, 263 (1970).
(25) A. Clearfield, *Rev. Pure Appl. Chem.*, **14**, 91 (1964).
(26) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 400.
(27) R. A. Daake and J. D. Corbett, unpublished research.
(28) A. S. Izmailovich, S. I. Troyanov, and V. I. Tsirel'nikov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **19**, 1597 (1974).
(29) H. F. Franzen and J. Graham, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **123**, 2 (1966).

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Sulfur Dioxide Bonding in Four-Coordinate Complexes. Crystal and Molecular Structure of the Toluene Solvate of Bis(sulfur dioxide)bis(triphenylphosphine)platinum

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Received February 6, 1976 AIC60101F

The crystal and molecular structure of the toluene solvate of bis(sulfur dioxide)bis(triphenylphosphine)platinum, $Pt(SO_2)_2(PPh_3)_2 \cdot C_7H_8$, has been determined at −63 °C. The compound crystallizes in the space group $P2_1/c$ with $a = 10.858$ (3) Å, $b = 20.570$ (6) Å, $c = 19.497$ (6) Å, and $\beta = 115.62$ (2)° with $\rho_{calcd} = 1.59$ g/cm^3 for $Z = 4$ (Mo Kα_1 radiation, λ 0.709 30 Å. The structure refined to an unweighted R value of 0.036 for 5592 reflections with $I > 3\sigma(I)$. The coordination geometry around the platinum is best described as a severely distorted tetrahedron with P1–Pt–P2 and S1–Pt–S2 angles of 158.58 (6) and 106.33 (8)°, respectively. The angles are consistent with arguments relating to the relative π-acceptor strength of the two ligands. Both sulfur dioxide groups are pyramidal with the average angle between the M–S vectors and SO_2 planes being 119° and an average M–S distance of 2.43 Å.

Introduction

The ability of terminally bound sulfur dioxide to exhibit at least two types of interactions with transition metal complexes has long been recognized. Conclusive structural evidence exists for complexes with bent MSO_2 moieties in which the geometry at the S atom is pyramidal (the angle between the M–S vector and the SO_2 plane being approximately 120°) as well as those for which the MSO_2 is planar.[1–6] It has been pointed out that SO_2 is similar to the nitrosyl ligand in this regard and that the behavior of both may be understood in terms of the number of d electrons and coordination geometry of the transition metal.[4,7–9] Thus, both ligands provide a readily observable