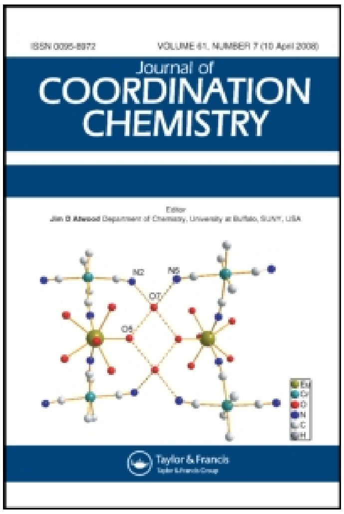

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THE POLYMERIC COPPER(II) COMPLEX, 2,2'-BIPYRIDINE-*N,N'*-(μ-NICOTINATO-*O, O'*:*N*) MONOAQUACOPPER (II) NITRATE DIHYDRATE

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THE POLYMERIC COPPER(II) COMPLEX, 2, 2'-BIPYRIDINE-*N*, *N*'-(μ-NICOTINATO-*O,O*' :*N*) MONOAQUACOPPER (II) NITRATE DIHYDRATE

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The nicotinate complex of Cu(II), 2,2'-bipyridine(nicotinato)monoaquacopper(II) nitrate dihydrate has been prepared and its crystal structure has been determined by means of X-ray methods. The nicotinate anions bridge adjacent Cu(II) atoms through both the pyridine N atom and the carboxyl group to form infinite chains. The carboxyl group of the nicotinate anion coordinates to the Cu(II) atom as a chelate. Based on the molecular structure the infrared spectrum is discussed.

Keywords: nicotinate bipyridyl; copper(II); crystal structure

INTRODUCTION

Because nicotinic and isonicotinic acid play important roles in the metabolism of all living cells, much interest have been directed towards their metal complexes. Previous structure determinations of nicotine or isonicotine complexes have revealed that the nicotinate or isonicotinate anion in transition metal complexes coordinates *via* either the pyridine N atom or one carboxylic O atom[1–5] while in lanthanide complexes they coordinate by a chelating carboxyl group.[6–7] In recent years, structural research on complexes bridged by heterocyclic aromatic molecules and their derivatives has been continuing in our laboratory.[8] As part of this research, a series of complexes bridged by nicotinate or isonicotinate has

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* On leave from Shangrao Normal School as a visiting scholar.

been synthesized, among which the structure of the title complex, [Cu(bipy)(nic)$(H_2O)]NO_3 \cdot 2H_2O$ (where bipy = 2, 2′-bipyridine, nic = the monoanion of nicotinic acid) has been determined by X-ray diffraction. The nicotinate anion in this complex is contrary to those found in other transition metal complexes reported but similar to that found in lanthanide complexes. We present here the crystal structure of the title complex and discuss its infrared spectrum, based on the molecule structure.

EXPERIMENTAL

Preparation

Some 0.604 g (2.5 mmol) of $Cu(NO_3)_2$ and 0.390 g (2.5 mmol) of 2, 2′-bipyridine were dissolved in 40 cm^3 of a mixture of ethanol and water. The mixture solution was heated for 1 h at 75 °C, then 20 cm^3 of an aqueous solution containing 0.308 g (2.5 mmol) of nicotinic acid and 0.100 g (2.5 mmol) of NaOH was slowly added with continuous stirring for 0.5 h at 75 °C. The resulting solution was filtered and slowly cooled to room temperature. After several days, well-shaped, dark blue single crystals were obtained.

Nitrogen, carbon and hydrogen were analyzed with a Carlo Erba 1160 Elemental Analyzer. Anal. calcd. for $CuC_{16}H_{18}N_4O_8$: C, 41.93; N, 12.23; H, 3.93%. Found: C, 42.41; N, 12.44; H, 4.19%.

Infrared Measurements

Infrared spectra were recorded with a Perkin-Elmer 683 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate and a Nicolet FTIR 170sx spectrophotometer (500–100 cm^{-1}) employing CsI pellets.

Crystal structure determination

Diffraction intensity data were collected on a Nonius CAD-4 diffractometer up to a 2θ value of 50° with graphite-monochromatized MoKα radiation. The ω-2θ scan technique was employed at a 2θ scan rate of 5.5° min^{-1} with scan width of $\Delta\theta = (0.95 + 0.35 \tan \theta)°$. Three standard reflections measured at regular intervals showed no intensity decrease throughout the data collection. A total of 3271 independent reflections was collected, of which 2181 were considered as observed [$I \geq 3\sigma(I)$] and used for the structure determination and refinement. Usual Lp and empirical absorption corrections were applied.

The structure was solved by Patterson method followed by Fourier syntheses. The structure refinement was carried out by full-matrix least-squares procedures using the TEXSAN program.[9] H atoms were located in a difference Fourier map. Anisotropic refinement including all the non-H atoms converged to agreement factors $R = 0.052$ and $R_w = 0.057$, where $w = 1/\sigma^2$ (F). Atomic scattering factors were taken from *International Tables for X-ray Crystallography.*[10] All computations were performed on a Micro VAX 3100 computer.

RESULTS AND DISCUSSION

Crystal structure

Crystal data: $C_{16}H_{18}CuO_8N_4$, M = 457.88, triclinic, space group $P1$, $a = 7.954(5)$, $b = 10.061(6)$, $c = 11.955(4)$Å, $\alpha = 92.47(4)$, $\beta = 96.64(5)$, $\gamma = 99.58(4)$°, $V = 935(2)$ Å^3, $Z = 2$, $Dc = 1.626$ g/cm^{-3}, $F(000) = 470$, μ(Mo-Kα) = 12.71 cm^{-1}.

Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table I.[†] Bond distances and angles are listed in Table II. The Cu(II) atom has distorted octahedral coordination as shown in Figure 1. Two N atoms of a 2,2′-bipyridine ligand coordinate to the Cu(II) atom in the equatorial plane with an average Cu—N distance of 1.997Å. A water molecule occupies another equatorial position with Cu—O 1.958Å. Two nicotinate anions related by translation along the *a* axis, coordinate to Cu (II) atom through the terminal carboxyl group and the pyridine N atom, respectively. The Cu—N3 distance of 2.227Å is about 0.23Å longer than (1.998Å) found in a copper (II) isonicotinate;[5] this suggests that the pyridine N atom in the title complex is axial and coordination is relatively weak. One remarkable feature of this structure is that the carboxyl group of the nicotinate anion coordinates to the Cu(II) atom as a chelate with a quite small 02*—Cu—03* chelating angle of 56.4°. This coordination mode is contrary to those found in six-coordinate nicotinate or isonicotinate complexes reported so far,[1–5] but similar to that found in nicotinate or isonicotinate complexes with a higher coordination number (for example, in the eight-coordinate Pb(II) complex of nicotinate,[11] in the Pb(II) complex of isonicotinate[12] and in the eight-coordinate lanthanide complexes of nicotinate).[6–7] One carboxylic O atom coordinates to the Cu(II) atom in the equatorial plane with a Cu—03* distance of 2.018Å while another carboxylic O atom makes a contact with the Cu(II) atom in the axial direction with Cu—02* equal to 2.547 Å. That the axial coordinate distance is about 0.5 Å longer than the value in the equatorial plane is consistent with other octahedral Cu(II) complexes.[13] With the small chelating angle, not only does

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[†] Full lists of H atom positions, an isotropic thermal parameters for non-H atoms and observed and calculated structure factors are available from the authors upon request.

the 02* atom deviate from the axial direction of the Cu(II) atom [02*—Cu—N3=153.7°] but the 03* atom also deviates by 0.457Å from the equatorial plane defined by Cu, 01, N1 and N2. This implies that the atomic orbitals of the carboxylic O atoms cannot maximally overlap with the *d* orbitals of the Cu(II) atom. Together with the fact that Cu—02* is much longer than Cu—03*, 02—C16 (1.233(8)Å) is significantlly shorter than 03—C16 (1.297(8)Å). The long Cu—02* distance may result in different ν(Cu—O) values in the IR spectra, as discussed below. The pyridine ring of the nicotinate anion is coplanar with the carboxyl group and perpendicular to the equatorial plane, its spatial orientation seems to depend on van der Waals contacts between the pyridine ring and the coordinated atoms, 03*—C11 and N1—C15 distances being 3.357 and 3.363Å, respectively.

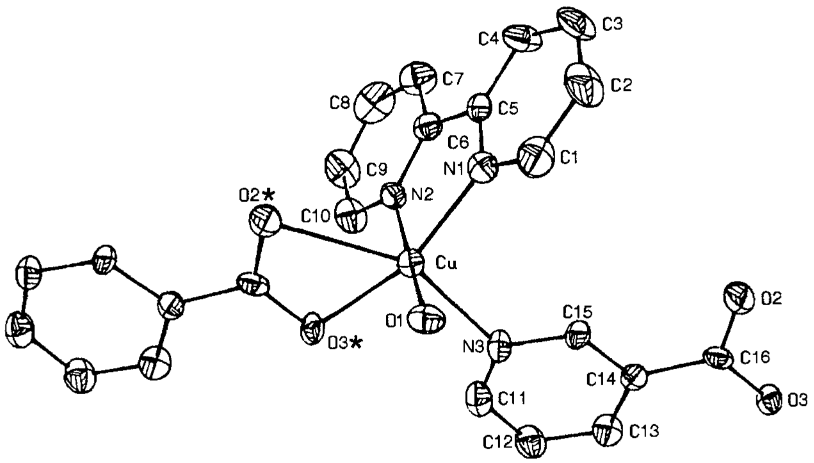

FIGURE 1 Molecular structure of the title complex with 50% probability displacement ellipsoids. H atoms are omitted for clarity.

TABLE I Fractional coordinates and equivalent isotropic thermal parameters for non-H atoms

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}(Å^2)$
Cu	0.1032(1)	0.0033(1)	0.21025(7)	1.73(3)
O1	0.0704(6)	−0.1527(5)	0.1014(4)	2.2(2)
O2	0.7820(6)	−0.0445(6)	0.2245(4)	2.9(2)
O3	0.9293(6)	0.0899(5)	0.1158(4)	1.9(2)
O4	0.446(1)	0.4142(8)	0.3046(7)	7.3(4)
O5	0.713(1)	0.4337(8)	0.2841(6)	5.5(3)
O6	0.554(1)	0.5603(8)	0.2013(7)	7.6(4)
O7	−0.1236(8)	−0.3949(6)	0.1057(5)	4.5(3)
O8	0.167(1)	−0.5083(8)	0.1251(6)	7.1(4)
N1	0.2118(8)	−0.0951(6)	0.3335(5)	2.0(2)

TABLE I *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}(Å^2)$
N2	0.1193(7)	0.1403(6)	0.3379(4)	1.8(2)
N3	0.3343(7)	0.0955(6)	0.1341(5)	2.0(2)
N4	0.572(1)	0.4720(8)	0.2641(6)	3.9(3)
C1	0.263(1)	-0.2155(8)	0.3246(7)	3.1(2)
C2	0.332(1)	-0.2741(9)	0.4147(8)	3.5(4)
C3	0.351(1)	-0.210(1)	0.5199(7)	3.7(4)
C4	0.299(1)	-0.086(1)	0.5297(6)	3.1(3)
C5	0.2332(9)	-0.0319(8)	0.4371(6)	1.9(3)
C6	0.1803(9)	0.1029(8)	0.4377(6)	1.9(3)
C7	0.192(1)	0.1865(9)	0.5348(6)	3.0(3)
C8	0.142(1)	0.310(1)	0.5245(8)	3.8(4)
C9	0.084(1)	0.3490(8)	0.4228(7)	3.2(4)
C10	0.071(1)	0.2614(8)	0.3293(6)	2.6(3)
C11	0.338(1)	0.1994(8)	0.0738(6)	2.6(3)
C12	0.485(1)	0.2646(8)	0.0324(6)	2.7(3)
C13	0.634(1)	0.2150(7)	0.0586(6)	2.3(3)
C14	0.6351(9)	0.1045(7)	0.1213(5)	1.7(3)
C15	0.4803(8)	0.0467(8)	0.1574(5)	1.7(3)
C16	0.787(1)	0.0432(7)	0.1553(5)	1.8(3)

TABLE II Selected bond distances (Å) and angles (°)

Cu—O1	1.958(5)	Cu—O2*	2.547(5)
Cu—O3*	2.018(5)	Cu—N1	2.004(6)
Cu—N2	1.990(6)	Cu—N3	2.227(6)
O2—C16	1.233(8)	O3—C16	1.297(8)
N1—C1	1.35(1)	N1—C5	1.347(8)
N2—C6	1.330(9)	N2—C10	1.34(1)
N3—C11	1.29(1)	N3—C15	1.340(9)
C1—C2	1.35(1)	C2—C3	1.37(1)
C3—C4	1.38(1)	C4—C5	1.35(1)
C5—C6	1.49(1)	C6—C7	1.39(1)
C7—C8	1.38(1)	C8—C9	1.35(1)
C9—C10	1.38(1)	C11—C12	1.39(1)
C12—C13	1.37(1)	C13—C14	1.37(1)
C14—C15	1.395(9)	C14—C16	1.47(1)
N4—O4	1.23(1)	N4—O5	1.25(1)
N4—O6	1.20(1)		
O1—Cu—O2*	88.7(2)	O1—Cu—O3*	91.9(2)
O1—Cu—N1	92.7(2)	O1—Cu—N2	170.5(2)
O1—Cu—N3	89.9(2)	O2*—Cu—O3*	56.4(2)
O2*—Cu—N1	105.6(2)	O2*—Cu—N2	86.2(2)
O2*—Cu—N3	153.7(2)	O3*—Cu—N1	161.3(2)
O3*—Cu—N2	91.8(2)	O3*—Cu—N3	97.5(2)
N1—Cu—N2	81.1(2)	N1—Cu—N3	100.6(2)
N2—Cu—N3	98.2(2)	Cu—N3—C11	123.4(5)
Cu—N3—C15	118.6(5)	O2—C16—O3	121.3(7)
O2—C16—C14	120.6(6)	O3—C16—C14	118.0(6)
C13—C14—C16	125.1(6)	C15—C14—C16	117.4(6)
O4—N4—O5	120 (1)	O4—N4—O6	119 (1)
O5—N4—O6	121.3(9)		

The crystal consists of polymeric molecules. Through both the terminal carboxyl group and the pyridine N atom, the nicotinate anions bridge Cu(II) atoms to form infinite chains along the *a* axis as shown in Figure 2. An extentive H-bonding network exists in the crystal, the adjacent polymeric chains being connected by H-bonding between O1 and O3* and the nitrate group being connected to the polymeric chain through H-bonding to oxygen atoms of coordinated and crystalline water.

Infrared spectra

The stretching vibration of the carboxyl group in nicotinate and isonicotinate complexes has been extensively discussed in the literature. For a pyridine *N*-coordinated complex both ν(C═O) and ν(C—O) values are similar to those found for the free ligand;[14] for the chelated lanthanide complex, both values shift to lower frequency,[7] and for unidentate complexes coordinated by the carboxyl group the ν(C—O) value decreases while the Δν[ν(C═O)-ν(C—O)] value increases with respect to the free ligand.[1,15] It is notable that for the title complex both ν(C═O) [1577 cm^{-1}] and ν(C—O) [1393 cm^{-1} bands move to lower frequency as in the lanthanide complex quoted above. The ν(C—O) value of 1393 cm^{-1} corresponds with that (1392 cm^{-1}) reported for a Cu(II) complex[1] and a Zn(II) complex.[15] The ν(C═O) value of 1577 cm^{-1} is 25 cm^{-1} smaller than the value for the free ligand.

Far infrared spectra of the title complex and nicotinic acid are shown in Figure 3. For the title complex below 450 cm^{-1}, three new bands were observed,

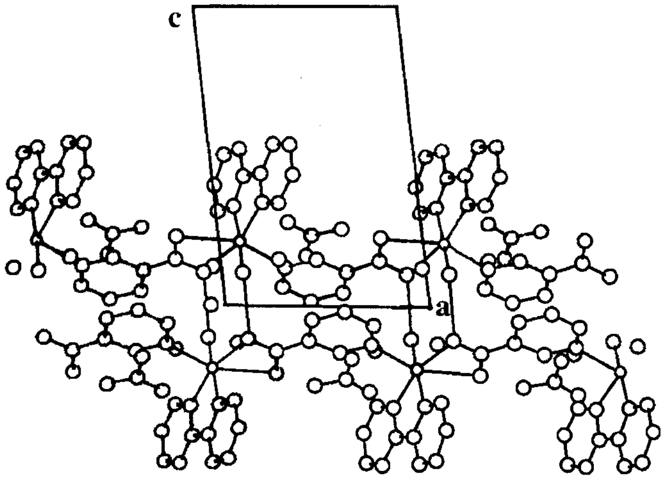

FIGURE 2 Packing diagram of polymeric chains in the unit cell.

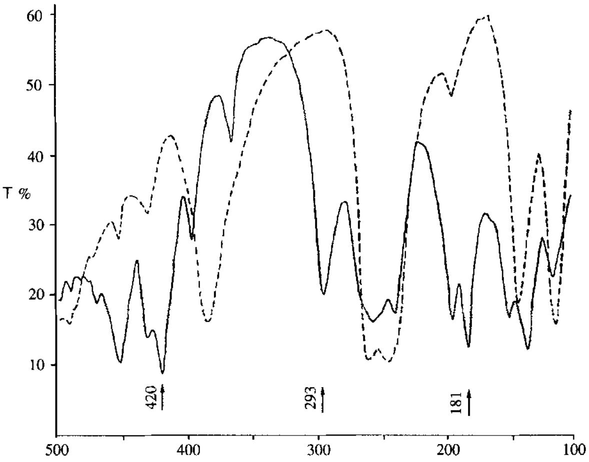

FIGURE 3 Far infrared spectrum of the title complexed (—) together with that of nicotinic acid (---)

among which the band at 293 cm^{-1} is assigned to ν(Cu—N). This is in agreement with frequencies found for Cu(nic)$_2$X$_2$[14] and Cu(i-nic)$_2$X$_2$[16] in that in each complex the pyridine N atom was proposed to coordinate to a Cu(II) atom in the axial direction, as in the title complex. However, the frequency is significantly smaller than values found in other transition metal complexes of nicotinate [Cr(II) 310 cm^{-1}, Co(II) 350 cm^{-1} and Ni(II) 365cm^{-1}][17] and seems to be contrary to the Irving-Williams series.[18] However, considering differences in coordination, *i.e.*, the pyridine N atom coordinates[2] to the Cr(II) atom in the equatorial plane with Cr—N 2.128Å but to the Cu(II) atom in the axial direction with Cu—N 2.227 Å, the ν(Cu—N) shift to lower frequency indicates weaker *N*-coordination in the axial direction for the title complex. The remaining bands at 420 cm^{-1} and 181 cm^{-1} are considered to be due to ν(Cu—O).

The 420 cm^{-1} band is in agreement with ν(Co—O) values for a series of cobalt(II) carbonates;[19] the band at 181 cm^{-1} is less than that at 222 cm^{-1} for the glycinate complex of Co(II) and that at 234 cm^{-1} for the glycinate complex of Ni(II)[20]. This difference is considered to result from the long Cu—O distance in the axial direction for the title complex.

Acknowledgments

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