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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 21. Single-Crystal and Powder Time-of-Flight Neutron Diffraction Studies of $Tl_4[Pt(CN)_4]CO_3$[1a]

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The crystal and molecular structure of the unusual complex $Tl_4[Pt(CN)_4]CO_3$, obtained by mixing $Tl_2[Pt(CN)_4]$ and Tl_2CO_3 in aqueous solution at 95 °C, was determined by both single-crystal and time-of-flight powder neutron diffraction. The complex is not a partially oxidized tetracyanoplatinate (POTCP) salt and contains Pt in an integral (2.0) oxidation state. The lustrous metallic green complex crystallizes in the tetragonal space group *P4/mcc* (D_{4h}^{2}, No. 124), with unit cell constants $a = b = 9.911$ (4) Å (9.908 (3) Å, powder study), $c = 6.490$ (3) Å (6.487 (2) Å), and $V_c = 637.5$ Å^3 at 298 K. In the single-crystal study diffracted intensities of 267 independent reflections were measured to a $(\sin\theta)/\lambda$ limit of 0.438 Å^{-1}, and of these 202 had $F_o^2 > \sigma(F_o^2)$. Full-matrix least-squares refinement of all structural parameters resulted in a final $R(F_o^2) = 0.075$ (all data) and $R(F_o^2) = 0.068$ (for $F_o^2 > \sigma(F_o^2)$). The time-of-flight (TOF) neutron powder data collected on the high-resolution powder diffractometer, HRPD, at the Argonne National Laboratory ZING-P′ prototype pulsed neutron source were refined with use of the Rietveld profile refinement technique starting from the single-crystal parameters which resulted in a profile $R = 0.025$. It is important to note that the structural parameters derived with use of the TOF and single-crystal methods are, in this case, virtually identical. The most pertinent structural feature in $Tl_4[Pt(CN)_4]CO_3$ is that the Pt atoms form perfectly linear chains with Pt–Pt separations crystallographically constrained to a value of $(c/2) = 3.245$ (3) Å. The intrachain Pt–Pt separation is much longer than in the partially oxidized salts (2.80–2.96 Å) and accounts for the low electrical conductivity in this salt ($\sigma_{\parallel} \leq 2.0 \times 10^{-7}$ Ω^{-1} cm^{-1}). The structure is composed of square-planar $Pt(CN)_4^{2-}$ groups linked by Tl^+ cations, all of which occupy the same molecular plane, and carbonate groups which lie between the $Pt(CN)_4^{2-}$ groups. The CO_3^{2-} group oxygen atoms are clearly disordered among at least two positions, creating six partially occupied oxygen atom sites per group. The Tl^+ and O separations are ~0.2 Å shorter than the sum of the ionic radii which is probably an artifact of disorder. The problems associated with the attempted preparation of Tl^+ partially oxidized tetracyanoplatinate salts, which should be possible because those of Rb^+ with the same ionic radius as Tl^+ can be prepared, are discussed. These combined neutron-scattering results highlight the utility of the TOF powder neutron diffraction method in small molecule crystallography. With the new generation of intense pulsed neutron sources about to come on line, it is likely that much more complex compounds, which can only be obtained as polycrystalline samples, will be studied in the near future.

Introduction

The single-crystal neutron diffraction and time-of-flight neutron powder diffraction studies of $Tl_4[Pt(CN)_4]CO_3$ were undertaken in order to test the feasibility of obtaining refined small molecule crystal structures with use of data derived from polycrystalline samples of chemically important compounds. Such studies are needed because of the rather frequent obstacle encountered in neutron diffraction studies, i.e., the inability to obtain single crystals of sufficient size. For materials with tetragonal or higher symmetry possessing unit cell constants of ~10 Å in each dimension, the TOF neutron powder diffraction method offers great promise as a solution to this problem. In order to rigorously test the TOF powder method, we chose $Tl_4[Pt(CN)_4]CO_3$ which has a unit cell volume of ~637.5 Å^3. The derived structural parameters compare very well with those obtained from a single-crystal neutron diffraction study (vide infra).

Experimental Section

Crystal Preparation. The preparation of $Tl_4[Pt(CN)_4]CO_3$ was carried out by direct interaction of Tl_2CO_3 and $Tl_2[Pt(CN)_4]$ in aqueous solution at 95 °C.[2] The product is a lustrous metallic green salt properly formulated after the structure analysis as $Tl_4[Pt(CN)_4]CO_3$. In the synthesis of starting material, 7.0 g of $Ba[Pt(CN)_4]\cdot 4H_2O$[3] was dissolved in 25 mL of hot distilled water (70–80 °C) and added to a solution of 7.0 g of Tl_2SO_4 in 210 mL of warm water (60–70 °C). $BaSO_4$ was removed by filtration, and the temperature was maintained at 70 °C for 1 h. After $BaSO_4$ was washed with two 10-mL portions of hot water (70–80 °C), the filtrates were combined and reduced to 200 mL on a steam bath. Slow cooling of the filtrate for 30 min followed by 90 min in an ice bath resulted in the crystallization of white $Tl_2[Pt(CN)_4]$. Then 0.73 g of recrystallized Tl_2CO_3 was dissolved in boiling water and added to a solution of 1.0 g of $Tl_2[Pt(CN)_4]$ previously dissolved in 20 mL of boiling water. Both solutes must be completely dissolved before mixing or the product will be contaminated with $Tl_2[Pt(CN)_4]$ starting material. The reaction vessel was covered with a watch glass and boiled in a hot air bath (a beaker placed inside another beaker on a hot plate), and the volume of the solution was reduced to ~10 mL. At approximately this point a red precipitate forms (*small* crystals of the desired product), and the volume is further reduced to 4–5 mL and then filtered hot with a fine-pore fritted glass filter. This procedure, when closely followed, yields fine needlelike crystals of the desired product which have a green metallic luster. Any starting material present can be removed by recrystallizing the mixture from a hot 0.05 M Tl_2CO_3 solution. The yield was ~1.4 g (85%) on the basis of $Tl_2[Pt(CN)_4]$. Anal. Calcd for $Tl_4[Pt(CN)_4]CO_3$: C, 5.10; N, 4.76; O, 4.08; Pt, 16.58; Tl, 69.48. Found (Galbraith Laboratories, Knoxville, TN): C, 4.97, 4.90; N, 4.40, 4.25; O, 4.17, 3.84; Pt, 16.68, 16.58; Tl, 69.30, 69.46, 69.53. The presence of Tl and Pt only was confirmed by emission spectrographic analyses (Argonne National Laboratory).

Collection of Neutron Diffraction Data. The crystal used for neutron data collection was needle-shaped with dimensions of 0.72 × 0.72 × 2.56 mm, with faces formed by the (110) planes and the (001) planes. Preliminary X-ray photographs indicated the tetragonal crystal system, with systematic absences *hhl*, *l* = odd, 0*kl*, *l* = odd, and *h*0*l*, *l* = odd, thus determining the space group as *P4/mcc* or *P4cc*.

The room-temperature neutron data were collected with use of an Electronics-and-Alloys four-circle automated diffractometer at the Argonne CP-5 reactor in a manner previously described.[4] The lattice constants were determined by a least-squares fit of the diffractometer setting angles for 19 intense reflections (40° < 2θ < 60°).

The calculated density, on the assumption of 2 two formula units

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(1) (a) Research performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. (b) Chemistry Division. (c) Solid State Science Division.

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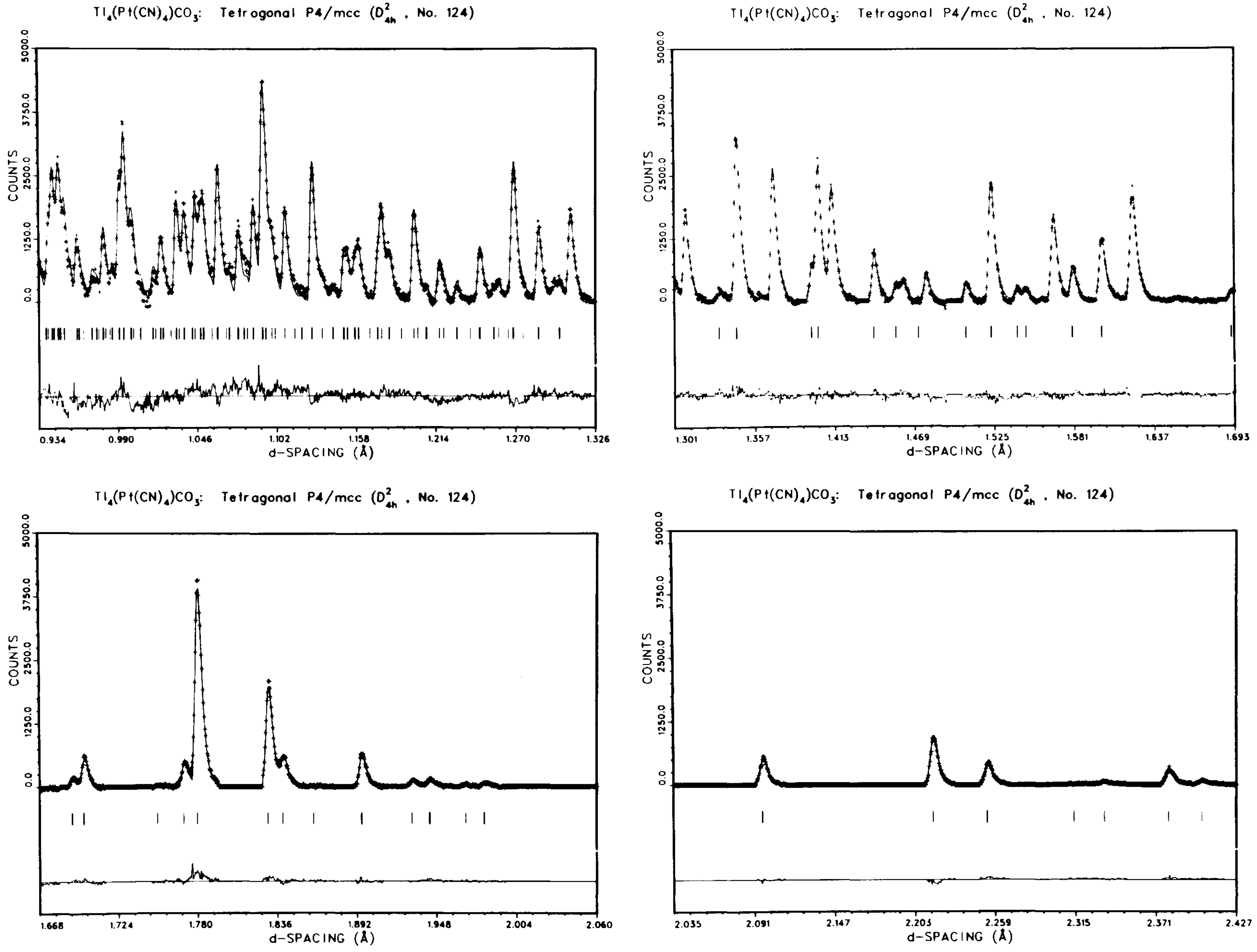

Figure 1. Final Rietveld refinement profile for $Tl_4[Pt(CN)_4]CO_3$. Plus marks (+) are the raw data points. The solid line is the calculated profile. Tick marks below the profile indicate the positions of all allowed reflections. Background has been removed before plotting. A difference plot appears at the bottom of the figure.

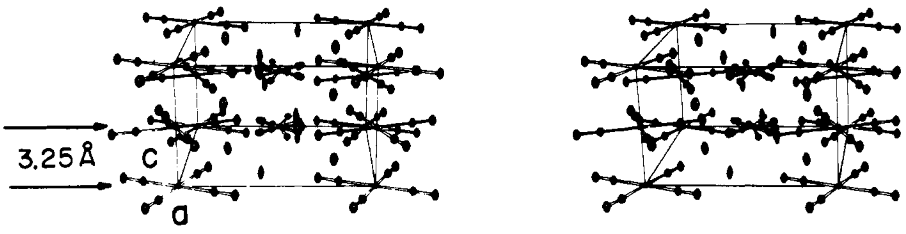

Figure 2. Stereodiagram of the structure of $Tl_4[Pt(CN)_4](CO_3)$ showing linear and parallel Pt atom chains ($d_{Pt-Pt} = 3.245$ (3) Å). The "chains" are derived from stacking of the square-planar $Pt(CN)_4{}^{2-}$ groups. The lattice also contains disordered $CO_3{}^{2-}$ anions between $Pt(CN)_4$ groups in the chains and Tl^+ cations which link the chains.

per unit cell, is 6.129 g/cm^3 which agrees well with the experimental density of 6.0 (2) g/cm^3 determined by displacement of a weighed sample. Individual reflections were corrected for absorption (μ_c = 0.455 cm^{-1}) with use of a Gaussian integration over the crystal volume,[5] and the minimum and maximum transmission coefficients were 0.89 and 0.97, respectively. Intensities were reduced to structure factors ($F_o{}^2$) in a manner previously described.[4]

The powder data were collected in the back-scattering detector banks of the high-resolution powder diffractometer (HRPD) at Argonne's ZING-P′ prototype pulsed neutron source.[14] The detectors are in two time-focussed arrays at $2\theta \approx \pm 160°$ and a nominal sample to detector distance of 1 m. Each array contains 15 6-atm ^{3}He counters ($^5/_8$ in. diameter × 10 in. long). The initial flight path (moderator to sample) is 18.37 m. The resolution of this instrument is $\Delta d/d$ = 0.003 (fwhm).

Structure Solution and Refinement. On the assumption that the title complex contains square-planar $Pt(CN)_4$ groups and with use of the single-crystal data, structure factor calculations were performed with use of logical positions for the platinum atoms in space group *P4/mcc*. After Fourier calculations were made, on the assumption of Pt at (0, 0, 0) and the carbonate carbon atom at ($^1/_2$, $^1/_2$, $^1/_4$), the locations of the cyanide group atoms and the Tl^+ ion were revealed on a Fourier map. Subsequent Fourier maps calculated with use of phases derived from these atom positions clearly established the presence of disordered carbonate oxygen atoms. The carbonate group oxygen atom disorder comprises O(1), at a site with twofold symmetry at (x, x, $^1/_4$) which results in four partially occupied oxygen atom positions about a single carbonate carbon atom, and O(2) at a general position which produces eight partially occupied oxygen atom sites. Full-matrix least-squares refinement of all atom positional parameters and isotropic temperature factors yielded discrepancy indices of

$$R(F_o) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.24 \qquad R(F_o{}^2) = \frac{\sum |F_o{}^2 - F_c{}^2|}{\sum F_o{}^2} = 0.33$$

$$R_w(F_o{}^2) = \left[\frac{\sum w_i |F_o{}^2 - F_c{}^2|^2}{\sum w_i F_o{}^4}\right]^{1/2} = 0.41$$

$$\mathrm{GOF} = \Sigma_1 = \left[\frac{\sum w_i |F_o{}^2 - F_c{}^2|^2}{n - p}\right]^{1/2} = 4.73$$

where n is the number of data and p the number of parameters varied in the least-squares refinement. The introduction of anisotropic temperature factors dramatically reduced these values as given in Table I. When the use of anisotropic values was attempted for the disordered carbonate group oxygen atoms O(1) and O(2), nonpositive definite temperature factors were obtained due probably to the inability to properly account for the disorder. In the final least-squares refinement these atoms were included with isotropic temperature factors only. A difference Fourier map calculated from the final least-squares parameters showed no peaks above background. In the last few cycles of least-squares refinement a secondary extinction parameter was refined ($g = 0.62 \times 10^{-4}$).[6] The data to parameter ratio was 8.9:1 with all data included and 6.7:1 where $F_o{}^2 > \sigma F_o{}^2$. The final agreement factors appear in Table I. The final positional and thermal parameters derived from the single crystal and TOF data are given in Table II, and the bond distances and angles are listed in Table III. The coherent neutron-scattering amplitudes used for Pt, N, C, O, and Tl were 0.950, 0.940, 0.665, 0.580, and 0.890, respectively (in units of 10^{-12} cm).[7]

Table I. Final Agreement Factors for $Tl_4[Pt(CN)_4]CO_3$

	single-crystal[a] data at 298 K				
data used	no. of data	$R(F_o)$	$R(F_o{}^2)$	$R_w(F_o{}^2)$	GOF
all data	267	0.098	0.075	0.093	1.09
$F_o{}^2 > \sigma(F_o{}^2)$	202	0.064	0.068	0.087	1.20

	powder data			
no. of reflctns	no. of data (time channels)	$R_{\mathrm{profile}}(I)$[b]	$R_{\mathrm{w,profile}}(I)$[c]	GOF[d]
222	2056	0.026	0.036	1.72

[a] See Experimental Section for the appropriate formulas for the single-crystal data. [b] $\Sigma|I_{\mathrm{obsd}} - I_{\mathrm{calcd}}|/\Sigma|I_{\mathrm{obsd}}|$. [c] $\{\Sigma w(I_{\mathrm{obsd}} - I_{\mathrm{calcd}})^2/\Sigma w(I_{\mathrm{obsd}})^2\}^{1/2}$. [d] $\{\Sigma w(I_{\mathrm{obsd}} - I_{\mathrm{calcd}})^2/(n-p)\}^{1/2}$.

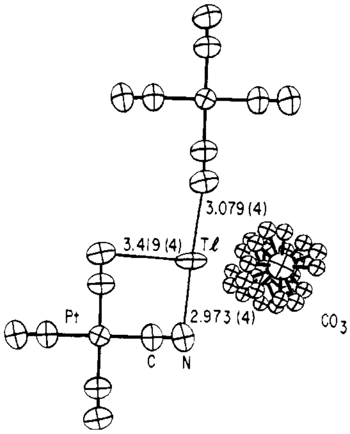

Figure 3. Tl^+ coordination sphere in $Tl_4[Pt(CN)_4]CO_3$. The Tl^+ ions and $Pt(CN)_4$ groups occupy the same molecular plane and are linked by CN^-- - -Tl^+- - -^-NC interactions. The disordered $CO_3{}^{2-}$ anions lie above and below the plane occupied by the Tl^+ anion.

The single-crystal data were also refined with use of the noncentrosymmetric space group *P4cc*. In spite of the larger number of parameters, no improvement in the agreement factors was observed nor were the parameter shifts of significant magnitude. Therefore the centrosymmetric space group *P4/mcc* (D_{4h}^2, No. 124) was indicated.

The powder data were refined with use of a Rietveld profile analysis code which has been modified for time-of-flight data from spallation pulsed neutron sources.[14] The refinement included 2056 data points (representing consecutive 5 μs wide time channels) and 222 allowed reflections. The 43 parameters refined included atomic coordinates, temperature factors, cell constants, scale and time zero factors, and background and profile parameters. The final agreement indices calculated with background included are given in Table I. The best-fit profile is shown in Figure 1.

Discussion

The structure of $Tl_4[Pt(CN)_4]CO_3$ is that of a one-dimensional tetracyanoplatinate comprising parallel and linear Pt

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Table II. Single Crystal and Time-of-Flight Positional and Thermal Parameters for $Tl_4[Pt(CN)_4](CO_3)$

	coordinates					
	single crystal			powder data		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Pt	0	0	0	0	0	0
C(1)	0.0744 (3)	0.1857 (3)	0	0.0738 (3)	0.1855 (3)	0
N	0.1211 (3)	0.2930 (3)	0	0.1200 (2)	0.2934 (2)	0
Tl	0.4077 (3)	0.2042 (3)	0	0.4074 (3)	0.2038 (3)	0
C(2)	0.5	0.5	0.25	0.5	0.5	0.25
O(1)	0.402 (2)	0.402 (2)	0.25	0.403 (1)	0.403 (1)	0.25
O(2)	0.4609 (9)	0.620 (1)	0.232 (2)	0.4588 (9)	0.6187 (9)	0.222 (1)

	temperature factors[a,b]					
atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.0040 (5)	0.0040 (5)	0.016 (1)	0	0	0
	0.0029 (3)	0.0029 (3)	0.005 (1)	0	0	0
C(1)	0.0042 (3)	0.0031 (4)	0.029 (1)	−0.0005 (3)	0	0
	0.0028 (4)	0.0029 (4)	0.014 (1)	0.0000 (2)	0	0
N	0.0081 (3)	0.0052 (3)	0.043 (1)	−0.0015 (2)	0	0
	0.0061 (3)	0.0039 (3)	0.034 (1)	−0.0022 (2)	0	0
Tl	0.0063 (4)	0.0091 (4)	0.042 (1)	−0.0002 (3)	0	0
	0.0069 (3)	0.0076 (4)	0.035 (1)	−0.0001 (2)	0	0
C(2)	0.0032 (7)	0.0032 (7)	0.015 (2)	0	0	0
	0.0046 (4)	0.0046 (4)	−0.002 (1)	0	0	0
O(1)[c,d]	2.4 (3)					
	1.1 (3)					
O(2)[c,d]	2.4 (2)					
	1.0 (2)					

[a] Single-crystal study data on top and powder study data on bottom. [b] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + ... + 2\beta_{12}hk + ...)]$. [c] Isotropic *B*'s (Å²). [d] O(1) and O(2) are oxygen atoms in disorder (see text).

Table III. Interatomic Distances (Å) and Bond Angles (Deg) for $Tl_4[Pt(CN)_4]CO_3$ Calculated from the Single-Crystal Study[a]

(A) Distances in the Pt(CN) Group			
Pt–C(1)	1.983 (3)	C(1)–N	1.160 (4)
Pt–Pt^{I}	3.245 (3)		
(B) Distances in the CO_3^{2-} Anion			
C(2)–O(1)	1.37 (2)	C(2)–O(2)	1.25 (1)
C(2)–C(2)^{I}	3.245 (3)		
(C) Thallium Ion Interactions			
Tl–O(1)	2.548 (3)	Tl–O(2)^{II}	2.52 (1)
Tl–O(2)^{III}	2.65 (1)	Tl–O(2)^{IV}	2.97 (1)
Tl–N	2.973 (3)	Tl–N^{V}	3.062 (2)
(D) Bond Angles of $Pt(CN)_4$ and CO_3 Groups			
Pt^{I}–Pt–Pt^{VI}	180	C(2)^{I}–C(2)–C(2)^{II}	180
Pt–C(1)–N	178.3 (3)	O(1)–C(2)–O(2)	115.6 (6)
C(1)–Pt–C(1)^{VII}	180	O(2)–C(2)–O(2)^{IX}	128.9 (8)
C(1)–Pt–C(1)^{VIII}	90		

[a] Superscripts refer to symmetry operations as follows: (I) $-x, y, \frac{1}{2} + z$; (II) $x, 1 - y, \frac{1}{2} - z$; (III) $x, y, -z$; (IV) $1 - x, 1 - y, -z$; (V) $1 - y, x, z$; (VI) $-x, y, z - \frac{1}{2}$; (VII) $-x, -y, -z$; (VIII) $-y, x, z$; (IX) $y, -x, \frac{1}{2} - z$. If no superscript is given (x, y, z) is implied.

atom chains (d_{Pt-Pt} = 3.245 (3) Å) derived from stacked $Pt(CN)_4^{2-}$ groups between which are highly disordered CO_3^{2-} anions (see Figure 2). As illustrated in Figure 3, these groups are linked by Tl^+ cations. The $Pt(CN)_4^{2-}$ groups and the Tl^+ cations occupy the same molecular plane ($z = 0, {}^1/_2$) while the CO_3^{2-} anions are located *between* the planes ($z = {}^1/_4, {}^3/_4$) with the result that $Tl_4[Pt(CN)_4]CO_3$ may be considered as the same structural type (type "I")[8] as the POTCP salts containing bifluoride anion, viz., $Cs_2[Pt(CN)_4](FHF)_{0.40}$. Salts in this category frequently have high electrical conductivity (>1000 Ω^{-1} cm^{-1}) if the intrachain Pt–Pt separations are ≤2.84 Å.[8] However, the long Pt atom spacings of 3.25 Å in the Tl^+ salt preclude it having high electrical conductivity even though it has a metallic luster in reflected light (for a discussion see ref 8). The measured four-probe electrical conductivity[9] $\sigma_{\parallel}$ is 2.0×10^{-7} Ω^{-1} cm^{-1}, which is characteristic of an insulator. For comparison purposes, the Pt–Pt spacing in $Ba[Pt(CN)_4]\cdot4H_2O$ is 3.32 Å,[10] the electrical conductivity[11] $\sigma_{\parallel}$ is ~1.0×10^{-6} Ω^{-1} cm^{-1}, and the Ba salt is greenish blue and has no metallic luster even in reflected light. Finally, the interatomic distances, viz., Pt–C (1.983 (3) Å), C–N (1.160 (4) Å), and Tl–N$_{min}$ (2.973 (3) Å), all appear to fall in normal ranges while Tl–O$_{min}$ appears short due to the oxygen atom disorder, etc.

Although Tl^+ and Rb^+ have very nearly the same radii (~1.65 Å) we have *not* been able to prepare a $Rb(TCP)CO_3$ salt analogous to the thallium compound reported here. In the case of the partially oxidized salts $Rb_2[Pt(CN)_4]\cdot xH_2O$ may be oxidized to form either $Rb_{1.75}[Pt(CN)_4]\cdot xH_2O$ or $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O$; however, we have been unable to prepare similar salts of Tl^+. This is probably due to the potential for oxidation of $Tl^+ \rightarrow Tl^{3+}$ in acid solution which is approximately the same as $Pt^{2.0} \rightarrow Pt^{2.2-2.4}$ (~0.75 V). In passing, it should be noted that there appears to be no evidence to date for POTCP complex formation for anything other than monovalent cations.[8]

The structural parameters derived with use of the single-crystal data and the Rietveld method of profile refinement,[12] as presented in Table II, are identical within the errors of the measurement and are (surprisingly) of comparable accuracy. Prince[15] has shown that the estimated standard deviations calculated in the Rietveld method are correct even though correlations do exist between the individual data points.

Since resolution of single diffraction peaks is not required when the Rietveld method is used, neutron diffraction studies using the time-of-flight powder method may possibly be undertaken, as judged from the present study, using samples having tetragonal (or higher) symmetry and unit cell volumes

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of up to ~1500 Å^3. Structures in which as many as 70 parameters were refined have been successfully determined with use of steady-state reactor sources and the Rietveld technique.[13]

The 0.2–0.3% resolution of the intense pulsed neutron source (IPNS-I) general purpose powder diffractometer, and the projected IPNS-I flux, should allow an entire powder spectrum to be collected in less than 1 day. Thus the use of polycrystalline samples, rather than large single crystals, opens the field of neutron diffraction to a large number of chemical problems not previously accessible.[16]

Acknowledgment. J.M.W. wishes to thank NATO (Research Grant No. 1276) for support which made it possible to visit and exchange information with European scientists. We wish to thank Professor W. A. Freeman, who assisted in early X-ray studies.

Registry No. $Tl_4[Pt(CN)_4]CO_3$, 76880-00-7.

Supplementary Material Available: A listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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(15) For a discussion, see: Prince, E. *J. Appl. Crystallogr.*, in press.

(16) ZING-P′ is the prototype of a new pulsed neutron source IPNS-I which will start operating in the spring of 1981. IPNS-I will be a national user facility for condensed matter research, available to all qualified scientists according to policies established by the Department of Energy. Inquiries should be addressed to Dr. T. G. Worlton, Scientific Secretary, IPNS Program, Argonne National Laboratory, Argonne, IL 60439.

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Crystal Structure of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. A Neutron Diffraction Study

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A neutron diffraction study of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ confirmed the square-planar coordination geometry inferred from spectroscopic data and accurately placed the hydride ligands at bridging positions. At 112.4 K, the crystal lattice was triclinic, of space group $P\bar{1}$, with a = 12.084 (3) Å, b = 13.505 (6) Å, c = 9.540 (2) Å, α = 97.49 (2)°, β = 105.18 (1)°, γ = 116.15 (2)°, V_c = 1074.4 Å^3, and Z = 1. The Rh–Rh distances were 2.65 (1) Å, and the Rh–H distances were 1.808 (14) Å with H–Rh–H and Rh–H–Rh angles of 85.9 (5) and 94.1 (4)°, respectively. With an only slightly expanded P–Rh–P angle of 94.7 (4)°, near 90° average H–Rh–P angles, and near coplanarity of the $H_2Rh_2P_4$ system, the square-planar coordination geometry about each rhodium atom was established unequivocally. The planar Rh_2H_2 system is rectangular with 2.65- and 2.46-Å diagonals. Two four-center (Rh_2H_2) two-electron bonds are responsible for the framework bonding in the dimer. The net Mulliken bond order for the direct Rh–Rh interaction is positive but very small whereas those for Rh–H are large, nearly 0.5, as indicated by a molecular orbital analysis.

Introduction

Chemical studies[2] of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ have been providing molecular and mechanistic insights to catalytic reactions that involve both metal atoms of a coordinately unsaturated dinuclear metal complex. Because of the chemical importance of this molecule and the related $\{HRh[P(OCH_3)_3]_2\}_3$ complex, a neutron structure determination was undertaken, and the crystallographic[3] results are reported here.

Experimental Section

Crystals of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ were obtained by slow cooling of pentane solutions of the dimeric hydride. A rectangular crystal with faces with indices of the forms [02$\bar{3}$], [$\bar{3}$10], and [010] and with a volume of ~17 mm^3 was used for data collection. The crystal was mounted in a glass capillary, and the capillary was affixed to a hollow aluminum pin. This pin was mounted in an aluminum housing in a helium atmosphere, and this sample holder was placed in a closed-cycle helium refrigerator. During the course of preliminary crystallographic investigations and data collection the crystal was maintained at 112.4 K. Neutron diffraction data were collected[4] at the Brookhaven National Laboratory high flux beam reactor. The neutron beam wavelength was 1.1617 (1) Å. This wavelength was determined prior to the experiment by a least-squares fit of 48 reflections using a KBr crystal (a = 6.6000 Å). For minimization of the scattering from the refrigerator walls, a 12 in. Masonite collimator with a LiF extender (i.d. $^5/_8$ in.) was utilized.

Table I. Details of Data Collection and Structure Refinement for $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$

cryst system	triclinic, $P\bar{1}$, Z = 1
cell const (112.4 K)	
a, Å	12.084 (3)
b, Å	13.505 (6)
c, Å	9.540 (2)
α, deg	97.49 (2)
β, deg	105.18 (1)
γ, deg	116.15 (2)
V_c, Å^3	1074.4
mol wt	1040.8
D(calcd), g/cm^3	1.61
abs coeff, cm^{-1}	3.39
min and max transmission factors	0.521–0.730
data collection limit, Å^{-1} ((sin θ)/λ)	0.581 Å^{-1} (4224 reflections)
final agreement factor[a]	$R_w(F_o^2)$ = 0.135 (0.119)
goodness of fit	2.13
observn to parameter ratio	6.25

[a] Number in parentheses refers to data with $F_o^2 > \sigma(F_o^2)$.

Despite its adequate size, the crystal was a poor scatterer. The average peak full width at half-height was 0.45° in ω; difficulty was encountered in finding intense reflections to center for accurate lattice constant determination. Additionally, a significant (sin θ)/λ falloff in intensities was noted at 112.4 K. However, because of the chemical importance of the dimer and the lack of more suitable crystals, it was

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(1) (a) Argonne National Laboratory. (b) Brookhaven National Laboratory. (c) University of California. (d) Department of Chemistry, Haverford College, Haverford, PA.

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