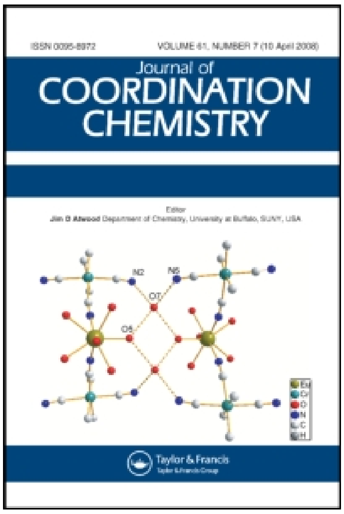

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THE POLYMERIC COMPLEX 1, 10-PHENANTHROLINE-N, *N'*-(μ-NICOTINATO-*N, O*)DIAQUACOPPER(II) NITRATE DIHYDRATE

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THE POLYMERIC COMPLEX 1,10-PHENANTHROLINE-*N,N'*-(μ-NICOTINATO-*N,O*)DIAQUACOPPER(II) NITRATE DIHYDRATE

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The title complex has been prepared and its structure determined by X-ray diffraction methods. The complex crystallizes space group $P2_1/a$ with a = 12.833(3), b = 10.443(2), c = 16.628(2)Å, β = 111.686(9)°. The nicotinate anions bridge adjacent Cu(II) atoms through both the pyridine N atom and the carboxyl O atom to form zigzag polymeric chains along the *b* axis. The carboxyl group of the nicotinate anion coordinates to the Cu(II) atom as a unidentate. Based on the molecular structure the infrared spectrum is discussed.

Keywords: nicotinate, phenanthroline, copper(II), crystal structure

INTRODUCTION

In recent years, structure research on complexes bridged by heterocyclic aromatic molecules and their derivatives has been continuing in our laboratory. [1]Because isonicotinic and nicotinic acids play important roles in the metabolism of all living cells and much interest have been directed towards their metal complexes, a series of complexes bridged by the nicotinate or isonicotinate anion has been synthesized, among which the structure of [Cu(bipy)(nic)(H_2O-)]NO_3·$2H_2O$ (bipy = 2,2'-bipyridyl) has been determined by X-ray methods and the chelating configuration of the carboxyl group of the nicotinate anion has been described. [2] As part of this research we present here the crystal structure of another nicotinate complex, [Cu(phen)(nic)$(H_2O)_2$]NO_3·$2H_2O$ (where nic = the monoanion of nicotinic acid, phen = 1,10-phenanthroline).

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EXPERIMENTAL

Preparation

The title complex was synthesized in a manner similar to the bipy complex[2] but 0.500 g of 1,10-phenanthroline was used instead of 0.390 g of 2,2′-bipyridyl. The resulting solution was filtered and slowly cooled to room temperature. After one month well-shaped, blue, single crystals were obtained. *Anal.* Calcd. for $CuC_{18}H_{20}N_4O_9$ (%): C, 43.23; N, 11.21; H, 4.04. Found: C, 43.55; N, 11.46; H, 4.29.

Infrared Measurements

Infrared spectra were recorded with a Perkin Elmer 683 spectrophotometer (4000-400 cm^{-1}) using 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 Rigaku AFC5R diffractometer up to a 2ϑ value of 50° with graphite-monochromatized Mo$K\alpha$ radiation. The ω-2ϑ scan technique was employed at a ω scan rate of 16.0° min^{-1} with scan width $\Delta\omega = (0.89 + 0.30 \tan\vartheta)°$. A total of 3873 independent reflections was collected, of which 2406 observed reflections $[I > 3\sigma(I)]$ were used for the structure refinement. Lp correction and empirical absorption $[T_{min} = 0.826, T_{max} = 0.999]$ correction were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Refinement was carried out by full-matrix least-squares methods. H atoms were located in a difference Fourier map. Anisotropic refinement including all the non-H atoms converged to agreement $R = 0.048$ and $R_w = 0.041$, where $w = 1/\sigma^2(F)$. The highest peak in the final difference Fourier map was 0.44 e $Å^{-3}$. Atomic scattering factors were taken from *International Table for X-ray Crystallography*.[3] All calculations were performed using the *TeXsan* crystallographic software package.[4]

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{18}H_{20}N_4O_9Cu$, $M = 499.92$, monoclinic, space group $P2_1/a$, $a = 12.833(3)$, $b = 10.443(2)$, $c = 16.628(2)$Å, $\beta = 111.686(9)°$, $V = 2070.7(6)Å^3$, $Z = 4$, $D_c = 1.603$ g cm^{-3}, $F(000) = 1028$, μ(Mo-Kα) = 11.15 cm^{-1}.

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

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cu	0.17545(6)	0.08457(7)	−0.20598(4)	2.30(1)
O(1)	0.1469(3)	0.1806(3)	−0.1156(2)	2.59(9)
O(2)	0.3089(3)	0.2886(4)	−0.0652(2)	3.5(1)
O(3)	0.8355(6)	0.396(1)	0.1673(4)	17.4(4)
O(4)	0.9769(5)	0.3118(5)	0.2547(4)	6.7(2)
O(5)	0.8485(5)	0.3900(6)	0.2917(4)	8.0(2)
O(6)	0.3348(3)	0.2133(4)	−0.2132(2)	3.5(1)
O(7)	0.0066(3)	−0.0483(4)	−0.2181(2)	3.9(1)
O(8)	0.5921(4)	0.4786(5)	0.0955(3)	6.9(2)
O(9)	0.2959(3)	0.4334(4)	−0.3241(2)	4.9(1)
N(1)	0.1858(3)	−0.0061(4)	−0.3120(3)	2.3(1)
N(2)	0.0777(3)	0.2052(4)	−0.2983(3)	2.2(1)
N(3)	0.2153(4)	0.4679(4)	0.1193(3)	2.5(1)
N(4)	0.8866(6)	0.3648(7)	0.2352(5)	5.7(2)
C(1)	0.2354(5)	−0.1143(5)	−0.3189(3)	2.8(1)
C(2)	0.2466(5)	−0.1531(6)	−0.3954(4)	3.6(2)
C(3)	0.2028(5)	−0.0781(7)	−0.4678(4)	3.7(2)
C(4)	0.1469(4)	0.0345(6)	−0.4646(3)	2.8(1)
C(5)	0.0932(5)	0.1179(6)	−0.5371(4)	3.5(2)
C(6)	0.0379(5)	0.2212(6)	−0.5308(4)	3.6(2)
C(7)	0.0275(5)	0.2572(6)	−0.4502(3)	2.9(1)
C(8)	−0.0332(5)	0.3625(6)	−0.4388(4)	3.9(2)
C(9)	−0.0368(5)	0.3864(6)	−0.3586(4)	3.9(2)
C(10)	0.0212(5)	0.3056(6)	−0.2888(4)	3.1(1)
C(11)	0.0814(4)	0.1799(5)	−0.3777(3)	2.3(1)
C(12)	0.1398(4)	0.0674(5)	−0.3848(3)	2.3(1)
C(13)	0.2451(4)	0.4084(5)	0.0593(3)	2.4(1)
C(14)	0.1749(4)	0.3240(5)	−0.0002(3)	2.2(1)
C(15)	0.0714(4)	0.2999(5)	0.0025(3)	2.6(1)
C(16)	0.0392(4)	0.3607(6)	0.0629(3)	2.9(1)
C(17)	0.1124(4)	0.4453(5)	0.1192(3)	2.6(1)
C(18)	0.2157(5)	0.2611(5)	−0.0657(3)	2.4(1)

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I[‡]. Selected bond distances and angles are listed in Table II. The Cu(II) atom has elongated octahedral coordination as shown in Figure 1. Two N atoms of a 1,10-phenanthroline ligand coordinate to a Cu(II) atom in the equatorial plane with an average Cu-N distance of 2.035Å. Two nicotinate anions, related by a screw axis, coordinate to the Cu(II) atom in the equatorial plane through a pyridine N atom and a terminal carboxyl group, respectively. The Cu-N(3) distance of 2.008(4)Å is significantly shorter than the

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

TABLE II Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses.

Cu-O(1)	1.951(3)	Cu-O(6)	2.487(4)
Cu-O(7)	2.518(4)	Cu-N(1)	2.048(4)
Cu-N(2)	2.023(4)	Cu-N(3)[a]	2.008(4)
O(1)-C(18)	1.278(6)	O(2)-C(18)	1.227(6)
N(1)-C(1)	1.322(6)	N(1)-C(12)	1.368(6)
N(2)-C(10)	1.318(6)	N(2)-C(11)	1.365(6)
N(3)-C(13)	1.345(6)	N(3)-C(17)	1.342(6)
C(1)-C(2)	1.392(7)	C(2)-C(3)	1.371(8)
C(3)-C(4)	1.389(8)	C(4)-C(5)	1.439(8)
C(4)-C(12)	1.406(6)	C(5)-C(6)	1.317(8)
C(6)-C(7)	1.444(7)	C(7)-C(8)	1.400(8)
C(7)-C(11)	1.402(7)	C(8)-C(9)	1.374(8)
C(9)-C(10)	1.406(8)	C(11)-C(12)	1.422(7)
C(13)-C(14)	1.382(7)	C(14)-C(15)	1.368(7)
C(14)-C(18)	1.522(7)	C(15)-C(16)	1.376(7)
C(16)-C(17)	1.374(7)		
O(1)-Cu-O(6)	98.7(2)	O(1)-Cu-O(7)	86.8(2)
O(1)-Cu-N(1)	172.4(2)	O(1)-Cu-N(2)	91.4(2)
O(1)-Cu-N(3)[a]	92.2(2)	O(6)-Cu-O(7)	173.1(2)
O(6)-Cu-N(1)	83.8(2)	O(6)-Cu-N(2)	85.2(2)
O(6)-Cu-N(3)[a]	89.7(2)	O(7)-Cu-N(1)	90.2(2)
O(7)-Cu-N(2)	90.5(2)	O(7)-Cu-N(3)[a]	94.3(2)
N(1)-Cu-N(2)	81.6(2)	N(1)-Cu-N(3)[a]	95.0(2)
N(2)-Cu-N(3)[a]	174.2(2)	Cu-O(1)-C(18)	123.9(3)
Cu-N(1)-C(1)	131.0(4)	Cu-N(1)-C(12)	111.0(3)
Cu-N(2)-C(10)	128.2(4)	Cu-N(2)-C(11)	112.4(3)
Cu-N(3)[a]-C(13)[a]	119.9(3)	Cu-N(3)[a]-C(17)[a]	122.2(3)
C(13)-N(3)-C(17)	117.9(4)	C(13)-C(14)-C(18)	118.8(5)
C(15)-C(14)-C(18)	122.6(5)	O(1)-C(18)-O(2)	126.6(5)
O(1)-C(18)-C(14)	114.3(5)	O(2)-C(18)-C(14)	119.1(5)

[a] Symmetry code: $0.5 - x, -0.5 + y, -z$.

value of 2.227Å found in the bipy complex as expected because the pyridine N atom in the latter complex coordinates to Cu(II) atom in the axial direction. Two water molecules occupy the axial direction in the present complex. The Cu-O distances in the axial direction [2.487(4) and 2.518(4)Å] are about 0.55Å longer than that in the equatorial plane. It is interesting that the carboxyl group coordinates to the Cu(II) atom as a unidentate unlike the chelate mode found in the corresponding bipy complex. The O(2) atom of the carboxyl group forms an H-bond with the coordinated water molecule, the distance between O(2) and O(6) atoms being 2.719(5)Å. It is obvious that the coordinated water molecule hinders the carboxyl group from chelating to the Cu(II) atom. It is noteworthy that the Cu-O(2) distance of 1.951(3)Å is about 0.07Å shorter than the coordination distance of 2.018(5)Å in the corresponding chelating complex.

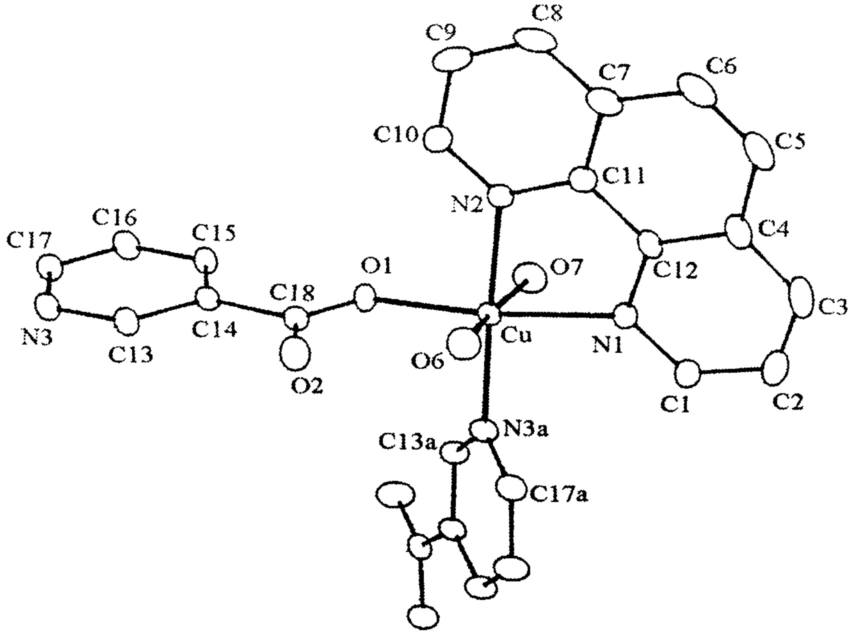

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoid. H atoms are omitted for clarity.

The crystal consists of polymeric molecules. Through both the terminal carboxyl O atom and the pyridine N atom, the nicotinate anions bridge the adjacent Cu(II) atoms to form infinite zigzag chains along the *b* axis as shown in Figure 2. An extensive H-bonding network exists between the carboxyl O(2) atom, coordinated water [O(6) and O(7)], crystalline water [O(8) and O(9)] and nitrate O atoms [O(4) and O(5)].

Infrared Spectra

The streching vibration of the carboxyl group in nicotinic acid has been reported, 1602 and 1418 cm^{-1} being assigned to ν(C=O) and ν(C-O), respectively. [5] In the present complex, the streching vibration of the carboxyl group was observed at 1605 and 1393 cm^{-1}. The ν(C-O) mode shifts to lower frequency by about 25 cm^{-1} as predicted by theory [6] and agrees with that reported for a Cu(I) nicotinate complex coordinated by a unidentate carboxyl group; 1392 cm^{-1} and 1605 cm^{-1} were observed for the carboxyl group. [7]

Below 500 cm^{-1}, two new bands were observed, that at 308 cm^{-1} being assigned to ν(Cu-N). This is in agreement with the value of 310 cm^{-1} reported for a Cr(II) nicotinate complex [8] and is higher than that found in the bipy

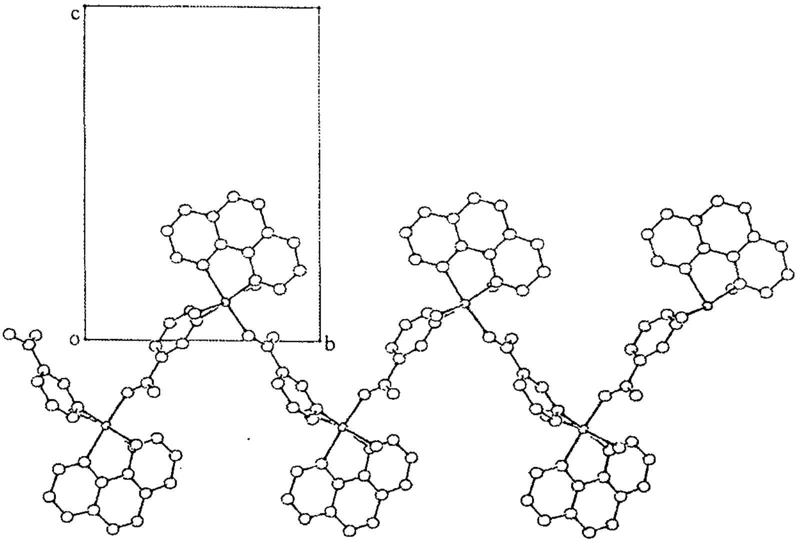

FIGURE 2 Packing diagram of polymeric chains in the unit cell.

complex because of the quite longer Cu-N distance of 2.227Å in the latter. The remaining band at 430 cm^{-1} is considered to be due to ν(Cu-O). This band shifts to higher frequency with respect to the bipy complex as expected because of the shorter Cu-O distance as mentioned above.

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References

[1] Xu D., Chen C., Xu Y., Cheng C., Chen J. and Tang W. (1991). *Acta Crystallogr.*, **C47**, 72.
[2] Xu D., Xie A., Xu Y., Zhang C. and Chen W. (1996). *J. Coord. Chem.*, 39, 273.
[3] *International Tables for X-ray Crystallography*, Vol. IV, (Kynoch Press, Birmingham, 1974), Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands.
[4] Molecular Structure Corporation (1985 and 1992), Crystal Structure Analysis Package.
[5] *The Sadtler Standard Spectra, 434-c*, (Sadtler Research Laboratories, inc., 1967), The United State of America.
[6] Nakamoto K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 4th Edition, (Wiley, New York, 1986), p. 194.
[7] Cariati F., Naldini L. and Panzanelli A. (1983). *Inorg. Chim. Acta*, **69**, 117.
[8] Cooper J. A., Bryan F. A., Paul D. B. and Leonard F. B. (1984). *Inorg. Chim. Acta*, **91**, 1.