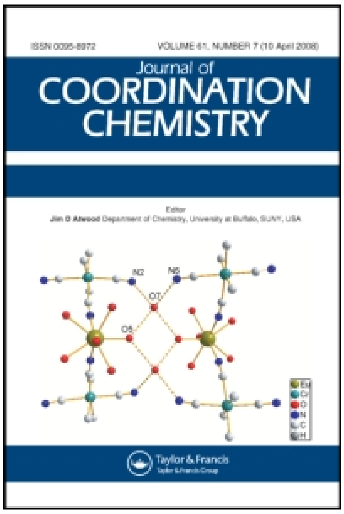

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE POLYMERIC COPPER(II) COMPLEX 1, 10-PHENANTHROLINE -*N, N'*-(μ-ISONICOTINATO-*N, O*) MONOAQUACOPPER(II) NITRATE DIHYDRATE

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To cite this Article Xu, Duanjun , Xie, Aili , Xu, Yuanzhi , Nishikawa, Kazuyoshi and Yasuoka, Noritake(1998) 'THE POLYMERIC COPPER(II) COMPLEX 1, 10-PHENANTHROLINE -*N, N'*-(μ-ISONICOTINATO-*N, O*) MONOAQUACOPPER(II) NITRATE DIHYDRATE', Journal of Coordination Chemistry, 43: 2, 237 — 242

To link to this Article: DOI: 10.1080/00958979808022672

URL: http://dx.doi.org/10.1080/00958979808022672

J. Coord. Chem., 1998, Vol. 43, pp. 237–242
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Printed in Malaysia

THE POLYMERIC COPPER(II) COMPLEX 1,10-PHENANTHROLINE-*N,N'*-(μ-ISONICOTINATO-*N,O*)MONOAQUACOPPER(II) NITRATE DIHYDRATE

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(Received 6 January 1997)

The title complex has been prepared and its structure determined by X-ray diffraction. The complex crystallizes in space group *C2/c* with $a = 26.892(5)$, $b = 10.479(4)$, $c = 14.179(2)$ Å, $\beta = 98.59(2)°$. Isonicotinate anions bridge adjacent Cu(II) atoms through the pyridine N atom and the carboxyl O atom to form zigzag polymeric chains along the *b* axis. The carboxyl group of the isonicotinate anion coordinates to the Cu(II) atom as a unidentate. Based on the molecular structure the infrared spectrum is discussed.

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

INTRODUCTION

As a part of a research programme on complexes bridged by heterocyclic aromatic molecules and their derivatives with a view to the investigation of magnetic superexchange interactions between adjacent magnetic nuclei, complexes bridged by isonicotinate or nicotinate anion have been synthesized. Of these, the structures of two nicotinate complexes have been determined by X-ray methods [1, 2]. The carboxyl group of the nicotinate anion shows different coordination modes in the two complexes; one coordinates to Cu(II) as a unidentate ligand but the other acts as a chelating ligand. In order to compare the coordination in corresponding isonicotinate complexes, we present here the crystal structure of the title complex.

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

EXPERIMENTAL

Preparation

The title complex was synthesized in a manner similar to the nicotinate complex [2] but isonicotinic acid was used instead of nicotinic acid. The resulting solution was filtered and slowly cooled to room temperature. After several weeks well-shaped, blue, single crystals were obtained. *Anal.* Calcd. for $C_{18}H_{18}N_4O_8Cu$ (%): C, 44.82; N, 11.62; H, 3.77. Found: C, 45.09; N, 12.01; H, 3.58. Infrared spectra were recorded using a Perkin Elmer 683 spectrophotometer (4000-400 cm^{-1}) with powdered sample spread on KBr plates 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 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 a scan width, $\Delta\omega$, of $(1.0 + 0.30 \tan \vartheta)°$. A total of 3677 independent reflections was collected, of which 1868 observed reflections $[I > 3\sigma(I)]$ were used for structure refinement. Usual Lp and empirical absorption $[T_{min} = 0.921, T_{max} = 0.996]$ corrections were applied.

The structure was solved by direct methods (MITHRIL90) [3] followed by Fourier syntheses. The structure 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 factors $R = 0.052$ and $R_w = 0.044$, where $w = 1/\sigma^2(F)$. The highest peak in the final difference Fourier map was 0.41 e $Å^{-3}$. The number of reflections per refined parameter is 6.7. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography* [4]. All calculations were performed using the TEXSAN crystallographic software package [5].

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{18}H_{18}N_4O_8Cu$, $M = 481.91$, monoclinic, space group $C2/c$, a = 26.892(5), $b = 10.479(4)$, $c = 14.179(2)$ Å, $\beta = 98.59(2)°$, $V = 3950(1)$ Å^3, $Z = 8$, $D_c = 1.620$ g cm^{-3}, $F(000) = 1976$, μ(Mo-Kα) = 1.162 mm^{-1}.

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

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cu	0.85570(3)	0.48550(8)	0.63181(6)	2.09(2)
O(1)	0.8218(2)	0.6377(5)	0.6707(3)	2.4(1)
O(2)	0.8490(2)	0.5910(5)	0.8238(4)	3.3(1)
O(3)	0.4167(3)	0.5080(10)	0.3922(6)	12.0(3)
O(4)	0.3917(4)	0.6020(8)	0.2660(6)	11.7(4)
O(5)	0.3562(3)	0.4424(8)	0.3024(6)	9.8(3)
O(6)	0.8213(2)	0.5330(5)	0.4797(3)	3.2(1)
O(7)	0.6605(2)	0.2952(5)	0.0252(4)	5.2(2)
O(8)	0.7989(2)	0.0257(6)	0.1020(4)	6.0(2)
N(1)	0.8986(2)	0.3281(5)	0.6170(4)	2.2(1)
N(2)	0.9218(2)	0.5751(5)	0.6291(4)	1.9(1)
N(3)	0.7024(2)	0.8797(6)	0.8386(4)	2.3(1)
N(4)	0.3897(3)	0.5185(8)	0.3205(5)	4.1(2)
C(1)	0.8860(3)	0.2077(8)	0.6092(5)	3.1(2)
C(2)	0.9208(3)	0.1098(7)	0.6033(6)	3.9(2)
C(3)	0.9706(3)	0.1412(8)	0.6067(6)	3.5(2)
C(4)	0.9855(3)	0.2683(7)	0.6136(5)	2.6(2)
C(5)	1.0366(3)	0.3125(8)	0.6169(6)	3.3(2)
C(6)	1.0480(3)	0.4350(8)	0.6207(5)	3.2(2)
C(7)	1.0102(2)	0.5322(7)	0.6242(5)	2.4(2)
C(8)	1.0194(3)	0.6639(8)	0.6291(6)	3.3(2)
C(9)	0.9811(3)	0.7467(8)	0.6336(6)	3.2(2)
C(10)	0.9310(3)	0.6989(7)	0.6336(5)	2.7(2)
C(11)	0.9603(2)	0.4921(7)	0.6246(4)	2.1(2)
C(12)	0.9481(2)	0.3600(7)	0.6184(5)	2.0(2)
C(13)	0.6973(2)	0.8183(8)	0.7552(5)	2.6(2)
C(14)	0.7358(3)	0.7474(7)	0.7269(5)	2.4(2)
C(15)	0.7809(2)	0.7365(7)	0.7877(5)	2.2(2)
C(16)	0.7865(3)	0.7994(8)	0.8730(5)	3.1(2)
C(17)	0.7465(3)	0.8731(8)	0.8970(5)	2.9(2)
C(18)	0.8220(2)	0.6485(7)	0.7621(6)	2.3(2)

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 square pyramidal coordination as shown in Figure 1. Two N atoms of a 1,10-phenanthroline ligand coordinate to a Cu(II) atom in the basal plane with an average Cu-N distance of 2.028 Å. Two isonicotinate anions, related by a screw axis, coordinate to the Cu(II) atom in the basal plane through the pyridine N atom and a terminal carboxyl group, respectively. The Cu-N(3)a distance of 2.009(5)Å is identical with that (2.008Å) in the nicotinate phenanthroline complex [2], and 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)	1.957(5)	Cu-O(6)	2.271(5)
Cu-N(1)	2.041(6)	Cu-N(2)	2.016(5)
Cu-N(3)a	2.009(5)	O(1)-C(18)	1.300(8)
O(2)-C(18)	1.209(8)	N(1)-C(1)	1.307(9)
N(1)-C(12)	1.371(8)	N(2)-C(10)	1.320(9)
N(2)-C(11)	1.361(8)	N(3)-C(13)	1.336(8)
N(3)-C(17)	1.344(9)	C(15)-C(18)	1.525(9)
O(1)-Cu-O(6)	87.0(2)	O(1)-Cu-N(1)	169.0(2)
O(1)-Cu-N(2)	94.3(2)	O(1)-Cu-N(3)a	89.0(2)
O(6)-Cu-N(1)	103.6(2)	O(6)-Cu-N(2)	96.6(2)
O(6)-Cu-N(3)a	95.7(2)	N(1)-Cu-N(2)	82.0(2)
N(1)-Cu-N(3)a	92.5(2)	N(2)-Cu-N(3)a	167.4(2)
Cu-O(1)-C(18)	114.8(4)	Cu-N(1)-C(1)	130.2(5)
Cu-N(1)-C(12)	111.4(4)	Cu-N(2)-C(10)	128.0(5)
Cu-N(2)-C(11)	112.5(4)	Cu-N(3)a-C(13)a	118.1(5)
Cu-N(3)a-C(17)a	122.9(5)	C(13)-N(3)-C(17)	119.0(6)
C(14)-C(15)-C(18)	120.1(6)	C(16)-C(15)-C(18)	120.9(6)
O(1)-C(18)-O(2)	126.2(7)	O(1)-C(18)-C(15)	113.2(6)
O(2)-C(18)-C(15)	120.5(7)		

value (2.227Å) found in the nicotinate bipyridine complex [1]. This is expected because in the latter complex the pyridine N atom coordinates to Cu(II) in the axial direction. One water molecule [O(6)] occupies the apical position to complete penta-coordinate geometry around Cu(II). The Cu-O(6) distance of 2.271(5)Å is about 0.3Å longer than that in the basal plane. N(1), N(2), N(3)a and O(1) atoms are coplanar, and the Cu(II) atom deviates 0.197Å from the average plane towards the apical O(6) atom, as usually found in square pyramidal Cu(II) complexes. It is notable that the carboxyl group in the present complex acts as a unidentate towards Cu(II) with Cu-O(1) 1.957 Å; neither the Cu-O(2) distance of 2.968Å nor the O(2)-Cu-O(6) angle of 135.8° suggests coordination of the O(2) atom. The polymeric catena structure seems to hinder the O(2) atom from bonding with Cu(II).

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

Infrared Spectra

The infrared spectrum of free isonicotinic acid was recorded along with the title complex for comparison. The stretching vibration of the carboxyl group was

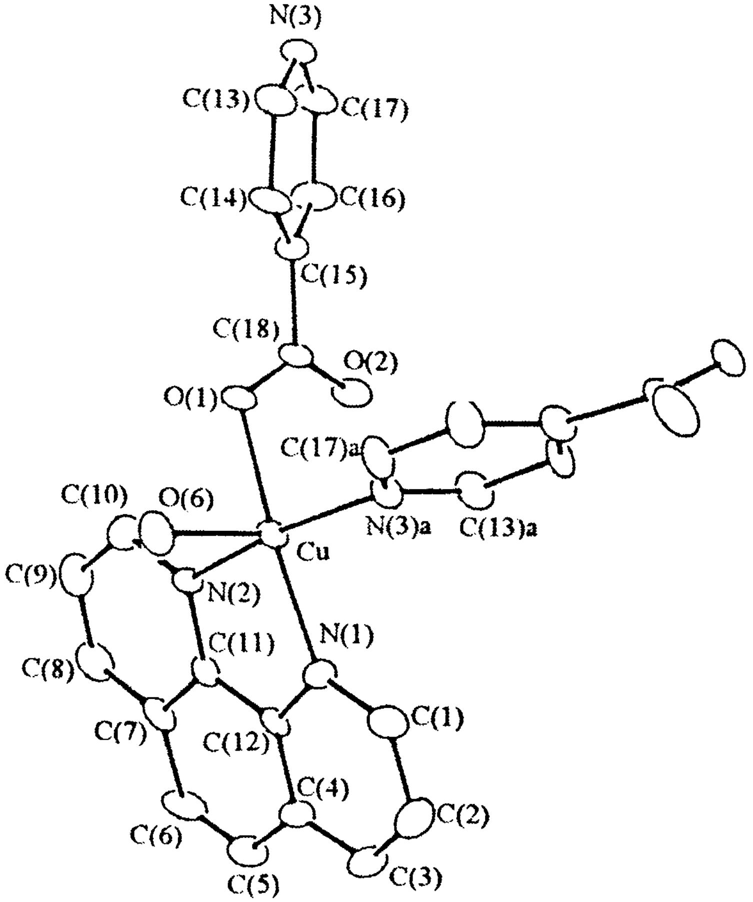

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

observed at 1602 cm^{-1} [ν(C=O)] and 1404 cm^{-1} [ν(C-O)] in free isonicotinic acid, and at 1600 cm^{-1} and 1378 cm^{-1} in the complex. The ν(C-O) frequency moves towards lower frequency by about 25 cm^{-1} as predicted by theory [6] and agrees with that reported for the unidentate nicotinate Cu(II) complex [2, 7]. The band at 310 cm^{-1} is tentatively assigned to ν(Cu-N). This is in agreement with the value of 308 cm^{-1} reported for a phenanthroline Cu(II) nicotinate complex [2] and is somewhat higher than the value of 293 cm^{-1} found in the bipyridine nicotinate complex [1] because in the latter the pyridine N atom is semi-coordinated to a Cu(II) atom in an axial direction with a long Cu-N distance of 2.227Å.

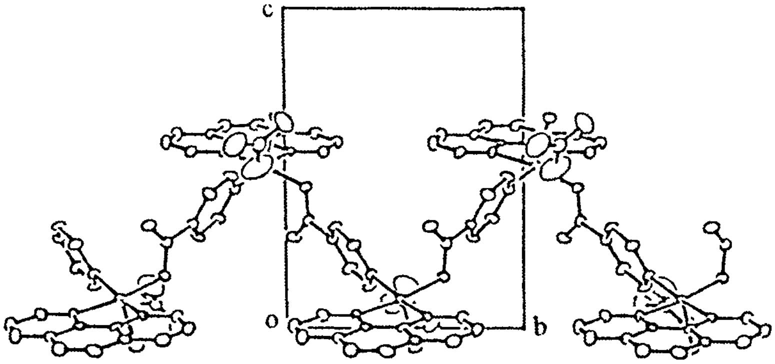

FIGURE 2 Packing diagram of polymeric chains in the unit cell.

Acknowledgements

This project was supported by the Zhejiang Province Natural Science Foundation and the National Natural Science Foundation of China.

References

[1] D. Xu, A. Xie, Y. Xu, C. Zhang and W. Chen, *J. Coord. Chem.*, **39**, 273 (1996).
[2] D. Xu, A. Xie, Y. Xu, K. Nishikawa and N. Yasuoka, *J. Coord. Chem.*, in press.
[3] C. J. Gilmore, *MITHRIL90 An Integrated Direct Methods Computer Program*, (University of Glasgow, Scotland, 1990).
[4] International Tables for X-ray Crystallography, Vol. IV, (Kynoch Press, Birmingham, 1974); present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands.
[5] *TEXSAN*, Molecular Structure Corporation (1985 and 1992), Crystal Structure Analysis Package.
[6] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edition, (Wiley, New York, 1986), p. 257.
[7] F. Cariati, L. Naldini and A. Panzanelli, *Inorg. Chim. Acta*, **69**, 117 (1983).