properties of these complexes. This research was supported by the National Science Foundation through Grant No. GP-38491X.

Registry No. Chloro(2-diethylaminoethanolato)copper(II), 51717-03-4; bromo(2-dibutylaminoethanolato)copper(II), 21331-08-8.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40473T.

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Crystal and Molecular Structure of Hexakis(pyridine *N*-oxide)cobalt(II) Perchlorate

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The crystal structure of hexakis(pyridine *N*-oxide)cobalt(II) perchlorate, $Co(C_5H_5NO)_6(ClO_4)_2$ has been determined from three-dimensional X-ray data collected on a three-circle automatic diffractometer using Mo Kα radiation. The complex crystallizes in the trigonal space group $R\bar{3}$ with cell constants $a = 12.512$ (3) and $c = 19.044$ (3) Å. The observed and calculated densities for three molecules per unit cell are 1.59 (2) and 1.601 g cm^{-3}, respectively. The structure was refined by full-matrix least squares to a final R value of 0.037 and a weighted R value of 0.052, for 590 independent reflections whose intensities were greater than twice their estimated standard deviations. The complex cation has S_6 ($\bar{3}$) symmetry and the coordination geometry about the cobalt atom is perfectly octahedral to within the estimated standard deviations, the Co–O distance being 2.088 (2) Å and the O–Co–O angles 89.97 (4) and 90.03 (4)°. The perchlorate ions have C_3 point symmetry and occupy the trigonal holes between the cations within each layer of the structure.

Introduction

Complexes of the transition metals with pyridine *N*-oxide and its substituted derivatives have been known for a decade or more and they have formed the subject of several recent reviews.[1] For the first-row metals several stoichiometries are known, but the series of hexakis complexes formed by these ligands are of considerable interest, in that they exhibit spectroscopic and magnetic properties indicative of large deviations from effective octahedral symmetry in their electronic structure.[2] For example, Lever and coworkers found appreciable splitting of the lower excited states in the spectra of the chromium(III) and nickel(II) complexes of the parent ligand, while the results of epr measurements on a variety of hexakis(pyridine oxide)manganese(II) complexes recently[3] are also consistent with a marked deviation from O_h symmetry as judged by the magnitude of the zero-field splitting.

In addition to the possibility of a large distortion from O_h (or near-octahedral) symmetry for the MO_6 moiety, a plausible explanation that has been advanced to account for these deviations is that they arise from the interactions of the metal d orbitals with the orbitals involving the ligand N–O bonds *via* the nonlinear M–O–N systems,[2] so that in crystal field terminology, the effective perturbing charges affecting the d orbitals are not centered at the coordinated oxygen atoms. As a large number of hexakis complexes, usually loosely described as octahedral, contain such nonlinear M–O–X groupings (X = C, S, P, N), it appeared appropriate to examine the molecular stereochemistry and electronic properties (in single-crystal form) of certain members of these series in some detail, to assess and develop various theoretical models useful in interpreting these properties. To date, few structural results on such species have been reported.

We have earlier investigated the stereochemistry and magnetic properties of the hexaurea complex of titanium, $Ti(OC(NH)_2)_6{}^{3+}$, which contains a nonlinear Ti–O–C system and a coordination polyhedron having D_3 symmetry.[4-6] In this instance, the deviation of the TiO_6 group from an octahedron is toward a trigonal prism, there being negligible distortion (*i.e.*, compression or extension) along the threefold axis. While the average magnetic properties were initially interpreted using a crystal field model based on the observed geometry,[6] sub-

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sequent measurement and analysis of the magnetic anisotropy by Figgis and coworkers[7] and by ourselves[8] have shown this model to be inadequate. Arguing within a crystal field framework, the former were led to the conclusion that a crystallographically undetected distortion of the octahedron along the threefold axis must be present in order to explain the magnitude and sign of the splitting of the $^2T_{2g}$ term deduced from the magnetic measurements.[9] Although there is evidence for magnetic interaction between neighboring units along the axial direction (threefold axis) in the isostructural $Cr(urea)_6{}^{3+}$ complex,[10] an angular overlap approach utilizing the highest filled molecular orbitals of the urea ligands accounts for the magnetism of the titanium complex equally as satisfactorily as the point charge model[8] and, being based on the structure of the complex, in this example is probably physically more reasonable.

The pyridine oxide complexes then offer a suitable series on which to test further details and the applicability of this simplified mo scheme in an extensive manner, and such investigations are currently under way in our laboratory. As a prerequisite for interpreting the single-crystal properties and for developing the interpretive model, the detailed stereochemistry of the cobalt complex $Co(pyO)_6(ClO_4)_2$ has been determined and this paper reports the results of the analysis. Shortly after this study was started, the structure of the mercuric complex $Hg(pyO)_6(ClO_4)_2$ was reported[11] and this proves to be isomorphous and isostructural with the first-row transition metal analogs. In addition, we learned that X-ray analyses of the iron, cobalt, and copper complexes were also being undertaken by Dr. D. Taylor at Australian National University.[12] Our X-ray work was therefore confined to the analysis of the cobalt complex.

Experimental Procedures

Data Collection. Crystalline samples of the hexakis(pyridine oxide) salts of the first-row metal perchlorates were prepared as described by Lever, *et al.*[2] Crystals of the cobalt complex suitable for a detailed structure analysis were obtained by recrystallization from an ethanol–methanol mixture. *Anal.* Calcd for $CoC_{30}H_{30}N_6Cl_2O_4$: C, 43.49; H, 3.66; N, 10.15. Found: C, 43.49; H, 3.72; N, 10.01.

Preliminary precession photographs recorded using Mo Kα radiation indicated that all the complexes $M(pyO)_6(ClO_4)_2$ (M = Fe–Zn) crystallize in the trigonal system (Laue symmetry $\bar{3}$), the systematic absences $-h + k + l \neq 3n$ being consistent with rhombohedral space groups $R3$ and $R\bar{3}$. In the absence of disorder, the cations are required to have point symmetry $\bar{3}$ (S_6) in space group $R\bar{3}$ and 3 (C_3) symmetry in $R3$, while the perchlorate ions will have threefold symmetry in both space groups. Preliminary cell constants established the isomorphism with the corresponding mercury complex[11] and so suggested $R\bar{3}$ as being correct.

A well-formed rhombohedral-shaped crystal of the cobalt complex, having dimensions 0.33 × 0.33 × 0.29 mm was chosen for data collection. Referred to hexagonal axes (obverse setting) the six crystal boundary faces all belong to the general form {101}, the crystal edges being parallel to the axes of the rhombohedral cell. The crystal was mounted on an Enraf–Nonius CAD3 diffractometer with its hexagonal c axis roughly parallel with the ϕ axis of the instrument. The source to crystal and crystal to detector aperture distances are 23.5 and 9.8 cm, respectively. Zirconium-filtered Mo radiation at an instrument takeoff angle of 4.5° was used for all measurements, the incident-beam collimator being 0.9 mm in diameter. Unit cell dimensions, obtained by least-squares refinement of the accurate setting angles of 36 reflections (12 independent) centered using the program SETANG,[13] are a = 12.512 (3) and c = 19.044 (3) Å. The corresponding rhombohedral cell dimensions are a = 9.617 Å and α = 81.16°. The observations were made at 29° and are based on an assumed wavelength for Mo Kα_1 of 0.7093 Å. The calculated density of 1.601 g cm^{-3} for 3 molecules per hexagonal unit cell agrees well with that of 1.59 (2) g cm^{-3} determined by flotation in a carbon tetrachloride–ethylene dibromide mixture.

Integrated diffraction data were collected using the θ–2θ scan technique, with a scan rate of 10°/min and a scan range of 1.0 + 0.5 tan θ degrees, centered about the average peak position. A scintillation counter equipped with a pulse height selector, set for a 95% window centered on the Mo Kα peak, was used to measure the data, the receiving aperture having a diameter of 2 mm. Each reflection was scanned up to a maximum of 4 times, the number of scans actually required being determined by a preset intensity value. For the strong reflections, attenuation filters of nickel foil of varying thickness were automatically inserted once a given count rate (approximately 2500 counts/sec) was exceeded, and a total of five filters with factors ranging from 1.50 to 12.10 were used in the data collection. Instrumental and crystal stabilities were monitored by alternately measuring the intensities of two internal standards (303 and 024) after every 30 reflections. No significant deviations from their average values were found.

Table I. Positional Parameters for $Co(C_5H_5NO)_6(ClO_4)_2$ with Standard Deviations in Parentheses

Atom	x	y	z
Co	0.0	0.0	0.0
O(1)	0.1536 (2)	0.1062 (2)	0.0633 (1)
N	0.2047 (2)	0.0514 (3)	0.0990 (2)
C(1)	0.2708 (4)	0.0104 (4)	0.0658 (3)
C(2)	0.3226 (4)	−0.0461 (5)	0.1024 (3)
C(3)	0.3091 (4)	−0.0584 (5)	0.1731 (4)
C(4)	0.2431 (4)	−0.0138 (5)	0.2064 (3)
C(5)	0.1909 (3)	0.0415 (4)	0.1690 (2)
C1H	0.274 (4)	0.018 (4)	0.018 (3)
C2H	0.364 (4)	−0.079 (5)	0.078 (3)
C3H	0.346 (6)	−0.092 (5)	0.200 (4)
C4H	0.227 (4)	−0.015 (4)	0.252 (3)
C5H	0.142 (4)	0.076 (4)	0.191 (2)
Cl	0.0	0.0	0.35135 (9)
O(2)	0.0	0.0	0.4239 (3)
O(3)	0.0094 (4)	−0.1030 (4)	0.3277 (3)

Stationary-background counts B_1 and B_2 were taken at each limit of the 2θ scan, for half the scan time. From these and the measured peak counts P, the net intensity for each reflection, I, was obtained as $I = [P - (B_1 + B_2)](F_m/n_s)$ where F_m is the appropriate attenuation factor and n_s the number of scans. The intensity data were assigned standard deviations according to the formula

$$\sigma(I) = [(P + B_1 + B_2)(F_m/n_s)^2 + (cI)^2]^{1/2}$$

with c introduced to account for random errors, other than those arising from counting statistics.[14] Initially c was assigned a value of 0.04, but in the later stages of refinement, this was computed to be too low and it was accordingly increased to 0.055.[15]

A total of 676 independent reflections in the range $1° \leq 2\theta_{Mo} \leq 46°$ were measured and of these, 86 had a net intensity less than $2\sigma(I)$ and were treated as unobserved. In addition to the independent set of data, the intensities of *ca.* 400 reflections in the two neighboring sectors of reciprocal space related by the threefold axis were also measured, together with 20 strong, low-angle Friedel pairs in the negative 2θ region. No significant differences between related members were observed, after application of corrections for background and absorption. Corrections for absorption (μ_{Mo} = 7.57 cm^{-1}) and for Lorentz and polarization effects were applied to reduce the intensities to relative F^2 values, the transmission factors for the former ranging from 0.797 to 0.830.[16]

Structure Solution and Refinement. Computations were carried out on a CDC 3800 computer using local modifications of Zalkin's FORDAP Fourier program, Prewitt's SFLS5 full-matrix least-squares routine, and various locally written programs. The scattering factors for all nonhydrogen atoms were taken from the tabulation by Cromer and Waber,[17] those for cobalt and chlorine being corrected for anomalous dispersion.[18] The hydrogen atom scattering factor used was that tabulated by Stewart.[19] The agreement factors are defined in the usual manner as $R = (\sum||F_o| - |F_c||)/(\sum|F_o|)$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, and in all least-squares refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ the weights w being evaluated as $w^{1/2} = 2LpF_o/\sigma(I)$. Examination of a three-dimensional Patterson function yielded cobalt and chlorine positions and strongly suggested $R\bar{3}$ as the correct space group.[20] While the perchlorate ions also have C_3 symmetry in $R3$, this space group would have two crystallographically independent ions, so that a different distribution of Co–Cl vectors would be anticipated. One electron density map, phased on the cobalt and chlorine atoms was sufficient to locate all nonhydrogen atoms and two cycles of isotropic refinement (38

Table II. Thermal Parameters for $Co(C_5H_5NO)_6(ClO_4)_2$ in Å^2 with Standard Deviations in Parentheses

Atom	B_{11}[a] or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co[b]	4.09 (9)	4.09	2.30 (5)	2.045	0.0	0.0
O(1)	3.28 (13)	3.24 (13)	3.93 (13)	1.74 (11)	−0.92 (10)	−0.28 (9)
N	2.16 (13)	2.78 (13)	3.34 (17)	0.97 (12)	−0.29 (11)	−0.12 (11)
C(1)	3.71 (20)	4.92 (24)	3.84 (26)	2.54 (19)	−0.75 (17)	−0.99 (18)
C(2)	4.39 (24)	5.44 (25)	6.10 (33)	3.38 (21)	−1.36 (20)	−1.33 (23)
C(3)	3.26 (22)	4.32 (24)	7.38 (39)	1.67 (19)	−1.52 (23)	0.98 (23)
C(4)	3.33 (21)	5.39 (25)	3.93 (27)	1.18 (19)	−0.05 (19)	1.28 (20)
C(5)	2.33 (18)	3.64 (20)	3.50 (25)	1.16 (15)	−0.25 (15)	0.04 (15)
Cl[b]	8.15 (15)	8.15	2.62 (8)	4.075	0.0	0.0
O(2)[b]	24.58 (95)	24.58	2.87 (30)	12.29	0.0	0.0
O(3)	10.52 (31)	7.63 (25)	11.76 (34)	5.52 (24)	0.41 (26)	−3.29 (22)
C1H	3.8 (9)					
C2H	5.1 (10)					
C3H	6.7 (15)					
C4H	4.6 (12)					
C5H	4.4 (9)					

[a] The form of the anisotropic thermal ellipsoid is given by $\exp[-\Sigma_i\Sigma_j h_i h_j r_i^* r_j^* B_{ij})/4]$ with $i, j = 1, 2, 3$, where r_i^* is the ith reciprocal axis. [b] For these atoms $B_{11} = B_{22} = 2B_{12}$ and $B_{13} = B_{23} = 0$.

variables including an overall scale factor) and led to values of $R = 0.124$ and $R_w = 0.157$. Assignment of anisotropic thermal parameters to all nonhydrogen atoms yielded $R = 0.072$ and $R_w = 0.098$ after a further two cycles and examination of a difference electron density map revealed the five independent hydrogen atoms of the ligand in regions of 0.5–0.7 e Å^{-3}. This difference map also indicated a very large anisotropy in the oxygen atom of the perchlorate ion situated on the threefold axis but did not give any evidence of an appreciable static disorder in the ion. Further refinement, including the hydrogen atoms, initially calculated as fixed contributions (one cycle) and then allowing their positional and isotropic thermal parameters to vary, led to $R = 0.042$ and $R_w = 0.056$ based on the observed reflections (*vide infra*) after two further cycles (101 variables). The B_{11} value for the threefold oxygen of the perchlorate ion converged to a very high value, indicative of an appreciable displacement of electron density away from the C_3 axis for this atom. In addition, there was considerable anisotropy of the same form in the thermal motion of the chlorine atom. However, an attempt to refine the perchlorate as a rigid group of T_d symmetry (with small adjustments in coordinates being made between cycles in which isotropic thermal parameters were refined), including a small static disorder with the "unique" Cl–O bond slightly offset from the threefold axis, led to significantly inferior agreement factors. We therefore concluded that our refinement model was essentially correct.

Three further cycles of least-squares refinement including a secondary extinction correction evaluated according to the formula given by Zachariasen[21] led to final values of $R = 0.037$ and $R_w = 0.051$ for the 590 observed reflections, the value of the extinction coefficient being 4.5 (8) × 10^{-8}. Of the 86 unobserved reflections, only one had a value of $|F_o - F_c|$ greater than 3 times the relevant $\sigma(F_o)$, and the R and R_w values for all reflections were 0.044 and 0.055, respectively. In the final cycle of refinement, the largest shift in any parameter was less than 0.15 times its estimated standard deviation. The positional and thermal parameters derived from the final cycle, along with their esd's estimated from the inverse matrix, are presented in Tables I and II. A compilation of observed and calculated structure amplitudes is available.[22] A final difference Fourier map revealed no peaks larger than 0.3 e Å^{-3}.

Results and Discussion

A view of one layer of the structure of $Co(pyO)_6(ClO_4)_2$ projected down the c axis of the hexagonal unit cell is illustrated in Figure 1. Relevant bond distances and angles are given in Table III, while the root-mean-square amplitudes of the thermal ellipsoids are listed in Table IV. In approximate terms, the overall structure may be viewed as a cubic close-packed array of cations with the perchlorate anions occupying the tetrahedral holes in the arrangement.

Table III. Bond Distances (Å) and Angles (deg) in $Co(C_5H_5NO)_6(ClO_4)_2$[a]

	Distances		
Co–O(1)	2.088 (2)	O(1)–N	1.334 (4)
N–C(1)	1.331 (5)	N–C(5)	1.343 (5)
C(1)–C(2)	1.365 (7)	C(4)–C(5)	1.365 (7)
C(2)–C(3)	1.357 (8)	C(3)–C(4)	1.362 (7)
C(1)–C1H	0.92 (5)	C(2)–C2H	0.94 (5)
C(3)–C3H	0.92 (6)	C(4)–C4H	0.89 (6)
Cl–O(2)	1.382 (6)	Cl–O(3)	1.424 (4)
		C(5)–C5H	1.00 (5)
	Angles		
O(1)–Co–O(11)	89.97 (4)	O(1)–Co–O(12)	90.03 (4)
O(1)–N–C(1)	120.5 (3)	O(1)–N–C(5)	118.7 (3)
N–C(1)–C(2)	120.3 (4)	N–C(5)–C(4)	119.5 (4)
C(1)–C(2)–C(3)	120.0 (5)	C(3)–C(4)–C(5)	120.3 (4)
C(1)–N–C(5)	120.8 (3)	C(2)–C(3)–C(4)	119.0 (4)
O(2)–Cl–O(3)	108.5 (4)	O(3)–Cl–O(31)	110.5 (1)
		Co–O(1)–N	119.5 (2)

[a] Least-squares plane parameters for the ligand: $l = 0.8309$, $m = 0.5441$, $n = 0.1165$, $d = 1.7227$ Å. Distances of atoms from plane (Å × 10^3): O(1), 1; N, −7; C(1), 9; C(2), 3; C(3), −5; C(4), 2; C(5), 4; C1H, −30; C2H, −46; C3H, 32; C4H, 2; C5H, 15. (Hydrogen atoms were not included in calculation of plane parameters.) Plane is of the form $lX + mY + nZ = d$, where Y and Z are coincident with the crystal axes. The weights used were for the ith atom $w_i = 1/(a\sigma_x b\sigma_y c\sigma_z)^{2/3}$.

Table IV. Rms Amplitudes of Vibration

	Axes		
Atom	Major	Intermed	Minor
Co	0.227 (2)	0.227 (2)	0.171 (1)
O(1)	0.241 (4)	0.200 (4)	0.180 (4)
N	0.208 (5)	0.200 (5)	0.162 (5)
C(1)	0.265 (6)	0.208 (6)	0.195 (6)
C(2)	0.307 (6)	0.236 (6)	0.190 (6)
C(3)	0.333 (7)	0.226 (7)	0.176 (7)
C(4)	0.306 (6)	0.212 (6)	0.196 (6)
C(5)	0.228 (5)	0.212 (5)	0.170 (5)
Cl	0.321 (3)	0.321 (3)	0.182 (3)
O(2)	0.558 (11)	0.558 (11)	0.191 (10)
O(3)	0.420 (5)	0.365 (5)	0.229 (5)

The Structure of the Cation. The view of the $Co(pyO)_6^{2+}$ complex ion given in Figure 1 clearly illustrates the crystallographically imposed S_6 point symmetry of this species. To within the estimated standard deviations, the CoO_6 grouping is perfectly octahedral, the angle θ between the Co–O bond and the threefold axis being 54.73 (3)°. The twist angle ϕ, being the angle of projection between the two sets of threefold related bonds, is in this instance crystallographically fixed at 60°, because of the $\bar{3}$ site symmetry of the cobalt atom. The S_6 configuration was one of the alternative structures with threefold symmetry suggested on the basis of infrared results,[2] and it is likely that this arrangement of ligands minimizes the nonbonded interactions between them. Apart from two orientations giving D_{3d} symmetry, the other general arrangement for a trigonal complex would belong to point group D_3 and would allow a variable ϕ angle. Such is the arrangement found

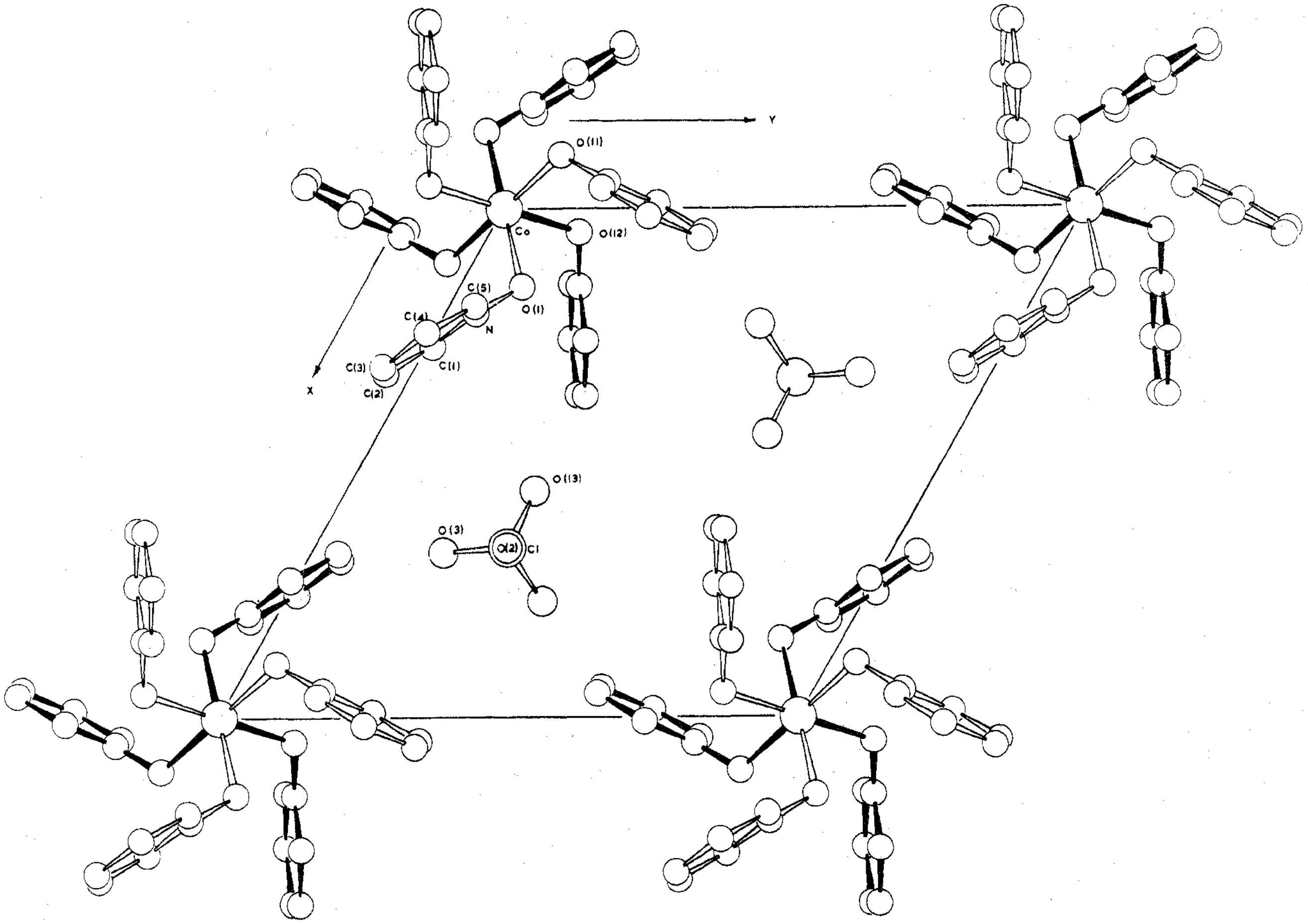

Figure 1. An [001] projection of one layer (at $z = 0$) of the unit cell of $Co(pyO)_6(ClO_4)_2$. The numbered atoms define the asymmetric unit (Table I).

in the $M(urea)_6{}^{3+}$ complexes.[4,5] For the $M(pyO)_6{}^{2+}$ complexes, however, a scale model indicates that D_3 symmetry introduces appreciable conflict between the rings of one threefold set of ligands with those of the other when ϕ is near 60° and the planes of the ligands are roughly parallel to the C_3 axis.[23] This angle of inclination in the present structure is 6.7°.

The geometry of the coordinated pyridine oxide is comparable with that observed for this ligand in other complexes[24] and with that for the free molecule.[25] The Co–O–N bond angle of almost 120° is in accord with that expected for sp^2 hybridization of the oxygen atom, although this angle varies between wide limits in other complexes.[11,24] The pyridine oxide ligand is planar (Table III); however, the metal atom lies 1.723 Å out of this plane and the dihedral angle between the ligand plane and the plane formed by Co, O(1), and N is 72.2°. The C_3 axis is inclined at 50.8° to this latter plane, so that in terms of a simplified molecular orbital or angular overlap model, which would take account of the orientation of the –N–O grouping relative to the threefold axis of the cation, magnetic and spectroscopic properties indicative of an octahedron extended along the threefold axis should be anticipated.[32]

The Perchlorate Ion. The ClO_4^- ions occupy the trigonal holes between the cations within each layer of the structure and, taking into account the orientation of the thermal ellipsoids of oxygens O(3), O(31), and O(32), have almost C_{3v} point symmetry. As noted earlier, the B_{11} and B_{22} thermal parameters for the threefold oxygen O(2) and the chlorine atom converged to high values, and while a model incorporating a small static disorder did not refine satisfactorily, extensive librational motion or a limited rotational disorder is not ruled out. Figure 2 illustrates the relative orientation and magnitudes of the thermal ellipsoids of the ClO_4^- group and the appearance of the ellipsoid for O(2), together with the short bond distance, 1.382 (6) Å (compared to 1.424 (4) Å for Cl–O(3)), is indicative of a large libration about an axis normal to the threefold axis.[26] The oxygen–oxygen distance along the C_3 axis is 2.898 (6) Å in accord with expectation for a nonbonded contact. In order to correct the observed dimensions of the ClO_4^- ion for the effects of libration, the rigid-body model was adopted as that being most suitable.[27] Given the nature of ClO_4^- group, a riding model would certainly seem inappro-

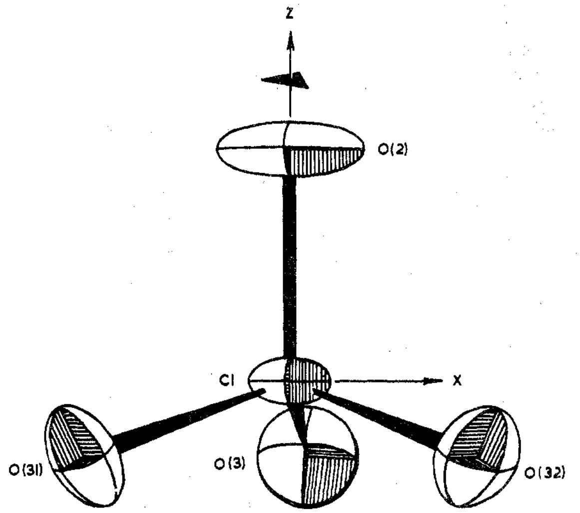

Figure 2. The perchlorate ion viewed normal to the C_3 axis. The thermal ellipsoids are drawn at the 50% probability level.

priate and, in fact, gives an excessively large correction for the Cl–O(2) distance. The components of the translational (T) and librational (ω) tensors, together with the axial tensor, **S**, which represents the coupling between **T** and ω,[27] were determined by a least-squares fit to the observed U_{ij} (10 independent) referred to orthogonal axes with z along the C_3 axis. For C_3 symmetry, the **T** and ω tensors are diagonal and the following values were obtained: $T_{11} = T_{22} = 0.0940$ (62) and $T_{33} = 0.0135$ (82) Å^2; $\omega_{11} = \omega_{22} = 0.0823$ (49) and $\omega_{33} = 0.0200$ (64) radian^2. The rms amplitudes of libration normal and parallel to the threefold axis are then 16.4° and 8.0°, respectively, the former value confirming the very large librations normal to the axis and being coupled with a large rectilinear oscillation of rms amplitude 0.31 Å, also normal to the axis. The only nonzero element of the **S** tensor ($S_{21} = -S_{12}$) has the value −0.0175 (32)[28] indicating that the effective origin of libration is at a distance of 0.21 Å (S_{12}/ω_{11}) along the Cl–O(2) bond from the chlorine atom. This displacement of the origin is in accord with the angles between the principal axes of the thermal ellipsoid of O(3) and the Cl–O(3) bond.

The adequacy of the rigid-body model in the present instance is reflected in the calculated corrections to the observed geometry and in its ability to reproduce the U_{ij}. Apart from U_{33} for Cl and O(2), for which the calculated values are much lower than the observed values (for these $U_{33} = T_{33}$), the agreement is reasonable. The corrected bond distances for both Cl–O(2) and Cl–O(3) are 1.495 (6) Å and the corrected O(2)–Cl–O(3) angle is 109.2°.[29] This distance is appreciably longer than that often quoted for a "normal" (uncorrected) Cl–O bond in perchlorate, namely, *ca.* 1.42–1.45 Å.[30] However, larger values (up to 1.485 Å) have been found in studies where corrections have been made for thermal motion.[31]

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40474L.

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(32) **Note Added in Proof.** Following the submission of this paper for publication, the crystal structure of the Ni(pyO)$_6{}^{2+}$ complex in the form of the tetrafluoroborate salt has been reported [A. D. Van Ingen Schenau, G. C. Vershoor, and C. Romers, *Acta Crystallogr., Sect. B*, **30**, 1686 (1974)]. The authors carried out refinements in both $R\bar{3}$ and $R3$ and suggested the latter as the correct space group, although they discuss the geometry of the cation on the basis of the centric space group. The BF$_4{}^-$ ions exhibit a static disorder in this structure.