Pergamon

0277-5387(95)00011-9

Polyhedron Vol. 14, No. 15–16, pp. 2165–2171, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

COPPER(II) NITRATE COMPOUNDS WITH HETEROCYCLIC LIGANDS: STRUCTURES OF $[Cu(NO_3)(2,2'\text{-DIPYRIDYL})_2][NO_3]\cdot H_2O$ AND $[Cu(H_2O)(1,10\text{-PHENANTHROLINE})_2][NO_3]_2$

K. J. CATALAN, S. JACKSON and J. D. ZUBKOWSKI*

Department of Chemistry, Jackson State University, Jackson, MS 39217, U.S.A.

D. L. PERRY*

Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.

E. J. VALENTE

Department of Chemistry, Mississippi College, Clinton, MS 39056, U.S.A.

L. A. FELIU* and A. POLANCO

Department of Natural Sciences, Universidad Metropolitana, Ana G. Mendez
University System, Rio Pedras, PR 00928, Puerto Rico

(*Received* 8 *November* 1994; *accepted* 8 *December* 1994)

Abstract—The crystal and molecular structures of $[Cu(NO_3)(2,2'\text{-dipyridyl})_2](NO_3)\cdot H_2O$ (**1**) and $[Cu(H_2O)(1,10\text{-phenanthroline})_2](NO_3)_2$ (**2**) have been determined by single crystal X-ray diffraction. The copper cation in **1** displays pseudo-octahedral geometry with ligand nitrogen donors occupying four positions, a coordinated nitrato oxygen a fifth and a non-bonded oxygen a sixth. The copper cation in **2** shows a trigonal bipyramidal geometry with ligand nitrogen donors occupying the axial and two of the equatorial positions, and a coordinated aqua oxygen the other.

Copper complexes of 2,2′-bipyridine and 1,10-phenanthroline have been observed as playing a role in a number of biochemical processes in natural systems. Antimycoplasmal activity has been observed[1] with copper(II) complexes of 2,2′-bipyridine, while the inhibition of the activity of the cyclic nucleotide phosphodiesterase of yeast involving 1,10-phenanthroline[2] and copper has been reported. The role of 2,2′-bipyridine in the uptake of *Gallisepticum* cells has been reported[3] and the incubation of rat liver nuclei with copper(II)/1,10-phenanthroline species to enhance the susceptibility of chromatin to the action of micrococcal nuclease[4] has also appeared in the literature. Differences in the toxicity of copper(II) to *Nitzschia closterium* in the presence of 1,10-phenanthroline have been reported.[5]

The copper(II)–2,2′-bipyridine/1,10-phenanthroline systems have also been used extensively in technology applications. Chang and Weil[6] have reported data concerning electrochemical processes in the electroplating of copper using copper(II) solutions in conjunction with 1,10-phenanthroline. Coal desulphurization involving coal liquids has been effected using catalysts of copper(II)–2,2′-bipyridine. This catalytic process was able to be conducted at relatively low temperatures, at which carbon–sulphur bonds in aryl sulphides were observed to be broken.[7] Copper(II) salts with 2,2′-bipyridine have been used in the electrodeless deposition of copper on printed electronic circuit

---

*Authors to whom correspondence should be addressed.

boards.[8] In this study, the effects of adding the 2,2′-bipyridine to the plating process resulted in smooth ductile deposits which had lower hydrogen concentrations and higher elongations.

Initial work in this area in this laboratory has involved the synthesis and structural characterization of the reaction products of copper(II) nitrate with 2,2′-dipyridine and related-type ligands. In the present paper $[Cu(NO_3)(2,2'\text{-dipyridine})_2](NO_3)\cdot H_2O$ (**1**) has been prepared. When the analogous reaction is effected with 1,10-phenanthroline, the compound $[Cu(H_2O)(1,10\text{-phenanthroline})_2](NO_3)_2$ (**2**) was isolated. The crystal and molecular structures of the two complexes are reported herein. Compound **2** has been investigated for its bonding properties,[9] electronic properties[10] and structure.[11]

EXPERIMENTAL

General

Copper(II) nitrate hydrate, $Cu(NO_3)_2\cdot 2.5H_2O$, 2,2′-dipyridine and 1,10-phenanthroline were purchased from Aldrich Chemical and used without further purification. IR spectra were obtained as KBr pellets on a Mateson Polaris FT-IR. UV–vis were obtained on a PE Lambda 3B spectrophotometer with water as solvent.

Analysis

Elemental analysis for carbon, hydrogen and nitrogen were in agreement with calculated values.

Synthesis of $[Cu(NO_3)(2,2'\text{-dipyridine})_2](NO_3)\cdot H_2O$ (**1**)

$Cu(NO_3)_2\cdot 2.5H_2O$ (1.00 g, 5.23 mmol) was dissolved in 50 cm^3 of ethanol. To this solution, 1.67 g (10.67 mmol) of 2,2′-dipyridine was added. The solution was refluxed for 30 min. Blue crystals were obtained from the cooled solution, specimens of which were suitable for study by single-crystal X-ray diffraction. The solid was filtered from solution and washed with cold ethanol. The decomposition point was 279–281°C. IR (KBr pellet): 3050, 1600, 1350 (s), 1100 (s), 770 cm^{-1} (s denotes a strong peak). UV–vis: 315 ($\varepsilon = 736.8\ cm^{-1}\ M^{-1}$) and 700 ($\varepsilon = 60.2\ cm^{-1}\ M^{-1}$).

Synthesis of $[Cu(H_2O)(1,10\text{-phenanthroline})_2](NO_3)_2$ (**2**)

$Cu(NO_3)_2\cdot 2H_2O$ (3.10 g, 13.32 mmol) was dissolved in 100 cm^3 of ethanol. To this solution 5.09 g (25.70 mmol) of 1,10-phenanthroline was added and the solution was stirred overnight at room temperature. A green precipitate formed which was filtered and washed with ethanol yielding 6.78 g (11.99 mmol, 90.0% yield).

Compound **2** (0.5 g) was dissolved in a 1 : 1 mixture of water and methanol. The solution was allowed to stand overnight at 80°C, and yielded green crystals which were suitable for study by single crystal X-ray diffraction. IR (KBr pellet): 3510, 3050, 1675, 1650, 1600, 1350 cm^{-1} (s). UV–vis: 330 nm ($\varepsilon = 904.0\ cm^{-1}\ M^{-1}$).

Crystallography

For **1**, data were collected on an Enraf–Nonius CAD-4 diffractometer fitted with a molybdenum source and a graphite monochromator (wavelength = Mo-K_α 0.71073 Å).[12] Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry.[13] Relevant crystallographic data are summarized in Table 1. The structure was solved by direct methods (SHELXS)[14] and refined using standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms, anisotropic vibrational amplitude features were found corresponding to the positions of the hydrogen atoms. Ligand hydrogen atom positions were assigned idealized locations. Hydrogen atoms were included in structure factor calculations, but not refined. Hydrogen atoms for water molecules were placed at the positions from subsequent difference Fourier maps. Their positions and isotropic vibrational amplitudes were refined.

Data for compound **2** were collected on a Siemens R3m/V automated diffractometer fitted with a molybdenum source and a graphite monochromator (wavelength = Mo-K_α 0.71073 Å). Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry.[13] Relevant crystallographic data are summarized in Table 1.

The structure was found by location of the copper atom in a Patterson function map, and the remaining atoms from subsequent difference Fourier calculation maps.[14] A model in $C2/c$ was first tried in which copper was placed in special positions at 0, 0.094, 1/4, as reported previously.[11] It eventually included all non-hydrogen atom positions with attendant anisotropic vibrational terms, and hydrogen atoms in calculated positions with isotropic vibrational factors. As the refinement (full-matrix

Table 1. Structural determination summary

	1	**2**
Empirical formula	$C_{20}H_{18}CuO_7N_6$	$C_{24}H_{18}CuN_6O_7$
Crystal form	Pale blue, irregular prisms	Blue, elongated prisms
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	Cc (no. 9)
Unit cell dimensions	$a = 12.0449(18)$ Å $b = 14.6299(21)$ Å $c = 15.0701(25)$ Å $\alpha = 61.789(13)^\circ$ $\beta = 86.352(13)^\circ$ $\gamma = 67.600(13)^\circ$	$a = 22.640(5)$ Å $b = 7.254(2)$ Å $c = 16.604(3)$ Å $\alpha = 90^\circ$ $\beta = 123.76(2)^\circ$ $\gamma = 90^\circ$
Z	4	4
Volume (Å^3)	2141.3(5)	2267.0(8)
D_{calc} (Mg m^{-3})	1.60	1.66
Size (mm)	$0.20 \times 0.20 \times 0.20$	$0.9 \times 0.45 \times 0.12$
Formula weight (amu)	517.9	564.0
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)	Mo-K_α ($\lambda = 0.71073$ Å)
Scan type	θ–2θ	θ–2θ
No. of reflections collected	5582	2929
No. of unique reflections	5582	2523
Temperature (°C)	−85	20
Solution	Direct methods (SHELXS)	Patterson
Refinement method	Standard least-squares	Full-matrix least-squares
No. of parameters refined	626	341
Final R indices (obs. data)	$R = 3.33\%$, $R_w = 3.71\%$	$R = 4.24\%$, $R_w = 5.88\%$
R indices (all data)	$R = 5.91\%$	$R = 5.45\%$, $R_w = 7.39\%$
Goodness-of-fit	1.37	0.63
Largest difference peak/hole (e Å^{-3})	0.44, −0.10	0.73, −0.77

$R = \Sigma \| F_0| - |F_c \| / \Sigma(|F_0|)$, $R_w = [\Sigma(w|F_0| - |F_c|)^2 / \Sigma(wF_0{}^2)]^{1/2}$.

Goodness-of-fit $= [\Sigma(w|F_0| - |F_c|)^2/(n_0 - n_v)]^{1/2}$, where n_0 = number of observations, n_v = number of parameters and w = weights.

least-squares minimizing differences in F values) approached convergence, the nitrates appeared to exhibit disorder and the coordinated water oxygen was poorly fitted. The final R (in $C2/c$) was 0.0470 for 187 variables. A model in the polar space group Cc was tried in which copper was again placed in special positions 0, 0.094, 1/4, and each phenanthroline was modelled separately. Nitrates became ordered and the coordinated water oxygen showed an improved model; however, the least-squares were unstable unless the nearly two-fold related phenanthroline and nitrate atom positions were refined in alternate cycles. The final R (in Cc) was 0.0424 for 341 variables, a model which fitted the data significantly better than the $C2/c$ model at the 0.5% confidence level; reflection statistics favour the choice of a non-centrosymmetric space group as well. R_w was 0.0588, goodness-of-fit = 0.61, final difference Fourier features did not exceed +0.73 and −0.77 e Å^{-3}, notably around the copper position.

Scattering factors for both structures were taken from the *International Tables for X-ray Crystallography*.[15]

RESULTS AND DISCUSSION

The reaction of copper nitrate with heterocyclic ligands can produce at least three different products depending on the nature of the ligand and the conditions of the reaction. For 2,2′-dipyridine and 4,4′-dimethyl-2,2′-dipyridine the product has the formula $[Cu(NO_3)L_2]^+$, where L = the bidentate nitrogen heterocyclic ligand. When the ligand is 1,10-phenanthroline, the product has the formula $[Cu(H_2O)L_2]^{2+}$. For the reaction of copper nitrate with 2,2′-dipyridine at pH 10, the product is $[Cu(\mu\text{-}OH)(NO_3)(2,2'\text{-dipyridine})]_2$.[16]

Structure of $[Cu(NO_3)(2,2'\text{-dipyridine})_2](NO_3) \cdot H_2O$ (**1**)

The structure of the cation of **1** (Fig. 1) is best approximated as having a distorted *cis*-octahedral

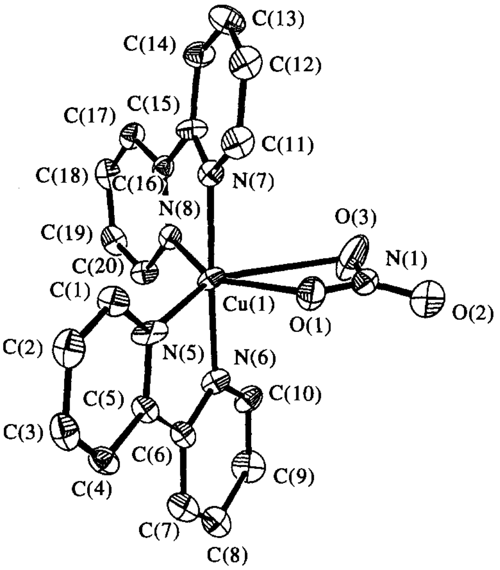

Fig. 1. ORTEP of $Cu(NO_3)(bipyridyl)_2^+$, 50% ellipsoids. Hydrogen atoms are omitted for clarity.

geometry. Selected bond distances and interbond angles are given in Table 2. The structure consists of two crystallographically independent copper complexes in the unit cell. Both complexes have the same molecular structure. The molecules are arranged with one dipyridine ligand overlapping a dipyridine ligand on the independent molecule at an average distance of 3.71 Å. Copper is coordinated to the nitrogen donors of two dipyridyl ligands and two oxygens of a nitrate. Two nitrogens are axially coordinated with linear N—Cu—N angles. Nitrate bonds in an unsymmetrical mode. One oxygen of the nitrate is coordinated to the copper at a distance of 2.12 (2.18) Å, while the other is more distant at 2.82 (2.72) Å. By comparison, the nitrito group in $[Cu(dipyridyl)_2(O_2N)][NO_3]$ is more symmetrically bonded at 2.27 and 2.35 Å;[17] the Cu—ONO_2 distance is 2.540 Å in $Cu(xanthine)_2(NO_3)_2 \cdot 2H_2O$.[18] The non-bonded oxygens of the nitrate are an average of 4.20 Å away from the copper. $Cu(2,2'\text{-dipyridine})_2(O_2N)][NO_3]$ is described as *cis*-distorted octahedral. While the two compounds are similar in geometry, bonding of the nitrito group is more symmetric and results in an approximate C_2 axis along the copper and nitrogen (of the nitrite group) vector. Distances for a Cu^{II}—O bond range from 2.23 to 3.97 (±0.06) Å, with an average bond distance of 2.66 Å.[15] A distance of 2.82 Å could suggest a weak interaction between the copper and oxygen. "Equatorial" N—Cu—N angles are 125.5° (130.1°), suggesting a distorted trigonal bypyramidal coordination. However, the adjacent N—Cu—O angle is about 90° in both molecules. The bite angle of O—Cu—O is 48°, suggesting that a second oxygen of the nitrate occupies a coordination site while not being sym-

Table 2. Selected bond distances (Å) and bond angles (°) for **1**

Molecule one		Molecule two	
Cu(1)—O(1)	2.116	Cu(2)—O(4)	2.184(3)
Cu(1)—O(3)	2.822(4)	Cu(2)—O(6)	2.717(3)
Cu(1)—N(5)	2.109(3)	Cu(2)—N(9)	2.097(3)
Cu(1)—N(6)	1.978(3)	Cu(2)—N(10)	1.981(3)
Cu(1)—N(7)	1.974(3)	Cu(2)—N(11)	1.969(3)
Cu(1)—N(8)	2.021(3)	Cu(2)—N(12)	2.036(3)
O(1)—Cu(1)—O(3)	48.25(11)	O(4)—Cu(2)—O(6)	50.66(10)
O(1)—Cu(1)—N(5)	90.64(12)	O(4)—Cu(2)—N(9)	94.69(11)
O(1)—Cu(1)—N(6)	89.88(13)	O(4)—Cu(2)—N(10)	88.00(12)
O(1)—Cu(1)—N(7)	88.86(13)	O(4)—Cu(2)—N(11)	89.74(12)
O(1)—Cu(1)—N(8)	143.77(13)	O(4)—Cu(2)—N(12)	135.28(12)
O(3)—Cu(1)—N(5)	138.11(12)	O(6)—Cu(2)—N(9)	144.49(11)
O(3)—Cu(1)—N(6)	90.62(14)	O(6)—Cu(2)—N(10)	89.53(12)
O(3)—Cu(1)—N(7)	86.56(13)	O(6)—Cu(2)—N(11)	88.14(12)
O(3)—Cu(1)—N(8)	96.10(12)	O(6)—Cu(2)—N(12)	85.13(11)
N(5)—Cu(1)—N(6)	80.13(13)	N(9)—Cu(2)—N(10)	80.63(13)
N(5)—Cu(1)—N(7)	102.55(13)	N(9)—Cu(2)—N(11)	100.72(13)
N(5)—Cu(1)—N(8)	125.52(13)	N(9)—Cu(2)—N(12)	130.01(13)
N(6)—Cu(1)—N(7)	177.05(14)	N(10)—Cu(2)—N(11)	177.46(13)
N(6)—Cu(1)—N(8)	97.88(14)	N(10)—Cu(2)—N(12)	99.40(13)
N(7)—Cu(1)—N(8)	81.60(14)	N(11)—Cu(2)—N(12)	81.40(13)

metrically bonded. The coordination geometry is therefore better described as a distorted octahedron rather than a trigonal bipyramid.

The water molecule and the uncoordinated nitrate form a hydrogen-bonding unit consisting of four water molecules and four nitrates. This is shown in Fig. 2. One nitrate [consisting of N(3), O(7), O(8) and O(9)] accepts two hydrogen bonds, O(7)···H(3)—O(14) and O(8)···H(1)—O(13), with an O···O distance of 2.88 and 2.93 Å, respectively. The other nitrate [consisting of N(4), O(10), O(11) and O(12)] accepts one hydrogen bond, O(11)···H(4)—O(14), with an O···O distance of 2.87 Å. O(14) (a water oxygen) accepts one hydrogen bond, O(14)···H(2)—O(13), with an O···O distance of 2.95 Å.

Bond distances and angles in the dipyridine ligands and the nitrates appear normal. The mean values for the C—N, C—C and pyridine–pyridine lengths are 1.35, 1.38 and 1.48 Å. An analogous compound for which this laboratory has gathered preliminary data, $[Cu(NO_3)(4,4'\text{-dimethyl-dipyridine})_2][NO_3]$,[19] is isostructural with **1** with respect to its coordination sphere.

Structure of $[Cu(H_2O)(1,10\text{-phenanthroline})_2][NO_3]_2$ (**2**)

The structure of the cation of **2** (Fig. 3) contains the CuN_4O core with an approximate trigonal bipyramid geometry. A comparison of selected bond lengths and interbond angles of **2**, the structure reported earlier,[11] and the related $[Cu(H_2O)(1,2\text{-bis}(9\text{-methyl-}1,10\text{-phenantrolin-}2\text{-yl})\text{ethane})][ClO_4]_2$, (**3**),[20] are given in Table 3. Axial and equatorial Cu—N bond lengths are similar for all three compounds. Oxygen from the water molecule occupies an equatorial position with a Cu—O distance of 2.190 Å, comparable to the Cu—O distance of 2.198 Å found in **2**, somewhat longer than the Cu—O distance of 1.938 Å in $Cu(\text{xanthine})_2(NO3)_2\cdot 2H_2O$ but similar to the longer Cu—O distance of 2.28(1) Å in $[Cu(\text{theo})_2(H_2O)_3]$.[21] The nitrate ligands hydrogen-bond to the coordinated water molecule; O—O distances are 2.78 and 2.84 Å. This compares to 2.79 Å in $Cu(NO_3)_2\cdot 21/2H_2O$[22] and 2.77 Å reported earlier. A similar five-coordinate geometry has recently been reported for $[Cu(1,10\text{-phenanthroline})_2Br][ClO_4]$.[23]

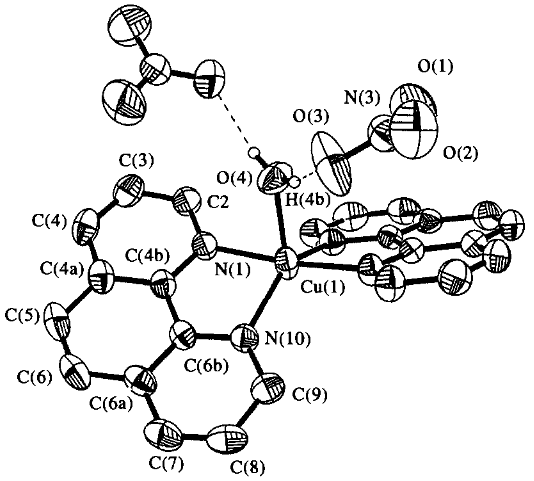

Fig. 3. ORTEP of $Cu(H_2O)(\text{phenanthroline})_2^+$, 50% ellipsoids, showing hydrogen bonding to nitrates. Hydrogens bonded to carbon are omitted for clarity.

Acknowledgements—We thank the Office of Naval Research (J. D. Z.) and the JSU/LBL/AGMEF Consortium (D. L. P., L. A. F. and A. P.) for support, as well as the U.S. Department of Energy under contract No. DE-AC03-76SF00098. The authors also wish to

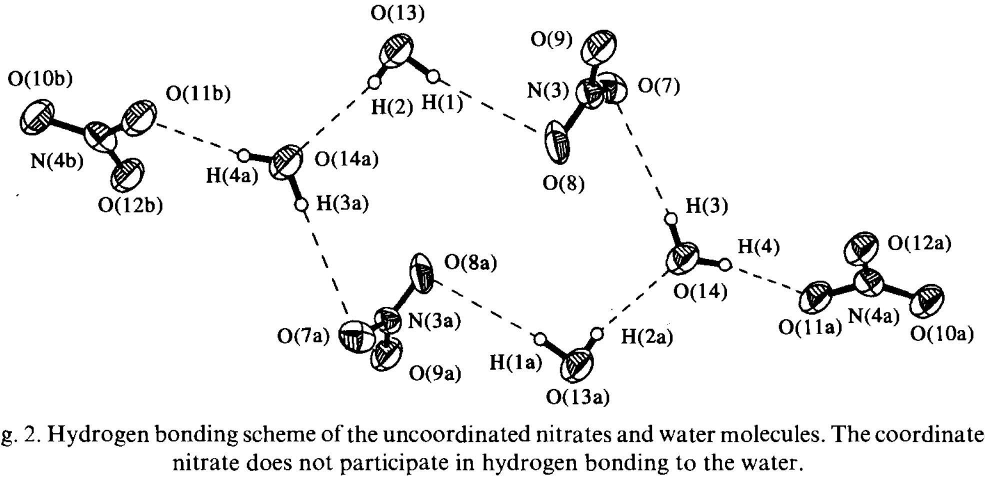

Fig. 2. Hydrogen bonding scheme of the uncoordinated nitrates and water molecules. The coordinated nitrate does not participate in hydrogen bonding to the water.

Table 3. A Comparison of selected bond distances (Å) and bond angles (°) for [Cu(H_2O)(1,10-phenanthroline)$_2$](NO_3)$_2$ (A), the previously reported structure (B) and [Cu(H_2O)(9-methyl-1,10-phenanthrolin-2-yl)$_2$](ClO_4)$_2$ (C)

	A	B	C
Cu(1)—N(10)	2.012(12)	2.03(1)	2.094(5)
Cu(1)—N(1a)	1.982(13)	1.99(1)	1.967(5)
Cu(1)—N(10a)	2.040(9)	2.03(1)	2.089(4)
Cu(1)—N(1)	2.018(14)	1.99(1)	1.984(5)
Cu(1)—4	2.190(5)	2.18(1)	2.198(4)
O(4)—O(3)	2.78	2.78 (ave)	[a]
O(4)—O(5)	2.84		[a]
N(1)—Cu(1)—N(10)	82.1(4)	83.0(4)	82.0(2)
N(10)—Cu(1)—N(1a)	101.9(5)	100.1(4)	102.5(2)
N(1)—Cu(1)—N(10a)	98.8(4)	—	99.3(2)
N(1)—Cu(1)—N(1a)	172.2(4)	171.0(4)	172.2(2)
N(10)—Cu(1)—N(10a)	139.7(4)	139.6(4)	132.6(2)
O(4)—Cu(1)—N(1)	84.9(5)	85.5(4)	83.7(2)
O(4)—Cu(1)—N(10)	113.0(5)	110.(4)	122.6(2)
O(4)—Cu(1)—N(1a)	87.3(6)	—	89.2(2)
O(4)—Cu(1)—N(10a)	107.2(6)	—	104.7(2)
O(5)—N(4)—O(6)	116.8(15)	114(1)	[a]
O(5)—N(4)—O(7)	130.3(12)	128(1)	[a]
O(6)—N(4)—O(7)	111.8(17)	118(1)	[a]

[a] Perchlorate anion.

thank F. J. Hollander for help with the initial collection of some of the data. K. J. C. and S. J. thank the JSU-MARC Program for support under NIH grant No. T32GMO7672-17.

REFERENCES

1. H. Van der Goot, P. J. Pijper and H. Smit, in *Inflammatory Dis. Copper* (*Proc. Symp.*) (Edited by J. R. J. Sorenson), pp. 409–422. Humana Press, Clifton, NJ (1983).
2. J. Londeborough and K. Suroanta, *J. Biol. Chem.* 1983, **258**, 2966.
3. H. O. Gaisser, H. Van der Goot and H. Timmerman, *Eur. J. Med. Chem.-Chim Ther.* 1985, **20**, 513.
4. G. Poznanovic and L. Sevaljevic, *Molec. Biol. Rep.* 1984, **9**, 231.
5. T. M. Florence, B. G. Lumsden and J. J. Fardy, in *Complexation of Trace Metal Natural Waters*, *Proc. Int. Symp.* (Edited by C. J. M. Kramer and J. C. N. Duinker), pp. 411–418. Kluwer, Boston, MA (1984).
6. J. W. Chang and R. Weil, *72nd Ann. Tech. Conf. Proc. Am. Electroplat. Soc.*, Session F, Paper F-3 (1985).
7. J. J. Eisch, L. E. Hallenbeck and M. A. Lucarelli, *Fuel* 1985, **64**, 440.
8. H. Honma and S. Mizushima, *Kinzoku Hyomen Gijutsu* 1983, **34**, 290.
9. R. J. Deeth and M. Gerloch, *Inorg. Chem.* 1984, **23**, 3853.
10. A. Bencini and D. Gatteschi, *Inorg. Chem.* 1977, **16**, 1994.
11. H. Nakai, Y. Deguchi, *Bull. Chem. Soc. Japan* 1975, **48**, 2557.
12. (a) Performed using locally modified versions of Enraf–Nonius MolEN structure solution and refinement package and other programs; (b) MolEN, Delft Instruments, X-Ray Diffraction, D.V. Delft, Netherlands (1990).
13. R. B. Roof Jr, *A Theoretical Extension of the Reduced-Cell Concept in Crystallography*, Publication LA-4038. Los Alamos Scientific Laboratory, Los Alamos, NM (1969).
14. SHELXTL PLUS (System of Crystallographic Programs). Siemens Analytical X-Ray Instruments, Madison, WI (1990).
15. *International Tables for X-ray Crystallography*, Vol. IV. D. Reidel, Dordrecht, Holland (1987).
16. R. J. Majeste and E. A. Meyers, *J. Chem. Phys.* 1970, **74**, 3497.
17. (a) I. M. Proctor and F. S. Stephens, *J. Chem. Soc.* (*A*)

1969, 1248; (b) I. M. Proctor, B. J. Hathaway, D. E. Billing, R. Dudley and P. Nicholls, *J. Chem. Soc.* (*A*) 1969, 1192.

18. E. Dubler, G. Hanggi and H. Schmalle, *Inorg. Chem.* 1992, **31**, 3728.
19. Selected data for [Cu(NO_3)(4,4′-dimethyl-2,2′-dipyridine)$_2$][NO_3]. Cell: $a = 7.555(6)$, $b = 11.550(10)$, $c = 15.221(11)$ Å, $\alpha = 73.09(6)°$, $\beta = 88.23(6)°$ and $\gamma = 71.60(6)°$. Space group $= P1$, $Z = 2$. K. Catalan, E. J. Valente and J. D. Zubkowski, unpublished results.
20. Y. Yao, M. W. Perkovic, D. P. Rillema and C. Woods, *Inorg. Chem.* 1992, **31**, 3956.
21. N. S. Begum and H. Manohar, *Polyhedron* 1994, **13**, 307.
22. B. Morosin, *Acta Cryst.* 1970, **B26**, 1203.
23. O. J. Parker, G. T. Greiner and G. L. Breneaman, *Polyhedron* 1994, **13**, 267.