steady increase in moment to values in considerable excess of the spin only at temperatures *well above* T_c, e.g., $\mu = 3.98\ \mu_B$ at 25.1 K, appears to indicate relatively strong 1-D ferromagnetism. To our knowledge, this novel behavior has not been previously observed in systems that also ultimately order three-dimensionally as ferromagnets and is the subject of further study in this laboratory. Finally the present work clearly establishes another member of a rather select group[32] of compounds, namely, three-dimensionally ordered ferromagnetic insulators.

Acknowledgment. The authors wish to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grant No. DMR-80-12625. They also express their appreciation to Dr. Arthur Heis of Bruker Instruments, Inc., Billerica, MA, for his assistance in obtaining X-band ESR spectra.

Registry No. Ni(bpy)$(NCS)_2$, 81340-50-3; Ni$(bpy)_2(NCS)_2$, 15748-25-1; Ni$(py)_2(NCS)_2$, 50388-33-5; α-Ni(2,9-dmp)Cl_2, 29115-92-2; β-Ni(2,9-dmp)Cl_2, 21361-04-6; Ni$(bpy)_3(NCS)_2$, 81340-41-2.

Supplementary Material Available: A table of magnetic moments vs. temperature and three figures of visible and infrared spectra (4 pages). Ordering information is given on any current masthead page.

---

[32] P. Day, *Acc. Chem. Res.*, **12**, 236 (1979).

Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Single-Crystal Structures of ZrX_3 ($X = Cl^-, Br^-, I^-$) and $ZrI_{3.40}$ Synthesized in Low-Temperature Aluminum Halide Melts

EDWIN M. LARSEN,* JULIE S. WRAZEL,[1] and LAURENCE G. HOARD

Received March 19, 1981

The single-crystal data for the zirconium trihalides and partially oxidized zirconium iodide, $ZrI_{3.40}$, confirm that all four structures consist of chains of face-shared zirconium halide octahedra with equally spaced metal atoms. The space group is $P6_3/mcm$. The trihalides were found to contain no crystallographically detectable metal absences or metal atoms disordered to other hexagonal sites in the unit cell. Thus, the trihalides as prepared here are stoichiometric and possess such a very narrow composition range that they may be considered line phases. The elongation of the halogen octahedra along the 3-fold axis, which is greatest for the trichloride, less for the bromide, and negligible for the iodides, may be explained in part by the necessity to reduce repulsive nearest-neighbor metal interactions. The following lattice parameters were found: $ZrCl_3$, $a = b = 6.383$ (1), $c = 6.139$ (2) Å; $ZrBr_3$, $a = b = 6.728$ (2), $c = 6.299$ (2) Å; ZrI_3, $a = b = 7.298$ (4), $c = 6.667$ (4) Å; $ZrI_{3.40}$, $a = b = 7.239$ (2), $c = 6.673$ (1) Å; $Z = 2$. The structures were refined to final R values and errors-of-fit as follows: $ZrCl_3$, $R_1 = 2.99\%$, $R_2 = 4.59\%$, error-of-fit = 1.79; $ZrBr_3$, $R_1 = 7.55\%$, $R_2 = 12.33\%$, error-of-fit = 1.97; ZrI_3, $R_1 = 5.96\%$, $R_2 = 10.41\%$, error-of-fit = 1.55; $ZrI_{3.40}$, $R_1 = 5.66\%$, $R_2 = 9.13\%$, error-of-fit = 1.44. The stoichiometry of the partially oxidized zirconium iodide, $ZrI_{3.40}$, was established by refinement of the zirconium site occupancy.

Introduction

The initial structure determinations of zirconium trichloride, tribromide and triiodide were derived from powder data.[2] These data yielded a structure consisting of linear chains of face-sharing ZrX_6 octahedra with the metal atoms equally spaced along the c axis. The structure determination by Watts,[3] which confirmed this structure, was also based on powder data. Single-crystal diffraction studies[4,5] on zirconium tribromide yielded more precise lattice parameters for the same structure. Recently Daake and Corbett,[6] using the Guinier powder camera technique, reported precise lattice parameters for the trihalides over a range of composition and drew correlations between shifts in the a and c lattice parameters with composition. Their comparison of parameters with those previously reported[2,4,5] suggests that the earlier data may have been obtained on materials that, in fact, were nonstoichiometric. Whether this correlation is applicable to all products independent of their method of preparation is worthwhile exploring, since the range of nonstoichiometry generally widens with temperature, and high-temperature structures may be retained upon cooling the preparation to room temperature.

The trihalide samples used for the initial powder pattern studies were prepared by the reduction of the zirconium tetrahalides with zirconium metal at high temperatures (500–700 °C) and high pressures (50–20 atm).[7] The products were contaminated with some residual metal. The reaction times ranged from 70 to 100 h, after which the reaction bomb was rapidly quenched. The Daake–Corbett products were obtained by the reaction of the corresponding tetrahalides with ZrCl, ZrBr, or $ZrI_{1.8}$ in a sealed tantalum tube at temperatures ranging from 435 to 775 °C and pressures of 5–20 atm. Both of these syntheses are considered to yield high-temperature preparations.

On the other hand, the powder data by Watts[3] were obtained on a zirconium trihalide sample prepared by the low-temperature (25 °C) reduction[8] of zirconium tetrachloride with atomic hydrogen in an electrodeless discharge. In the work reported here, the single crystals studied were prepared by using the technique of Larsen et al.[4] In this synthesis, the tetrahalides, dissolved in the corresponding liquid aluminum halide at the eutectic composition, are reduced by either metallic zirconium or aluminum at temperatures ranging from 220 (Cl) to 280–300 °C (I) to yield a homogeneous reduced-state solution. The crystals of the trichloride and tribromide grow at the lip of the tilted reaction ampule. In the

---

[1] Based in part upon a dissertation submitted by Julie Wrazel to the Graduate School of the University of Wisconsin, Madison, WI, in partial fulfillment of the requirement for the Ph.D. degree, 1979.

[2] Dahl, L. F.; Chiang, Tao-I.; Seabaugh, P. W.; Larsen, E. M. *Inorg. Chem.* **1964**, *3*, 1236–1242.

[3] Watts, J. A. *Inorg. Chem.* **1966**, *5*, 281–283.

[4] Larsen, E. M.; Moyer, J. W.; Gil-Arnao, F.; Camp, M. J. *Inorg. Chem.* **1974**, *13*, 574–581.

[5] Kleppinger, J.; Calabrese, J. C.; Larsen, E. M. *Inorg. Chem.* **1975**, *14*, 3128–3130.

[6] Daake, R. L.; Corbett, J. D. *Inorg. Chem.* **1978**, *17*, 1192–1195.

[7] Larsen, E. M.; Leddy, J. J. *J. Am. Chem. Soc.* **1956**, *78*, 5983–5986.

[8] Newnham, L. E.; Watts, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 2113–2115.

0020-1669/82/1321-2619$01.25/0

Table I. Zirconium Halide Parameters and Structural Solution Data

	$ZrCl_3$	$ZrBr_3$	ZrI_3	$ZrI_{3.40}$
cryst dimens, mm	0.35 × 0.15	0.6 × 0.25 × 0.2	0.5 × 0.15	0.6 × 0.3
lattice dimens				
$a = b$, Å	6.383 (1)	6.728 (2)	7.298 (4)	7.239 (2)
c, Å	6.139 (2)	6.299 (2)	6.667 (4)	6.673 (1)
V, Å^3	216.6 (1)	246.9 (2)	307.5 (4)	302.8 (1)
calcd D, g/cm^3	3.03	4.45	5.10	5.73
total data	979	831	566	495
total independent data	701	315	566	495
interatomic distances, Å				
Zr-Zr	3.0695 (8)	3.152 (1)	3.334 (2)	3.3365 (6)
Zr-X	2.5382 (6)	2.676 (3)	2.8997 (15)	2.8820 (9)
X-X	3.502 (1)	3.746 (6)	4.1098 (25)	4.075 (17)
X-X′	3.6754 (8)	3.822 (2)	4.0917 (17)	4.0811 (7)
(X-X′)-(X-X)	0.1738	0.0766	−0.0171	0.0106
angles, deg				
Zr-X-Zr	74.408 (24)	72.16 (9)	70.17 (5)	70.74 (3)
X-Zr-X′	92.78 (2)	91.16 (7)	87.75 (3)	90.15 (2)
X-Zr-X	87.225 (7)	88.84 (6)	90.25 (3)	89.85 (2)

case of the iodide at 300 °C, a purple crystalline form grows from the lip down into the melt, and below 280 °C, a black product grows from the lip up on the glass surface wetted by a thin film of the melt. These syntheses are considered to yield low-temperature preparations. Suitable crystals from the low-temperature preparation were examined by single-crystal X-ray diffraction to determine whether they were nonstoichiometric owing to significant dislocations or absences from ideal metal ion locations.

Crystal Data and Collection

The air-sensitive crystals were epoxied to a thin glass rod and sealed in 0.3-mm i.d. Lindemann glass capillaries. The approximate dimensions of the crystals used are given in Table I. Data were collected at room temperature on a Syntex P$\bar{1}$ automated diffractometer. Computer control was supplied by a Nova computer. Graphite-monochromated Mo Kα radiation was used with a takeoff angle of 4°. Hexagonal data sets were collected as the axial scans of crystals in all systems indicated hexagonal symmetry. There were no restrictions placed on h, k, or l in the chloride data collection, but a unique, $k \geq h$, data set was collected on the two iodide systems. The tribromide crystal was suspected of having a small satellite crystal and each datum was collected at an orientation of 0, 15, and 30° around the diffraction vector to observe the effects, if any, of the satellite. This resulted in a unique data set, each reflection having a 3-fold redundancy, for the tribromide system. The refined lattice parameters and unit cell volumes with errors are given in Table I. $Z = 2$ was found for all the compounds.

Two to three reflections in each system were monitored periodically during data collection as a check on the integrity of the crystal. Data were collected over the range $3° \leq 2\theta \leq 110°$ in the 2θ-θ mode for the collection parameters given in Table I. The scan speed range (deg/min) was 0.5–24.0. The background/scan time was 0.3 in the $ZrCl_3$ data collection. During the other three data collections the reflections were strong and the background was stable so the background was not scanned. The program MUCALC[9] was used to calculate absorption coefficients and densities.

The data were corrected for Lorentz–polarization[10] and absorption[11] effects. Analysis of the step-scan data[10] showed nothing unusual in the peak shapes. The program QUICKSAM[12] was used to sort and merge the data. The data considered as "observed" are those for which $I > 2\theta_I$. The space group chosen, $P6_3/mcm$ (No. 193), forbids $h0l$ reflections for odd values of l. In all four systems some violations of symmetry were observed. The 007 reflection was observed in the trichloride system, the 001, 003, 005, and 0,0,11 reflections were observed in the tribromide, the 003 and 007 in reflections were observed the triiodide, and the 001 reflection was observed in the nonstoichiometric iodide. In addition, $h0l$ data for $h \neq 0$ were observed above the $2\sigma_I$ cutoff with F_o values of 1.2–2.0 for eight $ZrCl_3$ reflections, 3.1 and 7.7 for two $ZrBr_3$ reflections, 4.5–10.4 for five ZrI_3 reflections, and 3.8–7.6 for four $ZrI_{3.4}$ reflections. Nevertheless Patterson maps of all four data sets strongly indicated $P6_3/mcm$ (D_{6h}^3).

$ZrCl_3$. In the chloride system, the two zirconium atoms in the unit cell were placed in the special set 2b (0, 0, 0 and 0, 0, $^1/_2$). The six chlorides were placed on the special set 6g (x, 0, $^1/_4$; 0, x, $^1/_4$; $\bar{x}$, $\bar{x}$, $^1/_4$; $\bar{x}$, 0, $^3/_4$; 0, $\bar{x}$, $^3/_4$; x, x, $^3/_4$). Initial isotropic and anisotropic refinements[13] were carried out on the complete data set, including unobserved reflections and those with F_o negative. The scattering factor tables used were those of Cromer and Mann.[14] The calculated absorption coefficient was 38.31 cm^{-1}. Anisotropic refinement of the scale factor, one chloride positional parameter (x), and symmetry-allowed thermal parameters on the metal and the chloride, with metal scattering factors corrected for anomalous scattering,[15] yielded $R_1 = 3.22\%$, $R_2 = 4.69\%$, an error-of-fit of 1.42, and a data-to-parameter ratio of 68.4.

$ZrBr_3$. The zirconium tribromide data were corrected for absorption and Lorentz–polarization effects and examined for evidence that the suspected satellite crystal had affected the reflection profiles. The absorption correction was substantial as the calculated absorption coefficient was 256.75 cm^{-1}. The reflection profiles appeared normal, and the data were merged to a unique set containing a total of 315 data. As in the chloride system, this set was used to examine the isotropic extinction correction. The atoms were assigned special positions in hexagonal symmetry as in the chloride system. The coefficient was negative (-4.03×10^{-5}), and no improvement in the refinement was achieved through its application. The data set was then modified to contain only those reflections for which $I > 2\sigma_I$ and pruned of symmetry-forbidden reflections. Trial refinements with additional metal atom density in the extra octahedral positions were made. Such refinements would not converge. Refinement of the multiplicities revealed 100% occupancy to within 1% of the zirconium atom sites in the chain. Anisotropic refinement, corrected for anomalous scattering, yielded final $R_1 = 7.55\%$, $R_2 = 12.33\%$, error-of-fit = 1.97, and data-to-parameter ratio of 15.4.

ZrI_3 and $ZrI_{3.40}$. The refinement of the two forms of the binary iodides proceeded in much the same manner as that of the trichloride and tribromide. The purple form had a negative isotropic extinction coefficient of -2×10^{-6} and proved to be stoichiometric. The calculated absorption coefficient was 158.25 cm^{-1} for both forms. The refinement

---

(9) Zalkin, Allan. "MUCALC: A Program to Calculate Absorption Coefficients, Density and $F(000)$"; Lawrence Berkeley Laboratory: Berkeley, CA, 1974; modified by L. G. Hoard, The University of Wisconsin—Madison, 1979.

(10) Broach, R. W. Ph.D. Thesis, The University of Wisconsin—Madison, 1977; Appendix I.

(11) "ALCOCK: An Analytical Absorption Program. Modified for the 4-Circle P$\bar{1}$ at the University of Wisconsin", modified by L. G. Hoard, The University of Wisconsin—Madison, 1979.

(12) Broach, R. W. Ph.D. Thesis, The University of Wisconsin—Madison, 1977; Appendix II.

(13) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFLS: A FORTRAN Crystallographic Least-Squares Program", Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

(14) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–324.

(15) Real and imaginary parts taken from: "International Tables for X-ray Crystallography"; The International Union of Crystallography: Birmingham, England, 1964; Vol. IV.

of the metal atom multiplicities again showed 100% occupancy of the metal atom sites in the chain and none in the extra octahedral sites. The final anisotropic refinement, corrected for anomalous scattering, gave R_1 = 5.96%, R_2 = 10.41%, error-of-fit = 1.55, and data-to-parameter ratio of 45.0.

The black form of the iodide was not stoichiometric. Refinements of the isotropic extinction coefficient yielded a value of 4.1×10^{-6}. This had the effect of increasing the size of the anisotropic thermal parameters by about 1%. Refinement of the multiplicity of the zirconium atom resulted in a drop from 1.0 to 0.882 (1) without the corresponding occupancy of the extra octahedral sites in the unit cell. This corresponds to a composition of $ZrI_{3.40}$. The anisotropic refinement of this model yielded final R_1 = 5.66%, R_2 = 9.13%, error-of-fit = 1.44, and data-to-parameter ratio of 38.6.

Anomalous Electron Density. The foregoing $ZrCl_3$ structure solution was carried out without the execution of an electron density map as the rapid convergence of R values did not suggest need for one. However, for the purposes of confirming the refinement, various chloride data sets were expanded[16] into triclinic $P\bar{1}$ symmetry after refinement. Maps,[17,18] corrected for anomalous scattering effects,[19] were run. The first electron density map run on the complete chloride data set showed two sets of peaks occurring at 0, $^1/_2$, 0; 0, $^1/_2$, $^1/_2$ and 0, $^1/_3$, 0; 0, $^1/_3$, $^1/_2$, the former set corresponding to just over 10% of the relative intensity of the zirconium peaks (the most intense in the map) and the latter to just under 10%. In a map that was divided into 48 sections along each axis, these extra peaks drop in intensity to essentially background in three to four steps on the x and z axes but require fully half of the y axis to drop to levels that are substantially above background. It is difficult to conceive of real atoms giving rise to such oddly shaped peaks. There is, seemingly, a two-dimensional ridge of electron density on the y axis with peaks at $y = {}^1/_3$, $^1/_2$, and $^2/_3$. This ridge appears to be totally unaffected by any attempt in refinement to alter its position or shape. Since the structure consisted of close-packed chlorine atoms and these positions corresponded to no sensible sites in such a lattice with an origin at 0, 0, 0, efforts were made to identify the source of these extra peaks. The presence of peaks of such intensity was paradoxical since a low anisotropic R value had been obtained.

Maps made with an without an appropriate absorption correction both showed the extra peaks, undiminished in relative intensity. The possible effects of extinction were examined at several stages in the investigation of the identity of the extra peaks. The downweighting of any large peak where $F_o < F_c$ nevertheless had no effect on the presence of the extra peaks in the map. A systematic isotropic extinction correction was applied to the data.[20] The structure was refined anisotropically with and without the extinction correction. As the atoms were on special positions, the positional parameters were not affected. The isotropic extinction coefficient refined to a value of 4.6×10^{-5}. The magnitude of the correction had no effect on the presence of the extra peaks and served to enhance the thermal ellipsoids of the metal by about 3% in the two independent thermal parameters, which were refined. When it was ascertained that the extinction correction did not affect the presence of the peaks, the refinement was continued on a sorted and merged data set for which $I > 2\sigma_I$ and for which no correction was made for extinction.

Table II. Zirconium Halide Positional[a] and Thermal Parameters[b]

	x	$U(11)$, Å^2	$U(22)$, Å^2	$U(33)$, Å^2
		$ZrCl_3$		
Zr	0.0000 (0)	0.0223 (1)	0.0223 (1)	0.0233 (2)
Cl	0.3167 (1)	0.0281 (2)	0.0466 (4)	0.0233 (2)
		$ZrBr_3$		
Zr	0.0000 (0)	0.0220 (20)	0.0220 (20)	0.0277 (19)
Br	0.3211 (5)	0.0238 (17)	0.0400 (25)	0.0216 (10)
		ZrI_3		
Zr	0.0000 (0)	0.0203 (5)	0.0203 (5)	0.0346 (14)
I	0.3255 (1)	0.0234 (4)	0.0385 (7)	0.0221 (5)
		$ZrI_{3.40}$		
Zr	0.0000 (0)	0.0192 (6)	0.0192 (6)	0.0488 (19)
I	0.3246 (1)	0.0238 (3)	0.0371 (5)	0.0235 (5)

[a] y for Zr and all halides = 0.000; z for Zr = 0.000; z for halides = 0.2500. [b] $U(11) = U(22) = 2U(12)$ for Zr; $U(22) = 2U(12)$ for halides.

Table III. Zirconium Halide Rms Thermal Displacements on the Principal Axes (Å)

	$\mu(1)$	$\mu(2)$	$\mu(3)$
		$ZrCl_3$	
Zr	0.1494 (5)	0.1494 (5)	0.1525 (6)
Cl	0.1481 (8)	0.1526 (7)	0.2158 (8)
		$ZrBr_3$	
Zr	0.1486 (91)	0.1486 (91)	0.1664 (57)
Br	0.1357 (75)	0.1470 (33)	0.2000 (63)
		ZrI_3	
Zr	0.1424 (24)	0.1424 (24)	0.1860 (37)
I	0.1356 (18)	0.1488 (16)	0.1961 (17)
		$ZrI_{3.40}$	
Zr	0.1384 (27)	0.1384 (27)	0.2209 (43)
I	0.1389 (14)	0.1533 (15)	0.1926 (14)

The effect of symmetry-forbidden reflections was tested by eliminating from the data set the $00l$ reflections for which l was odd. The map on the refined structure retained the extra peaks. The following refinements were executed and electron density maps generated to determine whether these peaks were the result of small populations of atoms located either at the extraneous peak sites or at other octahedral sites in the unit cell. In neither case was convergence obtained.

In the first, small fractions of zirconium atom density were placed at the odd positions, at either 0, $^1/_3$, 0; 0, $^1/_3$, $^1/_2$ or 0, $^1/_2$, 0; 0, $^1/_2$, $^1/_2$. Zirconium density was the reasonable choice as these positions were located in the zirconium atom layer and might represent disordered zirconium atoms. Refinement of the multiplicities indicated that no atoms resided in these positions. The second refinement consisted of placing a small fraction of zirconium atom density in the octahedral position at $^1/_3$, $^2/_3$, 0 and symmetry-related positions. In hexagonal symmetry, this model would not converge in anisotropic refinement. However, a modification of this model in triclinic symmetry could be refined with no more than 1% of the zirconium metal atom density at $^2/_3$, $^1/_3$, 0 and $^2/_3$, $^1/_3$, $^1/_2$, no longer symmetry related. This model, including two independent zirconium atoms at 0, 0, 0 and 0, 0, $^1/_2$ and three independent chlorine atoms at x, 0, $^1/_4$; 0, x, $^1/_4$; and $\bar{x}$, $\bar{x}$, $^1/_4$, where $x \approx {}^1/_3$, refined under triclinic $P\bar{1}$ symmetry to a final R_1 of 3.24%. The third refinement consisted of placing aluminum atom density in the octahedral site at $^1/_3$, $^2/_3$, 0 and its symmetry-related positions. Refinement in hexagonal symmetry resulted in isotropic temperature factors of over 100.

After all of the possible modifications of the data were investigated, the zirconium trichloride structure was refined anisotropically to final R_1 = 2.99%, R_2 = 4.39%, error-of-fit = 1.79, and data-to-parameter ratio of 68.4. Pertinent interatomic distances and angles are given in Table I, positional and thermal parameters[22,23] in Table II, and

---

(16) Hoard, L. G. "EXP: A Program to Expand Hexagonal Data Sets into Triclinic Symmetry for Use in the MAP Routine"; The University of Wisconsin—Madison: Madison, WI, 1979.

(17) Calabrese, J. C. "MAP: A Local FORTRAN Fourier Summation and Molecular Assemblage Program"; The University of Wisconsin—Madison: Madison, WI, 1972.

(18) Hoard, L. G. "MAPLOK, A Fourier Map Prints and Statistics Generator"; The University of Wisconsin—Madison: Madison, WI, 1979.

(19) Hoard, L. G. "PRE*4: A Program to Correct Fourier Input to the MAP Routine for Anomalous Scattering"; The University of Wisconsin—Madison: Madison, WI, 1979.

(20) Lapp, R. L.; Jacobson, R. A. "ALLS: A Generalized Crystallographic Least Squares Program"; Ames Laboratory, DOE, Iowa State University: Ames, IA, 1979. Unweighted $R = \sum||F_o| - |SF_c||/\sum|F_o|$. Weighted $R = (\sum w(F_o - SF_c)^2/\sum wF_o^2)^{1/2}$. Extinction correction based on $y = (1 + g\gamma F_c^2)^{-1/2}$, where g is the isotropic extinction coefficient and y is the correction applied.

(21) Least-squares refinement based on $\sum w_{HKL}(F_o(HKL) - F_c(HKL))^2$. Weights based on $w_{HKL} = (1/\sigma_{HKL})^2$.

(22) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE: A Fortran Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964.

(23) Szmanda, C. Ph.D. Thesis, The University of Wisconsin—Madison, 1979.

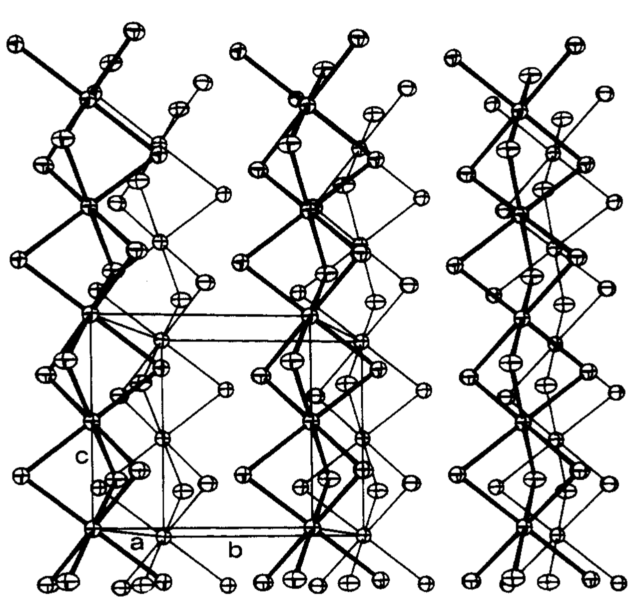


Figure 1. A unit cell in an array of chains.

rms thermal displacements[22] in Table III.

An electron density map, corrected for anomalous scattering effects, made on the zirconium tribromide data set expanded into triclinic symmetry, revealed the existence of the same set of odd peaks at 0, $^1/_3$, 0; 0, $^1/_3$, $^1/_2$; 0, $^1/_2$, 0; and 0, $^1/_2$, $^1/_2$ amounting to 2.5% of the zirconium atom density. An analysis of their identity as made on the chloride system gave no rationale for their existence. The electron density map on the two expanded zirconium iodide data sets contained the same extra peaks at $^1/_3$, $^1/_3$, 0; $^1/_3$, $^1/_3$, $^1/_3$; $^1/_3$, $^1/_2$, 0; and $^1/_3$, $^1/_2$, $^1/_2$ amounting to 10%–15% of the zirconium atom density. Again, analysis yielded no reasonable structural model for the peaks. In no case did the existence of these extra peaks interfere with the refinement to low R values for the space group $P6_3/mcm$.

Discussion

Structural Solution: Disorder-Free Zirconium Halides. The single-crystal data on zirconium halides confirmed the isomorphism of these compounds with β-$TiCl_3$. Figure 1 shows a unit cell delineated on an array of chains.[24] This figure is applicable to all four systems although the shapes of the atoms would be modified from system to system to account for differing values of rms thermal displacements. Analysis of Patterson maps supports the choice of the space group $P6_3/mcm$ for all four halide systems rather than $P\bar{6}2m$, fixing the zirconium positions at half the length of the c axis.

The refined multiplicities indicate complete zirconium atom site occupancy in the trihalides to within 1%. While the appearance of the symmetry-forbidden $h0l$ reflections is baffling, it is possible that the phenomenon of the unaccounted for electron density may be related to their appearance. Nothing in any of the manipulations of the data sets suggests the correspondence of this electron density to any realistic structural features. Furthermore the $h0l$, $h \neq 0$, data mysteriously do not appear to seriously affect the interpretation of the data in terms of a hexagonal unit cell as indicated by the axial scan data and the low R values achieved. Both the $h0l$, $h \neq 0$, data and the anomalous electron density appear to exist independently of the structure as refined. In addition, structural models containing metal atom density in the alternative octahedral sites ($x = {}^1/_3, {}^2/_3, y = {}^2/_3, {}^1/_3$) cannot be refined, suggesting a lack of even a statistical disordering over these positions. While such a model could be refined in the chloride system, the refinement required reduction of the symmetry to triclinic. This model differed from the final reported structure in that only small populations of additional zirconium were allowed to reside in these extra positions to an extent of not more than 1%, although this resulted in slightly higher R values. This model is reminiscent of Shelton's "shear plane"[25] model for the nonstoichiometric disproportionation products of the zirconium halides. The fact that the populations residing at the shear positions ($^1/_3$, $^2/_3$, 0 and $^1/_3$, $^2/_3$, $^1/_2$) are small, that the occupancies of the zirconium atom chains are essentially complete, and that this model did not refine significantly better than the ideal indicates that the *zirconium trihalides synthesized in this work are stoichiometric.*

The nonstoichiometric zirconium iodide, $ZrI_{3.40}$, has the same level of structural ideality. While not stoichiometric, the structure may also be viewed as chains of face-shared octahedra with no significant metal atom occupancy of the alternate octahedral sites. In this case, however, 11.75% of the octahedral metal atom sites along the chain itself are empty, 35.25% formally occupied by Zr(IV), and 53% occupied by Zr(III), the various kinds of metal atoms being statistically distributed over the available chain sites so that all of the metal atoms appear to be identical in the structure. Since $ZrI_{3.40}$ does not possess a unique structure, but rather one derived from the stoichiometric ZrI_3 structure in the manner just outlined, we will continue to write it as $ZrI_{3.40}$[33] rather than assign it the rational formula Zr_5I_{17}.

While the amount of disorder and nonstoichiometry in the crystals may vary from batch to batch and conceivably from crystal to crystal within a batch, the statistical likelihood is low of selecting the one crystal exhibiting a significant level of order and stoichiometry when the batch, as a whole, is analyzed as stoichiometric. Furthermore, a large metal atom population in the alternate sites would lend a three dimensionality to the microstructure of the crystal, thus binding the fibers more tightly together. Even in the crystals strong enough to survive the mounting process, this is not detected. These facts, coupled with the reproducibility of the analytical data on different synthetic batches, lead us to conclude that, at the lower temperatures employed in the aluminum halide melt method, the trihalides could also be considered as essentially line phases. With respect to $ZrI_{3.40}$, however, this conclusion is less firm, as its structure suggests the possibility of a finite variable composition range. We have not studied the composition of products over the temperature range spanning the temperature for the preparation of the pure purple ZrI_3 ($\geq$300 °C) and that for the preparation of the black $ZrI_{3.40}$ ($\leq$280 °C). However, visual observation of melts in the intermediate temperature range appeared to indicate that both the black and the purple are produced simultaneously, in different spatial locations in the reaction tube (see above).

All of the binary halides refined to satisfactory R values. However, the final R value obtained in this study on zirconium

---

(24) Johnson, C. K. "ORTEP-II, A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5738; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(25) Copley, D. B.; Shelton, R. A. J. *J. Less-Common Met.* **1970**, *20*, 359–366.

(26) Kleppinger, J. Ph.D. Thesis, University of Wisconsin—Madison, 1975.

(27) Lewis, J.; Machin, D. J.; Newnham, I. E.; Nyholm, R. S. *J. Chem. Soc.* **1962**, 2036.

(28) Keppert, D. L. "The Early Transition Metals"; Academic Press: New York, 1972.

(29) Clemmer, R. G. Ph.D. Thesis, University of Wisconsin—Madison, 1975.

(30) Magneli, A. *Acta Crystallogr.* **1953**, *6*, 495–500.

(31) Feldmann, C. D. Ph.D. Thesis, University of Wisconsin—Madison, 1979.

(32) Corbett, J. D.; Anderegg, J. W. *Inorg. Chem.* **1980**, *19*, 3822–3824.

(33) In light of its structure, $ZrI_{3.40}$ should actually be written as $Zr_{0.882}I_3$ in order to indicate that the nonstoichiometry is due to a metal atom deficiency rather than to excess iodine (see: Greenwood, N. N. "Ionic Crystals, Lattice Defects, and Nonstoichiometry"; Chemical Publishing Co.: New York, 1970; p 113). However, in order to facilitate comparison with Corbett's reported compositions, we have retained the $ZrI_{3.40}$ formula.

Table IV. Lattice Parameters for Compositions ZrX_n

X	*n*	reacn temp, °C	lattice parameters, Å		ref
			a	*c*	
Cl	2.94 (2)	600	6.3863 (5)	6.1374 (7)	6
	3.02 (2)	25	6.382 (5)	6.315 (7)	3
	3.00 (1)	220	6.383 (1)	6.139 (2)	*a*
	3.01 (3)	600-700	6.36 (1)	6.14 (1)	2
	3.02 (2)	450	6.3842 (4)	6.1341 (5)	6
Br	2.87 (2)	435	6.7565 (5)	6.3245 (5)	6
	2.95 (3)	700	6.75 (1)	6.315 (5)	2
	3.00 (2)	450	6.7472 (6)	6.3135 (6)	6
	3.01 (1)	240	6.728 (2)	6.299 (2)	*a*
	3.01 (-)	270	6.724 (2)	6.291 (2)	4
	3.01 (-)	270	6.7275 (20)	6.2992 (14)	5
	3.10 (2)	400	6.7399 (5)	6.3050 (5)	6
	3.23 (2)	435	6.7309 (5)	6.2995 (6)	6
I	2.83 (5)	775	7.2949 (5)	6.6672 (7)	6
	2.90 (3)	700	7.2907 (5)	6.6663 (5)	6
	2.93 (5)	600	7.25 (1)	6.64 (1)	2
	3.00 (3)	600	7.2850 (6)	6.6587 (9)	6
	3.00 (3)	300	7.298 (4)	6.667 (4)	*a*
	3.40 (-)	≤280	7.239 (2)	6.6733 (1)	*a*
	3.43 (5)	475	7.2346 (5)	6.698 (1)	6

[a] This work. Commerical analyses were performed by Galbraith Laboratories, Knoxville, TN, on preweighed samples sealed in small Pyrex ampules.

tribromide (R_1 = 7.55%) is to be contrasted with the R_1 = 2.3% obtained in our previous study.[5] Similar values for the primary structural parameters were obtained in each study. The lattice parameters and interatomic distances and angles are the same within the limits of error. The thermal parameters and rms thermal displacements are somewhat different, the former being decidedly smaller in this study and the latter only slightly smaller. The thermal parameters and rms thermal displacements within each study, however, bear the same relationships to each other (e.g., $\mu(1)_{Br} < \mu(2)_{Br} << \mu(3)_{Br}$). There are significant differences in the two data sets collected. The final data-to-parameter ratio reported here (15.4) is adequate but not as favorable as those obtained for the other three systems. In this study, the data set was collected out to a 2θ value of 110° (maximum *h*, *k*, or *l* = 12) whereas the earlier study[5] only contained data with a 2θ limit of 50° (maximum *h*, *k*, or *l* = 6). The minimum scan speed in this study was 0.5°/min, and many more weak reflections were detected than at the minimum scan speed of 2°/min used earlier. Both the extra weak reflections obtained and the weak and strong reflections with large 2θ values are associated with structural features occurring with less regularity than the highly symmetric chains of face-shared octahedra, which is the primary feature. The inclusion of these reflections contributed to the higher final *R* values obtained in this study. It should be pointed out here that bromide syntheses always seems to behave differently from the other syntheses. For reasons we have been unable to explain, the bromide synthesis is the least reproducible, and produces generally lower yields and crystals of more variable quality than the chloride and iodide systems. Variations in the crystal quality on the atomic level from one crystal to another may be more important in explaining the differences in *R* values than the differences in the data sets collected.

Finally, while it is conceivable that materials synthesized in aluminum halides could contain small amounts of aluminum, no such inclusion was detected crystallographically in any of the four halide systems. From the totality of evidence, it can be concluded that the binary halides synthesized in aluminum halides grow as chains of face-shared octahedra free of any significant number of crystallographically detectable metal atom inclusions, dislocations, or absences beyond those necessarily present along the chains in the black $ZrI_{3.40}$.

Table V. R_{Oh} (Å) vs. R_{Zr} (Å) in the Zirconium Halides

X	R_X	D_{M-X}	R_{Oh}	R_{Zr}
Cl	1.81	2.54	0.749	0.73
Br	1.95	2.68	0.807	0.73
I	2.16	2.90	0.894	0.74

Comparison of Lattice Parameters of Products from Different Synthetic Routes. The lattice parameters for ZrX_n as reported over a period of time[2-6] are presented in Table IV. Since the earlier data[2,3] are less precise than the recent data, it is difficult to involve them in any meaningful comparison.

The pairs of *a* and *c* lattice parameters for $ZrCl_3$ reported in the present work do not fall within the phase limits reported by Corbett, the *a* value being lower than *a* for *n* = 3.02 and the *c* value being higher than *c* for 2.94. However, since the stoichiometric range is small and the analytical uncertainty is at least ±0.02, the values for the *a* and *c* parameters in this work and those of Corbett agree reasonably well.

The tribromide and triiodide data show more of a variation with method of preparation. Whereas the tribromide data of this work and our previous[4,5] publications correspond reasonably well, the correspondence with the lattice parameters of the high-temperature products is not good. Our *a* value is consistently lower than the *a* value for the high-temperature preparation and our *c* value is consistently lower than the *c* value for the high-temperature preparation, except for *c* where *n* = 3.23. The purple form of the triiodide, which was determined to be stoichiometric in this work, has lattice parameters that correspond best to those values for Corbett's *n* = 2.83. The nonstoichiometric black form, which was determined to be $ZrI_{3.40}$ in this work, corresponds to either $ZrI_{3.5}$ or $ZrI_{2.8}$, depending upon which lattice parameter is used to make the comparison.

Within three significant figures the *c* lattice parameters (Table IV) for the stoichiometric compositions, except for Watt's[3] $ZrCl_3$, are in remarkable agreement. We suspect that variations in lattice parameters in the fourth and fifth significant figures are a function of synthetic route and handling as well as stoichiometry. It has been established[26] that the powder patterns of these trihalides do vary with annealing temperature and grinding of the crystals. Before a conclusive statement can be made regarding the correlation of lattice parameter shifts with stoichiometry, the reproducibility of lattice parameter measurements and elemental analyses from multiple preparations, which are handled in identical fashions, should be established. For resolution of this question single-crystal X-ray data should be collected for samples obtained via high-temperature synthesis for comparison with the parameters reported for compounds prepared via a low-temperature route.

Metal–Metal Distances and Their Significance. The bonding in these d^1 compounds has been described[2] as involving direct metal–metal interactions along the chain. The reported[27] diamagnetic character of these compounds was used to support this conclusion. However, the long metal–metal distances along the chain (Table I) raise questions about this hypothesis.

Comparison of the structural parameters of the zirconium trihalides with those of the ideal close-packed hard-sphere model shows that they are all consistent with an elongation of the halogen octahedra along the 3-fold axis rather than compression of the octahedra as would be expected if metal–metal bond formation played a dominant role in the structure of these compounds. The parameters examined include *c*/*a* ratios,[28] metal–metal distances, the angle between the 3-fold axis and the metal–halogen bond,[29] the X–M–X and X–M–X′ angles, and the difference between the interlayer interhalogen (X–X) distance and the interlayer interhalogen distance (X–X′). All show that the elongation is greatest for the trichloride, less for the tribromide, and negligible for the iodides. Alternatively we have calculated an experimental effective Zr^{3+} radius and compared it to the octahedral hole size calculated for an idealized hard-sphere model (Table V). In the chloride case the fit is good, while in the iodide case the site radius is almost 25% larger than the metal atom radius. For this series of zirconium halides a 3% excess in the site radius over the metal ion radius results in a 5% elongation of the metal–metal distance over the ideal interhole distance in the chloride; in the bromide an 11% excess in site radius results in a 2% elongation, and in the iodide a 25% excess in the site radius results in no elongation.

Consideration of the rms thermal displacements (Table III) reveals that the distribution of the metal atom electron density becomes progressively more elongated along the *c* axis in the series even though the site radius increases in size symmetrically. It appears that the metal ions with high formal charges compared to the counterion in an anisotropic structure require more space in the direction of the anisotropy to minimize nearest-neighbor metal ion repulsions. On the other hand, minimal oscillation is required perpendicular to the direction of structural anisotropy due to the lack of nearest-neighbor metal atoms at sufficiently short distances. A similar elongation of metal atom occupied octahedra has been observed by Magneli[30] along the *b* axis of the monoclinic homologous series M_nO_{3n-1} and M_nO_{3n-2} (M = Mo, W). If the zirconium trihalides are viewed as Magneli-type phases, the elongation of the octahedra is the result of the distortion necessary to reduce repulsive nearest-neighbor metal ion interactions when excess metal ion site radius is unavailable. However, the fact that distortion occurs does not necessarily totally eliminate bonding interactions between the d^1 electrons of the zirconiums, because the magnitude of the distortion must be the resultant of the repulsive electrostatic forces and the attractive bonding forces. It does seem clear that the d^1 electrons enter into a more complex behavior than simple σ-bond formation, as evidenced by the field-dependent, temperature-independent paramagnetism of the trihalides[31] and the valence photoelectron emission spectra[32] of the trichloride.

Acknowledgment. This work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation and in part by a National Science Foundation Departmental Instrument Grant (No. 28233), which allowed the purchase of the automated diffractometer. The authors also thank Mr. William B. Jensen for the many stimulating discussions.

Registry No. $ZrCl_3$, 10241-03-9; $ZrBr_3$, 24621-18-9; ZrI_3, 13779-87-8.

Supplementary Material Available: A listing of structure factor amplitudes for these compounds (8 pages). Ordering information is given on any current masthead page.

Contribution from the Science Research Laboratory,
3M Central Research Laboratories, St. Paul, Minnesota 55101

Partially Oxidized Cation Radical Complexes of Platinum(II)

A. R. SIEDLE,* M. C. ETTER, M. E. JONES, G. FILIPOVICH, H. E. MISHMASH, and W. BAHMET

Received November 30, 1981

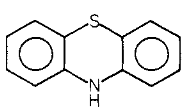
Metal complexes of the type L_2MCl_2 (M = Pd, Pt) were prepared from $KPtCl_3(C_2H_4)$ or $(PhCN)_2PdCl_2$ and the electrochemically active ligands (L) phenothiazine, phenoselenazine, and phenoxathiin. The stereochemistries of the compounds were deduced from vibrational spectra and X-ray powder diffraction data. From $KPtCl_3(C_2H_4)$ and phenoselenazine in acetonitrile were obtained both *trans*-bis(phenoselenazine)dichloroplatinum(II) and *cis*-bis(phenoselenazine)dichloroplatinum(II)–acetonitrile. This solvated cis isomer crystallizes in space group $Cmc2_1$ with $a = 14.693$ (4) Å, $b = 16.341$ (5) Å, $c = 10.643$ (8) Å, $V = 2555$ Å^3, $Z = 4$, $D_c = 2.07$ g cm^{-3}, and $D_m = 2.0$ g cm^{-3}. The structure, refined with 1061 reflections for which $I > 2\sigma(I)$, converged at at $R = 0.05$. The acetonitrile occupies a lattice site and is not coordinated to the metal. The two Pt–Se distances are 2.376 (2) and 2.400 (2) Å. The cis phenoselenazine ligands are nearly planar with dihedral angles through the Se–N vectors of 172.8 and 173.1°. Adjacent *c*-glide related molecules are packed so that a 3.48 Å interplanar spacing occurs between the coordinated phenoselenazine ligands on adjacent molecules. Iodine oxidation led to *trans*-$(PSZ)_2PtCl_2I_{4.0}$, *trans*-$(PSeZ)_2PtCl_2I_{3.5}$, and *cis*-$(PSeZ)_2PtCl_2I_{3.9}$, which had significantly greater electrical conductivity than the insulating precursors. Resonance Raman and X-ray photoelectron spectroscopies indicate that the hole sites are localized on the heterocyclic ligands and that the iodine is present predominantly as I_5^-.

Introduction

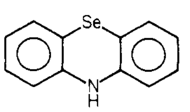
Partially oxidized compounds containing platinum(II), particularly the tetracyanoplatinates, have attracted considerable attention on account of their anisotropic electron transport properties.[1-3] In $Pt(CN)_4^{2-}$ derivatives, the cyanide ion can function as both a σ donor and a π acceptor. We have investigated the preparation and properties of related materials of the type L_2PtCl_2, where L is a neutral aromatic ligand which is both a good donor and capable of undergoing reversible electron-transfer reactions. This paper describes the synthesis and properties of a family of L_2MCl_2 compounds (M = Pd, Pt; L = phenothiazine, phenoselenazine, phenoxathiin), the crystal structure of one of these, *cis*-bis(phenoselenazine)dichloroplatinum(II)–acetonitrile, which reveals an unusual conformational change on complexation of the ligand, and partial oxidation reactions with iodine which afford cation radical complexes of platinum.

Results and Discussion

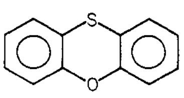
Synthesis and Properties of the Complexes. The ligands employed in this study were phenothiazine (PSZ), **1**, phenoselenazine (PSeZ), **2**, and phenoxathiin (POT), **3**. Phenothiazine (PSZ) and phenoselenazine (PSeZ) are particularly interesting ligands since (1) the ring chalcogen atom should serve as an effective donor site, (2) the ligand π^* system can back-bond with filled metal d orbitals, and (3) phenothiazine



1



2



3

---

(1) "Extended Linear Chain Compounds", J. S. Miller, Ed., Plenum Press, New York, 1982.

(2) A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, 429 (1980).

(3) "Highly Conducting One-Dimensional Solids", J. T. Devreese, R. P. Evrard, and V. E. Van Doyen, Eds., Plenum Press, New York, 1979.

0020-1669/82/1321-2624$01.25/0