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Structure of μ-Perchlorato-bis[*N*,*N*′-bis(β-carbamoylethyl)-*N*,*N*′-dimethylethylenediaminecopper(II)] Perchlorate*

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Abstract. $[\{Cu(C_{10}H_{22}N_4O_2)\}_2(ClO_4)](ClO_4)_3$, $M_r = 985{\cdot}5$, orthorhombic, *Pnma*, $a = 10{\cdot}367\ (1)$, $b = 27{\cdot}545\ (5)$, $c = 12{\cdot}876\ (2)$ Å, $U = 3676{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}75$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7093$ Å, $\mu = 1{\cdot}54$ mm^{-1}, $F(000) = 2024$, 298 (5) K, final $R = 0{\cdot}060$, $wR = 0{\cdot}049$ for 2353 observed reflections. The two copper(II)-diiminodiamide moieties of the binuclear complex are related to each other by a mirror plane containing a Cl and two O atoms of the perchlorate bridge. The Cu of each of these moieties is five-coordinate in a slightly distorted square-pyramidal geometry, and is displaced from the best plane of the two imino nitrogens and the two amide oxygens towards the apex of the pyramid, which is formed by a perchlorate O atom with the Cu—O distance 2·476 Å. The complex has the *RR* or *SS* configuration for the two chiral amine N centers, and the five-membered chelate ring adopts a stable *gauche* conformation. The two six-membered rings are in chair forms.

Introduction. In a previous paper we have reported the crystal structure of copper(II) with $H_2NOC(CH_2)_2$-$NH(CH_2)_2NH(CH_2)_2CONH_2$ (bcen) (Lee, Lu, Liu, Chung & Lee, 1984). As an extension, the crystal structure of the title compound is described here. Detailed structures of these two compounds are compared.

Experimental. The ligand *N*,*N*′-bis(β-carbamoylethyl)-*N*,*N*′-dimethylethylenediamine, *N*-Me$_2$bcen, was prepared by using the following procedure: 13·2 ml (0·2 mol) of *N*,*N*′-dimethylethylenediamine and 28·4 g (0·4 mol) of acrylamide in 50 ml acetonitrile were refluxed for 2 h. The solution was cooled and the product filtered off, washed with chloroform, recrystallized from chloroform, and dried in air; *N*-Me$_2$bcen was reacted with $Cu(ClO_4)_2.6H_2O$ in water. The title compound was crystallized from 9:1 ethanol–water solution (Chao & Chung, 1981; Wei, Chao & Chung, 1979).

CAD-4 diffractometer, graphite monochromator, blue rhombohedral crystal 0·2 × 0·3 × 0·5 mm used for data collection, unit-cell parameters from 25 reflections with $21 \le 2\theta \le 28°$, data collected by ω–2θ scans with scan parameters $2(0{\cdot}7 + 0{\cdot}35\tan\theta)°$ and with scan speed 20/10 ~20/3° min^{-1}, standard reflections 2,13,$\bar{3}$, 6$\bar{3}$0, $\bar{5}$41 checked every 2 h varied

* μ-Perchlorato-bis[3,3′-(*N*,*N*′-dimethylethylenediimino)dipropionamide]copper(II) perchlorate.

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within $2\sigma(I)$. Max. $\sin\theta/\lambda=0.76$ Å^{-1} ($0 \le h \le 15$, $0 \le k \le 41$, $0 \le l \le 19$), 6744 unique reflections collected, 2353 significant with $I \le 2.5\sigma(I)$. Empirical absorption correction based on azimuthal rotation from three reflections: $4\bar{4}1$, $5\bar{6}2$, $7\bar{7}2$ (North, Phillips & Mathews, 1968). Minimum, maximum and average correction factors are 0.9315, 0.9998 and 0.9713 respectively. The heavy atom Cu was solved by using Patterson syntheses. Other atoms were located successively by alternate difference Fourier analysis and least-squares fit. The function minimized in full-matrix refinement is $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics. 234 parameters with anisotropic temperature factors for non-hydrogen atoms. $R=0.060$, $wR=0.049$, $S=3.01$; $(\Delta/\sigma)_{max}=0.4$ in the final cycle. $(\Delta\rho)_{max} = 0.95$ e Å^{-3} [around N(2)]. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic positional parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq}
Cu	0·21666 (9)	0·12643 (3)	0·07731 (7)	2·73 (4)
Cl(1)	0·2383 (3)	¼	0·17099 (23)	3·15 (13)
O(11)	0·3525 (8)	¼	0·1109 (7)	5·1 (5)
O(12)	0·1644 (5)	0·20775 (18)	0·1490 (5)	5·1 (3)
O(14)	0·2705 (11)	¼	0·2761 (7)	7·6 (7)
Cl(2)	−0·2101 (4)	¼	−0·1148 (3)	5·05 (20)
O(21)	−0·3152 (19)	¼	−0·1864 (14)	18·8 (18)
O(22)	−0·2571 (10)	¼	−0·0126 (7)	6·6 (6)
O(23)	−0·2070 (15)	0·3000 (4)	−0·1429 (9)	18·3 (11)
O(24)	−0·0762 (14)	¼	−0·1087 (18)	18·3 (17)
Cl(3)	−0·31187 (22)	0·03341 (8)	−0·11499 (18)	3·80 (10)
O(31)	−0·2963 (7)	0·07496 (22)	−0·0511 (5)	6·4 (4)
O(32)	−0·2033 (7)	0·0271 (3)	−0·1744 (6)	8·6 (5)
O(33)	−0·4156 (7)	0·0405 (3)	−0·1794 (7)	10·4 (6)
O(34)	−0·3306 (9)	−0·0076 (3)	−0·0546 (6)	10·7 (6)
N(1)	0·0332 (6)	0·11269 (22)	0·0364 (5)	3·2 (3)
N(2)	0·2519 (6)	0·13848 (22)	−0·0714 (5)	3·3 (3)
N(3)	0·5850 (6)	0·17678 (23)	0·1143 (6)	3·8 (3)
N(4)	0·1128 (7)	0·05282 (23)	0·3412 (5)	3·4 (3)
O(1)	0·3950 (5)	0·13913 (18)	0·1175 (4)	2·97 (23)
O(2)	0·1894 (5)	0·09960 (17)	0·2153 (4)	2·97 (23)
C(1)	0·1054 (7)	0·0705 (3)	0·2473 (6)	2·6 (3)
C(2)	−0·0107 (8)	0·0562 (3)	0·1851 (7)	3·6 (4)
C(3)	0·0027 (8)	0·0620 (3)	0·0697 (7)	3·7 (4)
C(4)	−0·0619 (8)	0·1474 (3)	0·0836 (9)	4·8 (5)
C(5)	0·0251 (9)	0·1152 (4)	−0·0774 (7)	4·7 (5)
C(6)	0·1349 (12)	0·1404 (9)	−0·1226 (9)	12·5 (13)
C(7)	0·325 (3)	0·1010 (6)	−0·1150 (10)	14·5 (15)
C(8)	0·3410 (21)	0·1798 (6)	−0·0835 (9)	15·7 (14)
C(9)	0·4787 (9)	0·1652 (6)	−0·0439 (8)	6·6 (7)
C(10)	0·4806 (7)	0·1598 (3)	0·0680 (7)	3·1 (3)

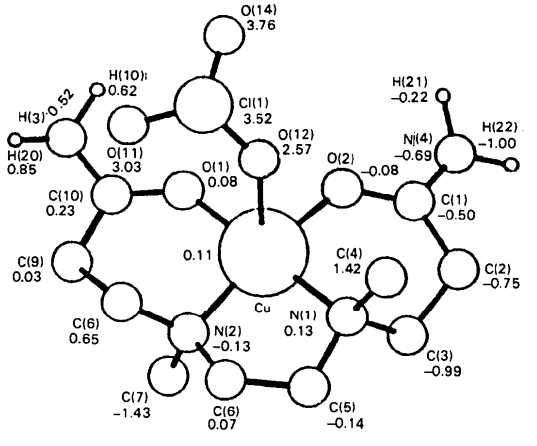

Fig. 1. Molecular structure of one moiety in the binuclear complex, showing displacements of atoms from the N_2O_2 plane (Å) (the atom positions below the plane are indicated by negative signs).

Discussion. The atomic coordinates and temperature factors are listed in Table 1.* An unusual aspect of this structure is the single perchlorate bridge between two copper-diiminodiamide moieties. These two moieties of the binuclear complex are related to each other by a mirror plane containing a Cl and two O atoms of the perchlorate bridge. In addition to the bridging ClO_4^-, there are three ClO_4^- acting as counter ions. A

* 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 43342 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu–N(1)	2·010 (6)	Cu–N(2)	1·977 (6)
Cu–O(1)	1·952 (5)	Cu–O(2)	1·945 (5)
Cl(1)–O(11)	1·414 (8)	Cl(1)–O(12)	1·422 (5)
Cl(1)–O(14)	1·395 (9)	Cl(2)–O(21)	1·427 (19)
Cl(2)–O(22)	1·403 (10)	Cl(2)–O(23)	1·425 (12)
Cl(2)–O(24)	1·390 (15)	Cl(3)–O(31)	1·419 (6)
Cl(3)–O(32)	1·372 (7)	Cl(3)–O(33)	1·371 (7)
Cl(3)–O(34)	1·384 (8)	N(1)–C(3)	1·495 (10)
N(1)–C(4)	1·502 (11)	N(1)–C(5)	1·469 (11)
N(2)–C(6)	1·382 (13)	N(2)–C(7)	1·398 (18)
N(2)–C(8)	1·473 (16)	N(3)–C(10)	1·321 (10)
N(4)–C(1)	1·305 (11)	O(1)–C(10)	1·233 (10)
O(2)–C(1)	1·253 (9)	C(1)–C(2)	1·498 (11)
C(2)–C(3)	1·501 (13)	C(5)–C(6)	1·455 (16)
C(8)–C(9)	1·568 (25)	C(9)–C(10)	1·449 (14)
Cu–O(12)	2·483 (13)		

N(1)–Cu–N(2)	87·3 (3)	N(1)–Cu–O(1)	179·4 (2)
N(1)–Cu–O(2)	91·8 (2)	N(2)–Cu–O(1)	92·9 (2)
N(2)–Cu–O(2)	167·2 (2)	O(1)–Cu–O(2)	87·9 (2)
O(11)–Cl(1)–O(12)	110·0 (3)	O(11)–Cl(1)–O(14)	109·3 (6)
O(12)–Cl(1)–O(12)A	109·9 (4)	O(12)–Cl(1)–O(14)	108·8 (4)
O(21)–Cl(2)–O(22)	109·9 (9)	O(21)–Cl(2)–O(23)	81·6 (6)
O(21)–Cl(2)–O(24)	143·0 (13)	O(22)–Cl(2)–O(23)	104·3 (6)
O(22)–Cl(2)–O(24)	107·1 (11)	O(23)–Cl(2)–O(23)A	150·4 (8)
O(23)–Cl(2)–O(24)	89·5 (7)	O(31)–Cl(3)–O(32)	109·4 (4)
O(31)–Cl(3)–O(33)	109·0 (5)	O(31)–Cl(3)–O(34)	110·4 (5)
O(32)–Cl(3)–O(33)	108·9 (6)	O(32)–Cl(3)–O(34)	109·0 (5)
O(33)–Cl(3)–O(34)	110·2 (6)	Cu–N(1)–C(3)	107·5 (5)
Cu–N(1)–C(4)	113·2 (5)	Cu–N(1)–C(5)	107·9 (5)
C(3)–N(1)–C(4)	109·8 (6)	C(3)–N(1)–C(5)	108·5 (6)
C(4)–N(1)–C(5)	109·7 (7)	Cu–N(2)–C(6)	107·8 (6)
Cu–N(2)–C(7)	111·4 (7)	Cu–N(2)–C(8)	110·4 (6)
C(6)–N(2)–C(7)	108·2 (15)	C(6)–N(2)–C(8)	118·1 (12)
C(7)–N(2)–C(8)	100·8 (14)	Cu–O(1)–C(10)	128·9 (5)
Cu–O(2)–C(1)	130·1 (5)	N(4)–C(1)–O(2)	120·2 (7)
N(4)–C(1)–C(2)	116·4 (7)	O(2)–C(1)–C(2)	123·4 (7)
C(1)–C(2)–C(3)	115·3 (7)	N(1)–C(3)–C(2)	113·8 (7)
N(1)–C(5)–C(6)	112·1 (8)	N(2)–C(6)–C(5)	118·6 (10)
N(2)–C(8)–C(9)	109·8 (13)	C(8)–C(9)–C(10)	111·2 (9)
N(3)–C(10)–O(1)	121·3 (8)	N(3)–C(10)–C(9)	115·1 (8)
O(1)–C(10)–C(9)	123·5 (8)		

O(12)A and O(23)A are the symmetry-related atoms of O(12) and O(23) respectively.

perspective view of a copper-diiminodiamide moiety with the numbering scheme and deviations of atoms from the least-squares plane through O(1)—N(2)—N(1)—O(2) is shown in Fig. 1. The equation of the least-squares plane formed by atoms N(1), N(2), O(1) and O(2) is $-2{\cdot}707x + 25{\cdot}75y + 3{\cdot}097z = 2{\cdot}798$.

As shown in Fig. 1, the Cu is five-coordinate in a slightly distorted square-pyramidal geometry, and is slightly displaced from the best plane of the two amine nitrogens and the two amide oxygens towards the apex of the pyramid, which is formed by a perchlorato O atom with Cu—O distance 2·483 Å. This bond is significantly longer than the equatorial Cu—O bond distances (1·952 and 1·945 Å). The two methyl groups attached to the asymmetric nitrogens N(1) and N(2) are axial. The bond angles and distances of the complex are normal for square-pyramidal copper(II) complexes, with alternating five- and six-membered chelate rings.

Comparing the results between this crystal and the crystal of $[Cu(NO_3)(bcen)(H_2O)].NO_3.H_2O$ (Lee *et al.*, 1984), we found the following significant results: (1) For each of these two complexes, the two asymmetric nitrogens are of the same *R* or *S* configuration, and the five-membered chelate ring adopts a stable *gauche* conformation. However, the bond angles and bond distances of this crystal shown in Table 2 are significantly different from those of $[Cu(NO_3)(bcen)H_2O]^+$. (2) The coordination numbers of these two complexes are different. $[Cu(NO_3)(bcen)(H_2O)]^+$ is of the 4+2 type; on the other hand, the Cu of each of these moieties of the present crystal is five-coordinate. This difference is mainly due to the steric effect of the two *N*-methyl groups of $[\{Cu(N\text{-}Me_2bcen)\}_2(ClO_4)](ClO_4)_3$. As shown in Fig. 1, the two bulky methyl groups are axial. Thus the coordination of a sixth ligand is inhibited sterically by the picket-fence effect of the axial *N*-methyl groups. For the present crystal, the hydrogen-bond lengths N(3)—H(20)···O(22) and N(4)—H(21)···O(31) are 3·07 (1) and 2·93 (1) Å respectively, and their bond angles are 143·9 (2) and 154·6 (2)° respectively. The O atoms around Cl(2) are disordered in the present crystal.

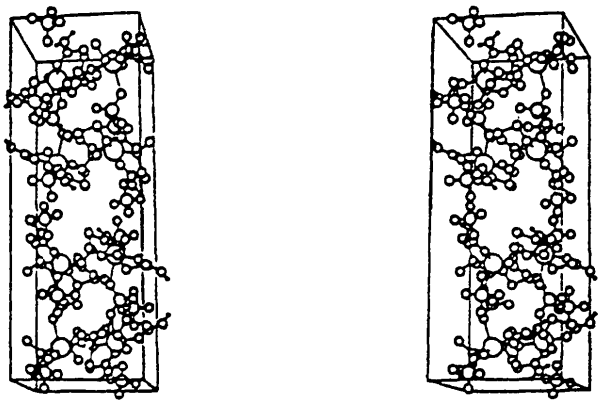

Fig. 2. Stereoview of the packing (viewed down the negative c direction).

Fig. 2 is a stereoview of the molecular packing.

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Structures of Three Copper Complexes with 2-Dimethylaminomethyl-4-phenylphenol

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Abstract. The crystal structures of three 2-dimethylaminomethyl-4-phenylphenolato (dapp) copper complexes were determined: (I) bis(2-dimethylaminomethyl-4-phenylphenolato)copper(II), $[Cu(C_{15}H_{16}NO)_2]$, $M_r = 516{\cdot}14$, monoclinic, $P2_1/n$, $a = 11{\cdot}051$ (2), $b = 9{\cdot}577$ (4), $c = 24{\cdot}436$ (12) Å, $\beta = 101{\cdot}29$ (3)°, V

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