(Cromer, Larson & Roof, 1960) which can be considered as an intergrowth of $CaCu_5$ and an ordering variant of the CsCl type, but here structural columns are intergrown instead of slabs (see Fig. 61 in Parthé & Chabot, 1984).

We would like to thank Dr J. L. Jorda for the preparation of the samples and Dr B. Chabot for many helpful discussions. Further, we would like to acknowledge the help of Mrs I. Jequier who typed the manuscript and Mrs B. Künzler who prepared the drawings. This study has been supported by the Swiss National Science Foundation under contract No. 2.858-0.83. One of us (KC) would like to thank the Stiftung Entwicklungsfonds Seltene Metalle, Zürich, for financial help.

References

AKSELRUD, L. G., KOMAROVSKA, L. P. & SKOLOZDRA, R. V. (1983). *Dopov. Akad. Nauk Ukr. RSR Ser. B*, pp. 33–35.

BROWN, I. D. (1983). *Acta Cryst.* A**39**, 216–224.

CHEVALIER, B., COLE, A., LEJAY, P. & ETOURNEAU, J. (1981). *Mater. Res. Bull.* **16**, 1067–1075.

CROMER, D. T., LARSON, A. C. & ROOF, R. B. (1960). *Acta Cryst.* **13**, 913–918.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DWIGHT, A. E. (1983). *J. Less-Common Met.* **93**, 411–413.

DWIGHT, A. E., HARPER, W. C. & KIMBALL, C. W. (1973). *J. Less-Common Met.* **30**, 1–8.

ESPINOSA, G. P., COOPER, A. S. & BARZ, H. (1982). *Mater. Res. Bull.* **17**, 963–969.

GLADYSHEVSKII, E. I., BODAK, O. I., YAROVETS, V. I., GORELENKO, YU. K. & SKOLOZDRA, R. V. (1978). *Ukr. Fiz. Zh.* (*Russ. Ed.*) **23**, 77–82.

HODEAU, J. L., CHENEVAS, J., MAREZIO, M. & REMEIKA, J. P. (1980). *Solid State Commun.* **36**, 839–845.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

ISHIKAWA, M., JORDA, J. L. & JUNOD, A. (1982). *Superconductivity in d- and f-Band Metals.* Proc. IVth Conf., Kernforschungszentrum Karlsruhe, Karlsruhe, June 28-30, edited by W. BUCKEL & W. WEBER, pp. 141–144.

JORDA, J. L. (1984). *J. Less-Common Met.* To be published.

KUZMA, YU. B., KRIPYAKEVICH, P. I. & BILONIZHKO, N. S. (1969). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 939–941.

PARTHÉ, E. & CHABOT, B. (1984). *Handbook on Physics and Chemistry of Rare Earths*, edited by K. A. GSCHNEIDNER JR & L. EYRING, Vol. 6, ch. 48, pp. 113–334. Amsterdam: North-Holland.

REMEIKA, J. P., ESPINOSA, G. P., COOPER, A. S., BARZ, H., ROWELL, J. M., MCWHAN, D. B., VANDENBERG, J. M., MONCTON, D. E., FISK, Z., WOOLF, L. D., HAMAKER, H. C., MAPLE, M. B., SHIRANE, G. & THOMLINSON, W. (1980). *Solid State Commun.* **34**, 923–926.

RYKHAL, R. M., ZARECHNYUK, O. S. & KUTEN, YA. I. (1978). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 1136–1138.

SKOLOZDRA, R. V., MANDZYK, V. M. & AKSELRUD, L. G. (1981). *Sov. Phys. Crystallogr.* **26**, 272–274.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY* 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TEATUM, E., GSCHNEIDNER, K. JR & WABER, J. (1960). Cited in *The Crystal Chemistry and Physics of Metals and Alloys* (1972) edited by W. B. PEARSON, p. 151. New York: John Wiley.

VANDENBERG, J. M. (1980). *Mater. Res. Bull.* **15**, 835–847.

Acta Cryst. (1984). C**40**, 1131–1135

Structures of Copper(II) Complexes with *N*,*N*′-Bis(*β*-carbamoylethyl)ethylenediamine and Its Deprotonated Form, $[Cu(NO_3)(C_8H_{18}N_4O_2)(H_2O)].NO_3.H_2O$ and $[Cu(C_8H_{16}N_4O_2)(H_2O)].H_2O$*

BY TSONG-JEN LEE, TIAN-HUEY LU, SI-HAN LIU, CHUNG-SUN CHUNG AND TSENG-YUH LEE

National Tsing Hua University, Hsinchu, Taiwan 300

(*Received* 21 *November* 1983; *accepted* 13 *February* 1984)

Abstract. (I) $[Cu(NO_3)(C_8H_{18}N_4O_2)(H_2O)].NO_3.H_2O$, $M_r = 425\cdot84$, triclinic, $P\bar{1}$, $a = 7\cdot663$ (3), $b = 10\cdot725$ (6), $c = 10\cdot767$ (5) Å, $\alpha = 91\cdot82$ (4), $\beta = 108\cdot18$ (9), $\gamma = 90\cdot14$ (4)°, $U = 840\cdot3$ (7) Å^3, $Z = 2$, $D_x = 1\cdot683$, $D_m = 1\cdot653$ (4) Mg m^{-3}, $F(000) = 476\cdot8$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot842$ mm^{-1}, $T = 296$ (4) K. (II) $[Cu(C_8H_{16}N_4O_2)(H_2O)].H_2O$, $M_r = 299\cdot82$, monoclinic, $P2_1/c$, $a = 6\cdot795$ (7), $b = 16\cdot872$ (8), $c = 12\cdot103$ (13) Å, $\beta = 118\cdot02$ (8)°, $U = 1224\cdot9$ Å^3, $Z = 4$, $D_x = 1\cdot660$, $D_m = 1\cdot653$ (4) Mg m^{-3}, $F(000) = 629\cdot2$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot736$ mm^{-1}, $T = 296$ (4) K. Final $R(F) = 0\cdot068$ and 0·060 for 2197 and 1861 observed reflections for (I) and (II), respectively. (I) is a six-coordinate octahedral complex with a nitrate O atom and a water O atom in *trans* positions. The quadridentate ligand bcen coordinates to the Cu atom with two tertiary N atoms and two O atoms. In contrast to this, (II) exhibits fivefold tetragonal pyramidal coordination, where the deprotonated ligand, $(H_{-2}bcen)^{2-}$, coordinates to the Cu atom with four N atoms and the fifth site is occupied by a water O atom.

---

* Aqua[3,3′-(ethylenediimino)dipropionamide]nitratocopper(II) nitrate monohydrate and aqua[3,3′-(ethylenediimino)dipropionamido(2−)]copper(II) monohydrate.

0108-2701/84/071131-05$01.50

Introduction. In our previous potentiometric and spectrophotometric studies of copper(II) complexes of *N,N'*-bis(*β*-carbamoylethyl)ethylenediamine, bcen (Wei, Chao & Chung, 1979), and *N,N'*-bis(*β*-carbamoylethyl)trimethylenediamine, bctn (Chao & Chung, 1981), it was noted that copper(II), after complexation with each of these ligands, can induce ionization of the amide protons, and the colour of the solution changes from blue to deep blue and finally to violet with an increase in pH. Quantitative equilibrium studies of the formations of the copper(II) complexes of these ligands and the Cu—O to Cu—N bond rearrangements at the two amide sites of these complexes (1–3) have been reported.

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+} \tag{1}$$

$$[CuL]^{2+} \rightleftharpoons [CuH_{-1}L]^{+} + H^{+} \tag{2}$$

$$[CuH_{-1}L]^{+} \rightleftharpoons [CuH_{-2}L] + H^{+} \tag{3}$$

These reactions are very fast and their kinetics and mechanisms have been studied (Chen, 1982). In this paper we report the crystal structures of (I) $[Cu(NO_3)(bcen)(H_2O)]NO_3.H_2O$ and (II) $[Cu(H_{-2}bcen)(H_2O)]H_2O$.

Experimental. *N,N'*-Bis(*β*-carbamoylethyl)ethylenediamine was prepared by the procedure described elsewhere (Wei, Chao & Chung, 1979) and then reacted with $Cu(NO_3)_2.6H_2O$ in water. Crystals of (I) were obtained by slow evaporation of the acid solution (pH = 5); crystals of (II) were obtained by evaporation of the basic solution (pH = 12).

Two crystals (blue and violet) were ground to spheres. Experimental data and structure-solution parameters are summarized in Table 1 together with some of the standard refinement procedures. Only Lorentz–polarization corrections were considered. Cu and nonhydrogen atoms were located by Patterson and Fourier methods. Two water molecules were found at the final stage of calculation. Full matrix least-squares refinement on *F* of coordinates, anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for H atoms reduced *R*(*F*) to 0·068 and 0·060 for (I) and (II), respectively. H atoms around the ring were positioned geometrically with C—H 0·95 Å, C—C—H and H—C—H 109·5°. Function minimized: $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma_F^2$, $\sigma_F = [k/2\sqrt{(Lp)}]\{[\sigma^2(I)_{\rm counting} + (0{\cdot}01I)^2]/I\}^{1/2}$.

Discussion. Final atomic parameters are given in Table 2, and bond lengths and bond angles in Table 3.* The

Table 1. *Experimental data and structure refinement parameters*

	(I)	(II)
Crystal size (mm)	0·3 × 0·35 × 0·4	0·3 × 0·35 × 0·3
Diffractometer and data-collection technique	Four-circle Syntex $P\bar{1}$ with graphite monochromator, ω–2θ scan	
Scan width	2·0° + 0·7° tanθ; starting 1° below $K\alpha_1$ and 1° above $K\alpha_2$; variable scan speed	
Lattice-parameter determination	15 reflections with 12° < 2θ < 25°	
Transmission factors	0·714 to 0·745	0·773 to 0·802
Stability	No significant variation	
Reflections measured	4366	3279
Unique reflections ($I > 3\sigma$)	2197	1861
Structure solution	Patterson and Fourier methods	
Range of *h, k, l*	$(0,\bar{13},\bar{13})$ to $(9,13,13)$	$(0,0,\underline{14})$ to $(8,23,\bar{14})$
Parameters refined		
Non-hydrogen atoms	(Coordinates & anisotropic temperature factors) 225	 153
H atoms	(Coordinates & isotropic temperature factors) 88	 80
Atomic scattering factors *f'* and *f''*	*International Tables for X-ray Crystallography* (1974)	
Number of reflections per parameter	7	8
Max. (sinθ)/λ	0·6497 Å^{-1}	0·6497 Å^{-1}
R (R_w)	0·068 (0·070)	0·060 (0·067)
Final max. residual electron densities (e Å^{-3})	0·31	0·27
S	not calculated	1·26
Programs	Tsing Hua *XTAL* Package and *ORTEP*	

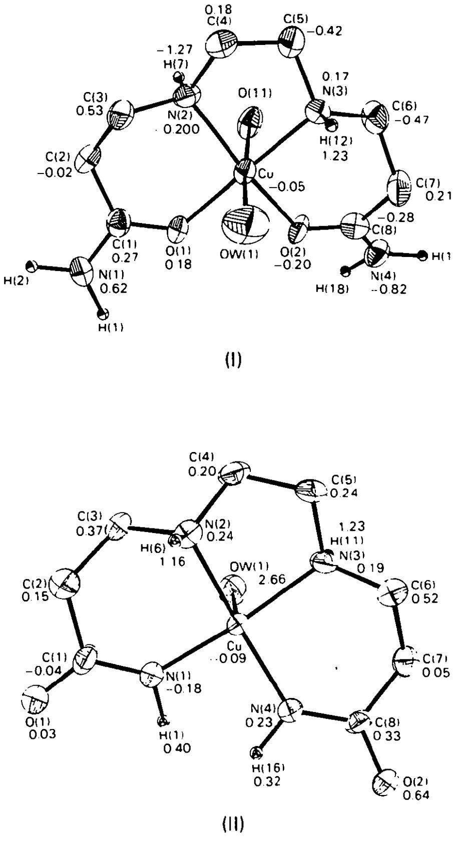


Fig. 1. Perspective view of the two complexes, showing deviations (in Å) from the major coordination plane (Johnson, 1976).

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and structure parameters for nitrate ions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39273 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic positional parameters and equivalent thermal parameters with e.s.d.'s in parentheses*

$B_{\rm eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j b_{ij}$, where the $\mathbf{a}_j$'s are the cell-length vectors in direct space.

	x	*y*	*z*	$B_{\rm eq}$(Å^2)
Compound (I)				
Cu	0·3625 (2)	0·2080 (1)	0·1995 (1)	2·42 (5)
O(1)	0·1324 (8)	0·1478 (5)	0·0725 (6)	2·91 (38)
O(2)	0·4692 (8)	0·0508 (5)	0·1580 (6)	2·80 (36)
O(11)	0·5100 (8)	0·2843 (6)	0·0335 (6)	3·54 (42)
O(12)	0·5257 (9)	0·3464 (7)	−0·1488 (7)	4·62 (49)
O(13)	0·3181 (9)	0·4204 (7)	−0·0696 (7)	4·74 (49)
O(21)	0·6605 (13)	0·1950 (11)	0·6251 (9)	8·65 (76)
O(22)	0·9145 (10)	0·1030 (7)	0·6935 (8)	6·08 (60)
O(23)	0·9072 (17)	0·2975 (9)	0·6843 (12)	10·11 (98)
O*W*(1)	0·2412 (10)	0·1365 (7)	0·3652 (7)	5·14 (54)
O*W*(2)	0·2465 (12)	0·2778 (8)	0·5915 (8)	7·18 (65)
N(1)	−0·1684 (10)	0·1437 (7)	−0·0304 (8)	3·58 (49)
N(2)	0·2817 (9)	0·3828 (6)	0·2069 (7)	2·43 (42)
N(3)	0·5861 (9)	0·2619 (6)	0·3460 (7)	2·47 (41)
N(4)	0·6987 (10)	−0·0742 (6)	0·1526 (7)	3·23 (47)
N(11)	0·4514 (10)	0·3528 (7)	−0·0621 (8)	3·26 (52)
N(22)	0·8253 (16)	0·2006 (10)	0·6669 (8)	4·78 (71)
C(1)	−0·0180 (12)	0·2060 (8)	0·0330 (8)	2·56 (52)
C(2)	−0·0300 (13)	0·3445 (8)	0·0558 (10)	3·36 (61)
C(3)	0·0828 (12)	0·3943 (8)	0·1908 (10)	3·24 (59)
C(4)	0·3949 (12)	0·4439 (8)	0·3295 (9)	2·11 (56)
C(5)	0·5937 (12)	0·4022 (8)	0·3466 (9)	3·29 (55)
C(6)	0·7631 (12)	0·2069 (9)	0·3416 (10)	3·33 (59)
C(7)	0·7450 (73)	0·0639 (9)	0·3444 (9)	3·56 (61)
C(8)	0·6289 (12)	0·0127 (8)	0·2121 (9)	2·76 (55)
Compound (II)				
Cu(1)	0·3171 (1)	0·4361 (0)	0·3225 (1)	2·34 (6)
O(1)	0·0457 (8)	0·6362 (3)	0·0996 (4)	4·00 (53)
O(2)	0·1579 (7)	0·4204 (3)	0·6137 (4)	3·27 (43)
O(3)	0·0482 (8)	0·1601 (3)	0·6520 (4)	4·19 (51)
O(4)	0·1649 (8)	0·3043 (3)	0·7759 (4)	3·54 (47)
N(1)	0·1453 (8)	0·5278 (3)	0·2267 (5)	2·44 (47)
N(2)	0·5226 (8)	0·4428 (3)	0·2451 (5)	2·90 (48)
N(3)	0·4867 (8)	0·3344 (3)	0·4020 (5)	2·52 (47)
N(4)	0·2045 (8)	0·4458 (3)	0·4436 (4)	2·79 (48)
C(1)	0·1647 (10)	0·5745 (4)	0·1471 (5)	2·36 (60)
C(2)	0·3405 (11)	0·5584 (4)	0·1079 (6)	3·35 (65)
C(3)	0·4222 (13)	0·4734 (5)	0·1194 (7)	4·32 (77)
C(4)	0·6203 (11)	0·3633 (4)	0·2536 (7)	3·47 (70)
C(5)	0·6813 (11)	0·3281 (4)	0·3792 (7)	3·61 (70)
C(6)	0·5495 (11)	0·3234 (4)	0·5340 (6)	3·07 (69)
C(7)	0·3530 (12)	0·3247 (4)	0·5598 (6)	3·32 (71)
C(8)	0·2308 (10)	0·4024 (4)	0·5383 (5)	2·05 (54)

Table 3. *Bond lengths* (Å) *and angles* (°)

	(I)	(II)
Cu—N(1)		1·957 (5)
Cu—N(2)	1·983 (7)	2·017 (7)
Cu—N(3)	2·002 (6)	2·040 (5)
Cu—N(4)		1·954 (6)
Cu—O(1)	1·957 (5)	
Cu—O(2)	1·974 (6)	
Cu—O*W*(1)	2·399 (9)	2·586 (4)
O*W*(1)—O*W*(2)	2·818 (11)	2·772 (6)
Cu—O(11)	2·548 (9)	
C(1)—O(1)	1·270 (10)	1·277 (7)
C(1)—N(1)	1·311 (10)	1·297 (7)
C(1)—C(2)	1·506 (12)	1·503 (12)
C(2)—C(3)	1·520 (12)	1·520 (11)
C(3)—N(2)	1·485 (12)	1·440 (9)
N(2)—C(4)	1·467 (10)	1·479 (9)
C(4)—C(5)	1·545 (13)	1·498 (11)
C(5)—N(3)	1·505 (10)	1·476 (11)
N(3)—C(6)	1·494 (11)	1·459 (9)
C(6)—C(7)	1·542 (14)	1·507 (13)
C(7)—C(8)	1·511 (11)	1·507 (9)
C(8)—N(4)	1·321 (12)	1·300 (9)
C(8)—O(2)	1·254 (10)	1·263 (10)
O(1)—Cu—O(2)	86·0 (2)	
O(1)—Cu—N(2)	95·3 (2)	
O(2)—Cu—N(3)	95·0 (2)	
N(1)—Cu—N(2)		91·8 (2)
N(2)—Cu—N(3)	85·6 (3)	84·6 (2)
N(3)—Cu—N(4)		92·9 (2)
N(4)—Cu—N(1)		92·5 (2)
Cu—O(1)—C(1)	127·3 (5)	
O(1)—C(1)—N(1)	119·1 (8)	124·4 (7)
Cu—N(1)—C(1)		132·8 (5)
N(1)—C(1)—C(2)	118·6 (7)	119·9 (6)
O(1)—C(1)—C(2)	122·4 (7)	115·7 (7)
C(1)—C(2)—C(3)	115·1 (7)	116·8 (7)
C(2)—C(3)—N(2)	109·8 (8)	114·0 (6)
C(3)—N(2)—Cu	113·7 (5)	115·0 (5)
Cu—N(2)—C(4)	109·0 (5)	107·7 (5)
N(2)—C(4)—C(5)	105·6 (7)	109·3 (7)
C(4)—C(5)—N(3)	105·1 (7)	108·4 (5)
C(5)—N(3)—Cu	106·7 (4)	109·2 (4)
Cu—N(3)—C(6)	115·8 (4)	115·7 (4)
N(3)—C(6)—C(7)	107·8 (7)	113·1 (5)
C(6)—C(7)—C(8)	110·0 (7)	116·6 (6)
C(7)—C(8)—O(2)	121·8 (8)	117·2 (6)
C(7)—C(8)—N(4)	118·5 (7)	118·6 (7)
Cu—N(4)—C(8)		132·4 (5)
Cu—O(2)—C(8)	126·7 (5)	

copper(II) and the four donor atoms of bcen lie more or less in a plane for both molecules. The deviations of atoms from the least-squares plane through the basal atoms are indicated in Fig. 1.

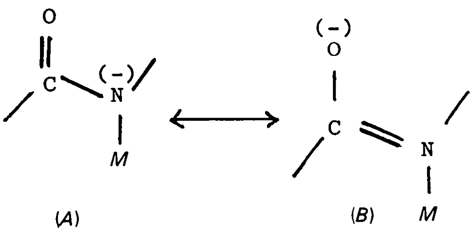
For (I), N(3) and O(1) are above the least-squares planes, while Cu, N(2) and O(2) are below it, so that the square-planar coordination geometry of the Cu$^{\rm II}$ undergoes a very slight tetrahedral distortion. Furthermore, the Cu—N(amino) and Cu—O(amide) bond lengths range from 1·983 (7) to 2·002 (6) Å and from 1·957 (5) to 1·974 (6) Å respectively. A nitrate oxygen and a water oxygen are coordinated axially. These axial Cu$^{\rm II}$—O bond lengths are significantly longer than the equatorial Cu$^{\rm II}$—O and Cu$^{\rm II}$—N bond distances, so that the coordination geometry of the copper(II) undergoes a significant tetragonal distortion, and is of the 4 + 2 type (Pavkovic & Brown, 1982), as would be predicted on the basis of the Jahn–Teller effect.

For (II), the copper is five-coordinate in a distorted square-pyramidal geometry as shown in Figs. 1 and 2. The Cu$^{\rm II}$—N(amino) bonds average 0·004 Å longer than the equivalent bonds in (I). The Cu—N(amide) bond lengths range from 1·955 to 1·957 Å, and the copper is displaced from the best plane of the two amino and the two amide nitrogens by 0·09 (1) Å toward the apex of the pyramid, which is formed by a water O atom with the Cu—O distance 2·586 Å. This bond is significantly longer than Cu—OH$_2$ in (I). No other donor atoms are located within reasonable bonding distance of the Cu$^{\rm II}$.

The two asymmetric nitrogens, N(2) and N(3), are of the same *R* or *S* configuration, and the five-membered chelate rings adopt a stable *gauche* conformation for both crystals.

Judging from these structures, it is clear that the Cu—O to Cu—N bond rearrangements at the two amide sites occur and the coordination number of Cu changes from six to five during deprotonation.

With deprotonation of the amide nitrogen, delocalization of the carbonyl double bond results in two important resonance forms, (*A*) and (*B*).



(*A*) (*B*)

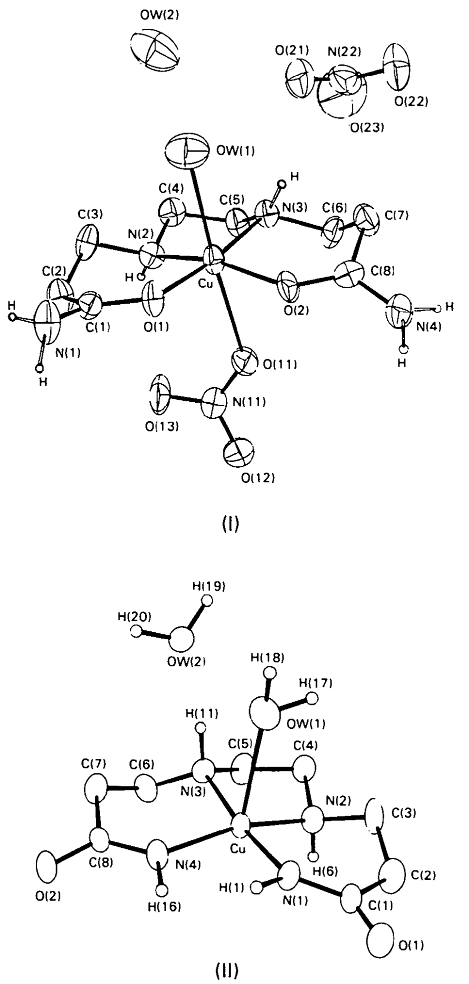


Fig. 2. Side view of the two molecules, showing more clearly the conformation and twisted orientation. The oxygen of the water molecule is indicated as O*W*.

Table 4. *Hydrogen-bond lengths* (Å) *and angles* (°)

Symmetry code for (I) and (II): None *x*, *y*, *z*; (i) $\bar{x}, \bar{y}, \bar{z}$.

	N···O or O···O distances (Å)	Bond angles (°)
(I)		
N(2)–H(7)···O(21)	3·114 (11)	151·6 (4)
N(3)–H(12)···O(21)	2·990 (12)	147·9 (4)
N(3)···O*W*(1)	3·030 (11)	
O*W*(1)···O*W*(2)	2·818 (11)	
O*W*(1)···O(22^i)	2·800 (10)	
(II)		
N(2)–H(6)···O(2^i)	3·078 (6)	176·2 (4)
N(3)–H(11)···O*W*(2)	3·074 (6)	170·8 (3)
N(3)–H(11)···O*W*(1)	3·094 (6)	113·1 (3)
O*W*(1)···O*W*(2)	2·772 (6)	

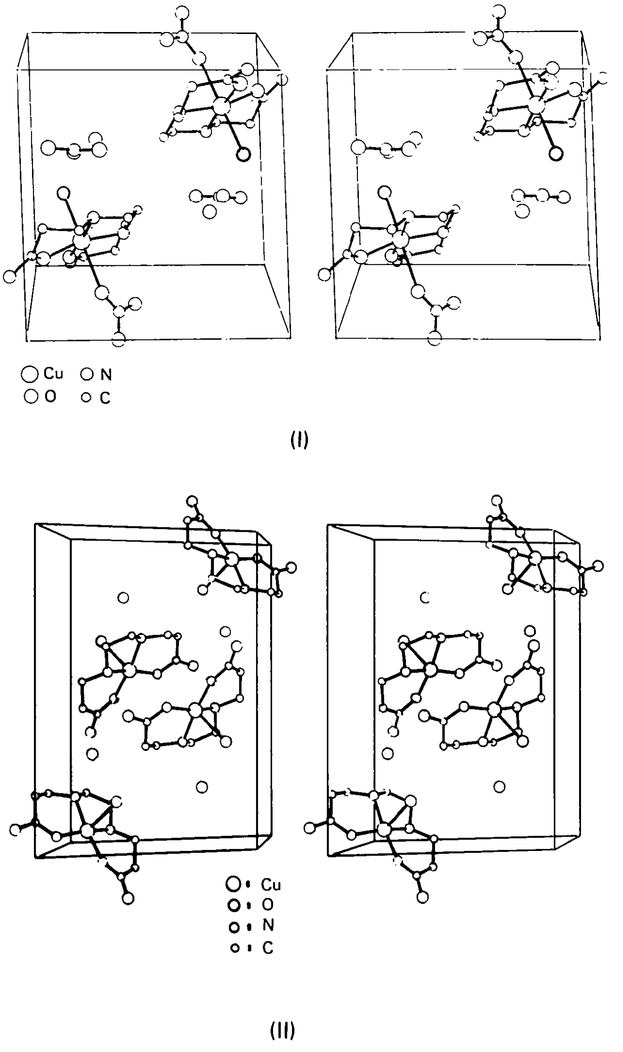


Fig. 3. Stereoscopic drawings of the crystal packing. (I) Origin: lower left corner, *a* axis towards the reader, *b* axis to the right, *c* axis up. (II) Origin: upper left corner, *a* axis towards the reader, *b* axis down, *c* axis to the right.

In (II) the C=O bonds are slightly longer while the OC—N bonds are slightly shorter than the corresponding bonds in (I). These differences are due to the increased contribution of resonance form (*B*) for (II).

It is interesting to note that the coordination numbers of these two $\mathrm{Cu^{II}}$ complexes are different. This difference in coordination number agrees with the tendency toward decreased coordination in the axial positions of six-coordinate metal complexes which contain strong in-plane fields (Busch, 1978). The deprotonated-amide nitrogen is a stronger donor than the amide oxygen. After the Cu—O to Cu—N bond rearrangements at the two amide sites, the in-plane ligand field increases, and the extent of axial addition decreases (Liang & Chung, 1980).

Some of the N···O and O···O distances are sufficiently short to indicate hydrogen bonding and are summarized in Table 4. Packing diagrams are shown in Fig. 3.

Thanks are due to the NSC of Taiwan for financial support.

References

Busch, D. H. (1978). *Acc. Chem. Res.* pp. 392–400.

Chao, M. S. & Chung, C. S. (1981). *J. Chem. Soc. Dalton Trans.* pp. 683–686.

Chen, J. Y. (1982). MS Thesis, Institute of Chemistry, National Tsing Hua Univ.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 202. Birmingham: Kynoch Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Liang, B. F. & Chung, C. S. (1980). *Inorg. Chem.* **19**, 572–574.

Pavkovic, S. F. & Brown, J. N. (1982). *Acta Cryst.* B**38**, 274–276.

Wei, L. W., Chao, M. S. & Chung, C. S. (1979). *J. Chin. Chem. Soc.* (*Taipei*), **26**, 145–151.

Acta Cryst. (1984). C**40**, 1135–1137

Structure of [2,2′-(1,4,10,13-Tetraoxa-7,16-diaza-7,16-cyclooctadecylene)dipropionato]-copper(II), $[\mathrm{Cu(C_{18}H_{32}N_2O_8)}]$

By J. W. Krajewski, P. Gluziński and Z. Urbańczyk-Lipkowska

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 *Warszawa, Poland*

and M. Dobler

Laboratory of Organic Chemistry, Federal Institute of Technology (*ETH*), *CH*-8092 *Zürich, Switzerland*

(*Received* 28 *November* 1983; *accepted* 3 *March* 1984)

Dedicated to Professor J. D. Dunitz (*ETH, Zürich*) *on the occasion of his* 60*th birthday*

Abstract. $M_r = 467{\cdot}99$, monoclinic, $P2_1/c$, $a = 7{\cdot}032\,(5)$, $b = 15{\cdot}533\,(2)$, $c = 9{\cdot}836\,(2)$ Å, $\beta = 113{\cdot}46\,(4)°$, $V = 985{\cdot}5\,(8)$ Å^3, $Z = 2$, $D_x = 1{\cdot}586\,(1)$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 11{\cdot}23$ cm^{-1}, $F(000) = 494$, $T = 293$ K, final $R = 0{\cdot}034$ for 1431 observed reflections. The molecule is centrosymmetric (C_i) with the Cu atom at the centre of symmetry. The Cu atom is coordinated to atoms N(1), C(13) and O(7) and to their symmetry-related equivalents, forming an irregular octahedron with one elongated and skewed [by 11·58 (7)°] diagonal.

Introduction. The title compound (αPRCU) (Koliński & Mroziński, 1983) is an α-propionic acid analogue of 1,4,10,13-tetraoxa-7,16-diaza-7,16-cyclooctadecanediacetatocopper(II) complexes (ACCU, $\mathrm{ACCU.CuCl_2}$) investigated recently by X-ray diffraction methods (Uechi, Ueda, Tazaki, Takagi & Ueno, 1982; Gluziński, Krajewski, Urbańczyk-Lipkowska, Bleidelis & Mishnyov, 1982; Gluziński, Krajewski, Urbańczyk-Lipkowska, Andreetti & Bocelli, 1984). The ligands of the above type are interesting because they seem to have a particular selectivity for $\mathrm{Cu^{II}}$ ions (Uechi *et al.*, 1982). The present X-ray diffraction investigation was undertaken in order to compare the structure of αPRCU with the already known structures of the complexes cited.

Experimental. Black crystal (0·28 × 0·18 × 0·12 mm) from reaction mixture. D_m not determined. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, $\omega/2\theta$ scan, $2\theta_{\max} = 55°$, $hkl_{\max} = 8, 19, 12$. Stability controlled with two reflections. 1935 unique reflections collected, 1431 with $I > 2\sigma_I$ regarded as observed. Cell constants

0108-2701/84/071135-03$01.50