Inorganica Chimica Acta, 114 (1986) 165–169

$[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$: Tetragonal Compression with Elongated Equatorial Bonds

FUSAO TAKUSAGAWA, PAULOS G. YOHANNES and KRISTIN BOWMAN MERTES*

Department of Chemistry, University of Kansas, Lawrence, Kans. 66045, U.S.A.

Received September 20, 1985

Abstract

The crystal and molecular structure of the dihydrate of $[Co(terpy)_2][NO_3]_2$ was determined. The complex crystallizes in the tetragonal space group $I4_1/a$ with $a = 12.408(2)$ and $c = 38.867(6)$ Å. The structure was refined using 2272 independent reflections to a final $R = 0.058$ and $R_w = 0.081$. The structure consists of $Co(terpy)_2{}^{2+}$ cations, disordered $NO_3{}^-$ anions, and two water molecules of crystallization. The cation exhibits compression along the molecular z axis along with significant elongation along the x and y axes with almost identical bond lengths (2.189(3) and 2.180(3) Å). These are the longest Co–N bonds observed in a cobalt(II) bisterpyridine complex to date.

Introduction

Interest in bis(2,2′:6′,2″-terpyridyl)cobalt(II) complexes $[Co(terpy)_2]^{2+}$ has been generated from findings that the spin state cross-over in these salts is apparently influenced by the anion and degree of hydration [1–7]. Furthermore, the aromatic, rigid, tridentate ligand provides a symmetrical environment about the metal which approximates D_{2d} symmetry. Structural studies have been performed on complexes for which the anions are Br^- [1], SCN^- [2], I^- [5], and $ClO_4{}^-$ [3, 6] for cobalt(II), Cl^- for cobalt(III) [7] and chromium(III) [8, 9], and $NO_3{}^-$ for copper(II) [10]. From the series of bis-terpyridine structures of divalent metal ions that have been reported, it has been observed that the crystals are either tetragonal or triclinic depending on the anion and water content. The general structural characteristic of the cations is compression of the complexes along the molecular z axis (which is coincident with the central nitrogen of both terpyridine ligands). Then, for metal ions for which a Jahn–Teller distortion is expected, elongation occurs along either the x or y axis, the net result being C_{2v} symmetry [1–3, 5, 6, 10].

Reinen and coworkers, in an investigation of high-spin–low-spin equilibria of $[Co(terpy)_2]X_2 \cdot nH_2O$ complexes, have reported the isolation and characterization of $[Co(terpy)_2][NO_3]_2 \cdot 0.5H_2O$ [4]. The complex crystallizes as brown plates in the tetragonal space group $I4_1/a$ and was reported to be isostructural with $[Cu(terpy)_2][NO_3]_2$ [10]. During a study of the hydrolysis of adenosine triphosphate assisted by cobalt(III) complexes in this laboratory, violet tetragonal bipyramidal crystals were isolated and analyzed as $[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$. In view of the interest in the degree of hydration on the structural aspects and spin states of these complexes, and the fact that this complex crystallized with a different crystal morphology and color than the previously reported nitrate complex, the crystal structure was undertaken.

Experimental

Synthesis

All chemicals were reagent grade. Trichlorodiethylenetriaminecobalt(III) ($Co(dien)Cl_3$) was prepared by adding diethylenetriamine to an aqueous solution of $Co(NO_3)_2$ and bubbling air through the resulting mixture. Further treatment with HCl gave a brown solid [11]. The pH of an aqueous solution (20 ml) of what was then thought to be $Co(dien)Cl_3$ (0.161 g, 0.6 mmol) and adenosine triphosphate (0.368 g, 0.6 mmol) was adjusted to 4.5 and let sit at room temperature for 8 h. At that time 2,2′:6′,2″-terpyridine (0.140 g, 0.6 mmol) in 10 ml of 30% ethanol was added. The solution was allowed to evaporate slowly over a period of four weeks, at which time violet crystals suitable for X-ray were isolated and separated mechanically from an additional residue. Since these crystals proved through analysis and crystal structure to be the nitrate salt of cobalt(II), it is assumed that the $Co(dien)^{3+}$ was contaminated with the starting reagent, $Co(NO_3)_2$. *Anal.* Calc. for $CoC_{30}H_{26}N_8O_8$: C, 52.56; H, 3.82; N, 16.35. Found: C, 52.50; H, 3.48; N, 16.30%.*

---

*Author to whom correspondence should be addressed.

*Elemental analyses for carbon, hydrogen, and nitrogen were performed at the Microanalytical Laboratory, University of Kansas, by Dr. Tho Nguyen.

0020-1693/86/$3.50

TABLE I. Crystallographic Data for $[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$

Compound	$CoC_{30}H_{22}N_8O_6 \cdot 2H_2O$
Formula weight	685.53
a (Å)	12.408(2)
b (Å)	12.408(2)
c (Å)	38.867(6)
V (Å^3)	5983.9(16)
D_c (g cm^{-3})	1.517
D_o (flotation) (g cm^{-3})	1.51(2)
Z	8
Space group	$I4_1/a$
Crystal dimensions (mm)	0.4 × 0.4 × 0.4
Temperature (°C)	25
Radiation	Mo Kα
Diffractometer	Syntex $P2_1$
μ (cm^{-1})	6.679
2θ range (deg)	4.0–45.0
Total number reflections	2886
Number independent reflections	2272
Final R	0.058
Final R_w	0.081

X-ray Data

Crystal data information is contained in Table I. Preliminary measurements indicated tetragonal symmetry with systematic absences for hkl, $h + k + l = 2n + 1$; $hk0$, $h = 2n + 1$ and $k = 2n + 1$; and $00l$, $l = 4n + 2$, indicative of space group $I4_1/a$. Unit cell parameters were derived from a least-squares fit of 15 reflections with $2\theta > 25.0°$. A correction for decay was made on the basis of three standard reflections, chosen and monitored every 50 reflections for which the maximum correction factor was 1.29. The data were collected on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). For $I_o < 0.2\sigma$, I_o was set to 0.2. Lorentz and polarization factors were applied to obtain structure factors, and an absorption correction was applied using an empirical method.* An extinction correction was also made, for which the maximum correction factor to F_c was 0.497 for reflection 132.

Solution and Refinement

The structure was solved by the heavy atom method. Subsequent Fourier maps revealed the positions of the remaining non-hydrogen atoms.** The cobalt ion was found to lie on the two-fold axis as were N1A, C4A, N1C, and C4C, the midpoints of each terpyridine ligand. Refinement was performed using full matrix and block-diagonal least-squares techniques during which the function $\Sigma w(|F_o| - k|F_c|)^2$ was minimized. The data were weighted according to $w = 1/\sigma^2$. Values of σ were calculated from $\sigma = \sigma(F_o^2)/2F_o$, where $\sigma(F_o^2) = \sigma(I_o)/LP$. Weights were changed in later refinements to $w = 1/\sigma_{new}^2$, where $\sigma_{new}^2 = \sigma^2 + 0.5A|F_o|^2 + 0.5B(\sin\theta/\lambda)^2$. Least-squares minimization of the function $\Sigma(\Delta F^2 - \sigma_{new}^2)^2$ for 20 separate segments in F_o and $\sin\theta/\lambda$ was applied to obtain values of A and B. For block-diagonal refinements, the scale and extinction factors and thermal parameters were placed in one block and positional parameters in another.

Initial refinements indicated disorder about the nitrate anion as shown in the electron density map in Fig. 1. Two sets of oxygen positions were chosen, and the positions of the atoms were varied using a restrained least-squares method. The idealized distance and angle were chosen as N–O = 1.26 Å and O–N–O = 120.0°. In early refinements, the occupancy parameters were varied, but were fixed in later refinements at 0.625 for N, O1, O2, and O3 and 0.375 for N′, O1′, O2′, and O3′. All hydrogen atoms were located in a difference map and added into final refinements with isotropic thermal parameters. Convergence was achieved at $R = 0.058$ and $R_w = 0.081$ (where $R = \Sigma||F_o| - k|F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - k|F_c|)^2/(\Sigma w|F_o|^2))^{1/2}$. The 'goodness of fit', $\{[\Sigma w(|F_o| - k|F_c|)^2]/(N_o - N_v)\}^{1/2}$, where N_o is the number of reflections and N_v is the total number of variables, was 1.430. The highest peak found in a difference Fourier map at this point was 0.57 e/Å^3. Atom numbering is shown in Fig. 2, a perspective view of the molecule. Final positional parameters and isotropic thermal parameters are found in Table II, bond lengths and angles of interest in Tables III and IV, respectively.

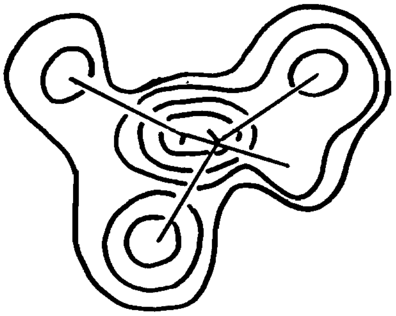

Fig. 1. Electron density map depicting the disordered NO_3^-.

Results and Discussion

The structure consists of $Co(terpy)_2^{2+}$ cations, disordered NO_3^- anions, and two water molecules of crystallization. The cobalt ion, the central nitrogen

---

*The programs were written in the DNA system by Dr. Fusao Takusagawa. The absorption correction was made according to the procedure reported [12a]. A Type I isotropic extinction correction was made according to ref. 12b. All calculations were performed on a Honeywell 66/6000 computer at the University of Kansas.

**Atomic scattering factors are from ref. 13.

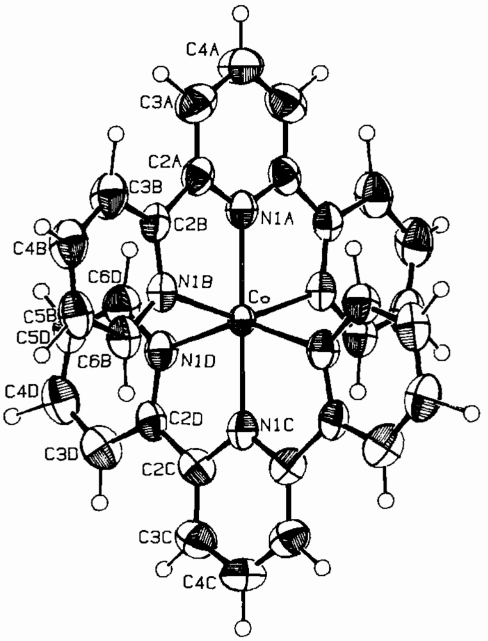

Fig. 2. Perspective view of the molecule.

TABLE II. Fractional Coordinates and Isotropic Thermal Parameters for $[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$

Atom	x	y	z	B
Co	0.5000	0.2500	0.12209(1)	2.45
N1A	0.5000	0.2500	0.1762(1)	3.42
C2A	0.4131(3)	0.2858(2)	0.19263(9)	3.70
C3A	0.4106(3)	0.2872(3)	0.2281(1)	5.01
C4A	0.5000	0.2500	0.2463(2)	5.19
N1B	0.3425(2)	0.3163(2)	0.13618(8)	3.54
C2B	0.3242(2)	0.3200(2)	0.17012(9)	3.60
C3B	0.2252(3)	0.3552(3)	0.1830(1)	4.95
C4B	0.1464(3)	0.3895(4)	0.1601(1)	5.39
C5B	0.1666(3)	0.3854(4)	0.1255(1)	4.97
C6B	0.2663(3)	0.3490(3)	0.1141(1)	3.87
N1C	0.5000	0.2500	0.0687(1)	3.55
C2C	0.5324(2)	0.3379(3)	0.05111(9)	3.83
C3C	0.5326(3)	0.3400(3)	0.0156(1)	4.71
C4C	0.5000	0.2500	−0.0020(2)	3.69
N1D	0.5619(2)	0.4080(2)	0.10759(8)	3.74
C2D	0.5686(2)	0.4277(2)	0.07356(9)	3.53
C3D	0.6069(3)	0.5249(3)	0.0608(1)	4.79
C4D	0.6392(3)	0.6042(3)	0.0840(1)	5.13
C5D	0.6334(4)	0.5853(3)	0.1186(1)	5.04
C6D	0.5953(3)	0.4857(3)	0.1298(1)	4.24
OW	0.7336(4)	−0.2192(4)	0.5331(1)	8.34
N	0.2408(5)	0.4258(7)	0.5327(2)	5.68
O1	0.2540(9)	0.3257(7)	0.5364(3)	6.59
O2	0.281(1)	0.4727(9)	0.5069(3)	11.82
O3	0.173(1)	0.475(1)	0.5513(3)	11.21
N′	0.261(1)	0.458(1)	0.5325(4)	12.57
O1′	0.241(2)	0.358(1)	0.5336(8)	12.03
O2′	0.192(2)	0.523(2)	0.521(1)	17.46
O3′	0.344(1)	0.493(1)	0.5475(5)	9.59
HC3A	0.661(4)	0.185(4)	0.243(1)	5.39
HC4A	0.5000	0.2500	0.272(2)	3.98
HC3B	0.780(7)	0.158(7)	0.213(2)	12.58
HC4B	0.934(3)	0.100(3)	0.168(1)	5.50
HC5B	0.893(3)	0.082(3)	0.1058(9)	3.44
HC6B	0.280(3)	0.350(2)	0.0871(8)	2.82
HC3C	0.437(3)	0.094(3)	0.001(1)	4.83
HC4C	0.5000	0.2500	−0.028(2)	4.46
HC3D	0.608(2)	0.529(2)	0.0336(8)	2.72
HC4D	0.682(8)	0.701(7)	0.076(3)	13.53
HC5D	0.653(3)	0.641(4)	0.137(1)	5.03
HC6D	0.587(3)	0.469(3)	0.1572(9)	2.98
HOW1	0.523(7)	0.015(7)	0.253(2)	12.47

TABLE III. Interatomic Distances and Hydrogen Bonding Interactions for $[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$

Atoms	Distances (Å)	Atoms	Distances (Å)
Interatomic distances			
Co–N1A	2.101(4)	C3D–C4D	1.394(6)
Co–N1B	2.189(3)	C4D–C5D	1.365(7)
Co–N1C	2.075(5)	C5D–C6D	1.394(5)
Co–N1D	2.180(3)	N–O1	1.261(12)
N1A–C2A	1.331(4)	N–O2	1.261(13)
C2A–C3A	1.379(5)	N–O3	1.260(14)
C2A–C2B	1.471(5)	N′–O1′	1.26(2)
C3A–C4A	1.394(5)	N′–O2′	1.26(3)
N1B–C2B	1.339(5)	N′–O3′	1.26(2)
N1B–C6B	1.340(4)	C3A–HC3A	1.11(4)
C2B–C3B	1.397(5)	C4A–HC4A	0.98(6)
C3B–C4B	1.390(6)	C3B–HC3B	1.18(9)
C4B–C5B	1.370(6)	C4B–HC4B	1.06(4)
C5B–C6B	1.388(5)	C5B–HC5B	1.14(3)
N1C–C2C	1.348(4)	C6B–HC6B	1.06(3)
C2C–C3C	1.381(5)	C3C–HC3C	1.06(4)
C2C–C2D	1.485(5)	C4C–HC4C	1.00(6)
C3C–C4C	1.371(5)	C3D–HC3D	1.06(3)
N1D–C2D	1.347(5)	C4D–HC4D	1.35(9)
N1D–C6D	1.360(5)	C5D–HC5D	1.02(4)
C2D–C3D	1.388(5)	C6D–HC6D	1.09(3)
Hydrogen bonding interactions			
OW–O1	3.010(9)	OW–O2′	2.648(18)
OW–O1′	3.129(12)	OW–O3′	3.014(15)

atoms of each terpyridine ligand, and the para carbon atoms lie on a twofold rotation axis, defined as the molecular z axis. The two halfs of each terpyridine ligand are thus bisected by the twofold axis and crystallographically related by symmetry. The two terpyridine rings are almost perpendicular as evidenced by the 89.6° angle between the two ligands. As observed in other bis-terpyridine complexes of cobalt(II), compression occurs along the molecular z axis, but significant elongation is observed along the x and y axes with almost identical bond lengths (2.189(3) and 2.180(3) Å). These are

TABLE IV. Bond Angles for $[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$

Atoms	Angle (deg)	Atoms	Angle (deg)
N1A–Co–N1B	75.51(8)	N1B–C6B–C5B	121.7(4)
N1A–Co–N1C	179.99(2)	C2C–N1C–C2C″	119.0(4)
N1A–Co–N1D	104.98(8)	N1C–C2C–C3C	121.6(3)
N1B–Co–N1B″[a]	151.03(12)	N1C–C2C–C2D	113.5(3)
N1B–Co–N1C	104.49(8)	N1C–C2C–C3C	121.6(3)
N1B–Co–N1D	92.37(9)	C3C–C2C–C2D	124.9(3)
N1B–Co–N1D″	95.05(9)	C2C–C3C–C4C	118.9(4)
N1B–Co–N1C″	104.49(8)	C3C–C4C–C3C″	120.1(5)
N1C–Co–N1D	75.02(8)	C2D–N1D–C6D	118.5(3)
N1D–Co–N1D″	150.03(10)	C2C–C2D–N1D	115.0(3)
C2A–N1A–C2A″	122.4(4)	C2C–C2D–C3D	123.1(3)
N1A–C2A–C3A	120.2(3)	N1D–C2D–C3D	121.9(3)
N1A–C2A–C2B	114.7(3)	C2D–C3D–C4D	118.8(4)
C3A–C2A–C2B	125.1(3)	C3D–C4D–C5D	120.0(4)
C2A–C3A–C4A	119.1(4)	C4D–C5D–C6D	118.6(4)
C3A–C4A–C3A″	119.0(5)	N1D–C6D–C5D	122.1(4)
C2B–N1B–C6B	120.0(3)	O1–N–O2	119.6(9)
C2A–C2B–N1B	116.6(3)	O1–N–O3	119.6(9)
C2A–C2B–C3B	122.4(3)	O2–N–O3	119.6(10)
N1B–C2B–C3B	121.0(3)	O1′–N′–O2′	120(2)
C2B–C3B–C4B	118.9(4)	O1′–N′–O3′	120(2)
C3B–C4B–C5B	119.4(4)	O2′–N′–O3′	119(2)
C4B–C5B–C6B	119.1(4)		

[a] The coordinates of atoms marked with ″ are applied the symmetry operation $(1 - x, \frac{1}{2} - y, z)$.

the longest M–N bonds observed in a cobalt(II) bis-terpyridine complex to date, previously an honor held by the ClO_4^- analog, which is isomorphous with the NO_3^- salt reported here and which exhibits a relatively similar coordination geometry [3, 6].

Generally, the NO_3^- salt follows the structural patterns of the other salts. The CoN_6 coordination sphere, in addition to being tetragonally compressed, is deformed angularly due to the restricted 'bite' of the terpyridine ligand. Thus the angles between the distal and central nitrogens of a given terpyridine are 75.51(8)° and 75.02(8)° for N1A–Co–N1B and N1C–Co–N1D, respectively, giving rise to a 'ruffled' equatorial plane. This gives N_{distal}–Co–N_{distal} angles of 151.03(12)° and 150.03(10)° for the two terpyridines, some of the smallest observed to date. As anticipated, each pyridine ring is essentially planar (within 0.008(5) Å) as shown in Table V, with a small twist between adjacent rings (2.7° between rings A and B and 1.9° between rings C and D) as determined from the dihedral angles between the planes. Likewise C$\overset{\cdots}{-}$C bonds reasonably average 1.384 and C$\overset{\cdots}{-}$N 1.344 Å, while intrapyridine angles exhibit only slight deviations from the idealized 120° (the largest being 122.4° observed for C2A–N1A–C2A′).

An interesting assessment of terpyridine deformation was described by Figgis, Kucharski and White in a comparison of a number of reported terpyridine structures [7]. Both the N_{distal}–$N_{central}$–N_{distal} angle, defined as θ, and the normalized 'bite' of the ligand, defined as $2 \sin(\alpha/2)$, where α equals the $N_{central}$–Co–N_{distal} angle, were used to ascertain the degree of terpyridine deformation. For the bis-

TABLE V. Least-squares Planes and Atom Displacements for $[Co(terpy)_2][NO_3]_2 \cdot 2H_2O$

Atom	Distance (Å)	Atom	Distance (Å)
A. N1A–C2A–C3A–C4A			
$0.383x + 0.924y - 0.001z = 5.236$			
N1A	0.001	C3A	0.001
C2A	−0.001	C4A	−0.001
B. N1B–C2B–C3B–C4B–C3B′–C2B′			
$0.359x + 0.933y + 0.038z = 5.389$			
N1B	−0.004	C4B	0.006
C2B	0.007	C3B′	−0.003
C3B	−0.008	C2B′	0.002
C. N1C–C2C–C3C–C4C–C3C′–C2C′			
$0.939x - 0.343y - 0.001z = 4.763$			
N1C	−0.001	C3C	−0.003
C2C	0.003	C4C	0.001
D. N1D–C2D–C3D–C4D–C3D′–C2D′			
$0.929x - 0.370y - 0.016z = 4.544$			
N1D	−0.007	C4D	−0.002
C2D	0.001	C3D′	−0.004
C3D	0.003	C2D′	0.008

terpyridine complexes reported, θ is found to range from 100.1° for the small, low spin cobalt(III) [Co(terpy)$_2$]Cl$_3$ [7] to 113.3° for the large d^9 [Cu(terpy)$_2$][NO$_3$]$_2$ [10], although for the Co^{2+} complexes, the range is narrower (104.9° to 109.0° for the SCN$^-$ [2] and Br$^-$ [1], respectively). In the case of the NO$_3^-$ complex reported here θ is at the larger end of the scale at 107.5(2)° for N1B–N1A–N1B′ and 108.7(2)° for N1D–N1C–N1D′, as anticipated from the rather long equatorial bond lengths. The angle θ, then, seems to be a reflection of general trend in metal ion size. The 'bite' found for [Co(terpy)$_2$][NO$_3$]$_2$ complex is 1.22, the lowest observed to date for the bis-terpyridine complexes. The closest approach is made by the analogous copper(II) complex, for which the terpyridine associated with the longer two equatorial bonds (2.288(4) Å) has a 'bite' of 1.23.

As mentioned previously the interest in the cobalt(II) complexes has revolved around the spin-state populations. It has been observed that the Co–N$_{\text{central}}$ bonds are the most sensitive to changes in spin state [6]. A large percentage (70%) of the high spin component at 298 K has been proposed for the ClO$_4^-$ salt, which has the highest room temperature magnetic moment of the [Co(terpy)$_2$]$^{2+}$ compounds studied crystallographically to date [6]. Two crystal structures have been separately reported for this compound, one of which contains 0.5 [6] and the other 1.3H$_2$O molecules [3] of crystallization. The two compounds are essentially isostructural, however, and have, in agreement with their large high spin component, until this report boasted the longest Co–N$_{\text{central}}$ distances, averaging 2.028 [6] and 2.022 Å [3] for the two structures as well as the longest distal bonds, averaging 2.136 [6] and 2.139 Å [3]. The NO$_3^-$ complex exhibits even longer Co–N bonds for both the central and distal nitrogen atoms, averaging 2.088(4) and 2.184(3) Å, respectively. The significant elongation, leading to an overall average of 2.152 Å compared to 2.100 Å for the ClO$_4^-$ complex [4], leads to the prediction that the NO$_3^-$ salt is possibly totally in the high spin form. Unfortunately, not enough crystalline product was isolated from the rather unique synthetic scheme to allow for magnetic measurements.

The crystal packing features of the cation and its accompanying anions and water molecules of hydration can be described as channels created by staggered layers of the Co(terpy)$_2^{2+}$ cations. The layers exist both parallel to the *ac* plane and the *bc* plane. The nitrates are situated approximately midway within the channels, although the less bulky water molecules seem to have more 'freedom' within the lattice network, sometimes approaching the cation walls. The projection of the unit cell on the *ac* plane at $y = 1/2$ is shown in Fig. 3. A degree of hydrogen bonding is found, especially between the water molecule and the less populated form of the disordered nitrate, as listed in Table III. The disordered, channel-like nature of the NO$_3^-$ positions suggest the possibility of potentially interesting electrical behavior of these crystals.

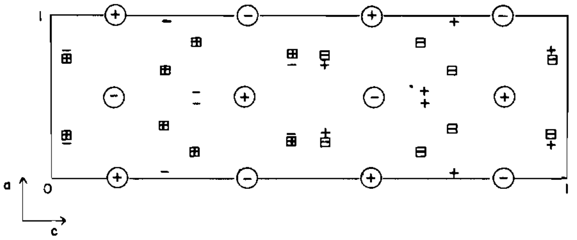

Fig. 3. Unit cell contents projected on the *ac* plane at $y = 1/2$. Key: ⊕ and ⊖ ≡ Co(terpy)$_2^{2+}$; ⊞ and ⊟ ≡ NO$_3^-$ for the more prevalent form, N, O1, O2, O3; + and − ≡ H$_2$O; + and − indicate above and below the $y = 1/2$ plane, respectively.

Supplementary Material

Tables of structure factors and anisotropic thermal parameters are available from author K.B.M. upon request.

Acknowledgement

The support of the National Institutes of Health (Grant GM 33922) is gratefully acknowledged.

References

1 E. N. Maslen, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1803 (1974).
2 C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 7 (1976).
3 W. Henke and S. Kremer, *Inorg. Chim. Acta, 65*, L115 (1982).
4 S. Kremer, W. Henke and D. Reinen, *Inorg. Chem., 21*, 3013 (1982).
5 B. N. Figgis, E. S. Kucharski and A. H. White, *Aust. J. Chem., 36*, 1527 (1983).
6 B. N. Figgis, E. S. Kucharski and A. H. White, *Aust. J. Chem., 36*, 1537 (1983).
7 B. N. Figgis, E. S. Kucharski and A. H. White, *Aust. J. Chem., 36*, 1563 (1983).
8 W. A. Wickramasinghe, P. H. Bird, M. A. Jamieson and N. Serpone, *J. Chem. Soc., Chem. Commun.*, 798 (1979).
9 W. A. Wickramasinghe, P. H. Bird and N. Serpone, *Inorg. Chem., 21*, 2694 (1982).
10 R. Allman, W. Henke and D. Reinen, *Inorg. Chem., 17*, 378 (1978).
11 J. Kleinberg (ed.), 'Inorganic Synthesis', Vol. 7, McGraw-Hill, New York, 1963, p. 211.
12 (a) A. North, D. Phillips and F. Matthews, *Acta Crystallogr. Sect. A, 24*, 351 (1968); (b) P. J. Becker and P. Coppens, *Acta Crystallogr., Sect. A, 31*, 417 (1975).
13 D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974, Tables 2.2A, 2.2B, and 2.3.1.