Table 3. *Selected bond distances* (Å) *and angles* (°)

*L*MoO(NCS)$_2$ (I)			
Mo—O	1·671 (5)	O—Mo—N(1)	99·1 (2)
Mo—N(1)	2·024 (5)	O—Mo—N(11)	175·8 (3)
Mo—N(11)	2·303 (6)	O—Mo—N(21)	95·2 (2)
Mo—N(21)	2·119 (4)	N(1)—Mo—N(1)′	91·4 (3)
		N(1)—Mo—N(11)	83·7 (2)
		N(1)—Mo—N(21)	90·0 (2)
		N(1)—Mo—N(21)	165·2 (2)
		N(11)—Mo—N(21)	81·8 (2)
		N(21)—Mo—N(21)	84·9 (2)
		Mo—N(1)—C(1)	171·0 (5)
*L*MoO(N$_3$)$_2$ (II)			
Mo—O	1·668 (8)	N(31)—Mo—O	91·0 (4)
Mo—N(4)	1·966 (10)	N(31)—Mo—N(11)	81·9 (3)
Mo—N(1)	2·030 (9)	N(31)—Mo—N(1)	88·2 (3)
Mo—N(11)	2·315 (9)	N(31)—Mo—N(4)	168·7 (4)
Mo—N(21)	2·137 (8)	N(31)—Mo—N(21)	85·1 (3)
Mo—N(31)	2·130 (8)	O—Mo—N(11)	171·3 (3)
N(5)—N(6)	1·18 (2)	O—Mo—N(1)	100·9 (4)
N(1)—N(2)	1·171 (12)	O—Mo—N(4)	100·2 (4)
N(2)—N(3)	1·155 (13)	O—Mo—N(21)	94·3 (4)
N(4)—N(5)	1·146 (13)	N(11)—Mo—N(1)	84·1 (3)
		N(11)—Mo—N(4)	86·8 (4)
		N(11)—Mo—N(21)	80·0 (3)
		N(1)—Mo—N(4)	90·7 (4)
		N(1)—Mo—N(21)	163·5 (4)
		N(4)—Mo—N(21)	93·0 (4)
		Mo—N(1)—N(2)	129·3 (8)
		Mo—N(4)—N(5)	136· (1)

Enemark, 1985). As expected, the Mo—N(11) distances *trans* to the oxo ligands [2·303 Å (I) and 2·315 Å (II)] are longer than the Mo—N(21) and Mo—N(31) distances *trans* to the N atoms of the NCS$^-$ or N$_3^-$ ligands [2·119 Å in (I), 2·137 and 2·130 Å in (II)]. The high thermal parameters of the solvate atoms in (I) may reflect loss of solvent during crystal decay. No evidence of disorder is present in the difference maps.

The study was carried out using the facilities of the Molecular Structure Laboratory, Department of Chemistry, University of Arizona. We thank the National Institutes of Environmental Health Sciences (ES00966) for partial support. We thank Dr Michael Bruck for valuable assistance and helpful discussions.

References

Cleland, W. E. Jr, Barnhart, K. M. Yamanouchi, K., Collison, D., Mabbs, F E., Ortega, R. B. & Enemark, J. H. (1986). Submitted for publication.

Collison, D., Mabbs, F. E., Enemark, J. H. & Cleland, W. E. Jr (1986). *Polyhedron*, **5**, 423–425.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.

Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 4.2. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Lincoln, S., Soong, S.-L., Koch, S. A., Sato, M. & Enemark, J. H. (1985). *Inorg. Chem.* **24**, 1355–1359 and references therein.

Acta Cryst. (1987). C**43**, 53–57

Structure of Tetraaqua-bis[μ-(glycylglycinato)-*NOO′*]-dicopper(II) Bis(diphenyl phosphate) Dihydrate

By T. Głowiak and I. Podgórska*

Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 *Wrocław, Poland*

(*Received* 18 *June* 1986; *accepted* 11 *August* 1986)

Abstract. $[Cu_2(C_4H_7N_2O_3)_2(H_2O)_4].2[P(C_6H_5O)_2O_2].2H_2O$, $M_r = 995·8$, orthorhombic, $Pca2_1$, $a = 16·994$ (4), $b = 5·953$ (2), $c = 41·537$ (8) Å, $V = 4202·1$ Å^3, $Z = 4$, $D_m = 1·57$ (1), $D_x = 1·57$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1·5418$ Å, $\mu = 2·72$ mm^{-1}, $F(000) = 2056$, $T = 294$ K, final $R = 0·032$ for 4132 non-zero reflections. The structure consists of discrete dimeric $[Cu_2(C_4H_7N_2O_3)_2(H_2O)_4]^{2+}$ units, uncoordinated diphenyl phosphate monoanions and water of crystallization. Within the dimeric complex unit each dipeptide molecule acts as a tridentate ligand through N(amino), O(peptide) and O(carboxyl) atoms. The square-pyramidal environment of each Cu is achieved by two coordinated water molecules, in each case one being in the axial position. There is also evidence of 'semi-coordination' of the second O(carboxylate) atom from an adjacent peptide molecule, at the second axial position of each Cu atom, Cu···O, 2·874 (3) and 2·727 (4) Å. The crystal structure is strongly stabilized by a three-dimensional network of N—H···O and O—H···O hydrogen bonds.

---

* To whom correspondence should be addressed.

Introduction. Molecules that contain only one peptide linkage, like N-substituted amino acids and dipeptides, offer the simplest systems in which the effect of various structural features of a protein-like donor molecule on the mode of coordination about a metal ion may be investigated (Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue & Pellacani, 1981; Antolini, Menabue, Saladini, Sola, Battaglia & Bonamartini Corradi, 1984; Mauguen, Vilkas & Amar, 1984, and references cited therein).

At low pH (<4) the peptide molecule binds through the terminal N-amino and the peptide O atom; in the pH range 4–7, however, coordination occurs preferentiaally through the N-amino and the deprotonated amide N atoms (Sigel & Martin, 1982). While chelation through the N-amide atom to transition metal ions has been frequently reported, coordination by the peptide O atom is less common. So far this type of coordination has been reported in the crystal structures of some Zn^{II}, Cu^{II} and Cd^{II} complexes (G = glycine): $[Zn(GG)_2].2H_2O$ (Freeman, 1967); $[Zn(GGG)].0\cdot5(SO_4).4H_2O$ (Van Der Helm & Nicholas, 1970); $[Cu(GGG)Cl].1\cdot5H_2O$ (Freeman, Robinson & Schoone, 1964); $[Cu_2$(G-L-Leu-L-Tyr$)_2].8H_2O$ (Franks & Van Der Helm, 1971); $[Cu_2$(*cyclo*-His-His$)_2(H_2O)].ClO_4.3\cdot5H_2O$ (Kojima, Hirotsu & Matsumoto, 1977); $[Cd(GG)_2Cl_2]$ and $[Cd$(G-GluO)$H_2O].H_2O$ (Flook, Freeman, Moore & Scudder, 1973).

The situation is more complicated when a second ligand is involved in the coordination (Sigel & Martin, 1982; Lim, Sinn & Martin, 1976).

In this paper we report the coordination behaviour of glycylglycine (GG) towards the Cu^{II} ion in the presence of diphenyl phosphate ligand (DPhP).

Experimental. Title compound prepared by direct reaction of the crystalline $[Cu(DPhP)_2(H_2O)_2]$ complex (Głowiak & Szemik, 1986) with a little excess of glycylglycine in water. The resultant blue solution warmed on a water bath until the reagents were dissolved. Evaporation of the filtered solution produced blue well developed crystals. Composition: calculated for $C_{16}H_{23}CuN_2O_{10}P$: C 38·59; H 4·66; N 5·63%; found: C 38·53; H 4·61; N 5·35%. Dimensions 0·22 × 0·24 × 0·20 mm; D_m by flotation in benzene/1,2-dibromoethane; orthorhombic $Pca2_1$ or $Pcam$ from Weissenberg photographs, $Pca2_1$ confirmed by refinement; Syntex $P2_1$ computer-controlled four-circle diffractometer, Cu $K\alpha$ radiation, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections with $22 < 2\theta < 32°$ measured on the diffractometer; 4390 independent reflections, $2\theta_{max} = 148°$; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1}, depending on intensity; three standards measured every 100 reflections, variation in their intensities ±3%. Corrections for Lorentz and polarization, not for absorption. 4132 reflections with $I > 1\cdot96\sigma(I)$ used for structure determination; index range h 0→20, k 0→7, l 0→51. Calculations performed on a Nova 1200 minicomputer with the Syntex (1976) *XTL/XTLE* system. Scattering factors for neutral atoms, corrected for anomalous dispersion, from *International Tables for X-ray Crystallography* (1974). Structure solved by heavy-atom method; full-matrix and block-diagonal least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$; non-H atoms refined with anisotropic temperature factors; H-atom coordinates and thermal parameters kept fixed ($B_{iso} = 6\cdot0$ Å²); 106 atoms, 540 variables; $(\Delta/\sigma)_{max} = 0\cdot01$, residual electron density in final difference map within −0·32 and +0·30 e Å^{-3}. Final R, wR and S 0·032, 0·037 and 3·047, respectively.

The diffuse reflectance spectrum of the undiluted well powdered sample was measured at room temperature in the 350–1000 nm region with a Beckman UV 5240 spectrophotometer.

The EPR spectra were obtained using a JEOL JES-ME-3X spectrometer equipped with an MJ-110 R magnetic field marker. The spectra were recorded for a powder sample at room and liquid nitrogen temperatures.

Magnetic susceptibility has been measured in the range 81–293 K with a Gouy balance using $HgCo(SCN)_4$ for calibration (Rade, 1973). The appropriate corrections for diamagnetism were calculated from Pascal's table (Earnshow, 1968).

Discussion. Final positional and equivalent isotropic thermal parameters for non-H atoms are listed in Table 1.* Selected bond lengths and angles are in Table 2. A perspective view of the $[Cu_2(GG)_2(H_2O)_4]^{2+}$ unit with the labelling scheme is shown in Fig. 1.

The crystal structure is composed of discrete binuclear units in which the two Cu^{II} are well separated [by 6·139 (1) Å] from each other. As predicted from potentiometric titrations of Cu^{II}–GG systems (Sigel & Martin, 1982), the metal is coordinated by the terminal N-amino and O-peptide atoms. The same type of coordination was found in a Cu^{II} mixed-ligand complex of ImH (imidazole) and GG (Bell, Freeman, Wood, Driver & Walker, 1969) and in a Cu^{II} complex of GGG crystallized at low pH (Freeman *et al.*, 1964). As in both these complexes the terminal carboxyl group of the peptide molecule is bonded to the second Cu^{II} ion (with the exception that in the two former structures the

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond lengths and angles, hydrogen-bond parameters, torsion angles and the results of least-squares-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43326 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

second copper atom originates from a symmetry-related molecule, thus forming infinite chains, while in our case there is no such symmetry relationship), and dimers are formed.

Each Cu^{II} atom within the dimeric unit displays a square-pyramidal coordination with N-amino, O-peptide atoms of one GG molecule, O-carboxylate atom of the second peptide molecule and O(water) in the basal plane, and with the axial position occupied by the O atom of the second water molecule. Both the second carboxylate O atoms interact weakly with the Cu atoms at 2·874 (3) and 2·727 (4) Å, and as a result the Cu atoms are six-coordinated, with ligand donor atoms forming distorted octahedra. These distortions are clearly indicated by the angles O(1)—Cu(1)—O(2) 50·7 (1)° and O(5)—Cu(2)—O(4) 53·8 (1)°, respectively.

This unsymmetrical coordination of the carboxylate group is reflected in the C—O bond lengths. The C—O bond lengths commonly lie in the ranges 1·25–1·30 Å for strongly bonded O and 1·22–1·27 Å for weakly bonded O, as in this structure (see Table 2).

The deviations of N(amino), O(peptide), O(carboxylate) and O(water) from their least-squares planes are between −0·075 (3) and 0·101 (4) Å for Cu(1) and −0·042 (4) and 0·056 (5) Å for Cu(2) respectively, such that these atoms form very flattened tetrahedra; Cu(1) and Cu(2) are 0·157 (1) and 0·172 (1) Å out of their basal planes.

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and* B_{eq}(Å^2) *values for non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	*y*	*z*	B_{eq}
Cu(1)	995 (1)	2284 (1)	2500	2·39 (3)
Cu(2)	−1540 (1)	−1565 (1)	3397 (1)	2·96 (4)
P(1)	1980 (1)	1357 (2)	4428 (1)	2·91 (7)
P(2)	2257 (1)	5867 (2)	1712 (1)	2·61 (6)
O(1)	1198 (2)	−644 (5)	2694 (1)	2·7 (2)
O(2)	1128 (2)	1089 (6)	3168 (1)	3·1 (2)
O(3)	−434 (2)	−2250 (6)	3266 (1)	3·3 (2)
O(4)	−1469 (2)	2112 (7)	3006 (1)	4·7 (3)
O(5)	−1876 (2)	−1426 (6)	2943 (1)	3·3 (2)
O(6)	−139 (2)	1485 (5)	2493 (1)	3·1 (2)
O(11)	2463 (2)	139 (6)	4186 (1)	3·6 (3)
O(12)	1240 (2)	2448 (8)	4330 (1)	4·3 (3)
O(13)	2482 (2)	3326 (6)	4596 (1)	3·3 (2)
O(14)	1866 (2)	−482 (6)	4706 (1)	3·9 (3)
O(21)	1461 (2)	6783 (6)	1783 (1)	3·1 (2)
O(22)	2672 (2)	4557 (6)	1971 (1)	3·3 (2)
O(23)	2758 (2)	7993 (6)	1605 (1)	3·1 (2)
O(24)	2241 (2)	4203 (6)	1416 (1)	3·2 (2)
O*W*(1)	2049 (2)	3691 (6)	2586 (1)	2·9 (2)
O*W*(2)	1436 (2)	1020 (7)	2023 (1)	4·2 (3)
O*W*(3)	−2570 (2)	−432 (7)	3558 (1)	4·1 (3)
O*W*(4)	−1857 (3)	−5137 (7)	3514 (1)	5·7 (4)
O*W*(5)	1850 (2)	6072 (7)	3958 (1)	4·0 (3)
O*W*(6)	236 (2)	2189 (8)	3784 (1)	4·8 (3)
N(1)	761 (2)	2989 (7)	3466 (1)	2·9 (3)
N(2)	−1024 (2)	−1095 (8)	3829 (1)	3·3 (3)
N(3)	−1336 (2)	2744 (7)	2357 (1)	3·0 (3)
N(4)	616 (2)	5229 (7)	2328 (1)	2·7 (3)
C(1)	1144 (2)	−653 (8)	3000 (1)	2·5 (3)
C(2)	1122 (3)	−2970 (9)	3149 (1)	3·1 (3)
C(3)	8 (3)	−2611 (8)	3501 (1)	2·8 (3)
C(4)	−339 (3)	−2622 (10)	3839 (1)	3·4 (4)
C(5)	−1681 (2)	539 (9)	2837 (1)	2·9 (3)
C(6)	−1734 (3)	739 (8)	2475 (1)	3·0 (3)
C(7)	−567 (3)	3021 (8)	2386 (1)	3·0 (3)
C(8)	−231 (3)	5244 (11)	2291 (2)	5·3 (5)
C(11)	1578 (3)	−104 (10)	5019 (1)	3·7 (4)
C(12)	1717 (4)	−1873 (12)	5227 (2)	5·7 (6)
C(13)	1446 (6)	−1651 (17)	5540 (2)	8·4 (9)
C(14)	1045 (5)	155 (18)	5631 (2)	7·8 (9)
C(15)	901 (4)	1987 (15)	5420 (2)	6·3 (7)
C(16)	1184 (3)	1843 (12)	5107 (1)	4·7 (5)
C(21)	3295 (3)	3324 (9)	4629 (1)	3·1 (3)
C(22)	3680 (3)	5271 (10)	4537 (1)	3·7 (4)
C(23)	4495 (3)	5361 (11)	4573 (1)	4·5 (5)
C(24)	4899 (3)	3575 (13)	4693 (2)	5·4 (5)
C(25)	4514 (4)	1639 (12)	4792 (2)	5·5 (6)
C(26)	3700 (3)	1486 (10)	4753 (1)	4·3 (4)
C(31)	3568 (2)	8027 (8)	1537 (1)	2·7 (3)
C(32)	3953 (3)	9996 (9)	1614 (1)	3·5 (4)
C(33)	4764 (3)	10127 (11)	1547 (2)	4·6 (5)
C(34)	5154 (3)	8429 (12)	1409 (2)	4·9 (5)
C(35)	4756 (3)	6486 (11)	1328 (2)	4·9 (5)
C(36)	3947 (3)	6251 (10)	1390 (1)	4·2 (4)
C(41)	1942 (3)	4698 (9)	1110 (1)	3·3 (4)
C(42)	2056 (4)	3025 (12)	888 (1)	5·5 (6)
C(43)	1772 (6)	3315 (17)	575 (2)	8·3 (9)
C(44)	1382 (6)	5262 (17)	491 (2)	7·5 (9)
C(45)	1272 (4)	6957 (15)	715 (2)	5·9 (6)
C(46)	1560 (3)	6648 (11)	1033 (1)	4·3 (4)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Copper(II) coordination			
Cu(1)—O(1)	1·950 (3)	Cu(2)—O(5)	1·970 (3)
Cu(1)—O(6)	1·986 (3)	Cu(2)—O(3)	1·998 (3)
Cu(1)—O*W*(1)	2·008 (3)	Cu(2)—O*W*(3)	1·992 (3)
Cu(1)—O*W*(2)	2·247 (4)	Cu(2)—O*W*(4)	2·247 (4)
Cu(1)—N(4)	2·000 (4)	Cu(2)—N(2)	2·016 (4)
Cu(1)···O(2)	2·874 (3)	Cu(2)···O(4)	2·727 (4)
O(1)—Cu(1)—O(6)	87·9 (1)	O(3)—Cu(2)—O(5)	91·2 (1)
O(1)—Cu(1)—O*W*(1)	98·2 (1)	O(3)—Cu(2)—O*W*(3)	170·8 (2)
O(1)—Cu(1)—O*W*(2)	90·3 (1)	O(3)—Cu(2)—O*W*(4)	95·3 (2)
O(1)—Cu(1)—N(4)	171·0 (1)	O(3)—Cu(2)—N(2)	82·1 (2)
O(6)—Cu(1)—O*W*(1)	165·4 (1)	O(5)—Cu(2)—O*W*(3)	93·0 (2)
O(6)—Cu(1)—O*W*(2)	103·3 (1)	O(5)—Cu(2)—O*W*(4)	100·2 (2)
O(6)—Cu(1)—N(4)	83·8 (1)	O(5)—Cu(2)—N(2)	166·2 (2)
O*W*(1)—Cu(1)—O*W*(2)	90·0 (1)	O*W*(3)—Cu(1)—O*W*(4)	92·0 (2)
O*W*(1)—Cu(1)—N(4)	89·2 (1)	O*W*(3)—Cu(2)—N(2)	92·1 (2)
O*W*(2)—Cu(1)—N(4)	95·0 (1)	O*W*(4)—Cu(2)—N(2)	92·5 (2)
O(1)—Cu(1)—O(2)	50·7 (1)	O(3)—Cu(2)—O(4)	87·7 (1)
O(6)—Cu(1)—O(2)	91·8 (1)	O(5)—Cu(2)—O(4)	53·8 (1)
O*W*(1)—Cu(1)—O(2)	82·0 (1)	O*W*(3)—Cu(2)—O(4)	88·2 (1)
O*W*(2)—Cu(1)—O(2)	137·9 (1)	O*W*(4)—Cu(2)—O(4)	154·0 (2)
N(4)—Cu(1)—O(2)	125·9 (1)	N(2)—Cu(2)—O(4)	113·5 (2)
Glycylglycinate			
O(1)—C(1)	1·275 (1)	O(5)—C(5)	1·294 (6)
O(2)—C(1)	1·251 (6)	O(4)—C(5)	1·225 (6)
C(1)—C(2)	1·512 (7)	C(5)—C(6)	1·511 (6)
C(2)—N(1)	1·454 (6)	C(6)—N(3)	1·457 (6)
N(1)—C(3)	1·307 (6)	N(3)—C(7)	1·323 (6)
C(3)—O(3)	1·251 (5)	C(7)—O(6)	1·251 (6)
C(3)—C(4)	1·520 (6)	C(7)—C(8)	1·492 (8)
C(4)—N(2)	1·477 (7)	C(8)—N(4)	1·447 (6)

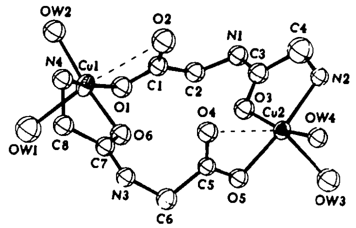

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the $[Cu_2(GG)_2(H_2O)_4]^{2+}$ complex with the atom-numbering scheme.

Within the dipeptide ligands, bond distances and angles are normal and in good agreement with those found in related structures. Both the carboxylate and peptide groups are planar. The two GG ligands have similar conformations although the values of corresponding torsion angles differ to some extent. The major differences between them are in the angles ψ_1^1 and ψ_1^2 [N(1)—C(3)—C(4)—N(2), O(3)—C(3)—C(4)—N(2) for the first GG molecule and N(3)—C(7)—C(8)—N(4), O(6)—C(7)—C(8)—N(4) for the second one], which differ by as much as 27°. These differences are probably caused by differences in the modes of hydrogen bonding.

The dimensions of the two independent DPhP monoanions compare well with those observed in glycinium diphenyl phosphate (Głowiak & Wnęk, 1985*a*) and certain other copper(II) diphenyl phosphate compounds (Głowiak & Wnęk, 1985*b*; Głowiak, Podgórska & Baranowski, 1986; Głowiak & Podgórska, 1986).

The (C)O—P—O(C) angles involving the esterified oxygen atoms are 104·4 (2) and 107·0 (2)° for the first and second DPhP ion, respectively. In both ions these angles are not the smallest ones, as was found in glycinium diphenyl phosphate, but instead, in each case, one of the (C)O—P—O angles is the smallest. The largest angles in both DPhP ions are the O—P—O angles. Both DPhP anions display the same *gauche–gauche* conformation about both P—O(C) bonds.

Besides the discrete dimeric complex cations and uncoordinated DPhP anions, the crystal structure also contains water of crystallization, which provides crystal stability by bridging the complex and DPhP through a network of hydrogen bonds. The packing arrangement, with hydrogen-bonding scheme, is illustrated in Fig. 2.

There are eighteen crystallographically independent hydrogen bonds or short van der Waals contacts, of the type O—H···O and N—H···O. Each water molecule [except O*W*(3)] forms two such contacts, with O-carboxylate, O-phosphate and O-water of an adjacent molecule. The O···O lengths are in the range 2·713 (4) to 3·044 (5) Å and O—H···O angles range from 135 to 179°. O*W*(3) is involved in three close contacts, one of the H atoms being shared between two acceptor O atoms, forming a 'bifurcated hydrogen bond'. The lengths of these H bonds are 2·769 (5) (normal H bond), 3·056 (6) and 2·874 (5) Å (bifurcated H bond), while the corresponding angles are 164, 149 and 123°.

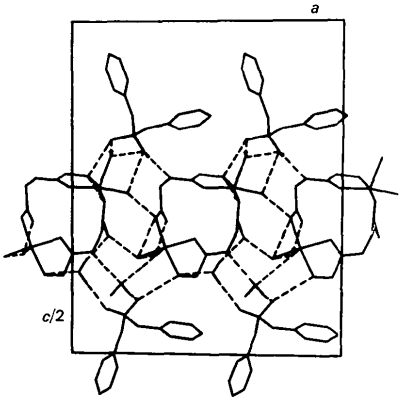

Fig. 2. Molecular packing viewed along **b**.

The H atoms of the coordinated amino groups and the N-peptide atoms serve as donors in six further hydrogen bonds or close van der Waals contacts of type N—H···O. These contacts occur with O-water (two contacts), O-phosphate (three contacts) and coordinated carboxyl oxygen (one contact). The corresponding N···O lengths and N—H···O angles are in the range 2·815 (5) to 3·053 (5) Å and 126 to 174°, respectively.

Magnetic and spectroscopic results. The X-band room-temperature as well as liquid-nitrogen-temperature EPR spectra of a polycrystalline sample show a single resonance line at $g = 2{\cdot}16$; there is no evidence in these spectra of any $\Delta M_s = 2$ transition, which would be indicative of a singlet–triplet transition.

The magnetic susceptibility over the whole temperature range measured shows no significant deviation from the behaviour predicted by the Curie law. Hence, the only possible conclusion is that any interaction between the two copper centres must be very small. Also the effective magnetic moment of 1·93 BM (1 BM $\equiv 9{\cdot}27 \times 10^{-24}$ J T^{-1}) (at room temperature) is typical of Cu^{II} complexes with well separated Cu centres. The absence of interaction between the two Cu^{II} ions of the dimeric unit is easy to explain. Each unpaired electron arising from a Cu^{II} ion is described by a magnetic orbital (Kahn, 1982) localized in the basal plane of the $CuNO_4$ square-based pyramid and pointing towards the four nearest neighbours of the metal ion. It follows that the two magnetic orbitals are separated by *ca* 6 Å, which is particularly unfavourable for their interaction. So in terms of metal–metal interaction, the title compound is not a genuine binuclear complex. The ground state must be described as two single-ion spin doublets and not as a molecular spin triplet and a molecular spin singlet.

In the solid-state electronic spectrum of the title compound only one broad and asymmetric '*d–d*' absorption band is observed ($\lambda_{max} = 715$ nm).

We are grateful to Dr A. Jezierski for his helpful discussion of the EPR spectra. This work has been supported by the Polish Academy of Sciences.

References

Antolini, L., Menabue, L., Saladini, M., Sola, M., Battaglia, L. P. & Bonamartini Corradi, A. (1984). *Inorg. Chim. Acta*, **93**, 61–66.

Battaglia, L. P., Bonamartini Corradi, A., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1981). *Inorg. Chem.* **20**, 1075–1080.

Bell, J. D., Freeman, H. C., Wood, A. M., Driver, R. & Walker, W. R. (1969). *J. Chem. Soc. Chem. Commun.* pp. 1441–1443.

Earnshow, A. (1968). *Introduction to Magnetochemistry.* London: Academic Press.

Flook, R. J., Freeman, H. C., Moore, C. J. & Scudder, M. L. (1973). *J. Chem. Soc. Chem. Commun.* pp. 753–754.

Franks, W. A. & van Der Helm, D. (1971). *Acta Cryst.* B**27**, 1299–1310.

Freeman, H. C. (1967). *Adv. Protein Chem.* **22**, 257–424.

Freeman, H. C., Robinson, G. & Schoone, J. C. (1964). *Acta Cryst.* **17**, 719–730.

Głowiak, T. & Podgórska, I. (1986). *Inorg. Chim. Acta.* In the press.

Głowiak, T., Podgórska, I. & Baranowski, J. (1986). *Inorg. Chim. Acta,* **115**, 1–10.

Głowiak, T. & Szemik, A. W. (1986). *J. Crystallogr. Spectrosc. Res.* In the press.

Głowiak, T. & Wnęk, I. (1985*a*). *J. Crystallogr. Spectrosc. Res.* **15**, 157–171.

Głowiak, T. & Wnęk, I. (1985*b*). *Acta Cryst.* C**41**, 507–510.

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

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

Kahn, O. (1982). *Inorg. Chim. Acta,* **62**, 3–14.

Kojima, Y., Hirotsu, K. & Matsumoto, K. (1977). *Bull. Chem. Soc. Jpn,* **50**, 3222–3231.

Lim, M. C., Sinn, E. & Martin, R. B. (1976). *Inorg. Chem.* **15**, 807–811.

Mauguen, Y., Vilkas, E. & Amar, C. (1984). *Acta Cryst.* C**40**, 82–85.

Rade, H. S. (1973). *J. Phys. Chem.* **77**, 424–426.

Sigel, H. & Martin, R. B. (1982). *Chem. Rev.* **82**, 385–426.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.

Van Der Helm, D. & Nicholas, H. B. (1970). *Acta Cryst.* B**26**, 1858–1866.

Acta Cryst. (1987). C**43**, 57–59

Dichloro(*N*,*N*-dimethylethylenediamine)platinum(II)

By R. Melanson, C. de la Chevrotière and F. D. Rochon

Département de Chimie, Université du Québec à Montréal, CP 8888, *succ. A, Montréal, Canada H*3*C* 3*P*8

(*Received* 16 *June* 1986; *accepted* 5 *August* 1986)

Abstract. $[PtCl_2(C_4H_{12}N_2)]$, $M_r = 354{\cdot}15$, monoclinic, $P2_1$, $a = 5{\cdot}639\ (2)$, $b = 10{\cdot}661\ (4)$, $c = 7{\cdot}244\ (3)$ Å, $\beta = 95{\cdot}88\ (3)°$, $V = 433{\cdot}2\ (3)$ Å^3, $Z = 2$, $D_x = 2{\cdot}714$, $D_m = 2{\cdot}71\ (2)$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 169{\cdot}1$ cm^{-1}, $F(000) = 324$, $T = 295$ K, $R = 0{\cdot}032$ for 905 unique observed reflections. Pt has square-planar coordination with a slight distortion caused by the bidentate ligand [N—Pt—N angle = 84·0 (5)°]. The bond distances are Pt—Cl 2·303 (4), 2·317 (4) and Pt—N 2·039 (14), 2·067 (12) Å. The crystal is stabilized by hydrogen bonds between the $-NH_2$ group and one chloride ligand.

Introduction. Recently, we have started a study on the reactions of platinum(II) compounds with ethylenediamine derivatives. We have synthesized as starting materials the dihalo complexes. In order to characterize well all the compounds involved in these reactions, we have decided to determine the crystal structure of some of these dihalo compounds. Up to now, only the dichloro Pt complex of *N*,*N*-dimethylethylenediamine $[PtCl_2\{N(CH_3)_2C_2H_4NH_2\}]$ has given suitable crystals for X-ray diffraction. Its structure is reported below.

Experimental. *Synthesis.* $[PtCl_2\{N(CH_3)_2C_2H_4NH_2\}]$ was synthesized from the aqueous reaction of K_2PtCl_4 with *N*,*N*-dimethylethylenediamine in a 1:1 ratio. The yellow compound was recrystallized from water at 333 K. Yield 70%. Dec. at 488–503 K. Elemental analysis: calc. 13·56% C and 3·41% H, exp. 13·49% C and 3·31% H.

The crystals used for the structure determination were obtained by slow evaporation of an aqueous solution.

Platelet, dimensions (mm): 0·084 (100–$\bar{1}$00) × 0·038 (001–00$\bar{1}$) × ~0·29 (0$\bar{1}$0–110 and $\bar{1}$10); density by flotation in bromoform–dibromomethane mixture; precession photographs showed space group $P2_1$; Syntex $P\bar{1}$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from refined angles of 15 centered reflections (2θ range: 10–21°); 1056 independent reflections measured up to $2\theta < 55°$ by θ–2θ scan technique; range of hkl: h: 0→7, k: 0→13, l: −9→9; standard reflections 060, 200 and 011, variations < 2·5%; reflections with $I_{\text{net}} < 2{\cdot}5\sigma(I)$ unobserved, $\sigma(I)$ calculated as in Melanson & Rochon (1975); absorption correction based on equations of crystal faces, transmission factors from 0·278 to 0·536; data corrected for Lorentz and polarization effects; 905 unique observed reflections; atomic scattering factors of Cromer & Waber (1965) for Pt, Cl, N, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt and Cl from Cromer (1965).

0108-2701/87/010057-03$01.50