Structural Studies in Metal–Purpurate Complexes. Part 6.† Crystal Structures of Bis(purpurato)-copper(II) and -zinc(II) Hydrates

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The crystal structures of the title compounds, $[CuL_2]\cdot5H_2O$ (1) and $[ZnL_2]\cdot4H_2O$ (2) (L = purpurate), have been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.083 (702 'observed' reflections) and 0.10 (522 'observed' reflections) respectively. Crystals of (1) are orthorhombic, space group *Fddd*, $a = 24.610(8)$, $b = 24.859(9)$, $c = 8.011(3)$ Å, $Z = 8$. Crystals of (2) are monoclinic, space group *C2/c*, $a = 10.404(3)$, $b = 25.355(7)$, $c = 9.695(3)$ Å, $\beta = 114.89(2)^\circ$, $Z = 4$. Both complexes contain ML_2 molecular species together with lattice water molecules. The symmetry of the zinc derivative is close to D_{2d}, while that of the copper is reduced to D_2. In each of the tridentate ligands, the central nitrogen co-ordination distance to the metal is equal to, or less than, that of the oxygens [Cu–N 1.931(9); Zn–N 2.07(3), 2.14(3); Cu–O 2.421(6); Zn–O 2.19(2), 2.10(2) Å] whereas in all derivatives previously studied the metal–nitrogen bond is long. In the copper derivative, a better model is obtained if the metal atom is disordered in *z* over two sites 0.61(1) Å apart; Cu(disordered)–N is 1.954(8), and Cu–O 2.246(8), 2.621(10) Å.

INTERDIFFUSION of aqueous copper(II) chloride and murexide {ammonium purpurate, $[NH_4][L]$ ($L = [C_8H_4N_5O_6]^-$)} solutions yielded a crystalline deposit at the interface; the bulk of this deposit comprises very fine elongated flakes but intermingled with these may be found a few small pseudo-tetragonal capped blocks, both phases being a reddish brown colour on crushing. The structure determination of the second phase, $CuL_2\cdot5H_2O$ (1), is described in this paper, a crystal 0.10 × 0.10 × 0.15 mm being used for the crystallographic work. Also described is the structure determination of $[ZnL_2]\cdot4H_2O$ (2), obtained as fine orange crystals by mixing an aqueous solution of zinc chloride with a less-than-stoicheiometric suspension of murexide and allowing the solution to stand after filtration of the initial fine precipitate; care must be taken to distinguish the product from the red crystalline $[ZnL_2]\cdot9H_2O$ [1] which is formed under very similar conditions but with an excess of *murexide*.

EXPERIMENTAL

Analysis for (2) (Found, calc. for $ZnL_2\cdot4H_2O$): C, 28.7, 28.70; H, 2.7, 2.41; N, 20.95, 20.91; Zn, 10.75, 9.76%. Previous work carried out on copper– and zinc–purpurate systems has been concerned with the determination of the formation [2,3] and rate constants [3,4] of the 1 : 1 complexes.

The definition of the atom numbering scheme within the purpurate anion together with other details common to all structure determinations in this series is given in Part 1.[5] Observed and calculated structure-factor tables have been deposited.‡

Crystallographic Data and Procedure.—(1): $C_{16}H_{18}CuN_{10}O_{17}$, $M = 686.0$, Orthorhombic, space group *Fddd* (D_{2h}^{24},

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† Part 5 is the preceding paper.

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[1] M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, Part 3, *J.C.S. Dalton*, 1977, 1350.

[2] G. Geier, *Helv. Chim. Acta*, 1967, **50**, 1879.

[3] G. Maass, *Z. phys. Chem.*, 1968, **60**, 138.

[4] G. Geier, *Helv. Chim. Acta*, 1968, **51**, 94; A. Bewick and P. M. Robertson, *Trans. Faraday Soc.*, 1967, **63**, 678.

[5] R. L. Martin, A. H. White, and A. C. Willis, Part 1, *J.C.S. Dalton*, 1977, 1336.

No. 70, second setting) (but see below), $a = 24.610(8)$, $b = 24.859(9)$, $c = 8.011(3)$ Å, $U = 4\,901(3)$ Å^3, $D_m = 1.86(1)$ g cm^{-3}, $Z = 8$, $D_c = 1.86$ g cm^{-3}, $F(000) = 2\,792$, crystal size $0.10 \times 0.10 \times 0.15$ mm (capped prism), $\mu(\text{Mo-}K_\alpha) = 9.3$ cm^{-1} (data corrected for absorption), data range $2\theta < 50°$ yielding 1 098 reflections [702 'observed' with $I > 3\sigma(I)$], final $R = 0.083$, $R' = 0.074$ ($n = 0$).

TABLE 1

Atomic fractional cell co-ordinates [(x, y, z); H $\times 10^3$; others $\times 10^4$], and thermal parameters ($U_{ij} \times 10^3$ Å^2) with least-squares estimated standard deviations in parentheses

(1) (The copper derivative) [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu [b]	1 250(—)	1 250(—)	1 250(—)	11(1)	22(1)	193(4)	0(—)	0(—)	0(—)
The purpurate ligand [r(Å) is N–H; γ, δ (°) are H(nm)–N(nm)–C($nm - 1, m + 1$)]									
N(0) [b]	2 035(4)	1 250(—)	1 250(—)	18(5)	23(5)	35(8)	0(—)	0(—)	11(6)
C(11)	2 278(3)	1 705(3)	1 764(13)	22(4)	14(4)	46(7)	−3(4)	−11(5)	6(5)
C(12)	1 942(3)	2 073(3)	2 649(13)	19(4)	22(5)	42(7)	−7(4)	−3(5)	3(5)
O(12)	1 476(2)	1 979(2)	3 127(9)	25(3)	37(4)	50(5)	−7(3)	9(3)	−9(4)
N(13)	2 170(3)	2 556(3)	3 100(10)	27(4)	28(4)	41(6)	−4(3)	7(4)	−9(4)
H(13)	195(—)	280(—)	383(—)	100(—)	$r = 1.00(—)$; $\gamma, \delta = 117(—), 118(—)$				
C(14)	2 674(4)	2 724(4)	2 620(14)	35(5)	38(6)	34(7)	−20(5)	3(4)	−18(6)
O(14)	2 840(3)	3 172(3)	3 021(11)	58(5)	56(5)	85(7)	−30(4)	18(5)	−35(5)
N(15)	2 961(3)	2 390(3)	1 613(11)	20(4)	31(4)	38(6)	−8(3)	2(4)	−1(4)
H(15)	332(—)	252(—)	120(—)	100(—)	$r = 1.00(—)$; $\gamma, \delta = 117(—), 116(—)$				
C(16)	2 807(3)	1 879(3)	1 123(13)	19(4)	29(5)	32(6)	0(4)	−1(5)	14(5)
O(16)	3 083(3)	1 645(3)	0 099(10)	31(4)	42(4)	59(6)	−4(3)	18(4)	−4(4)
Lattice-water molecules									
O(1) [b]	1 250(—)	1 250(—)	6 250(—)	23(6)	18(6)	76(12)	0(—)	0(—)	0(—)
O(2)	3 325(4)	1 639(3)	4 925(10)	126(8)	39(4)	31(5)	−1(4)	−2(5)	−16(4)

(2) (The zinc derivative)

Atom	x	y	z					
Zn [b]	0 000(—)	1 284(2)	2 500(—) [c]					
The purpurate ligands								
Atom	x	y	z	U	x	y	z	U
N(0) [b]	0 000(—)	0 468(11)	2 500(—)	19(9)	0 000(—)	2 126(11)	2 500(—)	14(9)
C(11)	0 987(27)	0 234(9)	2 190(29)	5(7)	0 436(28)	2 320(10)	3 919(31)	23(8)
C(12)	1 978(29)	0 597(10)	2 082(31)	21(8)	0 949(28)	1 935(9)	5 136(31)	15(7)
O(12)	1 945(18)	1 077(7)	2 276(21)	29(6)	1 025(9)	1 455(6)	4 839(19)	31(6)
N(13)	3 000(23)	0 396(8)	1 670(25)	21(7)	1 359(25)	2 126(6)	6 536(26)	35(7)
H(13)	374(—)	064(—)	165(5)	100(—)	165(—)	186(—)	737(—)	100(—)
C(14)	3 072(33)	−0 111(12)	1 287(36)	39(9)	1 435(32)	2 634(12)	6 964(37)	35(9)
O(14)	3 943(21)	−0 267(7)	0 776(23)	48(7)	1 889(22)	2 779(8)	8 301(25)	46(7)
N(15)	2 085(25)	−0 456(9)	1 308(26)	32(7)	0 842(25)	2 992(8)	5 785(28)	34(7)
H(15)	219(—)	−084(—)	115(—)	100(—)	095(—)	337(—)	606(—)	100(—)
C(16)	0 894(31)	−0 281(11)	1 549(34)	31(9)	0 125(28)	2 867(9)	4 260(31)	14(7)
O(16)	−0 127(21)	−0 596(7)	1 131(21)	43(6)	−0 651(19)	3 180(3)	3 329(21)	39(6)
The lattice water molecules								
O(1)	4 684(20)	0 965(7)	0 480(23)	42(6)				
O(2)	3 144(18)	3 503(6)	0 852(21)	32(5)				

[a] The above values are for the model in which the copper atoms resides on the special position at $R = 0.086$. In refining the model with the copper disordered in z, no non-copper parameter changes by more than σ. For the copper, z becomes 0.087 0(13), $U_{11} = 12(1)$, $U_{22} = 21(1)$, $U_{33} = 81(10)$, $U_{12} = 3(21)$, population = 0.5, at R 0.083. [b] Special position. [c] U_{11}, 26(3); U_{22}, 15(3); U_{33}, 19(3); U_{13}, 12(2).

The structure was solved by direct methods and refined by full-matrix least squares. Non-hydrogen-atom thermal motion was refined anisotropically; hydrogen atoms were not located and were fixed geometrically for the purpurate and included in the refinement with $r_{\text{N–H}}$ invariant at 1.0 Å. The structure presents a number of unsatisfactory aspects which it has not been possible to resolve. (*i*) In addition to those reflections required by space group *Fddd*, a number of significant weaker reflections were observed among $h0l$, $0kl$ which, while satisfying the $h, k, l = 2n$ requirement, violated the $h + l$, $k + l = 4n$ requirement, requiring only $2n$ instead. In all, one of these reflections (402) was observed at the 20σ level, another four at the 10σ level, and a further nine at the 5σ level. (*ii*) The thermal motion of the copper atom is extraordinarily anisotropic; this is not true, however, of the co-ordinated purpurate atoms or the remainder of the ligand. However, thermal motion of the lattice water molecule oxygen atoms may also be abnormally anisotropic. (*iii*) R is rather high; this might to some extent be a consequence of the weak data, but there is a systematic abnormal increase in R for those data zones with high l (not found with h and k) and it seems that this is a further dubious aspect of the structure. In an attempt to resolve these anomalies, further refinement was attempted in space groups *Fdd*2 and *F*222; in *Fdd*2, the copper atom exists in sites of symmetry 2 (rather than the sites 222 in *Fddd*) with the possibility of a displacement of the copper along z, providing a model both plausible and consistent with the observation of the large thermal anisotropy of the copper, a virtue lacking in *F*222. Presumably because of the scarcity and specialized nature of the lower-symmetry data, however, it was not possible to initiate a successful refinement with either of these lower symmetries and the attempt was abandoned. Following a referee's suggestion the model was finally refined with the copper atom disordered in z; this effected a significant improvement lowering R from 0.086 to 0.083 and R' from 0.09 to 0.074. The above difficulties concerning the anomalies in the data remain, however, for both the ' ordered ' model (in which the copper has an anomalously high thermal anisotropy) and the disordered model (in which the copper atom equally populates two sites along *z* on either side of $z = 0.125$ with somewhat reduced anisotropy). The anomalous *hk*0, *h*0*l*, and 0*kl* data are deposited together with the tables of structure amplitudes.

(2): $C_{16}H_{16}N_{10}O_{16}Zn$, $M = 669.7$, Monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), $a = 10.404(3)$, $b = 25.355(7)$, $c = 9.695(3)$ Å, $\beta = 114.89(2)°$, $U = 2\,320(1)$ Å^3, $D_m = 1.92(1)$ g cm^{-3}, $Z = 4$, $D_c = 1.92$ g cm^{-3}, $F(000) = 1\,360$, crystal size $0.10 \times 0.06 \times 0.25$ mm (prism), μ(Mo-K_α) = 10.9 cm^{-1} (data corrected for absorption), data range $2\theta < 40°$ yielding 1 099 reflections (522 ' observed '), final $R = 0.10$, $R' = 0.086$ ($n = 1$).

The structure was solved by the heavy-atom method and refined by full-matrix least squares. The weakness of the data set did not permit the thermal motion of any atoms other than the metal to be refined anisotropically in a meaningful manner and hydrogen atoms were not located but treated as for (1). Ligand numbering for (2) is suffixed ' a ' or ' b ' to denote the ligand referred to where necessary.

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses. Only ligand hydrogen-bonding interactions are given, since water-molecule hydrogen atoms have not been located

(*a*) The purpurate geometry; as in previous papers in this series, the geometries of the two halves of the barbiturate ring are tabulated in parallel columns. Entries within each column are for the ligand of (1) and ligands ' a ' and ' b ' of (2) respectively. The geometry in (1) is for the ' ordered copper ' model at *R* 0.086

N(0)–C(11)	1.345(9)	133(3), 1.35(3)
C(11)–C(12)	1.42(1)	1.42(4), 1.45(4)
C(12)–O(12)	1.23(1)	1.23(3), 1.26(3)
C(12)–N(13)	1.37(1)	1.38(4), 1.33(4)
N(13)–C(14)	1.37(1)	1.35(4), 1.35(4)
C(14)–O(14)	1.23(1)	1.27(5), 1.23(4)

C(11)–C(16)	1.46(1)	1.43(4), 1.49(4)
C(16)–O(16)	1.21(1)	1.26(4), 1.22(3)
C(16)–N(15)	1.38(1)	1.43(5), 1.38(4)
N(15)–C(14)	1.36(1)	1.35(4), 1.39(4)
O(16) · · · O(16$^{\rm I}$) [≡O(26)]	2.69(1)	2.55(3), 2.50(3)

C(11)–N(0)–C(11$^{\rm I}$)	127.1(9)	127(3), 137(3)
N(0)–C(11)–C(12)	115.7(7)	113(2), 116(2)
C(11)–C(12)–O(12)	125.2(8)	124(3), 120(3)
O(12)–C(12)–N(13)	117.6(8)	119(3), 124(2)
C(11)–C(12)–N(13)	117.1(7)	117(2), 116(2)
C(12)–N(13)–C(14)	124.3(8)	125(3), 128(3)
N(13)–C(14)–O(14)	120.3(9)	122(2), 124(3)
N(13)–C(14)–N(15)	117.0(8)	119(3), 115(3)
C(12)–C(11)–C(16)	120.2(2)	118(3), 119(3)
M–N(0)–C(11)	116.5(5)	117(2), 111(2)
M–O(12)–C(12)	99.3(6)	110(2), 113(2)

N(0)–C(11)–C(16)	122.4(8)	126(3), 124(2)
C(11)–C(16)–O(16)	126.4(7)	128(3), 125(2)
O(16)–C(16)–N(15)	118.6(8)	115(3), 122(2)
C(11)–C(16)–N(15)	114.5(8)	117(3), 112(2)
C(16)–N(15)–C(14)	126.1(7)	121(2), 126(2)
N(15)–C(14)–O(14)	122.6(9)	118(3), 121(3)

(*b*) Remaining geometry of (1):

(*i*) Metal-atom environment (independent geometry only) (' ordered copper ' model, *R* 0.086)

Cu–N(0)	1.931(9)	Cu–O(12)	2.421(6)
N(0)–Cu–O(12)	76.7(7)	O(12)–Cu–O(12$^{\rm II}$)	83.0(2)
N(0)–Cu–O(12$^{\rm II}$)	103.3(2)		
O(12)–Cu–O(12$^{\rm III}$)	103.2(2)	O(12)–Cu–O(12$^{\rm I}$) [≡O(22)]	153.4(2)

(*ii*) Ligand-hydrogen-bonding interactions (O · · · H <2.5 Å); the angle subtended at the hydrogen is given in parentheses

H(13) · · · O(2$^{\rm IV}$)	1.8(166)	H(15) · · · O(12$^{\rm V}$)	2.1(162)

(*iii*) Metal-atom environment (' disordered copper ' model)

Cu–N(0)	1.954(8)	Cu · · · Cu$^{\rm I}$	0.61(1)
Cu–O(12)	2.621(10)	Cu–O(12$^{\rm II}$)	2.246(8)
N(0)–Cu–O(12)	71.5(2)	N(0)–Cu–O(12$^{\rm II}$)	109.1(2)
N(0)–Cu–O(12$^{\rm I}$)	80.7(2)	N(0)–Cu–O(12$^{\rm VI}$)	95.9(3)
O(12)–Cu–O(12$^{\rm I}$)	151.1(2)	O(12)–Cu–O(12$^{\rm II}$)	81.9(2)
O(12)–Cu–O(12$^{\rm VI}$)	92.9(4)	O(12$^{\rm I}$)–Cu–O(12$^{\rm II}$)	115.5(5)

Transformations of the asymmetric unit (*x*, *y*, *z*) are denoted by the following Roman superscripts

I $(x, \frac{1}{4} - y, \frac{1}{4} - z)$
II $(\frac{1}{4} - x, y, \frac{1}{4} - z)$
III $(\frac{1}{4} - x, \frac{1}{4} - y, z)$
IV $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$
V $(\frac{1}{4} + x, \frac{1}{2} - y, z - \frac{1}{4})$
VI $(\frac{1}{4} - x, \frac{1}{4} - y, z)$

(*c*) Remaining geometry of (2):

(*i*) Metal-atom environment (independent geometry only)

Zn–N(0a)	2.07(3)	Zn–N(0b)	2.14(3)
Zn–O(12a)	2.19(2)	Zn–O(12b)	2.10(2)
N(0a)–Zn–O(12a)	76.1(5)	N(0b)–Zn–O(12b)	78.1(5)
N(0a)–Zn–O(12b)	101.9(5)	N(0b)–Zn–O(12a)	103.9(5)
O(12a)–Zn–O(12b)	94.9(7)	O(12a)–Zn–O(12b$^{\rm I}$)	90.8(9)

(*ii*) Ligand-hydrogen-bonding interactions (O · · · H <2.5 Å); the angle subtended at the hydrogen is given in parentheses

H(13a) · · · O(1)	2.0(148)	H(15a) · · · O(12b$^{\rm II}$)	2.1(139)
H(13b) · · · O(2$^{\rm III}$)	1.9(162)	H(15b) · · · O(1$^{\rm IV}$)	2.1(137)

Transformations of the asymmetric unit (*x*, *y*, *z*) are denoted by the following Roman superscripts

I $(\bar{x}, y, \frac{1}{2} - z)$
II $(x, \bar{y}, z - \frac{1}{2})$
III $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$
IV $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$

For both compounds, fractional cell co-ordinates are in Table 1 and bond lengths and angles in Table 2. The unit-cell contents are shown in Figure 1.

DISCUSSION

It is unfortunate that the structures of the present two derivatives are less accurately established than many of the remaining members of the present series, since in many respects they are among the most interesting. In both cases highly symmetric lattices containing highly symmetrical ML_2 molecules are found: in the copper complex only one segment of the ligand (and the associated copper) comprises the asymmetric unit with the copper atom lying on a special position of 222 site symmetry, while in the zinc derivative the molecule has symmetry 2, the twofold axis passing along N(0)–Zn–N(0) so that the asymmetric unit comprises one segment of each of the two independent ligands. Whereas in the zinc complex the two ' planes ' developed by the three donor atoms of each ligand with the metal lie approxim-

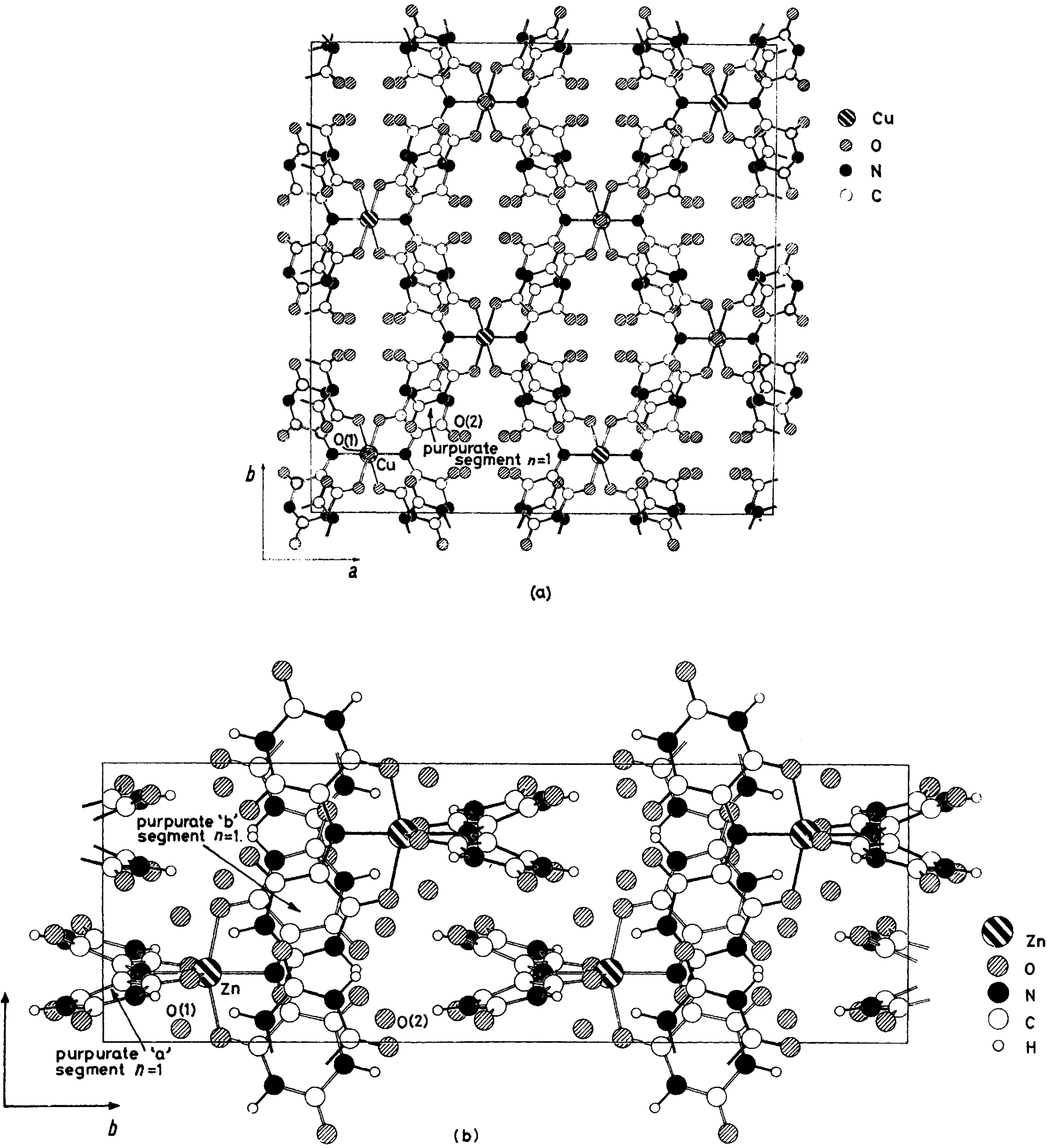

FIGURE 1 Unit-cell contents of (1)(a) and (2)(b) projected down c and a respectively. In (2), the bonds of the molecules in the top of the cell are shown as solids, in (1) those of the molecules with the central copper atom at $z = 3/8$, $7/8$. Hydrogen atoms in (1) omitted for clarity

ately normal (87.8°) to each other and almost parallel to the axial planes, it will be clear from Figure 2 that this is not the case for the copper derivative in which the metal environment departs seriously from D_{2d} symmetry, the molecule being considerably squashed towards planarity along one of the two-fold axes, the corresponding interplanar angle being 79.3°. Unlike the other derivatives studied the metal–oxygen distances are not *ca.* 0.1 Å greater than the metal–nitrogen ones; in particular, in the copper derivative, the Cu–N(0) distance is very clearly considerably shorter than the Cu–O(12) distances [1.931(9), *cf.* 2.421(6) Å] and the role of the ligand in bonding to the metal is more in keeping with the relative bonding strength of these two donors at the right-hand end of the transition series. The abnormality of the copper derivative in these respects is further reflected in its position relative to those of the other derivatives in the r_{M-O}/θ plot of ref. 1 in which different ligand strain is evidenced by the abnormally large angle between the two ligand ring planes (Table 3), the abnormally large O(16) ··· O(26) distance, and the diminished deviations of the atoms in their vicinity from the barbiturate plane. Although this suggests that the tendency toward overall ligand planarity is considerably enhanced by weakened M–O(12) bonding relative to that found in other derivatives in the series, this appears to be inconsistent with the tendency for the ligand to be non-planar in the unco-ordinated ligands found in the iron(II) and manganese(II) derivatives.[1]

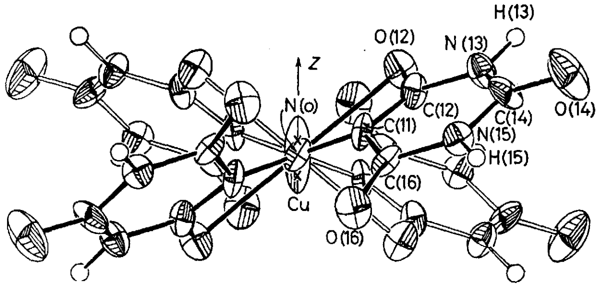

FIGURE 2 Diagram of the CuL_2 species (ordered model) projected along N(0)–Cu–N(0) showing 50% thermal ellipsoids. Attention is drawn to the large vibrational amplitude of the metal atom and the considerable deviation from orthogonality of the ligand 'planes.' The ligand nearest the viewer is shown with solid bonds. Points × mark the positions of the copper atoms in the disordered model.

It is apparent that the cause of the problems in achieving a total solution of the structure of (1) almost certainly lies in the real or apparent anisotropic thermal motion parallel to *c* with the likelihood that this is coupled with, or has its origin in, a slight positional displacement of the copper atom from the special co-ordinate $z = 1/8$ in *Fddd*. Why this should be so and yet not be reflected in correspondingly large anisotropy of the ligands is equally equivocal; a large thermal motion might be consistent with the presence of a dynamic Jahn–Teller effect, while a small disordered positional displacement of the metal along *c* might likewise be indicative of a static effect of the same type. [We note that the deviation of the copper atoms from the ligand ring planes is unusually large, presumably a consequence of the weak Cu–O(12) bonding, and as a result the potential minimum for thermal motion or positional displacement along *c* may be abnormally shallow in consequence.] However, it appears unlikely, given the possible symmetry of the metal environment, that the necessary orbital degeneracy exists for this to be a valid explanation of the origin of the effect.

In the present context, the structure of the 1 : 2 copper–dipicolinate complex is of unusual interest and relevance.[6] Unlike the purpurate ligand, the dipicolinate ligand together with the co-ordinated metal atom exhibit only trivial deviations from planarity throughout the system, and the pair of co-ordinated ligand planes lie almost orthogonal to each other. Here again there appears to be a tendency towards distortion within the molecule, but, because of the somewhat different nature of the ligand which retains a second readily ionizable hydrogen, an alternative and unusual resolution of the situation is found whereby these additional hydrogens from the two ligands are located on the one ligand so that the complex instead of being $[Cu(HP)_2]$ (H_2P = dipicolinic acid) becomes $[Cu(P)(H_2P)]$; both dipicolinate species are co-ordinated, but the Cu–O distances differ, that of the P^{2-} being 2.04 Å (mean) and for H_2P 2.36 Å, so that in effect a conventional tetragonal distortion is imposed within the system. A similar situation is found in $[Ag(P)(H_2P)]$,[7] but the nickel(II) analogue which

TABLE 3

Least-squares planes, calculated through the C(*n*1, *n*2, *n*4, *n*6),N(*n*3, *n*5) skeleton of each barbiturate segment of the ligand (*n* = 1) in the form $pX + qY + rZ = s$, where the right-handed orthogonal (Å) frame is defined with *X* parallel to *a*, *Z* in the *ac* plane. Atom deviations (Å) are in square parentheses, with values for (1) preceding those for (2) 'a' and (2) 'b'. The estimated standard deviations of the defining atoms are in Å. The angle between the normals to the two barbiturate planes of each ligand is θ°

Compound	(1)	(2) 'a'	(2) 'b'
10^4p	4 044	1 833	9 866
10^4q	−3 883	−2 433	1 629
10^4r	8 281	9 525	0 040
s	1.739	1.625	−0.264
σ	0.04	0.07	0.09
χ^2	70	220	360
θ	47.7	28.2	18.7

[C(11) 0.05 (0.09, 0.11), C(12) −0.05 (−0.03, −0.01), N(13) 0.01 (−0.02, −0.07), C(14) 0.03 (0.01, 0.05), N(15) −0.03 (0.05, 0.06), C(16) −0.01 (−0.10, −0.12), N(0) −0.09 (−0.01, 0.14), O(12) −0.11 (−0.18, −0.01), O(14) 0.03 (−0.12, 0.04), O(16) −0.19 (−0.42, −0.42), M −0.87 * (−0.51, −0.20)]

* Disordered model, metal deviations = −1.13, −0.62.

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[6] M. B. Cingi, A. C. Villa, C. Guastini, and M. Nardelli, *Gazzetta*, 1972, **102**, 1026; C. Sarchet and H. Loiseleur, *Acta Cryst.*, 1973, **B29**, 1345.

[7] M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1970, 1405.

requires no such distortion is simply $[Ni(HP)_2]$.[8] Clearly, the free energy of the system in the present purpurate derivative is lowered by the increased entropy; on the other hand, the relative decrease in entropy of the dipicolinate must be offset by the favourable enthalpy change of the more conventional 'tetragonal' distortion. (Such a distortion is not possible in the present complex because of the combined constraints of ligand symmetry *and* space group.)

The geometry of the zinc complex is inaccurate and not sufficiently unusual to warrant further discussion. In both complexes, lattice forces appear to be dominated by strong hydrogen-bonding interactions arising from the ligands and the lattice water molecules.

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[8] H. Gaw, W. R. Robinson, and R. A. Walton, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 695; A. C. Villa, C. Guastini, A. Musatti, and M. Nardelli, *Gazzetta*, 1972, **102**, 226; P. Quaglieri, H. Loiseleur, and G. Thomas, *Acta Cryst.*, 1972, **B28**, 2583.