Gable, R. W., Hoskins, B. F. & Robson, R. (1990). *J. Chem. Soc. Chem. Commun.* pp. 762–763.
Iwamoto, T. (1991). *Inclusion Compounds*, Vol. 5, edited by J. L. Atwood, J. E. D. Davies & D. D. MacNicol, ch. 6, pp. 177–212. Oxford University Press.
Iwamoto, T. (1996). *Comprehensive Supramolecular Chemistry*, Vol. 6, edited by D. D. MacNicol, F. Toda & R. Bishop, ch. 19, pp. 643–690. Oxford: Pergamon Press
Kim, J., Whang, D., Koh, Y. S. & Kim, K. (1994). *J. Chem. Soc. Chem. Commun.* pp. 637–638.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1996*a*). *XSCANS. Data Collection Software Programs.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *SHELXTL. Structure Determination Software Programs.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 1241–1243

Aqua(1,10-phenanthroline)(L-prolinato)-copper(II) nitrate monohydrate

RAMAIYER VENKATRAMAN,[a] JEFFREY D. ZUBKOWSKI[a] AND EDWARD J. VALENTE[b]

[a]*Department of Chemistry, Jackson State University, Jackson, MS 39217, USA, and* [b]*Department of Chemistry, Mississippi College, Clinton, MS 39058-4036, USA. E-mail: valente@mc.edu*

(*Received 20 January 1999; accepted 20 April 1999*)

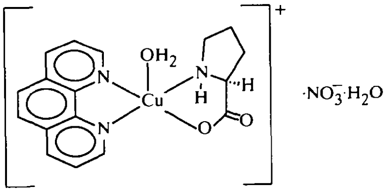
Abstract

The reaction of copper(II) nitrate hydrate with L-proline in the presence of one equivalent of 1,10-phenanthroline produces the title ternary complex, $[Cu(C_5H_8NO_2)(C_{12}H_8N_2)(H_2O)]NO_3 \cdot H_2O$. The enantiomorphous molecules contain two square-pyramidal complex cations as a loosely associated dimer. The bidentate proline ligands differ in conformation in the cations. In one cation, L-proline α-CH and NH groups lie on the same side as coordinated water and the Cu—OH_2 distance [2.382 (3) Å] is longer than in the other cation [2.234 (4) Å], in which the α-CH and NH groups lie below the pyramid base away from coordinated water. Additionally, copper is coordinated weakly by carboxyl oxygen from a neighboring inequivalent complex *trans* to water, with the longer C═O···Cu distance [3.390 (4) Å] opposite the shorter Cu—OH_2 distance, and the shorter C═O···Cu distance [3.102 (4) Å] opposite the longer Cu—OH_2 distance. Uncoordinated nitrates are hydrogen bonded to both coordinated and uncoordinated waters.

Comment

The role of ternary copper(II) complexes in biological systems is well documented (Baran, 1995; Sabat, 1996). Of particular interest are systems in which both purine and pyrimidine ligands and amino acids coordinate metal ions (Garcia-Raso *et al.*, 1998; Szalda & Kistenmacher, 1977). A variety of monomeric ternary complexes between copper(II), bidentate nitrogenous ligands like 2,2′-bipyridyl and 1,10-phenanthroline, and α-amino acids have been described (Griesser & Sigel, 1970; Fischer & Sigel, 1980; Kwik *et al.*, 1980; Antolini *et al.*, 1986). The typical structure involves an *O,N*-bidentate amino acid coordination, square-pyramidal coordination geometry and an apical water (Antolini *et al.*, 1983, 1985). Because L-proline, among the biologically important amino acids, is an unsymmetrical secondary amine, the resulting complexes are diastereomeric. A similar situation can occur in comparable 3-hydroxy-L-proline complexes. This leads to the possibility that on crystallization, diastereomers may form separate phases.

In the present case, the ternary complex of copper(II), 1,10-phenanthroline (*o*-phen) and L-proline, (I), crystallizes in space group $P2_1$, with two complex cations in the asymmetric unit. Copper ions in each cation have distorted square-pyramidal coordination geometry with bidentate phenanthroline, *O,N*-bidentate proline and apical water. The vacant coordination site is blocked distantly by the proline carboxyl oxygen of a neighboring complex cation, which serves to link the complexes weakly as dimers. Coordinated water in one complex cation is on the same side of the pyramid as the proline NH group. In this orientation, the NH group (N—H 1.0 Å) forms a hydrogen bond with an uncoordinated water oxygen [N6···O3*W* 2.87 (1) Å, H6*A*···O3*W* 1.89 (3) Å and angle at H6*A* 166 (3)°]. In the other cation, water is on the opposite side from the proline NH group, which makes a much weaker hydrogen bond to a nitrate oxygen [N3···O51^{i} 3.27 (1) Å, H3*B*···O51^{i} 2.44 (3) Å and angle at H3*B* 140 (3)°; symmetry code: (i) $2-x$, $\frac{1}{2}+y$, $-z$]. The configuration at the proline nitrogen and the α-carbon is *S* in each complex cation. The pyrrolidine rings adopt different conformations in the two cations. The proline coordinated to Cu1 has the C_2–C^{γ}-*exo* conformation and that coordinated to Cu2 has the C_s–C^{δ}-*endo* conformation (IUPAC–IUB Commission on Biochemical Nomenclature, 1970; Balasubramanian *et al.*, 1971). In one of the complex cations, considerable thermal motion is noted in the pyrrolidine



(I)

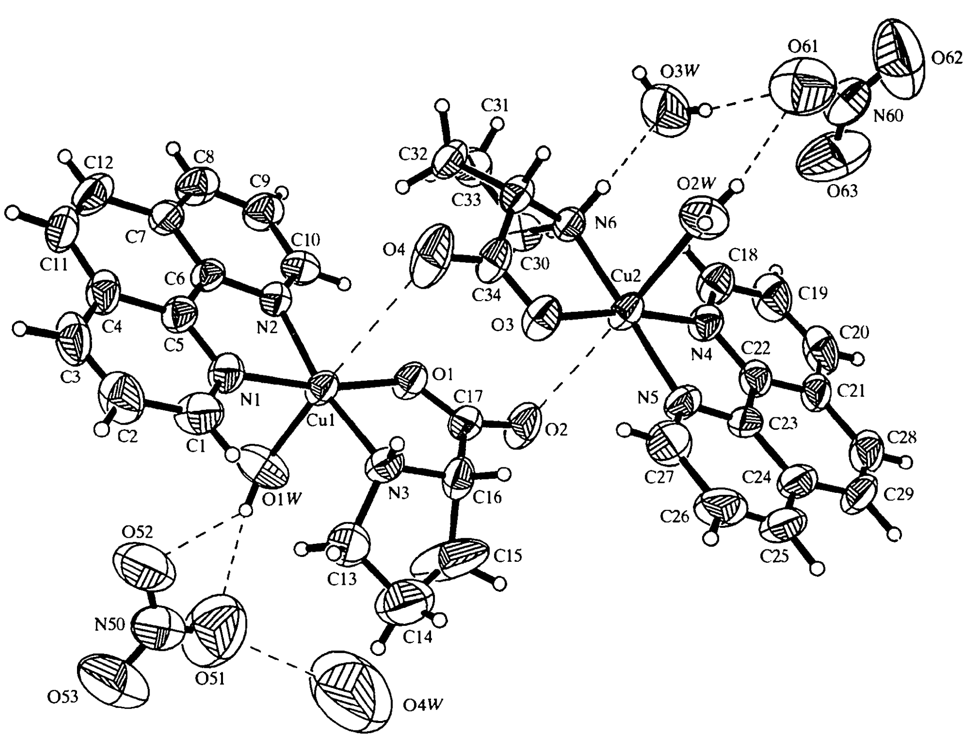


Fig. 1. Displacement ellipsoid plot (50% probability enclosure) of the loosely associated cation pairs, and hydrogen bonding to the anions and water solvate molecules.

ring at C13, C14 and C15, which produces abnormally short C—C distances. This is not unusual in prolinyl structures determined at ambient temperatures. A disorder model was tried without success.

In terms of the copper coordination sphere, the two independent cations have an approximate centrosymmetric relationship, ignoring the disparate Cu—O(water) distances. Cu atoms are displaced slightly from the mean N_3O plane toward the apical water O atoms, and the Cu—O(water) distances in the cations differ inversely with the length of the contacts with the distant carbonyl O atoms; Cu1—O1*W* 2.234 (4) and Cu2—O2*W* 2.382 (3) Å differ by 0.148 Å or 30 s.u.'s. In the similar ternary complex cation $[Cu(o\text{-phen})(\text{L-glu})(H_2O)]^+$, which also contains two independent molecules in the structure (Antolini *et al.*, 1985), apical Cu—O distances differ by 0.069 Å or 10 s.u.'s.

Experimental

An aqueous solution of copper(II) nitrate hydrate (1.0 mmol) in water (20 ml) was added slowly to an ethanolic solution of 1,10-phenanthroline (1.0 mmol). A blue precipitate formed immediately. A solution of L-proline (1.0 mmol) in water (10 ml) was added slowly followed by 1.0 *M* ammonium hydroxide until the solution was clear blue (pH 8–9). The solvent was allowed to evaporate slowly and blue–violet crystals separated after several days. Differential scanning calorimetry showed a single broad dehydration endotherm centered at 335 K, followed later by a sharp decomposition exotherm at 513 K. IR spectrum (KBr pellet; cm^{-1}): 3142 (*w*, NH), 2927 (*w*, CH), 1623 (*s*, C=O), 1518 (*s*, C—O), 1428 (*m*, CH_2), 1384 (*s*, C—O), 1148 (*m*), 1107 (*m*), 922 (*m*), 873 (*m*), 853 (*s*), 778 (*s*), 773 (*s*).

Crystal data

$[Cu(C_5H_8NO_2)(C_{12}H_8N_2)(H_2O)]NO_3{\cdot}H_2O$
$M_r = 911.82$
Monoclinic
$P2_1$
$a = 7.1732\,(17)$ Å
$b = 21.285\,(6)$ Å
$c = 12.280\,(3)$ Å
$\beta = 92.05\,(2)°$
$V = 1873.7\,(8)$ Å^3
$Z = 2$
$D_x = 1.616$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 11.5\text{–}31.5°$
$\mu = 1.22$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.70 × 0.40 × 0.40 mm
Clear blue–violet

Data collection

Siemens *R*3*m*/*V* diffractometer
ω scans (2.0° width)
Absorption correction: empirical (*XEMP* in *P*3 *Software*; Siemens, 1989)
$T_{min} = 0.483$, $T_{max} = 0.642$
7388 measured reflections
6942 independent reflections
3380 reflections with $I > 2\sigma(I)$

$R_{int} = 0.104$
$\theta_{max} = 32.57°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 32$
$l = -18 \rightarrow 18$
3 standard reflections every 197 reflections frequency: 180 min intensity decay: −1.7 (5)%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.101$
$S = 0.744$
6942 reflections
524 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0060 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.023 (13)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O1	1.918 (3)	Cu2—O3	1.941 (3)
Cu1—N3	2.004 (4)	Cu2—N5	1.992 (4)
Cu1—N2	2.020 (4)	Cu2—N6	1.997 (4)
Cu1—N1	2.033 (4)	Cu2—N4	2.031 (4)
Cu1—O1*W*	2.234 (4)	Cu2—O2*W*	2.382 (3)
C16—N3—C13—C14	8.5 (7)	C33—N6—C30—C31	38.0 (5)
N3—C13—C14—C15	−29.2 (8)	N6—C30—C31—C32	−40.2 (5)
C13—C14—C15—C16	38.3 (9)	C30—C31—C32—C33	27.0 (5)
C13—N3—C16—C15	15.3 (5)	C30—N6—C33—C32	−20.6 (5)
C14—C15—C16—N3	−32.8 (7)	C31—C32—C33—N6	−4.2 (5)

The absolute structure was determined from the known absolute configuration of one of the ligands (L-proline) in the complex. The Flack (1983) parameter was refined without Friedel data. In the development of the molecular model from X-ray data, H atoms were located in difference Fourier maps and included in the model at calculated positions and allowed to refine using a riding model, except for the water H atoms (on O4*W*), which could not be found. $U_{\rm iso}$ values for H atoms were assigned values 120% of the $U_{\rm eq}$ values of the attached non-H atoms or 150% in the case of water H atoms.

Data collection: *P*3 *Software* (Siemens, 1989). Cell refinement: *P*3 *Software*. Data reduction: *XDISK* in *P*3 *Software*. Program(s) used to solve structure: *SHELXS*93 (Sheldrick, 1993). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *P*3 *Software*. Software used to prepare material for publication: *SHELXL*97.

We thank the Office of Naval Research for support of instrumentation (EJV and JDZ) and the National Science Foundation (DUE-9250769).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1195). Services for accessing these data are described at the back of the journal.

References

Antolini, L., Battaglia, L. P., Corradi, A. B., Marcotrigiano, G., Menabue, L., Pellacani, G. C., Saladini, M. & Sola, M. (1986). *Inorg. Chem.* **25**, 2901–2904.
Antolini, L., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1983). *Inorg. Chem.* **22**, 141–145.
Antolini, L., Marcotrigiano, G., Menabue, L., Pellacani, G. C., Saladini, M. & Sola, M. (1985). *Inorg. Chem.* **24**, 3621–3626.
Balasubramanian, R., Lakshminarayanan, A. V., Sebesan, M. N., Tegoni, G., Venkatesan, K. & Ramachandran, G. N. (1971). *Int. J. Protein Res.* **3**, 25–33.
Baran, E. J. (1995). In *Quimica Bioinorganica*. Madrid: McGraw-Hill/Interamericana de Espana.
Fischer, B. E. & Sigel, H. (1980). *J. Am. Chem. Soc.* **102**, 2998–3008.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Garcia-Raso, A., Fiol, J. J., Adrover, B., Moreno, V., Molins, E. & Mata, I. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1031–1036.
Griesser, R. & Sigel, H. (1970). *Inorg. Chem.* **9**, 1238–1243.
IUPAC–IUB Commission on Biochemical Nomenclature (1970). *J. Mol. Biol.* **52**, 1–17.
Kwik, W. L., Ang, K. P. & Chen, G. (1980). *J. Inorg. Nucl. Chem.* **42**, 303–313.
Sabat, M. (1996). *Metal Ions in Biological Systems*, Vol. 32, edited by A. Sigel & H. Sigel. New York and Basel: Marcel Dekker.
Sheldrick, G. M. (1993). *SHELXS93. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1989). *P3 Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Szalda, D. J. & Kistenmacher, T. J. (1977). *Acta Cryst.* B**33**, 865–869.

Acta Cryst. (1999). C**55**, 1243–1246

$[Cu_2\{1,4\text{-bis}[(3\text{-methyl-2-pyridyl})\text{amino}]\text{phthalazine–H}\}(N_3)_3]$ at 40 K

Andres E. Goeta,[a] Laurence K. Thompson,[b] Christopher L. Sheppard,[b] Santokh S. Tandon,[b] Christian W. Lehmann,[a]† John Cosier,[c] Craig Webster[c] and Judith A. K. Howard[a]

[a]*Department of Chemistry, Durham University, Durham DH1 3LE, England,* [b]*Department of Chemistry, Memorial University of Newfoundland, St Johns, Newfoundland, Canada A1B 3X7, and* [c]*Oxford Cryosystems, 3 Blenheim Office Park, Lower Road, Long Hanborough, Oxford OX8 8LN, England. E-mail: a.e.goeta@durham.ac.uk*

(Received 21 December 1998; accepted 21 April 1999)

Abstract

The structure of the title compound, μ-azido-1:2κ^2N^1-[μ-4-(3-methyl-2-pyridyl-2κN-amino)-1-(3-methyl-2-pyridyl-1κN-imino)-1,2-dihydrophthalazin-2-yl-1:2κ^2N^2:N^3]-bis[(azido-κN^1)copper(II)], $[Cu_2(C_{20}H_{17}N_6)(N_3)_3]$, (I), determined from data recorded at 40 (1) K using a new open-flow He gas cryostat, is presented here as part of an extended study program on dicopper(II) azide-bridged compounds. Each pair of Cu^{II} centres in (I) is equatorially bridged by a μ_2-1,1-azide, with a bridge angle of 107.2 (1)°. The dinuclear centres form tetranuclear clusters through two μ_2-1,3-azide bridges, which in turn form chains along the *a* axis. Two C—

---

† Current Address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470-Mülheim an der Ruhr, Germany.