molecular symmetry of *mmm* is thus almost retained in the crystal structure. The complexes are parallel and equally spaced by symmetry in stacks along the *b* axis (Figs. 1 and 2). The normal to the molecular plane (all atoms) makes an angle of 18·5 (1)° with the *b* axis. The molecules in a stack are thus 'slipped' with respect to each other. The S···S contact distance within a stack is equal to the *b* axial translation of 3·75 Å. Between the stacks there is one shorter S1···S1 distance of 3·66 Å (marked on Fig. 2), indicating some transverse interaction. The van der Waals contact distance S···S is 3·60 Å (Bondi, 1964).

As mentioned above, a weak superstructure (a, $2b$, c) was observed and most clearly on long exposure rotation films. This additional scattering is rather diffuse with very extended Bragg spots. It was realized that these intensities were not correctly measured during data collection, and we chose to solve the structure in the subcell with $b = 3{\cdot}750$ Å. The resulting low residuals of the present analysis strongly suggest that the superstructure modulation is very small. The nature of this distortion is not yet known, but a weak Peierls or spin-Peierls distortion may be a possibility. The details of the magnetic and electrical properties of this interesting molecular solid are presently being investigated and will appear in a separate paper.

Financial support from the Danish Natural Science Research Council is gratefully acknowledged.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bray, J. W., Interrante, L. V., Jacobs, I. S. & Bonner, J. C. (1983). In *Extended Linear Chain Compounds*, Vol. 3, edited by J. S. Miller, pp. 353–441. New York: Plenum.

Brossard, L., Ribault, M., Bousseau, M., Valade, L. & Cassoux, P. (1986). *C.R. Acad. Sci. Sér.* II, **302**, 205–210.

Eisenberg, R. (1970). *Prog. Inorg. Chem.* **12**, 295–369.

Geiser, U., Schultz, A. J., Wang, H. H., Beno, M. A. & Williams, J. M. (1988). *Acta Cryst.* C**44**, 259–262.

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

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

Kobayashi, A., Kim, H., Sasaki, Y., Kato, R., Kobayashi, H., Moriyama, S., Nishio, Y., Kajita, K. & Sasaki, W. (1987). *Chem. Lett.* pp. 1819–1822.

Mazid, M. A., Razi, M. T. & Sadler, P. J. (1981). *Inorg. Chem.* **20**, 2872–2877.

Schultz, A. J., Wang, H. H., Soderholm, L. C., Sifter, T. L., Williams, J. M., Bechgaard, K. & Whangbo, M.-H. (1987). *Inorg. Chem.* **26**, 3757–3761.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS*86. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1990). C**46**, 1439–1441

Structure of a Dicopper(II) Complex of the Flexible, Dinucleating Ligand, *N*,*N*,*N'*,*N'*-Tetrakis(3-aminopropyl)-1,5-diamino-3-oxapentane

By Harry Adams, Neil A. Bailey,* W. Daniel Carlisle and David E. Fenton*

Department of Chemistry, The University, Sheffield S3 7HF, England

(*Received* 24 *August* 1989; *accepted* 4 *December* 1989)

Abstract. Tetrachloro-μ-[*N*,*N'*-di(3-aminopropyl)-4,10-diaza-7-oxatridecanediamine-*N*,*N'*,*N''*,*N'''*,*N''''*,*N'''''*]-dicopper(II) hydrate, $[Cu_2Cl_4\{[NH_2(CH_2)_3]_2N(CH_2)_2\}_2O.H_2O$, $C_{16}H_{42}Cl_4Cu_2N_6O_2$, $M_r = 619{\cdot}44$, monoclinic, $P2_1/c$ (C^5_{2h}, No. 14), $a = 13{\cdot}989\,(24)$, $b = 10{\cdot}568\,(22)$, $c = 16{\cdot}783\,(34)$ Å, $\beta = 90{\cdot}65\,(15)^\circ$, $V = 2481\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}658$ g cm^{-3}, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), μ(Mo $K\alpha$) = 21·80 cm^{-1}, $F(000) = 1287{\cdot}70$. 3097 independent reflections at 298 K gave $R = 0{\cdot}0599$. The copper(II) atoms are coordinated at either end of the ligand to a triamine fragment and to two chlorine atoms, leading to coordination geometries intermediate between trigonal bipyramidal and square-based pyramidal. The intermetallic separation is 8·875 Å.

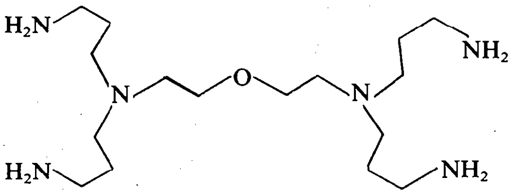
Introduction. Since the disclosure that the dioxygen binding site in deoxyhaemocyanin does not contain an endogenous protein bridge (Gaykema, Volbeda & Hol, 1986) efforts have been made to seek compatible model complexes which are capable of sustaining two copper atoms 3·6 Å apart as in the biological system (Sorrell, 1989; Tyeklar & Karlin, 1989). Copper(II) chloride complexes of the flexible, dinucleating ligand *N*,*N*,*N'*,*N'*-tetrakis(3-amino-

---

* Authors to whom correspondence should be addressed.

0108-2701/90/081439-03$03.00

propyl)-1,5-diamino-3-oxapentane (1) are preparable (Carlisle, 1988) and so it was of interest to determine the intermetallic separation and to see if the chloride anion could act as a bridging ligand in the corresponding dinuclear complex.



(1)

Experimental. *N*,*N*,*N'*,*N'*-Tetrakis(2-cyanoethyl)-1,5-diamino-3-oxapentane was synthesized by the literature method (Murase, Hamada & Kida, 1981) and reduced to (1) by dissolving sodium in absolute ethanol (Alcock, Kingston, Moore & Pierpoint, 1984). The reaction of (1) with $CuCl_2.H_2O$ in methanol gave the dinuclear complex $Cu_2(1)Cl_4.H_2O$. The FAB MS (fast-atom bombardment mass spectrum) of this complex exhibited a highest peak at 565 a.m.u. corresponding to the loss of a chloride anion from the neutral parent molecule to give a dinuclear monocation $[Cu_2(1)Cl_3]^+$.

The copper complex crystallizes from methanol as blue blocks; crystal dimensions $0{\cdot}20 \times 0{\cdot}15 \times 0{\cdot}30$ mm. Data were collected in the range $3{\cdot}5 < 2\theta < 50°$ (h $0\rightarrow16$, k $0\rightarrow12$, l $-20\rightarrow20$) on a Nicolet *R*3 diffractometer by the ω-scan method; unit-cell constants were determined from analysis of the setting angles of 12 reflections ($4 < \theta < 11°$). The 3097 independent reflections (of 4810 measured by variable-speed scan) for which $|F|/\sigma(|F|) > 3{\cdot}0$ ($R_{\text{merge}} = 0{\cdot}008$) were corrected for Lorentz and polarization effects, and for absorption, by analysis of seven sets of azimuthal scans (minimum and maximum transmission coefficients 0·304 and 0·335 respectively). Monitoring of a standard reflection throughout data collection indicated no significant crystal decay. The structure was solved by Patterson and Fourier techniques; hydrogen atoms were placed in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. The positions of the hydrogen atoms on the oxygen of the water molecule of solvation were constrained in O—H bond length and H—O—H bond angle and were sited close to the hydrogen-bonded contacts made by the water. Refinement on $|F|$ by blocked-cascade least-squares methods converged at a final $R = 0{\cdot}0599$ for 277 parameters, with allowance for thermal anisotropy of all non-hydrogen atoms. Maximum Δ/σ was 0·075; on the final difference map, minimum and maximum electron densities were $-0{\cdot}71$ and $+0{\cdot}70$ e Å^{-3}. Complex scattering factors were taken from the program package *SHELXTL* (Sheldrick, 1983), as implemented on the Data General Nova 3 computer, which was used for the structure solution and refinement. Unit weights were used throughout the refinement and proved to give satisfactory convergence. Atomic positional parameters with estimated standard deviations are listed in Table 1.*

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* (Å$^2 \times 10^3$)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	4336 (1)	2319 (1)	376 (1)	31 (1)
Cu(2)	1198 (1)	−3633 (1)	3007 (1)	34 (1)
Cl(1)	4563 (2)	4147 (2)	1334 (1)	42 (1)
Cl(2)	5892 (2)	1810 (3)	−116 (1)	48 (1)
Cl(3)	1389 (2)	−5988 (2)	3006 (1)	42 (1)
Cl(4)	732 (2)	−2274 (3)	4037 (1)	55 (1)
O(1)	1264 (4)	42 (5)	923 (3)	31 (2)
O(2)	3693 (5)	−6103 (8)	3121 (4)	58 (3)
N(1)	4177 (4)	3311 (7)	−618 (4)	37 (2)
N(2)	2834 (4)	2190 (6)	564 (4)	27 (2)
N(3)	4617 (5)	934 (7)	1145 (4)	40 (2)
N(4)	−173 (4)	−3722 (7)	2703 (4)	32 (2)
N(5)	1581 (4)	−3146 (6)	1809 (4)	27 (2)
N(6)	2546 (5)	−3477 (8)	3411 (4)	47 (3)
C(1)	3462 (6)	4320 (9)	−682 (5)	42 (3)
C(2)	2459 (6)	3824 (9)	−519 (5)	44 (3)
C(3)	2336 (6)	3395 (8)	328 (5)	37 (3)
C(4)	2639 (6)	2065 (8)	1436 (4)	35 (3)
C(5)	3077 (6)	943 (9)	1856 (5)	40 (3)
C(6)	4158 (7)	971 (9)	1935 (5)	44 (3)
C(7)	2464 (5)	1089 (8)	95 (4)	31 (2)
C(8)	1418 (5)	718 (8)	205 (4)	31 (2)
C(9)	1476 (6)	−1278 (8)	864 (4)	35 (3)
C(10)	1331 (5)	−1808 (7)	1689 (4)	27 (2)
C(11)	−470 (6)	−4422 (9)	1984 (5)	39 (3)
C(12)	−35 (5)	−3870 (8)	1244 (4)	33 (3)
C(13)	1057 (5)	−4001 (8)	1240 (4)	31 (2)
C(14)	2627 (5)	−3437 (9)	1707 (5)	37 (3)
C(15)	3304 (6)	−2646 (9)	2195 (5)	45 (3)
C(16)	3055 (6)	−2398 (9)	3070 (5)	49 (3)

Discussion. The molecular structure is shown in Fig. 1 and bond lengths and angles are given in Table 2. The structure comprises two well separated copper atoms (8·875 Å) coordinated at either end of an *N*,*N*,*N'*,*N'*-tetrakis(3-aminopropyl)-1,5-diamino-3-oxapentane molecule, with each copper coordinated to a triamine fragment, and by two chlorines. It would appear that in the absence of constraints imposed by either a bridging group or a molecular pocket, as provided by a proteinaceous environment, the metals fly as far apart as possible. Although both copper coordination polyhedra are intermediate between trigonal bipyramidal and square-based

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52828 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pyramidal, that around Cu(1) is much closer to the latter [axial ligand Cl(1)], and that of Cu(2) to the former [axial atoms N(4) and N(6)]. This seems to have had little effect on the copper–nitrogen bond lengths, which are approximately 0·15 Å shorter for the primary amines, compared to the tertiary amines. Conformations of both six-membered chelate rings on Cu(1), and that involving C(11)–C(13) on Cu(2), are chair-shaped and have torsion angles of magnitudes within 12° of 60°. However, the remaining chelate ring on Cu(2) has a distorted boat-shaped conformation [N—C—C torsion angles +44 (1) and +33 (1)°]. This is clearly necessary in order to permit the triamine to occupy two adjacent coplanar chelate planes in a trigonal bipyramid. The 1,5-diamino-3-oxapentane chain has synclinal conformation between N(2) and C(9), but antiperiplanar conformation between C(8) and N(5). The existence of two distinct coordination polyhedra does, at least in part, account for the variation of copper–chlorine bond lengths, of which the longest is that to the axial site of the square-based pyramidal polyhedron. The longer Cu—Cl bond of Cu(2) is to Cl(3), which is in the one of the two equatorial sites which would become axial in a square-based pyramidal polyhedron. A solvent water molecule links together molecules in adjacent unit cells, parallel to the *b* axis, through hydrogen bonds to Cl(1) and Cl(3).

Despite the flexible nature of the ligand it was found that addition of potentially bridging anions such as azide did not lead to the formation of a bridged dinuclear complex. The magnetic moments for these complexes were not reduced from the normal values found for $Cu_2(1)Cl_4.H_2O$ as would have been expected if the copper atoms were magnetically coupled. Strong antiferromagnetic coupling is observed in oxyhaemocyanin for which molecule both endogenous and exogenous bridges have been proposed from cumulative spectroscopic and EXAFS experiments (Solomon, 1983).

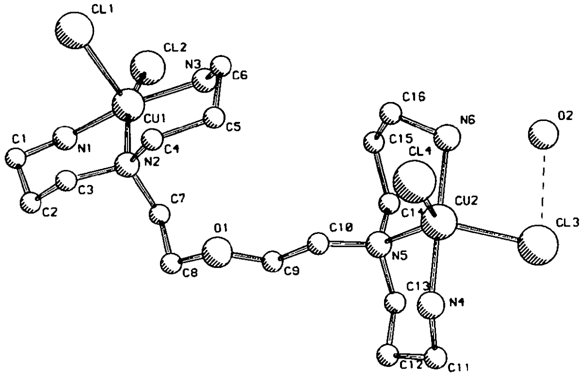


Fig. 1. View of the title compound.

Table 2. *Bond lengths* (Å) *and angles* (°)

Cu(1)—Cl(1)	2·531 (5)	Cu(1)—Cl(2)	2·398 (5)
Cu(1)—N(1)	1·980 (8)	Cu(1)—N(2)	2·132 (7)
Cu(1)—N(3)	1·987 (8)	Cu(2)—Cl(3)	2·503 (5)
Cu(2)—Cl(4)	2·346 (5)	Cu(2)—N(4)	1·981 (7)
Cu(2)—N(5)	2·150 (7)	Cu(2)—N(6)	2·002 (8)
O(1)—C(8)	1·420 (9)	O(1)—C(9)	1·430 (10)
N(1)—C(1)	1·465 (11)	N(2)—C(3)	1·502 (11)
N(2)—C(4)	1·498 (10)	N(2)—C(7)	1·494 (10)
N(3)—C(6)	1·481 (11)	N(4)—C(11)	1·472 (11)
N(5)—C(10)	1·470 (10)	N(5)—C(13)	1·499 (10)
N(5)—C(14)	1·507 (10)	N(6)—C(16)	1·464 (13)
C(1)—C(2)	1·526 (12)	C(2)—C(3)	1·503 (12)
C(4)—C(5)	1·506 (13)	C(5)—C(6)	1·518 (12)
C(7)—C(8)	1·528 (11)	C(9)—C(10)	1·509 (11)
C(11)—C(12)	1·507 (11)	C(12)—C(13)	1·534 (11)
C(14)—C(15)	1·499 (12)	C(15)—C(16)	1·536 (13)
O(2)···Cl(3)	3·229	H(2*C*)···Cl(3)	2·29
O(2)···Cl(1*a*)	3·260	H(2*D*)···Cl(1*a*)	2·31

Cl(1)—Cu(1)—Cl(2)	106·4 (1)	Cl(1)—Cu(1)—N(1)	98·2 (2)
Cl(2)—Cu(1)—N(1)	85·5 (2)	Cl(1)—Cu(1)—N(2)	94·1 (2)
Cl(2)—Cu(1)—N(2)	159·4 (2)	N(1)—Cu(1)—N(2)	93·3 (3)
Cl(1)—Cu(1)—N(3)	97·3 (2)	Cl(2)—Cu(1)—N(3)	83·4 (2)
N(1)—Cu(1)—N(3)	163·0 (3)	N(2)—Cu(1)—N(3)	92·6 (3)
Cl(3)—Cu(2)—Cl(4)	129·8 (1)	Cl(3)—Cu(2)—N(4)	93·2 (2)
Cl(4)—Cu(2)—N(4)	86·7 (2)	Cl(3)—Cu(2)—N(5)	102·1 (2)
Cl(4)—Cu(2)—N(5)	128·1 (2)	N(4)—Cu(2)—N(5)	91·2 (3)
Cl(3)—Cu(2)—N(6)	89·0 (3)	Cl(4)—Cu(2)—N(6)	88·2 (3)
N(4)—Cu(2)—N(6)	174·7 (3)	N(5)—Cu(2)—N(6)	93·1 (3)
C(8)—O(1)—C(9)	113·5 (6)	Cu(1)—N(1)—C(1)	121·1 (5)
Cu(1)—N(2)—C(3)	111·2 (5)	Cu(1)—N(2)—C(4)	109·9 (4)
C(3)—N(2)—C(4)	104·1 (6)	Cu(1)—N(2)—C(7)	107·9 (4)
C(3)—N(2)—C(7)	111·4 (6)	C(4)—N(2)—C(7)	112·3 (6)
Cu(1)—N(3)—C(6)	118·6 (6)	Cu(2)—N(4)—C(11)	119·9 (5)
Cu(2)—N(5)—C(10)	107·3 (4)	Cu(2)—N(5)—C(13)	109·1 (4)
C(10)—N(5)—C(13)	112·3 (6)	Cu(2)—N(5)—C(14)	108·0 (5)
C(10)—N(5)—C(14)	114·2 (6)	C(13)—N(5)—C(14)	105·9 (6)
Cu(2)—N(6)—C(16)	113·1 (6)	N(1)—C(1)—C(2)	111·5 (7)
C(1)—C(2)—C(3)	112·9 (7)	N(2)—C(3)—C(2)	116·6 (7)
N(2)—C(4)—C(5)	116·7 (7)	C(4)—C(5)—C(6)	115·2 (7)
N(3)—C(6)—C(5)	111·3 (7)	N(2)—C(7)—C(8)	117·5 (6)
O(1)—C(8)—C(7)	112·7 (6)	O(1)—C(9)—C(10)	105·6 (6)
N(5)—C(10)—C(9)	116·6 (6)	N(4)—C(11)—C(12)	111·6 (7)
C(11)—C(12)—C(13)	112·3 (6)	N(5)—C(13)—C(12)	115·0 (6)
N(5)—C(14)—C(15)	115·7 (7)	C(14)—C(15)—C(16)	117·9 (7)
N(6)—C(16)—C(15)	110·9 (8)	Cl(3)···O(2)···Cl(1*a*)	108·9

Note: Cl(1*a*) is related to Cl(1) by the symmetry operation *x*, *y* − 1, *z*.

We thank the Department of Education, Northern Ireland, for an award to WDC and SERC and Royal Society for funds towards the purchase of the diffractometer.

References

Alcock, N. W., Kingston, R. G., Moore, P. & Pierpoint, C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1937–1943.

Carlisle, W. D. (1988). PhD Thesis, Univ. of Sheffield, England.

Gaykema, W. J., Volbeda, A. & Hol, W. G. J. (1986). *J. Mol. Biol.* **187**, 255–275.

Murase, I., Hamada, K. & Kida, S. (1981). *Inorg. Chim. Acta*, **54**, L171–L173.

Sheldrick, G. M. (1983). *SHELXTL User's Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Solomon, E. I. (1983). In *Copper Coordination Chemistry; Biochemical and Inorganic Perspectives*, edited by K. D. Karlin & J. Zubieta, pp. 1–22. New York: Adenine Press.

Sorrell, T. N. (1989). *Tetrahedron*, **45**, 3–68.

Tyeklar, Z. & Karlin, K. D. (1989). *Acc. Chem. Res.* **22**, 241–248.