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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. IV. A Neutron Diffraction Study of Dirubidium Tetracyanoplatinate(IV) Dibromide*

BY GREGORY F. NEEDHAM,† PAUL L. JOHNSON, THOMAS F. CORNISH† AND JACK M. WILLIAMS‡

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Abstract. $Rb_2[Pt(CN)_4Br_2]$, monoclinic, $P2_1/c$ (C_{2h}^5), $a = 7.281$ (3), $b = 9.271$ (4), $c = 8.960$ (3) Å, $\beta = 106.65$ (2)°, $Z = 2$, $D_m = 3.5$ (1), $D_c = 3.61$ g cm^{-3}. A room-temperature, single-crystal neutron diffraction study was performed. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R(F_o^2) = 0.038$ for 1322 observed reflections $> \sigma(F_o^2)$. The structure consists of octahedrally coordinated platinum(IV) groups interacting with the rubidium ions.

Introduction. As part of a continuing study of partially oxidized tetracyanoplatinate conducting salts, and their starting materials, we have performed a room-temperature neutron diffraction analysis of $Rb_2[Pt(CN)_4Br_2]$. Use of the analogous compound $K_2[Pt(CN)_4Br_2]$ is a standard method in preparing the well-known one-dimensional conductor $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ (Abys, Enright, Gerdes, Hall & Williams, 1976) and therefore $Rb_2[Pt(CN)_4Br_2]$ is expected to be the precursor of a corresponding partially oxidized Br-deficient compound.

The compound $Ba[Pt(CN)_4].4H_2O$ [preparation described by Koch, Abys & Williams (1976)] was used to prepare single crystals of $Rb_2[Pt(CN)_4Br_2]$ by adding Rb_2SO_4 to a solution of $Ba[Pt(CN)_4].4H_2O$ heated to 70°C. After stirring, the $BaSO_4$ was removed by filtration. Br_2 was then added and the excess was driven off. Single, transparent, orange crystals were obtained from aqueous solution by slow evaporation.

Preliminary neutron observations gave the conditions for diffraction as $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$) which fixed the space group as $P2_1/c$. The crystal selected for data collection weighed 96 mg. After being sealed in a lead-glass capillary it was mounted on the Chemistry Division four-circle neutron diffractometer at the CP-5 research reactor. [This apparatus has been described by Petersen, Dahl & Williams (1974).] The neutron wavelength of 1.142 (1) Å was obtained with a Be crystal monochromator set at $\theta_m = 30°$. The cell parameters were determined from angular measurement of 30 automatically centered reflections, chosen in the 2θ range 40–60°. The least-squares-determined lattice parameters are given in the *Abstract*. 1557 data in the hkl octant, with 1322 $> \sigma(F_o^2)$, were automatically collected by the θ–2θ scan mode with 0.1° step-scan intervals. Background intensity measurements were taken on both sides of the peak. Two reference reflections were monitored every 80 measurements to assure that the crystal was neither decomposing nor drifting. These observations deviated only 1.5% from the mean. Data collection was complete out to $2\theta = 100°$. Structure factors were derived by applying Lorentz and ab-

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Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10^4$) *parameters for* $Rb_2[Pt(CN)_4Br_2]$ *and root-mean-square thermal displacements* (*in* Å $\times 10^3$) *of atoms along their principal ellipsoidal axes*

The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figure. The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	μ_1	μ_2	μ_3
Pt(1)	0	0	0	67(1)	42(1)	47(1)	−3(1)	17(1)	−1(1)	126(1)	132(1)	137(1)
C(1)	1908(1)	445(1)	2052(1)	86(1)	58(1)	55(1)	−3(1)	10(1)	−3(1)	136(1)	158(1)	160(1)
C(2)	2018(1)	324(1)	−1090(1)	87(1)	61(1)	67(1)	−6(1)	31(1)	1(1)	135(1)	160(1)	164(1)
N(1)	3063(1)	702(1)	3203(1)	127(1)	85(1)	70(1)	0(1)	−7(1)	−12(1)	140(1)	190(1)	212(1)
N(2)	3221(1)	516(1)	−1667(1)	135(1)	99(1)	111(1)	−8(1)	75(1)	7(1)	138(1)	209(1)	218(1)
Br(1)	903(1)	−2590(1)	327(1)	143(1)	49(1)	106(1)	8(1)	39(1)	6(1)	146(1)	186(1)	200(1)
Rb(1)	4952(1)	2771(1)	1199(1)	141(1)	65(1)	68(1)	−13(1)	29(1)	−4(1)	156(1)	164(1)	192(1)

sorption corrections ($\mu = 0.41$ cm^{-1}) and the magnitudes of the transmission factors ranged from 0.87 to 0.92. Standard errors were assigned to the data by means of the standard counting-statistics formula with $(0.05I)^2$ added to allow for systematic error.

The structure was solved with the program *MULTAN* (Germain, Main & Woolfson, 1971). Refinement was carried out by full-matrix least-squares techniques using first isotropic and then anisotropic thermal parameters, as well as a type 1 anisotropic extinction correction. The final $R(F^2) = \Sigma|F_o^2 - F_c^2|/ \Sigma F_o^2$ for the 1322 data $> \sigma(F_o^2)$ was 0.038; $R(F_o^2)$ for all the data was 0.038.* The largest peak in the difference Fourier map had a height of 0.6% of a Pt peak. We attributed this to background noise. The neutron scattering amplitudes used were as follows: $b_{Pt} = -0.950$, $b_C = 0.663$, $b_N = 0.940$, $b_{Rb} = 0.700$ and $b_{Br} = 0.680$, all in units of 10^{-12} cm. The refined positional and thermal parameters are given in Table 1 and important

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32305 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *for* $Rb_2[Pt(CN)_4Br_2]$

(*a*) Distances around Pt atom (Å)

Pt—C(1)	2.005 (1)
Pt—C(2)	2.006 (1)
Pt—Br	2.485 (1)

(*b*) C—N distances in cyanide groups (Å)

C(1)—N(1)	1.153 (1)
C(2)—N(2)	1.151 (1)

(*c*) Rb ion interactions (Å)

Rb—N(2^{iii})	3.025 (1)	Rb—N(2^i)	3.271 (1)
Rb—N(1^{iv})	3.052 (1)	Rb—N(1^i)	3.195 (1)
Rb—N(1^v)	2.998 (1)	Rb—Br^{iv}	3.678 (2)
Rb—N(2^{ii})	3.303 (2)	Rb—Br^{ii}	3.657 (2)

Symmetry positions

(i)	x, y, z	(iv)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(ii)	$1 - x, -y, -z$	(v)	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
(iii)	$x, \frac{1}{2} - y, \frac{1}{2} + z$		

(*d*) Angles within the coordination sphere of Pt (°)

Br—Pt—C(1)	90.02 (3)	Pt—C(1)—N(1)	177.25 (6)
C(1)—Pt—C(2)	89.78 (4)	Pt—C(2)—N(2)	177.70 (6)
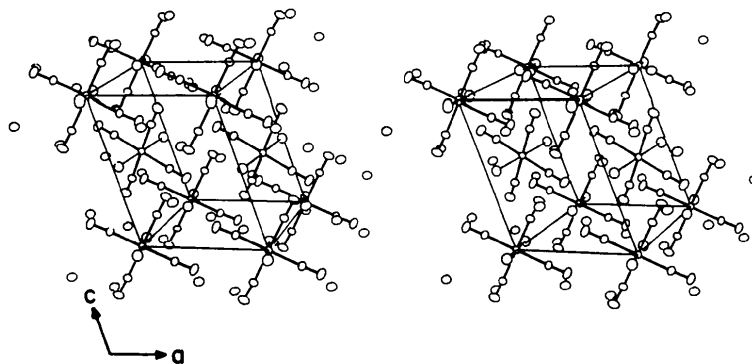
Fig. 1. Stereoscopic drawing of the unit-cell contents of $Rb_2[Pt(CN)_4Br_2]$.

bond lengths and angles in Table 2. A stereo drawing of the unit cell is shown in Fig. 1.

Discussion. As expected, the crystallographically non-equivalent Pt(1)–C(1), Pt(1)–C(2), and C(1)–N(1), C(2)–N(2) bond lengths are equal to within one e.s.d., as shown in Table 2.

The Pt atom is octahedrally coordinated, with the cyanides forming a square-planar arrangement around it. The Br atoms occupy axial positions around the Pt atom. The tetracyanoplatinate interatomic distances are in close agreement with those previously reported (Washecheck, Peterson, Reis & Williams, 1976; Williams, Keefer, Washecheck & Enright, 1976; Maffly, Johnson, Koch & Williams, 1977).

The Rb interacts with only two species, the cyanide N atoms and the Br atoms. It is at the center of a somewhat distorted bi-capped trigonal prism, with N atoms at the corners of the prism and Br atoms capping two of the side faces.

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4-Carboxy-1,2,4,8-tetramethyl-3,9-dioxatricyclo[5.2.1.0²,⁶]decane-8-carboxamide

BY A. W. HANSON

Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K 1A 0R6

Abstract. $C_{14}H_{21}NO_5$, F.W. 283·3; monoclinic, $P2_1/c$, $a = 11·770 (5)$, $b = 10·811 (5)$, $c = 11·346 (5)$ Å, $\beta = 91·79 (5)°$ (20°C); $D_m = 1·302$, $Z = 4$, $D_x = 1·304$ g cm^{-3}. The molecular configuration is found to be *rel*-(1R,2R,4R,6R,7S,8R).

Introduction. The title compound (I) was obtained by hydrolysis of a product of the AlCl₃-catalysed reaction of 2,5-dimethylfuran with ethyl cyanoformate (McCulloch & McInnes, 1976). The crystal-structure analysis was undertaken in order to establish the hitherto unknown molecular structure.

(I)
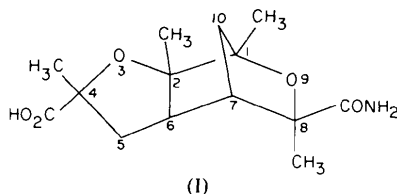
The crystals supplied were colourless, transparent, triangular plates ⟨100⟩. One of these was cut to yield a specimen of dimensions 0·13 × 0·20 ×0·35 mm. This was mounted on a four-circle diffractometer with the longest direction (corresponding to **b**) parallel to the φ

axis. The intensities of the 2457 independent reflexions within the limiting sphere $2\theta = 130°$ were measured with Cu $K\alpha$ radiation and a scintillation counter. The $\theta–2\theta$ scan mode was used, with scans of 2° for $2\theta < 100°$, and 3° otherwise. Background intensities were estimated from an experimentally derived function of θ. 236 reflexions were considered to be unobserved, as their net intensities were less than either 30 counts or 10% of the corresponding background intensity. No correction was made for absorption ($\mu = 8·3$ cm^{-1}).

The structure was readily determined by symbolic addition procedures, with all non-hydrogen atoms appearing in the first E map. Refinement was by block-diagonal least squares, minimizing $\Sigma\,w\Delta F^2$. The identification of atoms, initially based on chemical plausibility, was subsequently verified by a study of ΔF syntheses. (At a later stage in refinement, a persistent peak and trough in the ΔF synthesis gave warning that a presumed OH group was in fact NH₂; the substitution caused the R index to drop from 0·047 to 0·039.) The seven most intense reflexions were corrected for extinction, the largest correction being 14% of F_o. The weighting scheme used in the final stages was $w = w_1\,w_2$, where $w_1 = 5/F_o$ for $F_o > 5$, $w_1 = 1$ otherwise,