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Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 18. Synthesis, Crystal Structure, and X-ray Diffuse Scattering Studies of the New Partially Oxidized Tetracyanoplatinate Complex $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$[1]

RICHARD K. BROWN, DAVID A. VIDUSEK, and JACK M. WILLIAMS*

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We report the first synthesis and X-ray structure study of a partially oxidized tetracyanoplatinate complex containing azide ion, $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$. This one-dimensional conducting salt crystallizes in the tetragonal space group $P\bar{4}b2$ [D_{2d}^7, No. 117] with cell dimensions $a = 13.089$ (2) Å, $c = 5.754$ (1) Å, and $V = 985.8$ Å^3 and with a calculated density of 3.94 g/cm^3 for four formula units per cell. A total of 4358 observed data were averaged to yield 1584 independent reflections of which 1362 had $F_o^2 > \sigma(F_o^2)$. The structure was solved by standard heavy-atom methods and was refined by full-matrix least-squares to a final $R(F_o^2) = 0.068$ and $R_w(F_o^2) = 0.088$. The crystal structure consists of perfectly linear chains of Pt atoms with Pt–Pt separations crystallographically constrained to a value of $c/2 = 2.877$ (1) Å and interchain Pt–Pt distances of 9.255 (2) Å. Using X-ray diffuse scattering techniques we have established the Pt oxidation state as 2.25 (2). The crystal structure is pseudo body centered and nearly isomorphous with the tetracyanoplatinate complexes $M_2[Pt(CN)_4](FHF)_x$ [M = Cs ($x = 0.39$, 0.23) and M = Rb ($x = 0.40$)].

Introduction

The one-dimensional (1-D) properties of both cation- and anion-deficient, partially oxidized tetracyanoplatinate (POTCP) salts are of considerable intrinsic and practical interest to chemists and physicists. The practical interests were spawned in large part by Little's proposal in 1964 that these systems could model 1-D high-temperature excitonic superconductors.[2] One of the major continuing difficulties regarding study of these systems has been the paucity of materials available. Within the past few years this handicap has been greatly relieved by work in this[3] and other laboratories.[11] Since a detailed knowledge of the crystal structure is a necessary prerequisite to the understanding of the highly anisotropic properties of these systems, we have undertaken the crystal and molecular structure determinations of a number of these complexes.[4-10] In separate studies the electrical conduction properties of several of these materials have been determined over a range of temperatures.[11] The combined results of these studies have given rise to new speculation regarding the important structural factors which affect the anisotropic properties of these complexes. In a continuing effort to synthesize previously unknown POTCP conductors, and to confirm and clarify many of our recent observations, we have prepared and structurally and chemically characterized the one-dimensional POTCP azide complex $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$. In many respects the structure of this salt is closely related to several previously characterized POTCP complexes, especially $M_2[Pt(CN)_4](FHF)_x$ [M = Cs ($x = 0.39$, 0.23) and M = Rb ($x = 0.40$)][6,7] and to $Cs_2[Pt(CN)_4]Cl_{0.30}$.[10]

Experimental Section

Crystal Preparation. The preparation of $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$, CsCP($N_3$) hereafter, was carried out by electrolyzing an aqueous solution containing a 1:4 molar ratio of $Cs_2[Pt(CN)_4]\cdot H_2O$ and CsN_3,[23] respectively. A 9 mL aqueous solution containing 1.26 g (2.16 mmol) of $Cs_2[Pt(CN)_4]\cdot H_2O$ was acidified to a pH of ~5.5 with 0.2 mL of 9 M sulfuric acid. To the resultant white suspension was added 1.5 g (8.57 mmol) of CsN_3. After complete dissolution of the CsN_3, the solution was filtered and the filtrate transferred to an electrolytic cell consisting of two opposing 25-mm platinum electrodes which were separated by 6 mm. After 72 h of electrolysis at 1.00 V dc, the reddish bronze colored crystals were isolated by filtration. The crystals were washed with two 3-mL portions of cold water and allowed to air-dry. The yield of 1.15 g (1.96 mmol) represents a 91% yield based on $Cs_2[Pt(CN)_4]\cdot H_2O$. Anal. Calcd for $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$: Pt, 33.38; Cs, 45.48; C, 8.22; N, 11.39; O, 1.37; H, 0.17. Found[24] (Midwest Microlab Inc., Indianapolis, Ind.): Pt, 32.56; Cs, 44.54; C (12 determinations), 8.28 (1); N (18 determinations), 11.47 (2); O (4 determinations), 1.53 (1); H (10 determinations), 0.25 (41). The presence of Cs and Pt was also confirmed by emission spectrographic analyses at Argonne.[19]

Space Group Determination. A single crystal of CsCP(N_3) was sealed in a glass capillary to prevent dehydration and was aligned, using oscillation photographs, along the crystallographic *c* axis. Weissenberg photographs of the levels with $l = 0 \rightarrow 4$ and precession photographs of the levels with $h = 0 \rightarrow 3$ were obtained using Ni-filtered Cu Kα radiation. The crystal class is tetragonal and the unit cell constants and intensity distribution appear to be nearly identical with those for $Cs_2[Pt(CN)_4]Cl_{0.30}$[10] which belongs to the tetragonal space group $I4/mcm$ [D_{4h}^{18}, No. 140]. However, on long-exposure photographs of each level we observed a few (5–10) weak reflections which would be systematically absent in space group $I4/mcm$. The only systematic absence which could be positively identified was $0kl$

Table I. Positional and Thermal Parameters for $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$[a]

Positional Parameters

atom	x	y	z	atom	x	y	z
Pt(1)	0.0000	0.0000	0.0000	C(2)	0.4423 (5)	0.3588 (5)	0.515 (4)
Pt(2)	0.0000	0.0000	0.5000	N(1)	0.0800 (5)	0.2276 (5)	−0.004 (3)
Cs(1)	0.8307 (1)	0.3307	0.0000	N(2)	0.4092 (5)	0.2773 (5)	0.506 (3)
Cs(2)	0.6551 (1)	0.1551	0.5000	N(3)	0.0000	0.5000	0.0000
C(1)	0.0516 (5)	0.1447 (5)	−0.014 (4)	N(4)	0.0000	0.5000	0.214 (5)

Anisotropic Thermal Parameters[b]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0.0152 (3)	0.0152	0.0113 (3)	0.0	0.0	0.0
Pt(2)	0.0147 (3)	0.0147	0.0114 (3)	0.0	0.0	0.0
Cs(1)	0.0330 (4)	0.0330	0.0456 (5)	0.0037 (3)	0.004 (2)	−0.004
Cs(2)	0.0466 (5)	0.0466	0.0470 (6)	0.0099 (3)	−0.009 (2)	0.009
C(1)	0.022 (3)	0.018 (2)	0.012 (5)	−0.002 (2)	−0.002 (6)	0.007 (6)
C(2)	0.025 (3)	0.016 (2)	0.013 (5)	0.002 (2)	0.001 (6)	−0.004 (6)
N(1)	0.046 (4)	0.031 (3)	0.025 (4)	−0.008 (3)	0.015 (9)	−0.008 (9)
N(2)	0.053 (4)	0.030 (3)	0.044 (5)	−0.011 (3)	0.038 (8)	−0.007 (8)
N(3)[c]	0.07 (1)					
N(4)[c]	0.05 (1)					

[a] Standard deviation of least significant digit is given in parentheses. Occupancy of the N_3^- site was refined by least squares to an unreasonable value of 0.37 (4)[25] (see text for discussion of azide content). [b] The form of the anisotropic thermal ellipsoid is given by $\exp[(-\Sigma_i\Sigma_j h_i h_j r_i^* r_j^* U_{ij})/4]$ with $i,j = 1, 2, 3$, where r_i^* is the ith reciprocal axis. [c] For the azide ion the temperature factors are isotropic U's.

when $k = 2n + 1$ which indicated one of three possible space groups ($P4/mbm$, $P\bar{4}b2$, or $P4bm$). The structure could be successfully refined only in $P\bar{4}b2$ [D_{2d}^7, No. 117].

Collection of X-ray Diffraction Data. A well-formed crystal of approximate dimensions 0.15 × 0.15 × 0.22 mm was sealed in a glass capillary and mounted on a Syntex $P2_1$ diffractometer equipped with a molybdenum X-ray tube (λ 0.710 69 Å) and a graphite monochromator. The refined cell parameters, determined from 25 diffractometer centered reflections with $2\theta \geq 22.5°$, are $a = 13.089$ (2) Å, $c = 5.754$ (1) Å, and $V = 985.8$ Å^3 with $Z = 4$ and a calculated density of 3.94 g/cm^3. Intensity data were collected using a coupled ω–2θ scan for reflections in the region $\pm h$, $\pm k$, $+l$ with $5° \leq 2\theta \leq 60°$. The reflection scan ranges were from $[2\theta(K\alpha_1) - 1.3]°$ to $[2\theta(K\alpha_2) + 1.3]°$ with scan rates from $2.0°(2\theta)$/min to $10.0°(2\theta)$/min. The actual scan rate was determined from a preliminary peak intensity measurement for each reflection. Stationary background counts were taken at each extremity of the scan such that the total background counting time was equal to half of the total scan time. Three standard reference reflections ($13\bar{2}$, $31\bar{2}$, $\bar{1}32$) were measured after every 50 reflections and showed a maximum fluctuation of 4% during the course of data collection. Net intensities (I) were calculated using

$$I = \left(P - \frac{t_P}{t_B}(B_1 + B_2)\right)\mathrm{SR}$$

where P is the total scan count, B_1 and B_2 are the background counts, SR is the scan rate, and t_P and t_B are the counting times for the peak and background, respectively. The value of $\sigma(I)$ was evaluated as

$$\sigma(I) = \left[P + \left(\frac{t_P}{t_B}\right)^2 (B_1 + B_2) + (cI)^2\right]^{1/2} \mathrm{SR}$$

where c, a factor to account for errors other than those arising from counting statistics, was assigned a value of 0.05.

The 4358 reflections were averaged to yield 1584 symmetry-independent data. The "agreement index"

$$R(F_o^2) = \sum(F_{av}^2 - F_o^2)/\sum F_o^2$$

between averaged reflections was 0.043. The data were corrected for absorption ($\mu_c = 223.2$ cm^{-1}) and Lorentz–polarization effects.

Structure Solution and Refinement. Coordinates for the Pt and Cs atoms were obtained from a Patterson map. A difference Fourier map using the heavy-atom coordinates was sufficient to allow location of the two independent CN^- groups. After several cycles of isotropic full-matrix least-squares refinement, using all 1584 independent data, a difference Fourier map was calculated and revealed the position of the two independent nitrogen atoms [N(3) and N(4)] of the triatomic azide anion. Three additional cycles of full-matrix refinement, treating Cs, Pt, C, N(1), and N(2) anisotropically and N(3) and N(4) isotropically, led to $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum|F_o^2| = 0.068$ and $R_w(F_o^2) = [\sum w|F_o^2 - F_c^2|^2/\sum wF_o^4]^{1/2} = 0.088$. The quantity minimized was $\sum_i w_i|F_o^2 - S^2F_c^2|$, where S is the scale factor and the weight w for each reflection was calculated according to the expression

$$w_i = \sigma^{-2}(F_o^2)$$

Atomic scattering factors were obtained from ref 12, including corrections for anomalous scattering for the Pt and Cs atoms. Final positional and thermal parameters are presented in Table I. In the last cycle of least-squares refinement the largest shift-to-error ratio was 0.01. A final difference electron density map was nearly featureless, showing only small ripples of density with peak heights about one-sixth that found for the carbon atoms, in the near vicinity of the Pt and Cs atoms. We were unable to determine the absolute configuration by examination of the weighted R factors. This is not surprising in light of the fact that the position of the principal anomalous scatterer, Pt, remains unchanged upon coordinate transformation from one enantiomer (xyz) to the other (yxz).

X-ray Diffuse Scattering. The X-ray diffuse scattering photograph of a $CsCP(N_3)$ crystal was obtained, in a manner previously described,[13] on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. In order to reduce Bragg scattering, the c axis of the crystal was offset 10° from being exactly perpendicular to the incident beam. The stationary crystal–stationary film photograph was obtained with Mo $K\alpha$ X-radiation (λ 0.710 69 Å) after an exposure of 60 h with the X-ray tube at 1000 W.

The photograph was similar in appearance to those obtained with other POTCP materials, with diffuse lines observable about each row of Bragg reflections. The lines exhibited increasing scattering intensity at higher diffraction angles indicative of sinusoidal displacements of the platinum atoms along each chain, with phases not correlated with those in neighboring chains. The superlattice calculated from the diffuse lines is $7.9(3)c'$, where c' is the average Pt–Pt separation. This corresponds to a wave vector $k = 2\pi(1 - 1/7.9)c' = 1.75\pi/c'$, which is equal to twice the Fermi wave vector $2k_F$ for a Peierls-type distortion. Therefore, on the basis of the diffuse scattering, the Pt oxidation state is +2.25 (2), which yields a chemical stoichiometry of $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$.

Discussion

Pertinent bond distances and angles for $CsCP(N_3)$ are given in Table II. The crystal structure, comprising linear chains of square-planar $Pt(CN)_4^{1.75-}$ groups stacked parallel to c, is presented in Figure 1. Both Pt atoms have $\bar{4}$ site symmetry and both Cs^+ ions lie on a twofold axis. The central nitrogen atom, N(3), of the azide ion resides at a special position with 222 symmetry, and the terminal nitrogen atoms [N(4) and N(4)′] are on a twofold axis. Only the CN^- ligands occupy

Table II. Selected Bond Distances (Å) and Angles (deg) for $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$[a]

	Distances		
Pt–Pt (intrachain)	2.877 (1)	Pt–Pt (interchain)	9.255 (2)
Pt(1)–C(1)	2.013 (6)	Pt(2)–C(2)	1.998 (7)
C(1)–N(1)	1.15 (1)	C(2)–N(2)	1.15 (1)
	N(3)–N(4) 1.23 (3)		
	Angles		
C(1)–Pt(1)–$C(1)_{cis}$	90.09 (5)	C(2)–Pt(2)–$C(2)_{cis}$	90.11 (5)
C(1)–Pt(1)–$C(1)_{trans}$	175 (1)	C(2)–Pt(2)–$C(2)_{trans}$	175 (1)
Pt(1)–C(1)–N(1)	173 (2)	Pt(2)–C(2)–N(2)	175 (2)
	N(4)–N(3)–N(4) 180		

[a] Standard deviation of least significant digit is given in parentheses.

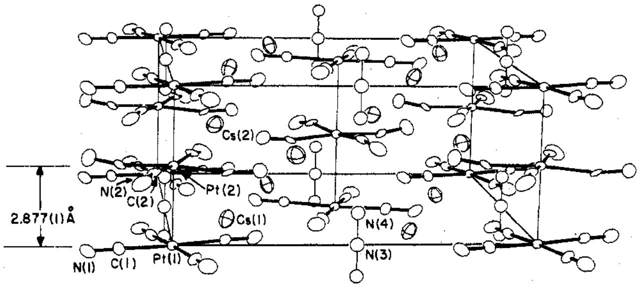

Figure 1. Perspective view of the unit cell of $Cs_2[Pt(CN)_4](N_3)_{0.25}\cdot 0.5H_2O$. Thermal ellipsoids are shown at the 50% probability level.

general positions in the space group. The Pt–Pt separation is crystallographically constrained to a distance of $(c/2)$ = 2.877 (1) Å and therefore the Pt–Pt separations are exactly equivalent. This salt is nearly isostructural with the POTCP salts $Cs[Pt(CN)_4](FHF)_{0.39}$,[7] $Rb[Pt(CN)_4](FHF)_{0.40}$,[6] and $Cs[Pt(CN)_4](Cl)_{0.30}$,[10] which possess intrachain Pt–Pt separations of 2.833 (1), 2.798 (1), and 2.859 (1) Å, respectively. The interchain Pt–Pt separations for these three salts are 9.233, 8.972, and 9.317 Å, respectively, whereas this distance for $CsCP(N_3)$ is 9.255 (2) Å. There is a linear correlation between inter- and intrachain Pt–Pt separations for the above-mentioned three complexes except $CsCP(N_3)$. This observation could be due to structural differences arising from the difference in space groups $I4/mcm$ vs. $P\bar{4}b2$ or more likely the difference in degree of partial oxidation (DPO) of the Pt atoms. Of the four POTCP salts discussed above, $CsCP(N_3)$ has both the lowest DPO and the highest intrachain Pt–Pt separation. Furthermore, there is a direct relationship between Pt–Pt separation and DPO for all four salts as we have discussed previously.[17]

The occupancy factor of the azide ion was refined to a value of 0.37 (4)[25] in the least-squares refinement of the structure. However, a value of 0.25 (2) for the DPO of the Pt atom was determined from the X-ray diffuse scattering experiments,[25] which in the past have been found to be considerably more reliable than least-squares-determined atomic occupancies, especially in cases such as this in which some azide sites may also be partially filled by water molecules (vide infra).[13] This is also partly due to severe correlation between atom multipliers and thermal parameters; this is especially true for a weakly scattering atom such as nitrogen in the presence of such powerful scatterers as platinum and cesium. However, and more to the point, chemical analysis of the title compound indicates the presence of water. Although the final difference Fourier map was exceedingly "clean", showing no possible sites for water molecules in the crystal lattice, it is our belief that the water molecules reside in some vacant azide anion sites. This is an obvious explanation for the larger value of the azide multiplicity factor as determined from the least-squares refinement. In the molecular formula for $CsCP(N_3)$ we have indicated $^1/_2$ H_2O molecule/Pt atom. This is a crudely estimated value determined from the oxygen chemical analysis which is very insensitive. Values as low as $^1/_4$ H_2O molecule/Pt atom or as high as 1 H_2O molecule/Pt atom cannot be ruled out. No thermogravimetric analysis has been carried out due to the explosive potential of the azide complex.

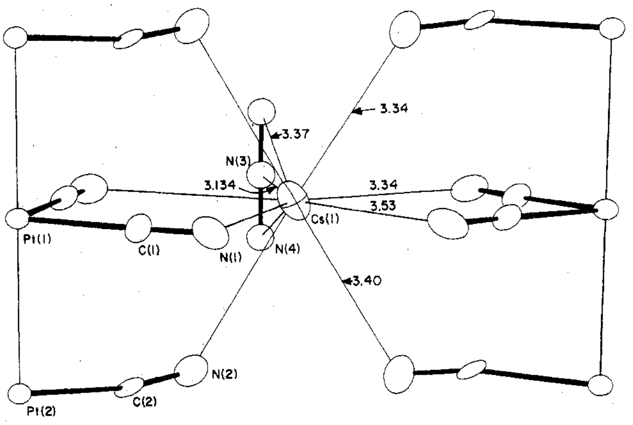

Figure 2. Perspective view showing the Cs(1) cation coordination sphere. Distances are in angstroms.

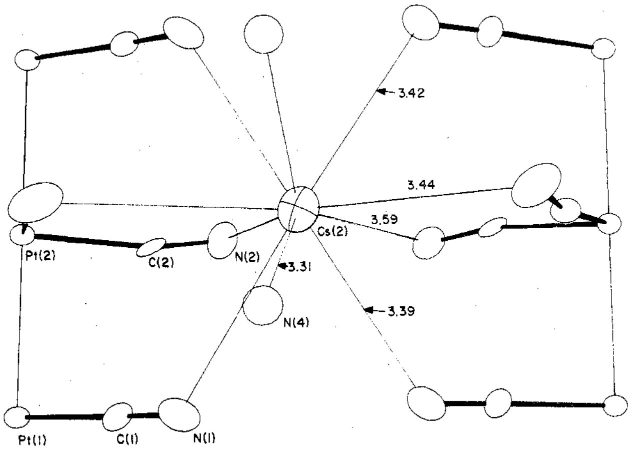

Figure 3. Perspective view showing the Cs(2) cation coordination sphere. Distances are in angstroms.

The coordination spheres of the two independent cesium ions are shown in Figures 2 and 3. For Cs(1) the shortest Cs–N contact [3.134 (1) Å] is that to N(3), the central nitrogen atom of the azide anion. This value may be compared with the $Cs\cdots O(H_2O)$ distances in $Cs_2[Pt(CN)_4]\cdot H_2O$[14] of 3.155 (8) and 3.125 (9) Å. The $Cs\cdots N$ distances in the parent $Cs_2[Pt(CN)_4]\cdot H_2O$[14] range from 3.236 (5) to 3.508 (6) Å. The azide ion terminal nitrogen atom to Cs(1) distances are equal at 3.37 (1) Å. There are four Cs(1)–N(1) contacts, two of 3.34 (2) Å and two of 3.532 (6) Å, and four Cs(1)–N(2) contacts, two at 3.34 (2) Å and two at 3.40 (2) Å, yielding a total of 11 Cs(1)–N contacts. For Cs(2) there are a total of 10 Cs–N contacts with the same range of Cs–N distances. There are two contacts between terminal azide nitrogen atoms and Cs(2) at 3.31 (1) Å. There are four Cs(2)–N(1) contacts, two at 3.39 (2) Å and two at 3.42 (2) Å, and four Cs(2)–N(2) contacts, two at 3.442 (7) Å and two at 3.59 (7) Å. These Cs–N distances are all comparable to those for $Cs_2[Pt(CN)_4]\cdot H_2O$[14] and $Cs_2[Pt(CN)_4]Cl_{0.30}$[10] for which the range is 3.236 (5)–3.508 (6) Å and 3.379 (4)–3.617 (9) Å, respectively.

The Pt–C bond distances [2.013 (6) and 1.998 (7) Å] and the C–N bond distances [both at 1.15 (1) Å] are in the normal range found for POTCP salts.

With regard to the azide ion we point out that the nitrogen atom positions of these partially occupied sites were clearly evident from a difference Fourier map phased using all but these atoms. The central nitrogen atom lies at $^1/_2$, 0, 0, and the terminal nitrogen atoms lie at $^1/_2$, 0, z and $^1/_2$, 0, $\bar{z}$ requiring the N_3^- group to be perfectly linear. The difference Fourier positions indicated an N–N separation of 1.16 Å, while the least-squares value converged to 1.23 (3) Å. The expected N–N separation in N_3^- is 1.16 Å[15] which is in essential agreement with our least-squares-determined value. Attempts to verify the presence of N_3^- ion using IR spectroscopy were unsuccessful, probably due to the very low concentration of azide ion in the crystal lattice.[20] We are continuing our studies of $CsCP(N_3)$ in an effort to determine if the anion content can be varied as is the case for the homologous series of MCP(FHF) complexes.[21]

Conclusions

One of the main structural findings reported here is the increased Pt–Pt separation and decreased DPO of $CsCP(N_3)$ relative to CsCP(FHF), RbCP(FHF), and CsCP(Cl). This observation is consistent with past observations[16] for these systems and with Pauling's resonating valence bond theory of metals.[17,18] A second interesting observation is that all POTCP salts that have been studied to date, which do not contain independent H_2O sites or are anhydrous, crystallize in the space group $I4/mcm$ or the nearly identical $P\bar{4}b2$. Those POTCP complexes which do contain independent H_2O sites seem most often to belong to space group $P4mm$. Another interesting point is that only POTCP complexes with "symmetrical" anions (e.g., F^-, Cl^-, Br^-, $(FHF)^-$, $(O_3SO{-}H{-}OSO_3)^{3-}$, and N_3^-)[4,6-10,22] have been prepared. As yet we have been unable to prepare salts with CN^-, OCN^-, SCN^-, or NCN^- anions. We are continuing our efforts to prepare and structurally characterize these unusual complexes and to obtain accurate temperature-dependent electrical conductivities for those salts which have already been structurally characterized.

Registry No. $Cs_2[Pt(CN)_4]\cdot H_2O$, 20449-75-6; CsN_3, 22750-57-8.

Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(25) Note that the chemical analyses, in addition to the XDS measurements, indicate the azide content to be $(N_3^-)_{0.25}$.

Contribution from the Departments of Chemistry, University of Illinois at Chicago Circle,
Chicago, Illinois 60680, and University of Virginia, Charlottesville, Virginia 22901

Structural and Magnetic Properties of Dimeric $[Ni_2(en)_4Cl_2]Cl_2$

K. O. JOUNG,[1a] C. J. O'CONNOR,[1b] E. SINN,*[1b] and R. L. CARLIN*[1a]

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The crystal structure of dimeric $[Ni_2(en)_4Cl_2]Cl_2$ has been determined at ambient temperatures. Crystal data: space group $P2_1/c$, $Z = 2$, $a = 6.327$ (3) Å, $b = 11.311$ (2) Å, $c = 15.811$ (4) Å, $\beta = 117.81°$, $R = 2.8\%$ for 1530 reflections. The complex consists of chlorine-bridged dimers with unsymmetrical Ni–Cl bridging. The Ni–Cl distances are 2.47 and 2.56 Å, the Ni–Cl–Ni angle is 96.55°, and the coordination octahedron is distorted. The single-crystal magnetic susceptibilities have been determined between 1.5 and 25 K and confirm the earlier report of ferromagnetic intradimer exchange interaction. The parameters resulting are: $\langle g \rangle = 2.25$, $D/k = 14 \pm 1$ K, $J/k = 5.0 \pm 0.5$ K, and $zJ'/k = -0.3 \pm 0.1$ K.

The compound di-μ-chloro-tetrakis(ethylenediamine)dinickel(II) chloride, $[Ni_2(en)_4Cl_2]Cl_2$, has been of importance in the development of our ideas about exchange interaction in dimers.[2] Specifically, measurements of the susceptibility over a wide temperature interval provided results which were interpreted in terms of a ferromagnetic intradimer exchange interaction.[3] The superexchange mechanism was also discussed in terms of Anderson's expanded orbital theory.[3,4] Zero-field-splitting effects, which are of dominant importance in nickel(II) chemistry and physics,[5] were explored, but it was not possible to determine the sign of the zero-field-splitting parameter, D, unambiguously. Partly, this was due to the fact that the effect of D on the dimer susceptibility is qualitatively similar to that of an antiferromagnetic interdimer interaction; the earlier measurements were also made only on powdered material. We thought it would be useful to determine the single-crystal susceptibilities of $[Ni_2(en)_4Cl_2]Cl_2$ at low temperatures, in the hope this might resolve some of the remaining ambiguities. Thus, we report here our measurements between 1.5 and 25 K on oriented single crystals. In order to interpret the magnetic studies, it was also necessary first to determine accurately the crystal structure at ambient

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