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Preparation and Crystal Structure of Diaquabis-(1,8-naphthyridine 1-oxide)cobalt(II) Nitrate

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The complex $[Co(napyo)_2(H_2O)_2](NO_3)_2$ was formed by the reaction of cobalt(II) nitrate with 1,8-naphthyridine 1-oxide (napyo) in methanol medium. The complex crystallizes in the monoclinic system, space group $P2_1/n$ with $Z=2$. Lattice parameters are: $a=7.165(2)$, $b=11.797(2)$, $c=11.830(3)$ Å, $\beta=95.14(3)°$, $V=995.9(4)$ Å^3, $D_c=1.705$ g cm^{-3}, $D_o=1.714$ g cm^{-3}, λ(Mo $K\alpha$)=0.71069 Å, $\mu=9.26$ cm^{-1}, $F(000)=522$. The final $R=0.036$ for 1433 unique observed reflections. Co^{2+} ion is coordinated by two nitrogen atoms and four oxygen atoms to form a distorted octahedron.

Many complexes of aromatic amine *N*-oxide with metal ions have been synthesized and characterized in recent twenty years.[1] However any complexes of 1,8-naphthyridine 1-oxide (napyo), which belongs to the kind of aromatic amine *N*-oxide, with transition metal ions have never been reported. In order to investigate the coordinating power of napyo with transition metal ions we recently synthesized a series of complexes of napyo with 3d metal ions. The present paper reports on the synthesis and crystal and molecular structure of the title compound.

Experimental

Preparation of $[Co(napyo)_2(H_2O)_2](NO_3)_2$. 0.1 mmol $Co(NO_3)_2\cdot 6H_2O$ and 0.2 mmol napyo[2] were dissolved in 40 ml methanol. Then the solution was placed in a desiccator with $CaCl_2$ at room temperature. After about two weeks pink needle-like crystals of the title compound were obtained. Calcd for $C_{16}H_{16}CoN_6O_{10}$: C, 37.59; H, 3.15; N, 16.44; Co, 11.53%. Found: C, 37.70; H, 3.21; N, 16.13; Co, 11.79%).

Crystal Structure Determination of $[Co(napyo)_2(H_2O)_2](NO_3)_2$. Crystal Data: $C_{16}H_{16}CoN_6O_{10}$, M=511.27, monoclinic, space group $P2_1/n$, $a=7.165(2)$, $b=11.797(2)$, $c=11.830(3)$ Å, $\beta=95.14(3)°$, $V=995.9$ Å^3, $Z=2$, $D_c=1.705$ g cm^{-3}, D_o (flotation in CCl_4/CH_2I_2)=1.714 g cm^{-3}, λ(Mo $K\alpha$)=0.71069 Å, $\mu=9.26$ cm^{-1}, $F(000)=522$.

A crystal of approximate dimension 0.2×0.2×0.3 mm was selected for the data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan. 25 reflections were used for measuring lattice parameters. 1928 independent reflections were collected in the range of $2°\leqslant 2\theta\leqslant 50°$. 1433 reflections with $I>3\sigma(I)$ were used in the structure determination and refinement. The intensity data were corrected for LP effect and empirical absorption. The structure was solved by the direct method and Fourier techniques, refined by full-matrix least-squares with anisotropic temperature parameters for all non-hydrogen atoms and isotropic thermal parameters for H atoms. Atomic scattering factors were taken from Ref. 3. All calculations were done by using computer programs from the Enraf-Nonius SDP package.[4] Final $R=0.036$, $R_w=0.038$.

Results and Discussion

The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1,[5] selected bond lengths and bond angles in Tables 2 and 3. The equations of the least-squares planes concerned, deviations of atoms and dihedral angles between these planes are given in Table 4. The structure of complex cation $[Co(napyo)_2(H_2O)_2]^{2+}$ and the packing of the molecules in the unit cell are presented in Figs. 1 and 2, respectively. The crystal of the complex consists of discrete $[Co(napyo)_2(H_2O)_2]^{2+}$ cations and nitrate group anions. All the atoms in both napyo rings are fairly coplanar, as shown in Table 4. It can be seen from Fig. 1 that the cobalt atom locates at the inversion center of the complex cation and is bonded to two oxygen atoms and two nitrogen atoms of two different napyo ligands and two oxygen atoms of two water molecules. The six coordinating bonds are nearly equal in length (2.037—2.096 Å) but the three coordinating planes (Table 4) are not strictly vertical with each other. So the coordinated configuration of Co atom is a distorted octahedron.

Table 1. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors

Atom	x/a	y/b	z/c	B_{eq}/Å$^{2\,a)}$
Co	0.0000	0.0000	0.0000	2.59(1)
O(1)	0.2120(4)	0.0498(2)	−0.0925(2)	3.73(5)
O(2)	0.1640(4)	0.0439(2)	0.1478(2)	4.36(6)
O(21)	−0.6090(4)	0.2315(2)	−0.8790(2)	4.42(6)
O(22)	−0.5608(5)	0.4070(3)	−0.8414(3)	6.42(8)
O(23)	−0.8117(4)	0.3313(3)	−0.8034(3)	7.49(8)
N(1)	0.2083(4)	0.1586(2)	−0.1170(2)	3.02(6)
N(2)	−0.0668(4)	0.1711(2)	−0.0293(2)	2.98(6)
N(21)	−0.6605(4)	0.3234(3)	−0.8417(2)	3.21(6)
C(1)	0.3434(5)	0.2052(4)	−0.1717(3)	4.04(8)
C(2)	0.3381(6)	0.3183(4)	−0.1995(3)	5.3(1)
C(3)	0.2000(6)	0.3844(3)	−0.1734(3)	4.83(9)
C(4)	0.0548(5)	0.3395(3)	−0.1151(3)	3.30(7)
C(5)	0.0614(5)	0.2250(3)	−0.0859(3)	2.63(6)
C(6)	−0.1026(6)	0.3997(3)	−0.0832(4)	4.62(9)
C(7)	−0.2320(6)	0.3443(4)	−0.0258(4)	4.47(9)
C(8)	−0.2073(5)	0.2302(3)	−0.0004(3)	3.54(8)

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3\cdot(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cdot\cos\alpha)$.

Table 2. Bond Lengths l/Å

Co-O(1)	2.037(3)	N(2)-C(5)	1.350(6)
Co-O(2)	2.083(3)	N(2)-C(8)	1.295(5)
Co-N(2)	2.096(3)	C(1)-C(2)	1.374(6)
O(1)-N(1)	1.316(4)	C(2)-C(3)	1.318(6)
O(21)-N(21)	1.239(4)	C(3)-C(4)	1.402(6)
O(22)-N(21)	1.218(4)	C(4)-C(5)	1.394(5)
O(23)-N(21)	1.215(4)	C(4)-C(6)	1.413(6)
N(1)-C(1)	1.330(5)	C(6)-C(7)	1.364(6)
N(1)-C(5)	1.388(4)	C(7)-C(8)	1.352(5)

Table 3. Bond Angles θ/°

O(1)-Co-O(2)	89.3(1)	C(3)-C(4)-C(6)	125.9(3)
O(1)-Co-N(2)	101.3(1)	C(5)-C(4)-C(6)	115.5(3)
O(2)-Co-N(2)	89.9(1)	N(1)-C(5)-C(4)	119.4(3)
O(1)-Co-O(1′)	180.0(0)	N(2)-C(5)-C(4)	124.2(3)
O(2)-Co-O(2′)	180.0(0)	N(2)-C(5)-N(1)	116.4(4)
N(2)-Co-N(2′)	180.0(0)	C(4)-C(6)-C(7)	119.2(4)
O(1)-N(1)-C(1)	120.5(3)	C(6)-C(7)-C(8)	120.3(3)
O(1)-N(1)-C(5)	119.6(3)	C(7)-C(8)-N(2)	123.4(4)
C(1)-N(1)-C(5)	119.9(3)	C(8)-N(2)-C(5)	117.4(3)
N(1)-C(1)-C(2)	120.8(4)	O(21)-N(21)-O(22)	121.1(3)
C(1)-C(2)-C(3)	121.6(4)	O(21)-N(21)-O(23)	120.3(3)
C(2)-C(3)-C(4)	119.8(4)	O(22)-N(21)-O(23)	118.6(3)
C(3)-C(4)-C(5)	118.6(3)		

Table 4. Least-Squares Planes,[a] the Deviations of Atoms (l/Å)[b] and Dihedral Angles between the Planes (θ/°)

Plane (1) [C(1), C(2), C(3),C(4), C(5), C(6), C(7), C(8), N(1), N(2)]
$-0.4376X-0.2277Y-0.8699Z-0.0468=0$
C(1), 0.006; C(2), −0.010; C(3), −0.009; C(4), −0.004; C(5), −0.003; C(6), 0.015; C(7), 0.009; C(8), −0.012; N(1), 0.019; N(2), −0.011

Plane (2) [C(1′), C(2′), C(3′), C(4′), C(5′), C(6′), C(7′), C(8′), N(1′), N(2′)]
$-0.4376X-0.2277Y-0.8699Z+0.0468=0$
C(1′), −0.006; C(2′), 0.010; C(3′), 0.009; (4′), 0.004; C(5′), 0.003; C(6′), −0.015; C(7′), −0.009; C(8′), 0.012; N(1′), −0.019; N(2′), 0.011

Plane (3) [Co, O(1), O(2), O(1′), O(2′)]
$-0.3742X+0.9257Y-0.0563Z=0$

Plane (4) [Co, O(1), N(2), O(1′), N(2′)]
$-0.4774X-0.2497Y-0.8425Z=0$

Plane (5) [Co, O(2), N(2), O(2′), N(2′)]
$0.8460X+0.0979Y-0.5241Z=0$

Plane No.	Plane No.	Dihedral Angle
(1)	(2)	0.0
(1)	(3)	89.9
(1)	(4)	3.0
(1)	(5)	86.4
(2)	(3)	89.9
(2)	(4)	3.0
(2)	(5)	86.4
(3)	(4)	90.3
(3)	(5)	101.3
(4)	(5)	89.2

a) X, Y, and Z in the equations of the planes are orthogonalized coordinates. b) Deviations of the atoms in Planes (3), (4), and (5) are 0.000.

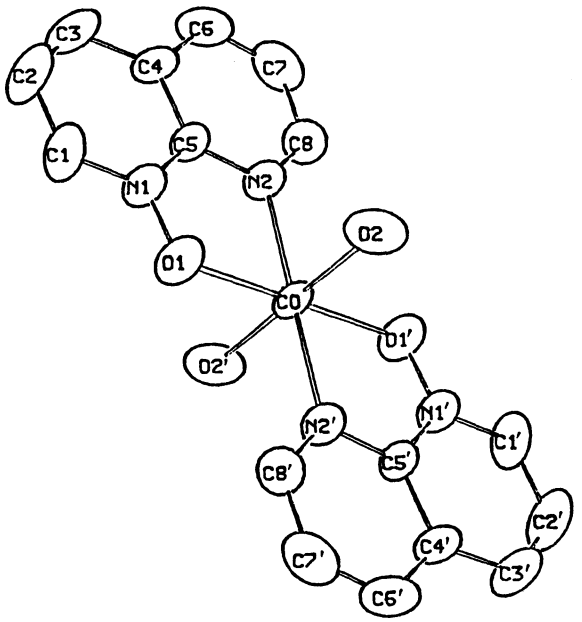

Fig. 1. The structure of the complex cation $[Co(napyo)_2(H_2O)_2]^{2+}$.

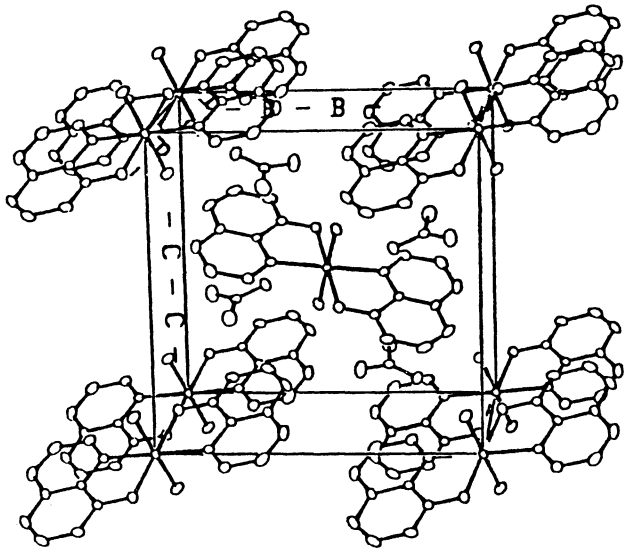

Fig. 2. The packing of the molecules in the unit cell.

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5) Atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and F_o-F_c tables are deposited as Document No. 8846 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.