Table 9. *Intermolecular hydrogen bonding scheme*

O(6′) is at symmetry position $[-\frac{1}{2}+x, y, \frac{1}{2}+z]$.
O(7′) is at symmetry position $[1+x, y, z]$.

H(1)···O(7′)	1·92 Å	H(3)···O(6′)	1·98 Å
N(1)···O(7′)	2·84	N(3)···O(6′)	2·78
N(1)–H(1)–O(7′)	176·3°	N(3)–H(3)–O(6′)	173·3°

Undoubtedly, it is this hydrogen-bonding scheme that restrains the hydantoin atoms from exhibiting the large thermal motion exhibited by the unfettered phenyl groups.

Most of the experimental work was performed in Seattle and we thank Professor L. H. Jensen for the use of his facilities and for advice and encouragement. We thank Professor R. E. Marsh for helpful criticism. This work was supported by USPHS Grant GM-10828 from the National Institutes of Health.

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Crystal and Molecular Structure of Nitratobis-(2,2′-dipyridyl)cobalt(III) Hydroxide Nitrate Tetrahydrate, $[Co(C_{10}H_8N_2)_2(NO_3)](NO_3)(OH).4H_2O$

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(*Received* 6 *October* 1970)

The structure of nitratobis-(2,2′-dipyridyl)-cobalt(III) hydroxide nitrate tetrahydrate, $[Co(C_{10}H_8N_2)_2(NO_3)](NO_3)(OH).4H_2O$, has been determined by single-crystal X-ray diffraction techniques. Crystals of this complex are monoclinic with $a=10{\cdot}923(2)$, $b=15{\cdot}998(4)$, $c=14{\cdot}442(2)$ Å, $\beta=101{\cdot}93(2)^\circ$, space group $C2/c$, $\varrho_c=1{\cdot}57$ g.cm^{-3}, $\varrho_o=1{\cdot}54$ g.cm^{-3}, and $Z=4$. The structure was solved by Patterson and Fourier methods. The cobalt atom is octahedrally coordinated by two molecules of 2,2′-dipyridyl and by a bidentate nitrate group. Water molecules, nitrate groups, and the hydroxide ions are involved in hydrogen bonds which extend continuously in the **a** and **c** directions. The final refinement of the structure by full-matrix anisotropic least-squares analysis resulted in an R value of 6·2%, based on 2995 observed reflections.

Introduction

Most of the information on the stereochemistry of first-row transition metal ion complexes that contain coordinated nitrate groups and nitrogen donor ligands is derived from spectroscopic data (Addison & Sutton, 1967). From the analysis of the spectroscopic data it is inferred that the nitrate groups may act as monodentate, bidentate, or bridging ligands. But very few crystal-structure data are available to confirm the spectroscopic interpretations and to provide accurate bond distances and angles for coordinated nitrate groups.

As part of a series of studies of amine complexes of transition metal nitrates, a crystalline hydrate containing two molecules of 2,2′-dipyridyl, two nitrate groups, and one hydroxide ion per cobalt(III) ion was selected for an X-ray diffraction analysis. In this complex the 2,2′-dipyridyl molecules may assume either a *cis* or *trans* configuration, each permitting several possibilities for the overall coordination, including coordination by one or both of the nitrate groups. The presence of water molecules and hydroxide ions, moreover, indicates that hydrogen bonding would occur in the structure. Therefore, determination of the structure was undertaken, to determine the role of the nitrate groups in the structure, to provide accurate values of the bond distances and angles for the nitrate groups and the 2,2′-dipyridyl molecule, and to obtain information on the hydrogen-bonding network.

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Experimental

Crystals of nitratobis-(2,2′-dipyridyl)cobalt(III) hydroxide nitrate tetrahydrate were prepared by slow evaporation of an aqueous solution of $Co(NO_3)_2$ and 2,2′-dipyridyl. In the presence of strong field ligands such as 2,2′-dipyridyl, Co(II) oxidizes slowly to Co(III) (Vlček, 1967). As the oxidation proceeds, the absorption band at ~10700 cm^{-1}, corresponding to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition in $\text{Co(dipyridine)}_3^{2+}$, disappears. After a few days, blood-red crystals which show no indication of absorption in the 10–11000 cm^{-1} region separate from the solution.

Table 1. *Crystal data for nitratobis*(*dipyridine*)*cobalt*(III) *hydroxide nitrate tetrahydrate*, $[Co(C_{10}H_8N_2)_2(NO_3)]\ (NO_3)\ (OH)\ .\ 4H_2O$

a = 10·923 (2)* Å	Space group: $C2/c$
b = 15·998 (4)	Z = 4
c = 14·442 (2)	ϱ_o = 1·54 g.cm^{-3}
β = 101·93° (2)	ϱ_c = 1·57 g.cm^{-3}

Systematic extinctions:
hkl: $h+k=2n+1$
$h0l$: $l=2n+1$

* Numbers in parentheses are standard deviations in the last significant figures. Lattice parameters were measured at room temperature.

Crystal symmetry and approximate cell parameters were obtained from zero- and upper-level precession photographs. The approximate cell parameters were then refined by least-squares analysis using 25 2θ angles measured on a diffractometer. The density was measured by the flotation method in a mixture of chloroform and tetrabromoethane. A summary of the crystal data is given in Table 1.

The crystal used for intensity measurements was an approximately spherical fragment of average diameter ~0·4 mm. Intensities of 4303 unique reflections with $2\theta \leq 65°$ were measured with niobium-filtered Mo $K\alpha$ radiation on a three-circle automatic diffractometer with a 4° take-off angle. The stationary-crystal stationary-counter method was used with background intensities measured at $2\theta \pm \Delta 2\theta$, where $\Delta 2\theta = 1{\cdot}8 + 1{\cdot}0$ tan θ (Alexander & Smith, 1964). The counting time for each background and for the peak intensity was 10 seconds.

Observed peak-height intensities (I_o) were converted into integrated intensities (I_i) by utilizing a curve of I_i/I_o *versus* 2θ. This curve was determined by manually measuring both the integrated and peak-height intensities of reflections covering the entire 2θ range. The data from which the peak-to-integrated curve was prepared gave a smooth curve, in which the ratio I_i/I_o increases as a function of θ in the expected way (Alexander & Smith, 1962). The crystal orientation

Table 2. *Atomic coordinates and anisotropic thermal parameters* for* $[Co(C_{10}H_8N_2)_2(NO_3)]\ (NO_3)\ (OH)\ .\ 4H_2O$

	x	y	z	$10^4\times\beta_{11}$	$10^4\times\beta_{22}$	$10^4\times\beta_{33}$	$10^4\times\beta_{12}$	$10^4\times\beta_{13}$	$10^4\times\beta_{23}$
Co	0	−0·00644 (3)†	$\frac{1}{4}$	52·2 (4)	27·3 (2)	21·5 (2)	0	−1·1 (2)	0
C(1)	0·1289 (3)	0·0418 (2)	0·4276 (2)	63 (2)	31 (1)	28 (1)	−6 (1)	−3 (1)	1·5 (8)
C(2)	0·2181 (3)	0·0419 (2)	0·5115 (2)	82 (3)	44 (1)	32 (1)	−9 (2)	−12 (2)	0 (1)
C(3)	0·3233 (3)	−0·0079 (2)	0·5175 (2)	81 (3)	50 (2)	44 (2)	−6 (2)	−22 (2)	8 (1)
C(4)	0·3379 (3)	−0·0549 (2)	0·4405 (3)	64 (3)	48 (2)	61 (2)	5 (2)	−9 (2)	8 (1)
C(5)	0·2460 (3)	−0·0527 (2)	0·3588 (2)	64 (2)	40 (1)	45 (2)	7 (1)	0 (1)	2 (1)
C(6)	0·0139 (3)	0·0914 (2)	0·4109 (2)	68 (2)	32 (1)	27 (1)	−5 (1)	3 (1)	0 (1)
C(7)	−0·0143 (3)	0·1500 (2)	0·4729 (2)	90 (3)	44 (1)	35 (1)	−1 (2)	9 (2)	−10 (1)
C(8)	−0·1249 (4)	0·1948 (3)	0·4470 (3)	106 (4)	49 (2)	56 (2)	7 (2)	19 (2)	−15 (2)
C(9)	−0·2034 (4)	0·1784 (3)	0·3618 (3)	84 (3)	52 (2)	63 (2)	19 (2)	11 (2)	−9 (2)
C(10)	−0·1706 (3)	0·1190 (2)	0·3026 (2)	68 (3)	46 (1)	43 (2)	12 (2)	0 (2)	−2 (1)
N(1)	0·1428 (2)	−0·0059 (1)	0·3532 (2)	62 (2)	31 (1)	29 (1)	1 (1)	−2 (1)	2 (1)
N(2)	−0·0629 (2)	0·0765 (2)	0·3260 (2)	61 (2)	33 (1)	28 (1)	2 (1)	3 (1)	−1 (1)
N(3)	0	0·1495 (3)	$\frac{3}{4}$	138 (6)	40 (2)	64 (3)	0	−13 (3)	0
N(4)	0	0·6657 (4)	$\frac{3}{4}$	157 (7)	50 (2)	74 (3)	0	28 (4)	0
O(1)	0	0·2269 (2)	$\frac{3}{4}$	207 (7)	27 (1)	132 (5)	0	−4 (5)	0
O(2)	0·0568 (2)	0·1032 (1)	0·6968 (2)	88 (2)	36 (1)	39 (1)	−7 (1)	1 (1)	7 (1)
O(3)	0·2557 (4)	0·2651 (3)	0·5909 (4)	166 (5)	89 (3)	149 (4)	−4 (3)	−13 (4)	13 (3)
O(4)	0·0494 (5)	0·3389 (3)	0·6227 (3)	215 (6)	80 (2)	104 (3)	25 (3)	15 (4)	5 (2)
O(5)	0·0820 (6)	0·3722 (4)	0·3011 (4)	273 (9)	123 (9)	147 (5)	−68 (5)	−53 (5)	−18 (3)
O(6)	0	0·4548 (4)	$\frac{3}{4}$	316 (12)	66 (3)	112 (5)	0	−26 (6)	0
O(7)	0	0·7398 (4)	$\frac{3}{4}$	490 (21)	47 (3)	226 (10)	0	113 (12)	0
H(2)‡	0·204	0·074	0·566						
H(3)	0·387	−0·009	0·575						
H(4)	0·412	−0·089	0·443						
H(5)	0·259	−0·086	0·306						
H(7)	0·043	0·162	0·532						
H(8)	−0·146	0·236	0·490						
H(9)	−0·282	0·208	0·344						
H(10)	−0·228	0·109	0·243						

* The anisotropic temperature factor has the form $\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.
† Numbers in parentheses are standard deviations in the last significant figures.
‡ Hydrogen atoms are labeled with the same number as the carbon atoms to which they are bonded.

was checked every few hours to ensure that all reflections were well centered. Several standard reflections were measured intermittently to monitor source intensity and possible decomposition. Intensities of the standard reflections were constant within 2% during data collection. Reflections for which the net number of counts did not exceed zero by at least twice the standard deviation (based on counting statistics) were labeled 'unobserved' and were assigned a value equal to one standard deviation. Intensity data were cor-

Table 3. *Observed and calculated structure factors*

The columns are h, l, $10F_o$ and $10F_c$. Unobserved reflections are marked with an L.

h	l	$10F_o$	$10F_c$
[illegible]	[illegible]	[illegible]	[illegible]

Table 3 (*cont.*)

[illegible]

rected for Lorentz and polarization factors. No absorpsorption correction was supplied as the crystal and the linear absorption coefficient (8·0 cm^{-1}) were both small and the crystal was approximately spherical. The average error due to neglect of this correction is estimated to be less than 6%.

Determination and refinement of the structure

All atoms of the structure, except hydrogen atoms, were located by Patterson and Fourier methods, assuming the centric space group. The trial model was then refined anisotropically* to an R factor of 7%. A

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* In the least-squares refinement, (*a*) the quantity minimized is $\sum w^2(|F_o|-|F_c|)^2$; (*b*) the F_o of an 'unobserved' reflection is weighted 0 or 1 depending on whether the corresponding F_c is less or greater than the assigned values of the F_o; (*c*) scattering factors for neutral cobalt, nitrogen, carbon, and hydrogen atoms and for the single negative oxygen atom are taken from *International Tables for X-ray Crystallography*, 1962; (*d*) the conventional R and the weighted R_w indices are defined by the expressions

$$R=\frac{\sum||F_o|-|F_c||}{\sum|F_o|} \text{ and } R_w=\left[\frac{\sum w^2(|F_o|-|F_c|)^2}{\sum w^2 F_o^2}\right]^{\frac{1}{2}};$$

(*e*) no correction for anomalous dispersion is applied as $\Delta F'$ and $\Delta F''$ for Co are small; (*f*) the weighting scheme is $w=1$ for $F_o \leq 46$ and $w=46/F_o$ for $F_o<46$.

difference Fourier synthesis (F_o-F_c), calculated at this point, showed well defined peaks outside the 2,2′-dipyridyl rings near the calculated hydrogen atom positions (Santoro, Mighell, Zocchi & Reimann, 1969). Evidence for the location of the hydrogen atoms attached to the hydroxide ion and to the water molecules was less convincing. Therefore, the final anisotropic refinement was carried out by including only the hydrogen atoms of the 2,2′-dipyridyl rings. These atoms were located at positions calculated after each cycle of refinement and were given an isotropic temperature factor of 4·0 Å^2. After this refinement the R and R_w values were 6·2 and 7·8% respectively. The standard deviation of an observation of unit weight was 1·7.

A difference map calculated at this point revealed no defined peaks or anomalous regions of electron density. Final atomic coordinates, anisotropic thermal parameters, calculated and observed structure factors, and bond distances and angles are given in Tables 2, 3 and 4, respectively. As the refinement of the structure was satisfactory in the space group $C2/c$, no further consideration was given to the acentric space group Cc.

Table 4. *Bond distances and angles for nitratobis-*(2,2′-*dipyridyl*)*cobalt*(III) *hydroxide nitrate tetrahydrate*

Coordination sphere:	
Co—N(1)	1·922 (2) Å
Co—N(2)	1·936 (2)
Co—O(2)	1·888 (2)
N(1)—Co—N(2)	83·27 (9)°
N(1)—Co—O(2)	88·31 (9)
N(2)—Co—N(2′)	93·53 (10)
N(2)—Co—N(1′)	96·35 (9)
O(2)—Co—O(2′)	69·92 (11)
O(2)—Co—N(1′)	92·13 (9)
2,2′-Dipyridyl molecule:	
N(1)—C(5)	1·342 (4) Å
C(5)—C(4)	1·382 (4)
C(4)—C(3)	1·378 (5)
C(3)—C(2)	1·387 (5)
C(2)—C(1)	1·389 (4)
C(1)—N(1)	1·352 (3)
N(2)—C(6)	1·355 (3)
C(6)—C(7)	1·375 (4)
C(7)—C(8)	1·386 (5)
C(8)—C(9)	1·373 (5)
C(9)—C(10)	1·374 (6)
C(10)-N(2)	1·341 (4)
C(1)—C(6)	1·462 (4)
C(5)—N(1)—C(1)	119·9 (2)°
N(1)—C(5)—C(4)	121·2 (3)
C(5)—C(4)—C(3)	119·3 (3)
C(4)—C(3)—C(2)	119·7 (3)
C(3)—C(2)—C(1)	118·5 (3)
C(2)—C(1)—N(1)	121·3 (3)
C(6)—N(2)—C(10)	119·0 (2)
N(2)—C(6)—C(7)	122·0 (3)
C(6)—C(7)—C(8)	118·4 (3)
C(7)—C(8)—C(9)	119·5 (4)
C(8)—C(9)—C(10)	119·6 (4)
C(9)—C(10)-N(2)	121·5 (3)
N(1)—C(1)—C(6)	114·1 (2)
C(1)—C(6)—N(2)	113·8 (2)
C(2)—C(1)—C(6)	124·6 (3)
C(1)—C(6)—C(7)	124·2 (2)
Nitrate groups:	
N(3)—O(2)	1·312 (4) Å
N(3)—O(1)	1·237 (6)
N(4)—O(7)	1·185 (9)
N(4)—O(5)	1·200 (6)
O(2)—N(3)—O(2′)	111·2 (4)°
O(2)—N(3)—O(1)	124·4 (2)
O(7)—N(4)—O(5)	120·3 (4)
O(5)—N(4)—O(5′)	119·3 (6)

Description and discussion of the structure

The cobalt atom, oxygen atom of the hydroxide group, nitrogen atom, and one of the oxygen atoms in each nitrate group are located on the twofold axis. All other atoms occupy general positions. Therefore, the asymmetric unit consists of $\frac{1}{2}$ a cobalt ion, one 2,2′-dipyridyl molecule, two water molecules, $\frac{1}{2}$ of each nitrate ion, and $\frac{1}{2}$ of a hydroxide ion. The crystal structure consists of discrete complex cations $[Co(C_{10}H_8N_2)_2(NO_3)]^{2+}$, hydroxide ions, nitrate ions, and water molecules linked by a network of hydrogen bonds. The packing in the cell and the distances between atoms connected by hydrogen bonds are shown in Fig. 1. For clarity, most of the atoms repeated by the C centering translation have been omitted from Fig. 1. A stereo view of the complex cation is shown in Fig. 2.

The coordination polyhedron is a distorted octahedron (Fig. 3) consisting of a cobalt atom, four nitrogen atoms, and two oxygen atoms. Two 2,2′-dipyridyl molecules and one nitrate group are coordinated to the cobalt atom through four nitrogen atoms and two oxygen atoms. Cobalt–nitrogen bond distances 1·936 (2) and 1·922 (2) Å, are in excellent agreement with those found in $[Co(NH_3)_6]I_3$, [1·936 (15) Å], by Kime & Ibers (1969). These workers indicate that a Co–N bond distance of approximately 1·9 Å is characteristic of Co(III) and is about 0·18 Å shorter than the corresponding distance in Co(II) complexes. Thus, the conclusion regarding the oxidation state of cobalt obtained from spectroscopic data is supported by the bond-distance data.

The 2,2′-*dipyridyl molecule*

This molecule consists of two pyridine rings bonded through C(1)–C(6). Atoms in each ring were found by least-squares analysis to be coplanar to within experimental error. The two rings, however, are not coplanar, the angle between the normals to the planes being 6·25°. The least-squares plane for each ring and the distances of the ring atoms to these planes are given in Table 5. Corresponding bonds in the two crystallographically independent pyridine rings agree with their average to within about one standard deviation. The single bond C(1)–C(6), 1·462 (4) Å, which connects the pyridine rings is shorter than the classical C–C bond, but it is within two standard deviations of the distance reported for molecular 2,2′-dipyridyl, 1·50 (3) Å, by Merritt & Schroeder (1956). The angles N(1)–C(1)–C(6), C(2)-

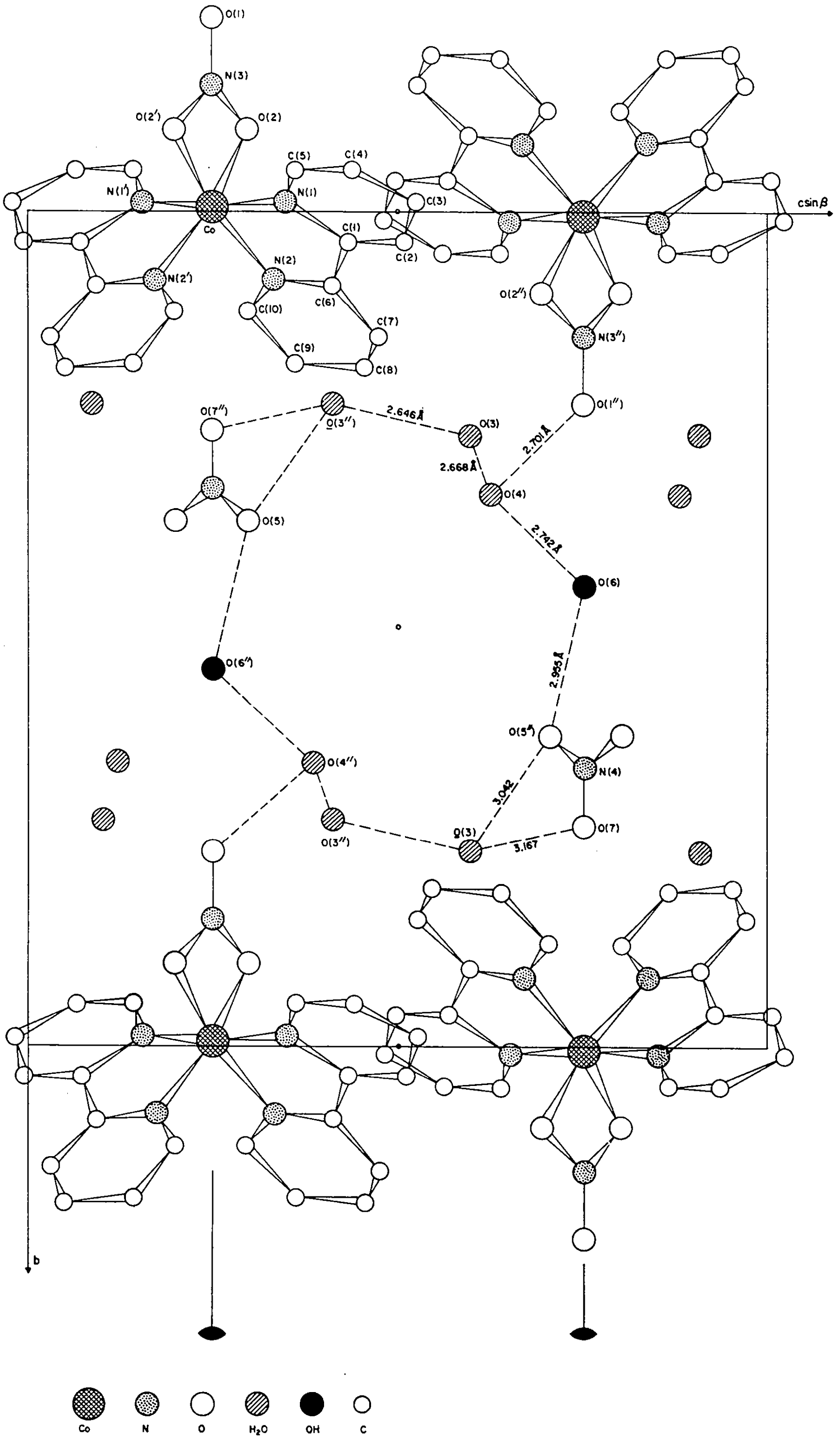


Fig. 1. Crystal structure of $[\mathrm{Co(C_{10}H_8N_2)_2(NO_3)]\ (NO_3)\ (OH).4H_2O}$ projected perpendicularly to the *a* axis. To simplify this figure, atoms repeated by the *C* centering translation are not shown except for O(3). Postulated hydrogen bonds are shown by dashed lines, and all unique distances (Å) are given. Each oxygen atom O(3) is hydrogen-bonded to four oxygen atoms: two hydrogen bonds [O(3)···O(3'') and O(3)···O(4)] are shown near the top of the Figure and the bifurcated one $\left[(\mathrm{O(3)}<\begin{matrix}\mathrm{O(7)}\\ \mathrm{O(5'')}\end{matrix}\right]$ is shown in the lower part of the Figure. Atoms $\underline{\mathrm{O}}(3)$ and O(3) are related by the *C* centering translation.

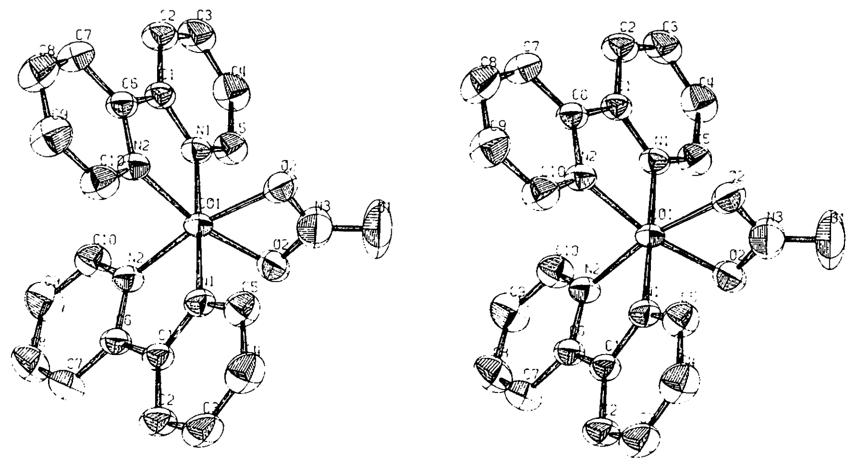


Fig. 2. Stereo view of the complex cation $\mathrm{Co(C_{10}H_8N_2)_2(NO_3)^{2+}}$.

C(1)–C(6), N(2)–C(6)–C(1), and C(7)–C(6)–C(1) show that the 2,2′-dipyridyl molecule is distorted by coordination (Fig. 2). This distortion is very similar to that found in iodobisbipyridinecopper(II) iodide (Barclay, Hoskins & Kennard, 1963) and in diaquo-bis-(2,2′-biimidazole) nickel(II) dinitrate (Mighell, Reimann & Mauer, 1969).

Table 5. *Distances from the ring atoms to the least-squares planes of the two rings of* 2,2′-*dipyridyl*

The equation of a plane in direct space is given by $PX+QY+RZ=S$. For ring I, $P=6{\cdot}0260$, $Q=12{\cdot}179$, $R=-6{\cdot}4607$, $S=-1{\cdot}4829$. For ring II, $P=6{\cdot}2397$, $Q=11{\cdot}196$, $R=-7{\cdot}7643$, $S=-2{\cdot}0763$.

Ring I		Ring II	
N(1)	−0·010 Å	N(2)	0·009 Å
C(1)	0·006	C(6)	−0·003
C(2)	0·003	C(7)	−0·006
C(3)	−0·008	C(8)	0·009
C(4)	0·005	C(9)	−0·004
C(5)	0·005	C(10)	−0·005

The angle between the normals to the two planes is 6·25°.

Nitrate ions

Two crystallographically independent nitrate ions exist in the structure. One coordinates to the cobalt atom through two oxygen atoms, and the other bonds to the hydroxide ion and to the water molecules through hydrogen bonds. The four unique N–O distances range from 1·185(9) to 1·312(4) Å. The shortest of these distances involves the oxygen atom O(7) which is weakly hydrogen-bonded to two water molecules O(3). The longest corresponds to the oxygen atoms coordinated to the cobalt atom. Of the two intermediate N–O distances, the larger one, 1·237(6) Å, involves the oxygen atoms O(1) which form two strong hydrogen bonds with water molecules O(4). The shorter distance, 1·200 (6) Å, involves the oxygen atoms O(5) which are weakly hydrogen-bonded with the hydroxide ion and the water molecule O(3). The O(2)–N(3)–O(2′) angle in the coordinated nitrate group is unusually small (111·2°). The deviation from 120° in this angle forces a 4° decrease of the O–Co–O angle. Reduction in both these angles is probably due to repulsion between Co(III) and N(3) which, even with the angular distortion, are separated by only 2·289 Å.

In a recent review, Addison & Sutton (1967) summarized the available data on the structural properties of nitrate groups in complexes containing coordinated nitrate ions. None of the cases cited by these workers involves crystallographic evidence for bidentate nitrate groups in amine complexes. However, bond distances and angles for bidentate nitrate groups in nitrato complexes are given. Most of the reported $-\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}$ bond angles in $-\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{M}$ structures fall in the 105°–115°

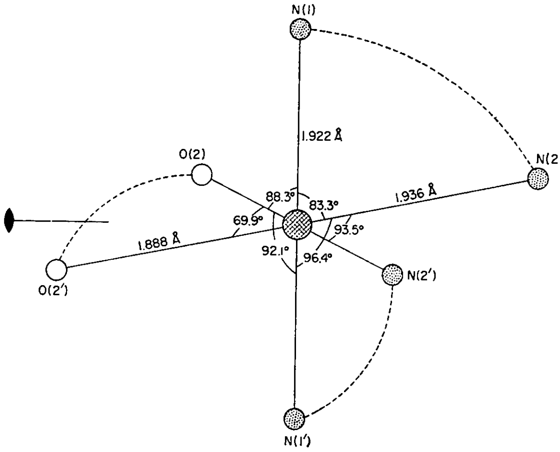
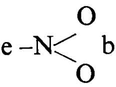
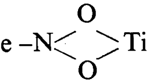
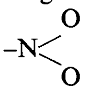


Fig. 3. Sketch of the octahedral coordination about the cobalt atom. Unique bond distances (Å) and angles are indicated. Atoms belonging to the same dipyridine or nitrate group are joined by broken lines.

range, and it is found that the N–O bond distances are longer when the oxygen atoms are coordinated than when they are not. Our results concerning the coordinated nitrate group can be compared with the nitrate groups found in the structure of $\mathrm{Ti(NO_3)_4}$ (Garner & Wallwork, 1966). In this structure, the bidentate configuration is symmetrical as in the present compound. The observed N–O bond distances in the titanium complex are 1·292(8) Å when the oxygen atoms are coordinated and 1·185(4) Å when they are not. The  $-\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}$ bond angle in the  $-\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Ti}$ group is 110·9°. In the cobalt complex, the corresponding distances are 1·313(4) and 1·237(6) Å and the  $-\mathrm{N}{<}^{\mathrm{O}}_{\mathrm{O}}$ bidentate angle is 111·2(4)°. Thus, the bidentate bond angles and the longer N–O bond distances are approximately equal. However, the shorter N–O (noncoordinated) bond distance is longer in the cobalt complex. This greater length is probably due to the fact that in the cobalt complex this oxygen atom is involved in two relatively strong hydrogen bonds.

Hydrogen bonding

The oxygen–oxygen intermolecular distances are shown in Fig. 1. These distances are consistent with hydrogen bonding. However, considering that the hydrogen atoms of the water molecules and of the $\mathrm{OH^-}$ ions have not been located, the existence and nature of such bonding in the structure can only be assumed. In the proposed scheme, the hydroxide ion O(6) acts as a donor in a symmetrical bifurcated hydrogen bond with the nitrate oxygen atoms [O(6)···O(5) distance, 2·955 Å] and as an acceptor in hydrogen bonds with two symmetrically related water molecules [O(6)···O(4), distance 2·742 Å]. Water molecule O(4) is involved in three relatively strong hydrogen bonds. In addition to the hydrogen bond with the hydroxide ion, O(4) is a donor in a hydrogen bond with the oxygen atom O(1) and is an acceptor with a water molecule O(3) having (–O···O–) distances of 2·701 and 2·663 Å, respectively. Finally, water molecule O(3) participates in three hydrogen bonds, one with water molecule O(4), one bifurcated bond with nitrate oxygen atoms O(5) and O(7), and one with a second water molecule symmetrically related to itself. Of the two hydrogen atoms attached to O(3), the first is always involved in the hydrogen bond with O(4). The second is always involved in either the bifurcated hydrogen bond, or the single hydrogen bond with another O(3) molecule. We assumed that for half the time O(3) acts as a donor in the bifurcated hydrogen bond and for the other half O(3) acts as a donor in forming the O(3)···O(3) bond. Therefore on the average, in this proposed scheme, the space-group symmetry is preserved.

All computer calculations on this structure were performed with the *Program System for X-ray Crystallography* (1967) developed at the University of Maryland in collaboration with the National Bureau of Standards and the Geological Survey, and with program *ORTEP* (C. K. Johnson, 1966). The authors would like to thank Mr J. Ritter for having suggested this problem.

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