C(12)—C(13)		1.42 (5)
C(13)—C(14)		1.40 (5)
C(14)—C(15)		1.57 (5)
P—C	1.79 (1)	1.83 (4)
C—C	1.38 (2)	1.42 (5)
Te(1)—Hg(1)—Te(2)		107.8 (1)
Te(1)—Hg(1)—Te(3)		130.0 (1)
Te(2)—Hg(1)—Te(3)		122.2 (1)
Hg(1)—Te(1)—C(1)		100.2 (9)
Hg(1)—Te(2)—C(6)		93.9 (9)
Hg(1)—Te(3)—C(11)		96 (1)
C(1)—S(1)—C(4)	93.4 (7)	94 (2)
C(6)—S(2)—C(9)		95 (2)
C(11)—S(3)—C(14)		93 (2)
Te(1)—C(1)—S(1)	119.6 (7)	124 (2)
Te(1)—C(1)—C(2)	130.0 (9)	128 (2)
S(1)—C(1)—C(2)	110.3 (8)	108 (2)
C(1)—C(2)—C(3)	110 (1)	116 (3)
C(2)—C(3)—C(4)	117 (1)	114 (3)
S(1)—C(4)—C(3)	109 (1)	108 (3)
S(1)—C(4)—C(5)		119 (3)
C(3)—C(4)—C(5)		132 (3)
Te(2)—C(6)—S(2)		120 (2)
Te(2)—C(6)—C(7)		125 (2)
S(2)—C(6)—C(7)		114 (2)
C(6)—C(7)—C(8)		103 (3)
C(7)—C(8)—C(9)	124 (4)	
S(2)—C(9)—C(8)	103 (3)	
S(2)—C(9)—C(10)		117 (3)
C(8)—C(9)—C(10)		140 (4)
Te(3)—C(11)—S(3)		123 (2)
Te(3)—C(11)—C(12)		128 (2)
S(3)—C(11)—C(12)		108 (2)
C(11)—C(12)—C(13)		117 (3)
C(12)—C(13)—C(14)		109 (3)
S(3)—C(14)—C(13)		112 (3)
S(3)—C(14)—C(15)		120 (3)
C(13)—C(14)—C(15)		128 (3)
C—P—C	109 (1)	109 (2)
P—C—C	120.2 (9)	117 (4)
C—C—C	120 (1)	120 (4)

Structure solution: direct methods. Structure refinement: full-matrix least-squares on F. As (II) crystallizes in a chiral space group, refinement was carried out for both enantiomeric conformations; the reported coordinates correspond to the model which gave lower residuals (residuals for the incorrect model are: $R = 0.0768$, $wR = 0.0840$, $S = 1.89$). The refinement of (I) included positional and anisotropic thermal parameters for all non-H atoms; H atoms other than those of the methyl C atom (which were not located) were included in idealized positions with a group isotropic thermal parameter [$U_{\text{iso}} = 0.072\ (8)$ Å^2]. The refinement of (II) included positional parameters and anisotropic thermal parameters for the non-H atoms other than C, which were refined isotropically; H atoms were not included. Computer programs: *SHELXTL* (Sheldrick, 1985). Corrections: Lorentz and polarization, real and imaginary anomalous dispersion (Cromer, 1974).

We are grateful to the National Science Foundation (CHE-9102548) for support of this work.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71113 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1024]

References

Behrens, U., Hoffman, G. & Klar, G. (1977). *Chem. Ber.* **110**, 3672–3677.

Blower, P. G. & Dilworth, J. R. (1987). *Coord. Chem. Rev.* **76**, 121–185.

Christou, G., Hagen, K. & Holm, R. H. (1982). *J. Am. Chem. Soc.* **104**, 1744–1745.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Engman, L. & Cava, M. P. (1982). *Organometallics*, **1**, 470–473.

Gysling, H. J. (1986). *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1, edited by S. Patai & Z. Rappoport, pp. 679–855. New York: John Wiley.

Lee, G. S. H., Craig, D. C., Ma, I., Scudder, M. L., Bailey, T. D. & Dance, I. G. (1988). *J. Am. Chem. Soc.* **110**, 4863–4864.

Money, J. K., Huffman, J. C. & Christou, G. (1988). *Inorg. Chem.* **27**, 507–514.

Pulla Rao, C., Dorfman, J. R. & Holm, R. H. (1986). *Inorg. Chem.* **25**, 428–439.

Sheldrick, G. M. (1985). *SHELXTL User's Manual*. Revision 5.1. Nicolet Instruments Corporation, Madison, Wisconsin, USA.

Zhao, J., Adcock, D., Pennington, W. T. & Kolis, J. W. (1990). *Inorg. Chem.* **29**, 4358–4360.

Acta Cryst. (1993). C49, 1756–1761

Structures of Bis(di-2-pyridylamine)dinitratocopper(II) and Bis(acetato)bis(di-2-pyridylamine)copper(II) Monohydrate

M. CARMEN MUÑOZ*

Departamento de Física Aplicada,
Universidad Politécnica de València,
Camino de Vera s/n, 46071-València, Spain

JOSÉ MIGUEL LÁZARO, JUAN FAUS AND MIGUEL JULVE

Departament de Química Inorgànica,
Facultat de Química de la Universitat de València,
Dr. Moliner 50, 46100-Burjassot, València, Spain

(*Received* 13 *November* 1992; *accepted* 18 *March* 1993)

Abstract

Both complexes consist of neutral mononuclear units, the copper(II) environment being distorted 4+2 octahedral for (I) and distorted square pyramidal for (II). Compound (I) is centrosymmetric. Its equatorial plane comprises the four N atoms of two di-2-pyridylamine (dpyam) ligands with the axial positions filled by two O atoms of two unidentate nitrate anions. The equatorial plane in (II) is composed of the two N atoms of dpyam and two O atoms of two acetate groups, with the apical position occupied by another O atom of one of the acetate

ligands. A structural comparison is made with other dpyam-containing copper(II) complexes and the influence of the counterion is discussed.

Comment

Di-2-pyridylamine (dpyam) has been used widely as a chelating ligand in transition-metal complexes (McWhinnie, 1970). Restricting ourselves to its complexes with copper(II), the structures of mononuclear and polynuclear compounds have been reported. The four-coordinate $[Cu(dpyam)_2](ClO_4)_2$ (Johnson, Beineke & Jacobson, 1971), the five-coordinate $[Cu(dpyam)_2I]_2I(ClO_4)_9$ (Johnson & Jacobson, 1973*a*), $[Cu(dpyam)_2Cl]Cl.4H_2O$ (Jensen & Jacobson, 1981), $[Cu(dpyam)_2Cl]Cl$ (Jacobson & Jensen, 1986), $[Cu(dpyam)(H_2O)_2F]F$ (Jacobson & Jensen, 1981) and $[Cu(dpyam)(H_2O)(CO_3)].2H_2O$ (Akhter, Fitzimmons & Hathaway, 1991) and six-coordinate $[Cu(dpyam)_2(CH_3COO)]NO_3$ and $[Cu(dpyam)_2(HCOO)]BF_4$ (Aduldecha, Keniry, Akhter, Tyagi & Hathaway, 1991) complexes belong to the former group, whereas the oxamidato (oa)-bridged $[Cu_2(dpyam)_2(oa)(NO_3)_2]$ (Sletten, 1982) and dihydroxo-bridged $[Cu_2(dpyam)_2(OH)_2(BF_4)_2]$ and $[Cu(dpyam)_2(OH)_2(H_2O)]Cl_2.2H_2O$ (Wu, Keniry & Hathaway, 1992) dinuclear species and the carbonato-bridged $[Cu(dpyam)(CO_3)].3H_2O$ (Sletten, 1984) and chloro-bridged $[Cu(dpyam)Cl(NO_3)].0.5H_2O$ (Mathews & Manohar, 1991) one-dimensional polymeric compounds correspond to the latter one. This variety of geometries including four-, five and six-coordinate species illustrates well the flexible nature of dpyam. In recent years, increasing attention has been paid to this ligand because its copper(I) complexes have been investigated as models of copper-containing plant hormone binding sites (Thompson & Whitney, 1984; Pyrka, Seeney & Pinkerton, 1991) and a very recent electrochemical study (Cinquantini, Opromolla & Zanello, 1991) has shown that dpyam favours the one-electron reduction from $[Cu(dpyam)_2]^{2+}$ to $[Cu(dpyam)_2]^+$ to a higher extent than the related less-flexible 2,2′-bipyridine and 1,10-phenanthroline ligands.

In the framework of our current work concerning the synthesis and characterization of polynuclear compounds of Cu^{II} using bidentate and tridentate nitrogen donor groups as end-cap ligands (Castro, Faus, Julve & Gleizes, 1991; Castro, Faus, Julve, Journaux & Sletten, 1991; Castro, Julve, De Munno, Bruno, Real, Lloret & Faus, 1992), copper(II) complexes with the dpyam ligand have been examined and the structures of the title compounds (I) and (II) are reported herein.

The structure of (I) consists of discrete neutral centrosymmetric monomers in which each Cu atom is surrounded by two chelating dpyam ligands and two unidentate nitrate anions. The coordination polyhedron around the metal ion can be described as a tetragonally distorted CuN_4O_2 octahedron with the pyridyl N atoms of the dpyam ligands forming the equatorial plane and two nitrate groups filling the axial sites. The two independent Cu—N distances are somewhat different [2.002 (2) and 2.016 (2) Å for Cu—N(1) and Cu—N(3), respectively]; this is most likely a result of steric effects which are evident in other parts of the structure.

The nitrate anion is weakly coordinated [2.477 (2) Å for Cu—O(3)]. It is planar and exhibits reasonable O—N—O bond angles (mean 120°). However, the average value of the N—O bond [1.234 Å] is slightly greater than that normally found in uncoordinated nitrate (Aduldecha, Keniry, Akhter, Tyagi & Hathaway, 1991, and references therein). The semi-coordination of nitrate and the weak intermolecular interactions [3.162 (3) Å for O(1)···N(2)] account for this elongation.

The bite angle of the dpyam ligand, N(1)—Cu—N(3) is 85.6 (1)°. In the other dpyam complexes, this value ranges between 86 and 96°. The six-membered chelate Cu—N(1)—C(5)—N(2)—C(6)—N(3) ring adopts the boat configuration with the Cu and N(2) atoms 0.37 and 0.34 Å, respectively, below the plane defined by the remaining four atoms. The bond lengths and bond angles in the dpyam ligand are in agreement with the structure of its low-melting polymorph (Johnson & Jacobson, 1973*b*) (average values of intra-ring C—C and C—N bond distances are 1.376 and 1.344 Å, respectively). The bond distances and bond angles about chemically equivalent atoms in the two pyridine rings are practically identical. There is no distortion about the bridging nitrogen [1.376 (4) and 1.380 (4) Å for N(2)—C(5) and N(2)—C(6)] in contrast to the related complex $[Cu(dpyam)_2](ClO_4)_2$ for which these distances are significantly different (1.41 and 1.32 Å, respectively). The individual pyridine rings in the dpyam ligand are essentially planar [maximum deviation 0.038 Å at C(6)], but the ligand itself is not, with a 37.3° dihedral angle between the plane defined by the pyridine rings. This value lies in the range observed for dpyam complexes (9.8–41.4°). It seems interesting to compare the structures of $[Cu(dpyam)_2(NO_3)_2]$ and $[Cu(dpyam)_2](ClO_4)_2$. The Cu atom occupies a $\bar{1}$ symmetry site in the former whereas it is on a twofold site in the latter. The steric hindrance between the two dpyam ligands in both complexes is relieved in a quite different manner. In the nitrato complex, the ligand twists such that the dihedral angle between the pyridine rings reaches 37.3°. However, in the perchlorate compound this dihedral angle is much smaller (9.8°) because the dpyam ligands try to define a tetrahedral environment around the metal atom. This is an example of structure change associated with the different coordinating ability of the counterion. The mononuclear complexes are stacked along the *b* axis of the unit cell following a 2_1 screw axis; the shortest intermolecular Cu···Cu^{ii} [(ii) $1+x$, y, z] separation is 7.61 Å.

The structure of (II) is made up of discrete [Cu(dpyam)($CH_3COO)_2$] units and water of crystallization linked by van der Waals forces and hydrogen bonds. The Cu atom exhibits a very distorted square-pyramidal CuN_2O_3 chromophore comprising a bidentate dpyam ligand [1.971 (8) and 2.000 (8) Å for Cu—N(1) and Cu—N(3), respectively] and two types of acetate groups, one with a marked asymmetric chelating coordination [1.962 (7) and 2.471 (7) Å for Cu—O(1) and Cu—O(2), respectively] and the other one unidentate [1.975 (7) Å for Cu—O(3)]. In fact, although this compound can be considered as basically five-coordinate, O(4) is occupying a sixth coordination position at a distance of 2.700 (8) Å. Some of the angles subtended at the ligating atoms are far from the ideal 90 and 180° [155.1 (3), 156.7 (3), 106.3 (3) and 57.6 (3)° for N(1)—Cu—O(1), N(3)—Cu—O(3), N(3)—Cu—O(2) and O(1)—Cu—O(2), respectively]. The Cu atom is displaced by 0.36 Å toward O(2) from the N(1)—N(3)—O(3) plane and significant deviations from it occur when O(2) is included in the mean-plane calculation. The chelating coordination mode of one of the acetate ligands is most likely the cause of these structural features.

Both acetato groups are planar. Although the mean C—O value is 1.25 Å in the two cases, the separate C—O distances [1.282 (12) and 1.217 (13) Å for C(11)—O(1) and C(11)—O(2) and 1.262 (11) and 1.246 (12) Å for C(13)—O(3) and C(13)—O(4), respectively] are consistent with their different coordination modes. The angles around carboxylate C atoms are very close to 120° as expected for a trigonal planar anion (Fitzgerald, Murphy, Tyagi, Walsh, Walsh & Hathaway, 1981). The dihedral angles between Cu—N(1)—N(3) and the carboxylate planes are 70.10 [C(11)] and 89.84° [C(13)].

The bite angle of the dpyam ligand [92.0 (3)° for N(1)—Cu—N(3)] is only slightly greater than 90°. No unusual bond lengths or bond angles are observed in the dpyam ligand and the individual pyridyl rings are quite planar [maximum deviation 0.015 Å for C(2)]. However, as in the preceding structure, the dpyam ligand is not planar. The pyridyl planes form a dihedral angle of 25.3°, a value which is very close to that of free dpyam (23°). Again the six-membered chelate ring Cu—N(1)—C(5)—N(2)—C(6)—N(3) adopts the boat configuration [Cu and N(2) atoms are 0.36 and 0.25 Å, respectively, below the mean plane defined by the other four atoms].

The shortest intermolecular Cu···Cu^{iii} [(iii) $-x$, $1-y$, $-z$] separation is 7.32 Å. Hydrogen bonds occur between the water molecule of crystallization and carboxylate O atoms [2.787 (12) and 2.836 (12) Å for O(5)···O(2) and O(5)···O(3^{iv}), respectively; (iv) $-x$, $1-y$, $1-z$].

The electronic spectra of (I) and (II), recorded as Nujol mulls on filter paper, involve twin peaks of comparable intensity at 10 800 and 16 100 cm^{-1} for (II) and a peak centred at 18 000 cm^{-1} with a shoulder at 15 000 cm^{-1} for (I), corresponding to the different chromophores they contain [CuN_4O_2 and CuN_2O_3 for (I) and (II), respectively].

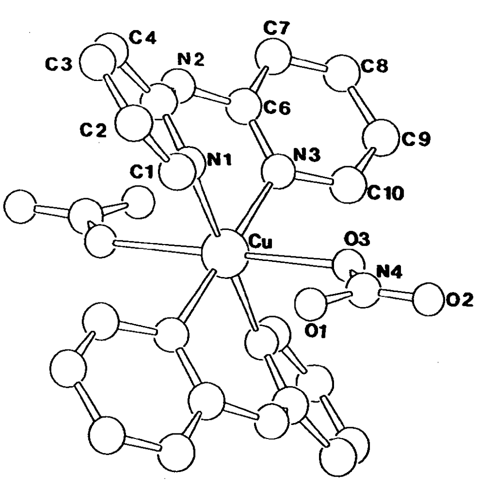

Fig. 1. Perspective view of the molecular structure of [Cu(dpyam)$_2$($NO_3)_2$] (I) and the atom-numbering scheme. H atoms have been omitted for clarity.

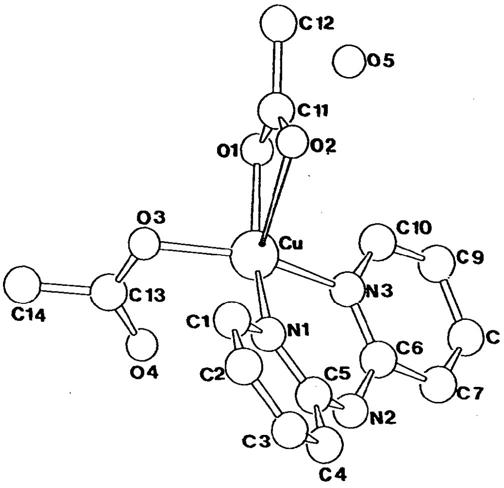

Fig. 2. Perspective view of the molecular structure of [Cu(dpyam)($CH_3COO)_2$].H_2O (II) and the atom-numbering scheme. H atoms have been omitted for clarity.

The most relevant feature of the infrared spectra of (II) is the evidence for the chelating coordination of acetate. The occurrence of ν_{as}(COO) and ν_s(COO) at 1570 and 1400 cm^{-1}, respectively, leads to a $\Delta\nu$ value of 170 cm^{-1} which is consistent with the presence of chelating carboxylate (Deacon & Philips, 1980). Finally, the ESR spectra of (I) and (II), recorded both at room temperature and 77 K, look like axial doublets with $g_\parallel = 2.23$ and $g_\perp = 2.07$ for the former and $g_\parallel = 2.28$ and $g_\perp = 2.08$ for the latter. The trend exhibited by the g values, $g_\parallel > g_\perp > 2.0$, points towards a $d_{x^2-y^2}$ ground state in both cases (Hathaway, 1984). Moreover, the smaller difference between $g_\parallel$ and $g_\perp$ values for (I) with respect to (II) is in full agreement with their different copper environment (elongated tetragonal octahedral and square pyramidal, respectively). A weak spin-forbidden transition $\Delta M_s = 2$ is observed in both spectra and is most likely a result of dipolar interactions between copper centres of the mononuclear entities.

Experimental

Compound (I)

Crystal data

$[Cu(NO_3)_2(C_{10}H_9N_3)_2]$
$M_r = 529.96$
Monoclinic
$P2_1/a$
$a = 7.607$ (2) Å
$b = 17.091$ (4) Å
$c = 8.416$ (2) Å
$\beta = 94.18$ (3)°
$V = 1091.37$ Å^3
$Z = 2$
$D_x = 1.59$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12$-18°
$\mu = 1.041$ mm^{-1}
$T = 293$ K
Cubic
0.3 × 0.3 × 0.2 mm
Dark green

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.95$, $T_{max} = 0.99$
4470 measured reflections
3616 independent reflections
2614 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.03$
$\theta_{max} = 26$°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.0426$
$wR = 0.0426$
2614 reflections
196 parameters
Riding model for H atoms
Unit weights applied

$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (I)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0.0	0.0	0.0	0.0287 (2)
N(1)	0.0902 (3)	0.0765 (1)	0.1665 (3)	0.0288 (13)
C(1)	0.0500 (5)	0.0701 (2)	0.3212 (4)	0.0370 (19)
C(2)	0.0811 (6)	0.1273 (2)	0.4315 (4)	0.0482 (20)
C(3)	0.1603 (6)	0.1956 (2)	0.3850 (4)	0.0521 (21)
C(4)	0.2087 (5)	0.2030 (2)	0.2330 (4)	0.0410 (20)
C(5)	0.1756 (4)	0.1412 (2)	0.1256 (3)	0.0295 (15)
N(2)	0.2377 (4)	0.1463 (1)	−0.0235 (3)	0.0349 (14)
C(6)	0.2986 (4)	0.0854 (2)	−0.1120 (3)	0.0300 (16)
C(7)	0.4264 (5)	0.1006 (2)	−0.2188 (4)	0.0395 (18)
C(8)	0.4999 (5)	0.0398 (3)	−0.2941 (4)	0.0463 (20)
C(9)	0.4468 (5)	−0.0368 (2)	−0.2624 (4)	0.0452 (22)
C(10)	0.3163 (5)	−0.0464 (2)	−0.1635 (4)	0.0387 (20)
N(3)	0.2359 (3)	0.0132 (1)	−0.0913 (3)	0.0293 (14)
N(4)	0.1507 (4)	−0.1673 (2)	0.1839 (3)	0.0372 (16)
O(1)	0.1653 (4)	−0.1936 (1)	0.0475 (3)	0.0574 (16)
O(2)	0.1823 (5)	−0.2093 (2)	0.2981 (3)	0.0835 (19)
O(3)	0.1063 (3)	−0.0978 (1)	0.2020 (3)	0.0422 (13)

Table 2. *Geometric parameters* (Å, °) *for* (I)

Cu—N(1)	2.002 (2)	N(4)—O(1)	1.246 (3)
Cu—N(3)	2.016 (2)	N(4)—O(2)	1.209 (3)
Cu—O(3)	2.477 (2)	N(4)—O(3)	1.248 (3)
N(1)—Cu—N(3)	85.6 (1)	Cu—O(3)—N(4)	129.5 (2)
N(1)—Cu—N(3^i)	94.4 (1)	O(1)—N(4)—O(3)	119.9 (3)
N(1)—Cu—O(3)	83.2 (1)	O(2)—N(4)—O(3)	120.6 (3)
N(3)—Cu—O(3)	94.7 (1)	O(1)—N(4)—O(2)	119.5 (3)

Symmetry code: (i) $-x, -y, -z$.

Compound (II)

Crystal data

$[Cu(C_2H_3O_2)_2(C_{10}H_9N_3)].H_2O$
$M_r = 370.85$
Triclinic
$P\bar{1}$
$a = 7.309$ (1) Å
$b = 10.917$ (1) Å
$c = 11.183$ (2) Å
$\alpha = 83.45$ (1)°
$\beta = 76.70$ (1)°
$\gamma = 73.36$ (1)°
$V = 830.91$ Å^3

$Z = 2$
$D_x = 1.47$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12$-18°
$\mu = 1.332$ mm^{-1}
$T = 293$ K
Rods
0.4 × 0.4 × 0.3 mm
Blue-green

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.81$, $T_{max} = 0.99$
3354 measured reflections
2868 independent reflections
2726 observed reflections [$I > 3\sigma(I)$]

$\theta_{max} = 26$°
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.071$
$wR = 0.071$

$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

2726 reflections
227 parameters
Riding model for H atoms
Unit weights applied

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (II)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.12685 (17)	0.26114 (11)	0.24629 (7)	0.0329 (5)
N(1)	−0.0352 (10)	0.1467 (7)	0.3277 (7)	0.0343 (2)
C(1)	−0.1972 (13)	0.2017 (10)	0.4140 (9)	0.0403 (3)
C(2)	−0.3113 (13)	0.1290 (11)	0.4869 (10)	0.0462 (3)
C(3)	−0.2668 (13)	0.0003 (10)	0.4692 (10)	0.0487 (3)
C(4)	−0.1074 (14)	−0.0551 (9)	0.3835 (9)	0.0460 (3)
C(5)	0.0092 (12)	0.0215 (8)	0.3137 (8)	0.0343 (2)
N(2)	0.1693 (11)	−0.0359 (7)	0.2296 (7)	0.0543 (2)
C(6)	0.3475 (12)	−0.0049 (8)	0.1908 (8)	0.0319 (2)
C(7)	0.5116 (15)	−0.1033 (10)	0.1431 (9)	0.0476 (3)
C(8)	0.6867 (14)	−0.0780 (11)	0.1037 (10)	0.0484 (3)
C(9)	0.7047 (14)	0.0442 (11)	0.1121 (10)	0.0497 (3)
C(10)	0.5381 (13)	0.1358 (10)	0.1595 (9)	0.0433 (3)
N(3)	0.3600 (10)	0.1132 (7)	0.1983 (7)	0.0363 (2)
O(1)	0.2812 (11)	0.3828 (7)	0.2406 (6)	0.0478 (2)
O(2)	0.1676 (12)	0.3405 (8)	0.4342 (7)	0.0656 (3)
C(11)	0.2559 (13)	0.4009 (9)	0.3552 (9)	0.0420 (3)
C(12)	0.3432 (16)	0.4978 (11)	0.3897 (11)	0.0645 (3)
O(3)	−0.0990 (10)	0.4054 (6)	0.2218 (6)	0.0443 (2)
O(4)	−0.0687 (11)	0.2972 (7)	0.0621 (7)	0.0547 (2)
C(13)	−0.1433 (12)	0.3957 (9)	0.1214 (8)	0.0353 (3)
C(14)	−0.2885 (15)	0.5071 (11)	0.0745 (10)	0.0523 (3)
O(5)	0.1425 (13)	0.3545 (7)	0.6851 (7)	0.0663 (3)

Table 4. *Geometric parameters* (Å, °) *for* (II)

Cu—N(1)	1.971 (8)	C(11)—O(1)	1.282 (12)
Cu—N(3)	2.000 (8)	C(11)—O(2)	1.217 (13)
Cu—O(1)	1.962 (7)	C(11)—C(12)	1.506 (14)
Cu—O(2)	2.471 (7)	C(13)—O(3)	1.262 (11)
Cu—O(3)	1.975 (7)	C(13)—O(4)	1.246 (12)
Cu—O(4)	2.700 (8)	C(13)—C(14)	1.501 (14)
N(1)—Cu—N(3)	92.0 (3)	O(3)—Cu—O(2)	95.2 (3)
N(1)—Cu—O(3)	94.0 (3)	Cu—O(1)—C(11)	101.3 (6)
N(1)—Cu—O(1)	155.1 (3)	O(1)—C(11)—O(2)	121.5 (9)
N(1)—Cu—O(2)	97.6 (3)	O(1)—C(11)—C(12)	117.8 (10)
N(3)—Cu—O(1)	94.3 (3)	O(2)—C(11)—C(12)	120.7 (10)
N(3)—Cu—O(2)	106.3 (3)	Cu—O(3)—C(13)	109.4 (6)
N(3)—Cu—O(3)	156.7 (3)	O(3)—C(13)—O(4)	121.4 (9)
O(1)—Cu—O(3)	89.6 (3)	O(3)—C(13)—C(14)	117.9 (9)
O(1)—Cu—O(2)	57.6 (3)	O(4)—C(13)—C(14)	120.7 (9)

The complex [Cu(dpyam)$_2$(NO$_3$)$_2$] (I) was prepared by adding a solution containing 0.241 g (1 mmol) of Cu(NO$_3$)$_2$.3H$_2$O in 6 ml of water to a warm solution of 0.342 g (2 mmol) of dpyam in 5 ml of acetone. The olive-green microcrystals which separated from the deep-green solution by slow evaporation were recrystallized from hot water. Cubic dark-green single crystals of (I) were formed by slow evaporation at room temperature. For (I), analysis found C 45.21, H 3.20, N 20.95%; calculated for $C_{20}H_{18}CuN_8O_6$ C 45.33, H 3.42, N 21.14%. For the complex [Cu(dpyam)(CH$_3$COO)].H$_2$O (II), a hot solution containing 0.199 g (1 mmol) of Cu(CH$_3$COO)$_2$.H$_2$O in 15 ml of a water-acetone (1:1) mixture was added to a warm solution of 0.171 g (1 mmol) of dpyam in 5 ml of acetone. After a few days, blue-green rods of (II) appeared in the resulting dark green solution. For (II), analysis found C 47.48, H 4.10, N 11.78%; calculated for $C_{14}H_{17}CuN_3O_5$ C 47.66, H 4.29, N 11.91%.

The structures were solved using three-dimensional Patterson and Fourier-synthesis techniques. Least-squares refinements were carried out with anisotropic thermal parameters for all non-H atoms. All H atoms were located from a difference synthesis, except H(5*a*) and H(5*b*) of compound (II), and were refined with an overall isotropic temperature factor using a riding model for computed atoms [0.06 and 0.08 Å^2 for (I) and (II), respectively]. All calculations were carried out using *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986), *XANADU* (Roberts & Sheldrick, 1975) and *SCHAKAL* (Keller, 1987) on an IBM 3090 computer.

This work was partially supported by the CICYT (Spain) (project PB91-0807-C02-01). Instrumental and computing facilities of the Servicio de Espectroscopia y Centro de Cálculo de la Universitat de Velència are gratefully acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71179 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1036]

References

Aduldecha, S., Keniry, M. E., Akhter, P., Tyagi, S. & Hathaway, B. J. (1991). *Acta Cryst.* C**47**, 1378–1383.

Akhter, P., Fitzsimmons, P. & Hathaway, B. J. (1991). *Acta Cryst.* C**47**, 308–310.

Castro, I., Faus, J., Julve, M. & Gleizes, A. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1937–1944.

Castro, I., Faus, J., Julve, M., Journaux, Y. & Sletten, J. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2533–2538.

Castro, I., Julve, M., De Munno, G., Bruno, G., Real, J. A., Lloret, F. & Faus, J. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1739–1744.

Cinquantini, A., Opromolla, G. & Zanello, P. (1991). *J. Chem. Soc. Dalton Trans.* pp. 3161–3163.

Deacon, G. B. & Philips, R. J. (1980). *Coord. Chem. Rev.* **33**, 227–250.

Fitzgerald, W., Murphy, B., Tyagi, S., Walsh, A., Walsh, B. & Hathaway, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2271–2279.

Hathaway, B. J. (1984). *Struct. Bonding* (*Berlin*), **57**, 55–117.

Jacobson, R. A. & Jensen, W. P. (1981). *Inorg. Chim. Acta*, **52**, 205–209.

Jacobson, R. A. & Jensen, W. P. (1986). *Inorg. Chim. Acta*, **114**, L9–L10.

Jensen, W. P. & Jacobson, R. A. (1981). *Inorg. Chim. Acta*, **49**, 199–204.

Johnson, J. E., Beineke, T. A. & Jacobson, R. A. (1971). *J. Chem. Soc. A*, pp. 1371–1374.

Johnson, J. E. & Jacobson, R. A. (1973*a*). *J. Chem. Soc. Dalton Trans.* pp. 580–584.

Johnson, J. E. & Jacobson, R. A. (1973*b*). *Acta Cryst.* B**29**, 1669–1674.

Keller, E. (1987). *SCHAKAL. Fortran Program for the Graphical Representation of Molecular and Crystallographic Models.* Univ. of Freiburg, Germany.

Mathews, I. I. & Manohar, H. (1991). *Acta Cryst.* C**47**, 1621–1624.

McWhinnie, W. R. (1970). *Coord. Chem. Rev.* **5**, 293–311.

Pyrka, G., Seeney, R. J. & Pinkerton, A. A. (1991). *Acta Cryst.* C**47**, 510–513.

Roberts, P. & Sheldrick, G. M. (1975). *XANADU. Program for Crystallographic Calculations*. Univ. of Cambridge, England.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELX86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sletten, J. (1982). *Acta Chem. Scand. Ser. A*, **36**, 345–351.
Sletten, J. (1984). *Acta Chem. Scand. Ser. A*, **38**, 491–496.
Thompson, J. S. & Whitney, J. F. (1984). *Inorg. Chem.* **23**, 2813–2819.
Wu, L. P., Keniry, M. E. & Hathaway, B. J. (1992). *Acta Cryst.* C**48**, 35–40.

Acta Cryst. (1993). C**49**, 1761–1762

Structure of the Copper(II) Complex of Isonicotinic Acid

Nobuo Okabe, Tomoko Nakamura
and Hatsuko Fukuda

*Department of Pharmaceutical Sciences,
Kinki University, Kowakae, 3-4-1, Higashi Osaka,
Osaka 577, Japan*

(*Received* 25 *September* 1992; *accepted* 25 *March* 1993)

Abstract

In crystals of diaquabis(isonicotinato-*N*)copper(II) dihydrate, the Cu atom is four-coordinate with the two N atoms of the pyridine rings and the two O atoms of the two water molecules in a *trans* orientation. The coordination geometry is square planar with distances Cu—O 1.985 (2) and Cu—N 2.004 (2) Å.

Comment

Both isoniazid and iproniazid are well known isonicotinic acid derivatives which are used as antituberculosis drugs (Carrington, Bird & Levence, 1984; Pinelopi, 1988), and have bacterial mutagenecity (Parodi *et al.*, 1981). These derivatives inhibit copper(II)-containing serum amine oxidase (Morpurgo *et al.*, 1988; Masuda, Nakamura & Shimomura, 1990). In order to obtain structural information on the mode of interaction between copper(II)-containing amine oxidase and isoniazid and/or iproniazid, we thought it worthwhile to investigate the crystal structure of the complex of isonicotinic acid with copper(II). To date, the crystal structures of the complexes of isonicotinic acid with calcium(II) (Cole & Holt, 1989) and with copper(I) chloride (Goher & Mak, 1985) have been determined, but the complex with copper(II) has not been subjected to crystal-structure analysis.

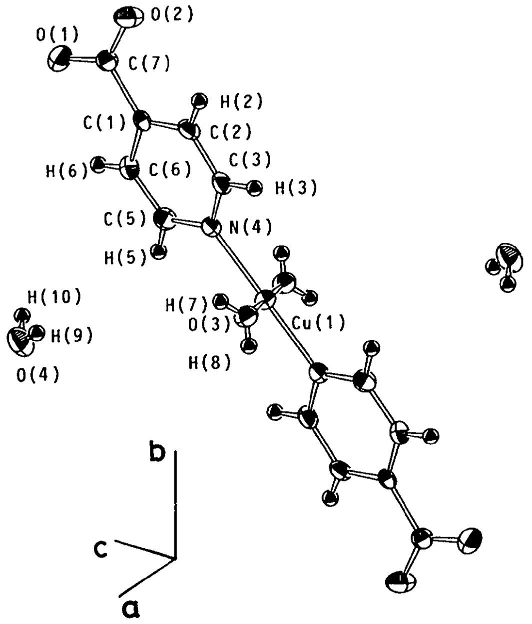

Fig. 1. Perspective view of diaquabis(isonicotinato)copper(II) dihydrate with atomic numbering, along the *a* and *c* axes.

Experimental

Crystal data

$[Cu(C_6H_4NO_2)_2(H_2O)_2]$.-$2H_2O$
$M_r = 379.81$
Triclinic
$P\bar{1}$
$a = 6.895\ (1)$ Å
$b = 9.181\ (1)$ Å
$c = 6.3377\ (8)$ Å
$\alpha = 105.24\ (1)^\circ$
$\beta = 108.20\ (1)^\circ$
$\gamma = 99.45\ (1)^\circ$
$V = 354.2\ (1)$ Å^3
$Z = 1$
$D_x = 1.781$ Mg m^{-3}
$D_m = 1.780\ (1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 43.5\text{–}48.3^\circ$
$\mu = 1.588$ mm^{-1}
$T = 296$ K
Plate
0.40 × 0.40 × 0.30 mm
Blue
Crystal source: solution of isonicotinic acid-$CuCl_2$ (1:7) in 10% ethanol

Data collection

Rigaku AFC-5*R* diffractometer
ω-2θ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{min} = 0.79$, $T_{max} = 1.29$
1756 measured reflections
1621 independent reflections
1487 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.013$
$\theta_{max} = 55.0^\circ$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -8 \rightarrow 7$
3 standard reflections monitored every 150 reflections
intensity variation: none

Acta Crystallographica Section C
ISSN 0108-2701 ©1993