

Structure and Stability of Carboxylate Complexes. XIX. The Structures of Diamminebis(glycolato)copper(II), Tetraamminebis(ethoxyacetato)copper(II), Bis(glycolato)bis(pyridine)copper(II) and Bis(ethoxyacetato)bis(pyridine)copper(II)

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Abstract

(a) Diamminebis(glycolato)copper(II), $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_3)_2(\text{NH}_3)_2]$, $M_r = 247.7$, monoclinic, $C2/c$, $a = 13.858$ (3), $b = 5.499$ (3), $c = 15.076$ (4) Å, $\beta = 132.2$ (2)°, $V = 851.1$ Å³, $Z = 4$, $D_x = 1.93$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.67$ mm⁻¹, $F(000) = 508$, $T = 298$ K, $R = 0.0277$ for 1513 observed reflexions with $I > 3\sigma(I)$. (b) Tetraamminebis(ethoxyacetato)copper(II), $[\text{Cu}(\text{C}_4\text{H}_7\text{O}_3)_2(\text{NH}_3)_4]$, $M_r = 337.9$, triclinic, $P\bar{1}$, $a = 5.055$ (3), $b = 7.012$ (2), $c = 11.768$ (2) Å, $\alpha = 80.32$ (1), $\beta = 79.92$ (2), $\gamma = 73.77$ (4)°, $V = 391.2$ Å³, $Z = 1$, $D_x = 1.43$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.42$ mm⁻¹, $F(000) = 179$, $T = 298$ K, $R = 0.053$ for 2061 observed reflexions with $I > 3\sigma(I)$. (c) Bis(glycolato)bis(pyridine)copper(II), $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$, $M_r = 371.8$, monoclinic, $C2/c$, $a = 22.383$ (6), $b = 5.755$ (3), $c = 17.629$ (4) Å, $\beta = 137.86$ (4)°, $V = 1524$ Å³, $Z = 4$, $D_x = 1.62$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.55$ mm⁻¹, $F(000) = 764$, $T = 298$ K, $R = 0.0412$ for 1149 observed reflexions with $I > 3\sigma(I)$. (d) Bis(ethoxyacetato)bis(pyridine)copper(II), $[\text{Cu}(\text{C}_4\text{H}_7\text{O}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$, $M_r = 427.9$, monoclinic, $C2/c$, $a = 9.579$ (5), $b = 14.22$ (1), $c = 13.904$ (3) Å, $\beta = 99.19$ (2)°, $V = 1870$ Å³, $Z = 4$, $D_x = 1.52$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.19$ mm⁻¹, $F(000) = 892$, $T = 298$ K, $R = 0.0494$ for 2642 observed reflexions with $I > 3\sigma(I)$. The copper(II) ion is in an elongated tetragonally distorted octahedral environment in all four compounds. The ethoxyacetate ligand is unidentate in the tetraammine compound, but the hydroxy- and alkoxycarboxylate ligands form *trans*-planar five-membered chelate rings in the other three compounds. Cooperative variations in the dimensions of the copper(II) coordination sphere may be ascribed to the different σ -donor powers of the ligand atoms.

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Introduction

Earlier structure determinations reported in this series have indicated that in copper complexes of the form $\text{Cu}(\text{Ch})_2L_2$, where the chelating ligand, Ch, is glycolate, 2-hydroxypropionate, methoxyacetate, ethoxyacetate, phenoxyacetate or substituted phenoxyacetates (Prout, Grove, Harridine & Rossotti, 1975, and references therein), the Cu—O bond lengths in the chelate rings appear to be influenced by the σ -donor properties of the unidentate ligands L , water or pyridine. Here we present four more examples of cooperative changes in bond lengths, in (a) diamminebis(glycolato)copper(II), (b) tetraamminebis(ethoxyacetato)copper(II), (c) bis(glycolato)bis(pyridine)copper(II) and (d) bis(ethoxyacetato)bis(pyridine)copper(II).

Experimental

The compounds were prepared by treating an aqueous solution of the appropriate copper carboxylate with an excess of aqueous ammonia or pyridine. Solutions were placed in a desiccator under an atmosphere of the appropriate base. On slow evaporation, pale blue needles crystallized from the mother liquor. Selected crystals were sealed in Lindemann tubes for X-ray photography and diffractometry. Preliminary cell dimensions were determined from oscillation and Weissenberg photographs. Crystals were then mounted on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. 25 reflexions with $\theta > 14^\circ$ were centred and used to calculate the orientation matrix and cell dimensions. Lorentz and polarization corrections were applied, but no absorption correction was made. After averaging equivalent reflexions, those independent reflexions with $I > 3\sigma(I)$ were used for structure solution and refinement. The structures were solved by Patterson heavy-atom methods. All non-H atoms were located from the

Table 1. Details of the observation of diffraction intensities and structure refinement

	(a)	(b)	(c)	(d)
Crystal size (mm)	0.4 × 0.4 × 0.3	0.6 × 0.4 × 0.15	0.6 × 0.3 × 0.2	0.6 × 0.4 × 0.2
Scan angle (°)	1.2 + 0.35tanθ	1.3 + 0.35tanθ	1.25 + 0.35tanθ	1.3 + 0.35tanθ
(sinθ/λ) _{max} (Å ⁻¹)	0.90	0.75	0.79	0.79
h _{min} , h _{max}	-24, 19	-7, 7	-31, 17	-15, 14
k _{min} , k _{max}	-1, 9	-10, 10	-1, 8	-1, 22
l _{min} , l _{max}	-1, 26	-1, 17	-1, 24	-1, 21
No. of reflexions measured	5962	3197	4081	4674
R _{int}	3.7	4.2	9.2	9.4
No. of reflexions observed [I > 3σ(I)]	1513	2061	1149	2642
R	0.0277	0.0530	0.0412	0.0494
wR	0.0333	0.0699	0.0452	0.0514
Σ(shift/e.s.d.) ²	0.01	0.01	0.01	0.01
ρ _{max} (e Å ⁻³)	0.13	0.60	0.13	0.13

Cu-phased Fourier syntheses. The structures were refined by the full-matrix least-squares method with isotropic temperature factors for H atoms and anisotropic temperature factors for all other atoms. H atoms were located in the difference electron density maps, but were placed geometrically. In the final cycles, an isotropic extinction parameter was included in the refinement and account was taken of the real and imaginary parts of the anomalous dispersion for Cu atoms. Each reflexion was assigned a weight according to a three-term Chebyshev weighting scheme (Carruthers & Watkin, 1979) and Σw|ΔF|² was minimized. The final difference map showed no electron density of chemical significance. Details of the observation of diffraction intensities and the structure refinement are given in Table 1. All calculations were performed using *CRYSTALS* (Watkin & Carruthers, 1983) on a VAX 11/750 computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic parameters are listed in Table 2. Bond lengths and angles are given in Table 3. The molecular structures of (a)–(d) are shown in Figs. 1–4.*

Results

Under the preparative conditions used, the chelate rings in the parent compounds were retained in the glycolates (a) and (c) and in the ethoxyacetate (d), with only two unidentate nitrogen bases coordinated to the Cu atom, but in a similar reaction of diaqua-bis(ethoxyacetato)copper(II), ammonia displaced both the aqua ligands and the ether O atoms of the ethoxyacetate ligands from the coordination sphere to form the tetraammine (b).

* Lists of observed and calculated structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55423 (71 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA096]

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$, where U_{11} , U_{22} and U_{33} are the mean-square displacements (Å²) along each of the principal axes of the thermal ellipsoid.

	x	y	z	U _{eq}
(a) Diamminebis(glycolato)copper(II)				
Cu	0.0000	0.5000	0.0000	0.0173
N(1)	0.0083 (1)	0.3319 (3)	-0.1113 (1)	0.0239
O(1)	-0.0935 (1)	0.2044 (2)	0.0076 (1)	0.0230
O(2)	-0.2766 (1)	-0.0053 (3)	-0.1015 (2)	0.0276
O(3)	-0.2257 (1)	0.5890 (2)	-0.1587 (1)	0.0259
C(1)	-0.2158 (1)	0.1836 (3)	-0.0857 (1)	0.0192
C(2)	-0.2990 (2)	0.3957 (3)	-0.1674 (2)	0.0235
(b) Tetraamminebis(ethoxyacetato)copper(II)				
Cu	0.000	0.000	0.000	0.0227
N(1)	-0.2388 (7)	-0.0977 (5)	0.1453 (3)	0.0290
N(2)	0.2999 (7)	-0.2570 (5)	0.0256 (4)	0.0255
O(1)	0.1742 (6)	0.1572 (4)	0.1392 (3)	0.0319
O(2)	-0.1329 (6)	0.4563 (4)	0.1480 (3)	0.0334
O(3)	0.1438 (7)	0.5552 (4)	0.2961 (3)	0.0344
C(1)	0.0750 (7)	0.3243 (5)	0.1782 (4)	0.0249
C(2)	0.2297 (10)	0.3568 (6)	0.2691 (4)	0.0312
C(3)	0.2923 (13)	0.5834 (8)	0.3810 (5)	0.0411
C(4)	0.1862 (18)	0.7969 (9)	0.4062 (7)	0.0532
(c) Bis(glycolato)bis(pyridine)copper(II)				
Cu	0.2500	0.2500	0.5000	0.0287
N(1)	0.1946 (3)	0.3074 (6)	0.3453 (3)	0.0306
O(1)	0.1727 (2)	-0.0277 (5)	0.4427 (3)	0.0308
O(2)	0.0602 (3)	-0.1856 (6)	0.3996 (4)	0.0404
O(3)	0.1262 (2)	0.4012 (6)	0.4422 (4)	0.0377
C(1)	0.1040 (3)	-0.0168 (8)	0.4187 (4)	0.0272
C(2)	0.0692 (3)	0.2226 (10)	0.4098 (5)	0.0363
C(8)	0.1983 (4)	0.1484 (10)	0.2939 (5)	0.0401
C(9)	0.1616 (4)	0.1804 (11)	0.1886 (5)	0.0464
C(10)	0.1168 (4)	0.3845 (11)	0.1316 (5)	0.0438
C(11)	0.1121 (4)	0.5503 (10)	0.1838 (5)	0.0427
C(12)	0.1520 (4)	0.5085 (9)	0.2894 (5)	0.0360
(d) Bis(ethoxyacetato)bis(pyridine)copper(II)				
Cu	0.0000	0.1418 (1)	0.2500	0.0245
N(1)	0.0000	-0.0042 (2)	0.2500	0.0250
N(2)	0.0000	0.2872 (2)	0.2500	0.0287
O(1)	0.2001 (2)	0.1446 (2)	0.3015 (1)	0.0319
O(2)	0.3808 (3)	0.1392 (2)	0.4219 (2)	0.0476
O(3)	0.0117 (2)	0.1280 (2)	0.4237 (1)	0.0337
C(1)	0.2541 (3)	0.1375 (2)	0.3913 (2)	0.0312
C(2)	0.1553 (4)	0.1297 (2)	0.4662 (2)	0.0349
C(3)	-0.0832 (4)	0.1353 (3)	0.4932 (2)	0.0391
C(4)	-0.2310 (4)	0.1344 (4)	0.4418 (3)	0.0498
C(11)	-0.1178 (3)	-0.0523 (2)	0.2556 (2)	0.0312
C(22)	-0.1212 (4)	-0.1510 (2)	0.2566 (3)	0.0368
C(33)	0.0000	-0.2000 (2)	0.2500	0.0378
C(111)	-0.0102 (4)	0.3364 (2)	0.1665 (2)	0.0343
C(222)	-0.0094 (4)	0.4339 (2)	0.1638 (3)	0.0399
C(333)	0.0000	0.4830 (3)	0.2500	0.0403

Both glycolates have the Cu atom at an inversion centre, coordinated by two chelating glycolato groups forming planar five-membered *trans* rings and also by two *trans* ammonia ligands [in (a)] or two *trans* pyridine ligands [in (c)] (Figs. 1 and 3). The maximum and mean deviations of the atoms of the chelate rings from the least-squares best plane are 0.043 and 0.027 Å, respectively, in (a) and 0.074 and 0.044 Å, respectively, in (c). In each case the Cu atom has an elongated octahedral coordination, the long bonds going to the hydroxy O atoms of the chelating glycolate with the Cu—O(3) bond lengths being 2.388 (1) Å in (a) and 2.299 (3) Å in (c). Cu—O(carboxylate) contacts, Cu—O(1), are also longer in (a) [2.034 (1) Å], than in (c) [1.944 (3) Å] but the Cu—N(1) bonds are shorter in the diammine (a) [1.986 (1) Å] than in the pyridine complex (c)

Table 3. Bond lengths (Å) and interbond angles (°) with *e.s.d.*'s in parentheses(a) Diamminebis(glycolato)copper(II) (molecular symmetry $\bar{1}$)

Cu—N(1)	1.986 (1)	O(2)—C(1)	1.256 (2)
Cu—O(1)	2.034 (1)	C(1)—C(2)	1.517 (2)
Cu—O(3)	2.388 (1)	C(2)—O(3)	1.415 (2)
O(1)—C(1)	1.262 (2)		
O(1)—Cu—O(3)	75.58 (5)	O(1)—C(1)—C(2)	120.1 (1)
O(1)—Cu—N(1)	88.65 (6)	O(2)—C(1)—C(2)	115.7 (1)
O(3)—Cu—N(1)	91.64 (6)	C(1)—C(2)—O(3)	113.3 (1)
Cu—O(1)—C(1)	122.1 (1)	C(2)—O(3)—Cu	108.4 (1)
O(1)—C(1)—O(2)	124.2 (2)		

Dimensions involving hydrogen bonding

N(1)···O(2')	3.018 (2)
O(3)···O(2'')	2.654 (2)

Ligand bite

O(1)···O(3)	2.724 (2)
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(b) Tetramminebis(ethoxyacetato)copper(II) (molecular symmetry $\bar{1}$)

Cu—N(1)	2.048 (4)	C(1)—C(2)	1.511 (6)
Cu—N(2)	2.021 (3)	C(2)—O(3)	1.410 (5)
Cu—O(1)	2.515 (3)	O(3)—C(3)	1.418 (6)
O(1)—C(1)	1.268 (4)	C(3)—C(4)	1.504 (8)
O(2)—C(1)	1.250 (4)		
N(1)—Cu—N(2)	89.0 (2)	O(1)—C(1)—C(2)	114.3 (3)
O(1)—Cu—N(1)	84.6 (1)	O(2)—C(1)—C(2)	120.1 (4)
O(1)—Cu—N(2)	91.1 (1)	C(1)—C(2)—O(3)	112.6 (3)
Cu—O(1)—C(1)	130.5 (3)	C(2)—O(3)—C(3)	111.9 (3)
O(1)—C(1)—O(2)	125.6 (4)	O(3)—C(3)—C(4)	108.6 (5)

Dimensions involving hydrogen bonding

N(2)···O(2'')	3.010 (6)
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(c) Bis(glycolato)bis(pyridine)copper(II) (molecular symmetry $\bar{1}$)

Cu—N(1)	2.017 (4)	N(1)—C(8)	1.332 (6)
Cu—O(1)	1.994 (3)	C(8)—C(9)	1.375 (8)
Cu—O(3)	2.299 (3)	C(9)—C(10)	1.379 (8)
O(1)—C(1)	1.256 (5)	C(10)—C(11)	1.382 (9)
O(2)—C(1)	1.237 (5)	C(11)—C(12)	1.363 (8)
C(1)—C(2)	1.533 (7)	C(12)—N(1)	1.352 (6)
C(2)—O(3)	1.390 (6)		
O(1)—Cu—O(3)	76.8 (1)	C(2)—O(3)—Cu	109.9 (3)
O(1)—Cu—N(1)	90.8 (1)	Cu—N(1)—C(8)	121.4 (4)
O(3)—Cu—N(1)	90.5 (2)	Cu—N(1)—C(12)	121.3 (3)
Cu—O(1)—C(1)	121.1 (3)	N(1)—C(8)—C(9)	123.3 (5)
O(1)—C(1)—O(2)	125.3 (4)	C(8)—C(9)—C(10)	118.8 (6)
O(1)—C(1)—C(2)	118.8 (4)	C(9)—C(10)—C(11)	118.4 (5)
O(2)—C(1)—C(2)	115.9 (4)	C(10)—C(11)—C(12)	119.5 (5)
C(1)—C(2)—O(3)	112.3 (4)	C(12)—N(1)—C(8)	117.3 (5)

Dimensions involving hydrogen bonding

O(2)···O(3'')	2.599 (4)
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Ligand bite

O(1)···O(3)	2.676 (4)
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(d) Bis(ethoxyacetato)bis(pyridine)copper(II) (molecular symmetry 2)

Cu—N(1)	2.076 (3)	O(3)—C(3)	1.432 (4)
Cu—N(2)	2.068 (3)	C(3)—C(4)	1.481 (3)
Cu—O(1)	1.936 (2)	N(1)—C(11)	1.333 (3)
Cu—O(3)	2.408 (2)	C(11)—C(22)	1.405 (6)
O(1)—C(1)	1.278 (3)	C(22)—C(33)	1.369 (4)
O(2)—C(1)	1.220 (4)	N(2)—C(111)	1.346 (4)
C(1)—C(2)	1.519 (5)	C(111)—C(222)	1.388 (4)
C(2)—O(3)	1.408 (4)	C(222)—C(333)	1.377 (5)
O(1)—Cu—O(3)	75.31 (8)	Cu—O(3)—C(3)	137.6 (2)
O(1)—Cu—N(1)	91.16 (7)	O(3)—C(3)—C(4)	109.6 (3)
O(3)—Cu—N(1)	85.33 (6)	Cu—N(1)—C(11)	120.9 (3)
O(1)—Cu—N(2)	88.84 (7)	Cu—N(2)—C(111)	121.3 (2)
O(3)—Cu—N(2)	94.67 (6)	N(1)—C(11)—C(22)	122.4 (3)
Cu—O(1)—C(1)	125.6 (2)	C(11)—C(22)—C(33)	119.1 (3)
O(1)—C(1)—O(2)	124.3 (3)	C(22)—C(33)—C(22')	118.9 (4)
O(1)—C(1)—C(2)	118.5 (3)	C(11')—N(1)—C(11)	117.4 (3)
O(2)—C(1)—C(2)	117.2 (3)	C(11')—N(2)—C(111)	118.2 (4)
C(1)—C(2)—O(3)	112.8 (3)	N(2)—C(111)—C(222)	122.9 (3)
C(2)—O(3)—Cu	107.8 (2)	C(111)—C(222)—C(333)	118.9 (4)
C(2)—O(3)—C(3)	113.5 (3)	C(222)—C(333)—C(222')	119.1 (5)

Ligand bite

O(1)···O(3)	2.680 (3)
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Symmetry codes: (i) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x, 1 + y, z$; (iii) $-x, -y, -z$; (iv) $x, y - 1, z$; (v) $-x, y, \frac{1}{2} - z$.

[2.017 (4) Å]. In (c), the planes of the pyridine rings roughly bisect the angle $O(1)—Cu—O(3') = 103.2 (1)^\circ$ between the two chelate rings, with torsion angles $C(12)—N(1)—Cu—O(3) = 43.6 (4)$ and $C(8)—N(1)—Cu—O(1) = -59.5 (4)^\circ$. In the chelate rings of (a) and (c), a decrease in the angle $O(1)—Cu—O(3)$ accompanies the increase in the Cu—O bond lengths in spite of a small increase in the ligand bite, $O(1) \cdots O(3)$. In the crystals, the glycolate complexes (a) and (c) are linked into a hydrogen-bonded network with $O(3)—H \cdots O(2')$ 2.654 (2) and 2.599 (4) Å, respectively. Compound (a) also contains $N(1)—H \cdots O(2')$ intermolecular hydrogen bonds (Table 3).

Bis(ethoxyacetato)bis(pyridine)copper(II), (d), has a similar structure to (a) and (c) but with different crystallographic symmetry (Fig. 4). The Cu atom lies on a crystallographic twofold symmetry axis and is coordinated by two chelating ethoxyacetato groups

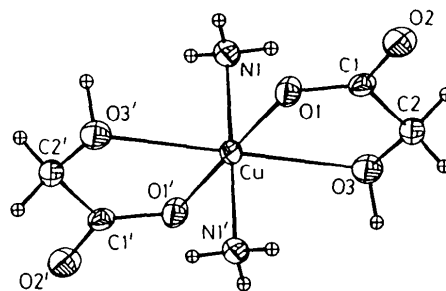


Fig. 1. Diamminebis(glycolato)copper(II): a view of the molecule showing the atom numbering. The primed atoms are related to the unprimed atoms by the symmetry operator $(-x, 1-y, -z)$.

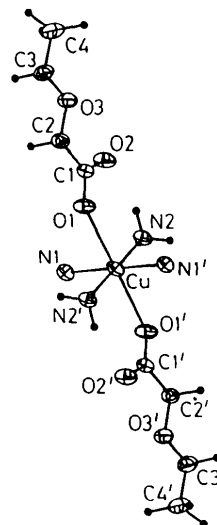


Fig. 2. Tetramminebis(ethoxyacetato)copper(II): a view of the molecule showing the atom numbering. The primed atoms are related to the unprimed atoms by an inversion centre at the Cu atom.

related by the twofold symmetry axis and by two crystallographically independent *trans* pyridine ligands, in which the twofold axis of the pyridine utilizes the crystallographic twofold axis. The planes of the two crystallographically independent pyridine molecules in the complex are approximately perpendicular, with the torsion angle C(11)—N(2)—N(1)—C(11) being 81.8(3)°. The torsion angle O(3)—Cu—N(2)—C(11) is -177.8(5)° so that the plane of the pyridine ring containing N(2) also contains the O(3)—Cu—O(3') vector. The immediate Cu-atom coordination is centrosymmetric, although

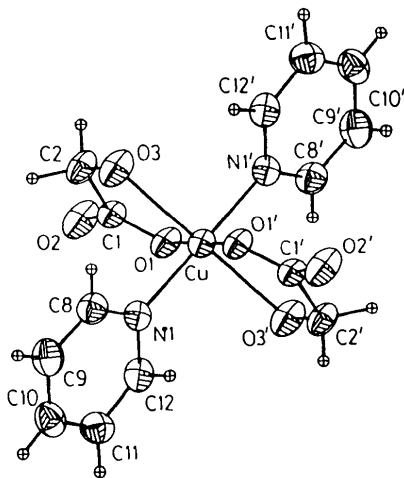


Fig. 3. Bis(glycolato)bis(pyridine)copper(II): a view of the molecule showing the atom numbering. The primed atoms are related to the unprimed atoms by the symmetry operator $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$.

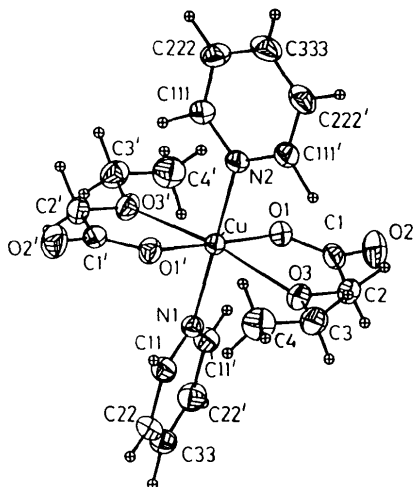


Fig. 4. Bis(ethoxyacetato)bis(pyridine)copper(II): a view of the molecule showing the atom numbering. The atoms C(33), N(1), Cu, N(2) and C(333) lie on a crystallographic twofold axis and the primed atoms are related to the unprimed atoms by the symmetry operator $(-x, y, \frac{1}{2} - z)$.

Table 4. Cu—N bond lengths and long contacts to the Cu atom (Å) in some tetraammine and tetrakis(pyridine) elongated CuN_4X_2 octahedra

	Cu—N(mean)	Long contacts*	Reference
$[\text{Cu}_2(\text{NH}_3)_4]$	2.013	3.224 (l)	(a)
$[\text{Cu}_2(\text{NH}_3)_4]\text{I}_3$	2.04	3.294 (l)	(b)
$[\text{Cu}(\text{MnO}_4)_2(\text{NH}_3)_4]$	2.015	2.456, 2.512	(c)
$[\text{Cu}(\text{SO}_4)(\text{H}_2\text{O})(\text{NH}_3)_4]$	2.032	2.339, 3.475	(d)
$[\text{CuSeO}_4(\text{NH}_3)_4]$	2.005	2.451, 2.607	(d)
$[\text{Cu}(\text{Cu}_2)_2(\text{NH}_3)_4]$	2.14	3.171 (l)	(e)
$[\text{Cu}(\text{C}_2\text{H}_5\text{OCH}_2\text{CO}_2)_2(\text{NH}_3)_4]$	2.035	2.515	(f)
$[\text{Cu}(\text{CF}_3\text{COO})_2(\text{py})_4]$	2.048	2.367	(g)
	2.044	2.356	(h)
$[\text{Cu}(\text{H}_2\text{O})_2(3\text{-Mepy})_2](\text{ClO}_4)_2$	2.03	2.47, 2.52	(i)

References: (a) Dubler & Linowsky (1975); (b) Trebbe (1982); (c) Seferiadis, Dubler & Oswald (1986); (d) Morosin (1969); (e) Baglio, Weakliem, Demelio & Vaughan (1970); (f) this work; (g) Pradilla, Chen, Koknat & Fackler (1979); (h) Pretorius & Boeyens (1978); (i) Hu, Barton, Johnson & Robertson (1981). Earlier values are cited in Hathaway & Tomlinson (1970).

* Cu—O contact unless specified.

the complete molecule is not (Fig. 4). Again, the Cu atom has an elongated octahedral coordination with long bonds, Cu—O(3) [2.408 (2) Å], within the chelate rings. The Cu—O(carboxylate) bond, Cu—O(1), is shorter [1.936 (2) Å] than in the glycolates (a) and (c) and the two crystallographically independent Cu—N bonds, Cu—N(1) [2.076 (3) Å] and Cu—N(2) [2.068 (3) Å], are substantially longer than in (c). The chelate ring is planar, with maximum and mean deviations from the least-squares best plane of 0.011 and 0.006 Å, respectively. The C(3) and C(4) atoms of the ethyl group are 0.221 and 0.215 Å, respectively, above the chelate plane. The terminal C(4) atom of the ethyl group is curled back towards the Cu atom and is thus only 3.445 (5) Å from the O(1') atom of the second chelate ring, as in the diaqua analogue (Prout, Carruthers & Rossotti, 1971). There are only van der Waals interactions between the molecules.

In the tetraammine (b), the Cu atom is at a crystallographic symmetry centre with four ammonia ligands in a square plane and two *trans* unidentate carboxylate groups completing the long contacts of a distorted coordination octahedron, with bonds Cu—N(1) of 2.048 (4), Cu—N(2) of 2.021 (3) and Cu—O(1) of 2.515 (3) Å (Fig. 2). The Cu atom and the non-H atoms of the ethoxyacetate ligand are all coplanar with maximum and mean deviations from the least-squares best plane of 0.104 and 0.057 Å, respectively. There is an intramolecular hydrogen bond N(2)—H...O(2') [3.010 (6) Å].

Discussion

The structure of the tetraammine (b) resembles that of tetrakis(imidazole)bis(methoxyacetato)copper(II) (Prout, Allison & Rossotti, 1971). The Cu—OOC contact is unusually long [2.515 (3) Å], though not as long as in the latter compound (2.825 Å) where there is some evidence of protonation of the carboxylate

Table 5. Some bond lengths (Å) and angles (°) in hydroxy- and alkoxy-carboxylato-copper(II) chelates

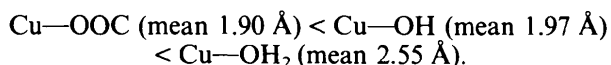
Complex	Cu—OOC	Cu—OR	Cu—OH ₂	Cu—N	O(1)···O(3)	O(1)—Cu—O(3)	Reference
CuG ₂	1.91	1.93	(2.54)*	—	2.56	83.4	(a)
[CuG ₂ (py) ₂]	1.994	2.299	—	2.017	2.676	76.8	(b)
[CuG ₂ (NH ₃) ₂]	2.034	2.388	—	1.986	2.724	75.58	(b)
[Cu(HMP) ₂ (H ₂ O) ₂]	1.89	2.01	2.56	—	2.58	82.7	(a)
[Cu(DHMP) ₂ (H ₂ O) ₂]	1.890	1.974	2.542	—	2.574	83.5	(c)
[CuM ₂ (H ₂ O) ₂]	1.93	2.13	2.16	—	2.61	79.9	(a)
[CuM ₂ (py) ₂].4H ₂ O	1.94	2.36	—	2.01	2.65	75.5	(d)
[CuE ₂ (H ₂ O) ₂]	1.97	2.38	1.99	—	2.68	75.2	(e)
[CuE ₂ (py) ₂]	1.936	2.408	—	2.072 (mean)	2.680	75.31	(b)
[CuP ₂ (H ₂ O) ₂]	1.94	2.47	1.98	—	2.70	74.4	(a)
	1.95	2.50	1.99	—	2.72	74.3	(a)
[Cu(4-MP) ₂ (H ₂ O) ₂]	1.955	2.432	1.945	—	2.691	74.8	(f)
[Cu(4-CIP) ₂ (H ₂ O) ₂]	1.956	2.406	1.960	—	2.667	74.6	(g)
[Cu(4-FP) ₂ (H ₂ O) ₂]	1.942	2.471	1.940	—	2.659	73.0	(h)

* Cu atom to carboxylate contact in a neighbouring ring.

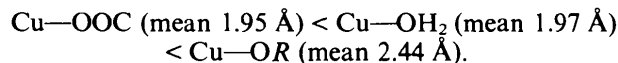
Abbreviations: G = glycolate; HMP = 2-hydroxy-2-methylpropionate; DHMP = 2,3-dihydroxy-2-methylpropionate; M = methoxyacetate; E = ethoxyacetate; P = phenoxyacetate; 4-MP = 4-methoxyphenoxyacetate; 4-CIP = 4-chlorophenoxyacetate; 4-FP = 4-fluorophenoxyacetate.

References: (a) Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti (1968); (b) this work; (c) Miller, Powell, Jacobson & Kulprathipanja (1976); (d) Prout, Barrow & Rossotti (1971); (e) Prout, Carruthers & Rossotti (1971); (f) Prout, Grove, Harridine & Rossotti (1975); (g) Smith, O'Reilly, Kennard, Studnicka & Oleksyn (1981); (h) O'Reilly, Smith & Kennard (1984).

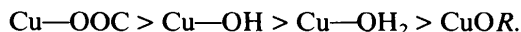
group. A marked tetragonal distortion appears to be a common feature in CuN₄X₂ octahedra (Table 4). All the remaining hydroxy- and alkoxy-carboxylates (Table 5) have planar *trans* five-membered chelate rings with copper(II) in approximately tetragonally distorted elongated octahedral coordination [except for the diaquabis(methoxyacetato) complex, which has a tetragonally compressed coordination at room temperature]. In the anhydrous glycolate, the long axis is perpendicular to the chelate plane with axial positions occupied by carboxylate O atoms of neighbouring molecules (Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti, 1968). In the diaquabis(hydroxycarboxylates) (Prout *et al.*, 1968; Miller, Powell, Jacobson & Kulprathipanja, 1976), it is the water molecules that occupy the axial positions, but at approximately the same Cu—O distances (Table 5). The bond lengths and hence the inverse bond strengths (Brown & Altermatt, 1985) are in the order:



By contrast, the diaquabis(alkoxy-carboxylates) (except the methoxyacetate) are elongated in the plane of the chelate rings along the Cu—OR axis with bond lengths:



Hence, the overall order of bond strengths in the quasi-homogeneous coordination spheres (Gažo, Bersuker, Garaj, Kabešová, Kohout, Langfelderová, Melnik, Serátor & Valach, 1976) appears to be:



An analysis of the energies of electronic transitions and of *g* values for some of the compounds had suggested that Cu—OH and Cu—OH₂ were in the

reverse order (Dawson, Hitchman, Prout & Rossotti, 1972).

In the ammine- and pyridine-substituted glycolates (a) and (c) the long Cu—O bonds in the unsubstituted glycolate have been replaced by shorter Cu—N bonds comparable in length to the Cu—OOC bonds. Hence, the tetragonal axis is no longer perpendicular to the chelate ring plane, but is in that plane along the Cu—OH bonds. The dimensions of the chelate rings and the distances of the axial substituents from the Cu atom resemble closely those in the diaquabis(ethoxyacetate) (Table 5). By comparison with the hydroxycarboxylate CuO₆ systems there is a lengthening of the Cu—OOC bond by about 0.1 Å and a more pronounced lengthening by about 0.3–0.4 Å of the Cu—OH bond in the chelate rings. Thus the long Cu—O bond is in the chelate ring of the CuN₂O₄ compounds as with the alkoxy-carboxylates. The changes in the bond lengths suggest that the nitrogen ligands weaken and lengthen the Cu—O bonds in the chelating glycolato group in the increasing order of the σ -donor properties of pyridine and ammonia. Indeed, the Cu—OOC bond in the glycolate (a), at 2.034 (1) Å, is the longest that we have found in related compounds (Table 5). The length of the Cu—OH bond appears also to depend on the hydrogen-bonding environment of the hydroxyl group with the shorter Cu—O bond accompanying the shorter hydrogen bond. Hydroxyl groups that form stronger hydrogen bonds as hydrogen donors are also themselves stronger σ -electron donors. Analogous cooperative effects have been noted previously in crystals containing hexaaquacopper(II) (Couldwell, Prout, Robey, Taylor & Rossotti, 1978). Replacement of the aqua ligands in the diaquabis(ethoxyacetate) by two pyridines in (d) causes little change in the dimensions of the chelate rings, as the Cu—OEt bonds already form the elongated axis. The structure of (d) resembles that of the

Table 6. Cu—N bond lengths (Å) in some diammines in elongated CuN₂O₄ octahedra

Complex	Cu—N	Reference
[Cu(N ₃) ₂ (NH ₃) ₂]	1.985	(a)
[CuBr(CH ₃ CO ₂)(NH ₃) ₂]	1.984	(b)
[Cu(C ₂ O ₄)(H ₂ O) ₂ (NH ₃) ₂]	1.960	(c)
[Cu(C ₂ H ₂ N ₂ O ₄)(NH ₃) ₂]*	1.960, 1.996	(d)
[Cu(HOCH ₂ CO ₂) ₂ (NH ₃) ₂]	1.986	(e)

References: (a) Agrell (1966); (b) Belicchi Ferrari, Calzolari Capacchi, Gasparri Fava & Nardelli (1972); (c) Garaj, Langfelderová, Lundgren & Gažo (1972); (d) Mutikainen & Lumme (1980); (e) this work. Earlier values are cited in Hathaway & Tomlinson (1970).

* C₂H₂N₂O₄ = orotonato.

Table 7. Cu—N bond lengths (Å) in some bis(pyridine) complexes in elongated CuN₂O₄ octahedra

Complex	Cu—N	Reference
[CuCl ₂ (py) ₂]	2.004	(a)
[CuBr ₂ (py) ₂]	2.013	(a)
[Cu(HCO ₂) ₂ (H ₂ O) ₂ (py) ₂]*	2.017	(b)
[Cu(HOCH ₂ CO ₂) ₂ (py) ₂]	2.017	(c)
[Cu(CH ₃ OCH ₂ CO ₂) ₂ (py) ₂]·4H ₂ O	2.01	(d)
[Cu(C ₂ H ₃ OCH ₂ CO ₂) ₂ (py) ₂]	2.068, 2.076	(c)
[Cu(N-ionicO) ₂ (H ₂ O) ₂ (py) ₂]	2.006	(e)
[Cu(acs) ₂ (py) ₂]	2.003	(f)

Abbreviations: N-ionicO = isonicotinato *N*-oxide; acs = acetylalicylato.

References: (a) Morosin (1975); (b) Bernard, Borel, Busnot & Leclaire (1979); (c) this work; (d) Prout, Barrow & Rossotti (1971); (e) Knuuttila & Knuuttila (1983); (f) Greenaway, Pezeshk, Cordes, Noble & Sorenson (1984).

* See Busnot, Busnot, Leclaire & Bernard (1983) and references therein for some methylpyridines.

bis(methoxyacetato)bis(pyridine) compound (Table 5), although the Cu—N bond is significantly longer.

The Cu—N bond length in the diammine (a) is close to those reported for other copper(II) diammines (Table 6, mean 1.977 Å) and is significantly shorter than those found in the bis(pyridine) complexes (c), (d) and others (Table 7, mean 2.024 Å). This cannot be a steric effect and may be attributed to the greater σ -donor power of the ammonia ligand relative to pyridine. The Cu—N bond lengths in (a) and other copper(II) diammines are also significantly shorter than those in (b) and other tetraammines (Tables 4 and 6, mean 2.040 Å). The latter bonds, in turn, are shorter than the equatorial mean Cu—N bond lengths in hexaamminecopper(II) chloride and bromide (2.11 Å) (Distler & Vaughan, 1967). Similarly, the Cu—N bond length in the bis(pyridine) (c) is in good agreement with other values (Table 7) and is shorter than in tetrakis(pyridine) complexes (Table 4, mean 2.038 Å). Thus, the more Cu—N bonds there are in the Cu-atom coordination sphere, the longer and weaker are the individual Cu—N bonds. These effects may be attributed to a decrease in the net electron-acceptor capacity of the Cu atom with an increase in the number of coordinated donor N atoms.

The hydroxy- and alkoxycarboxylates provide a good example of the plasticity of the coordination

sphere of copper(II) and the mutual influence of ligands (Gažo, Boča, Jóna, Kabešová, Macáškova & Šima, 1982). The bidentate carboxylate ligands all have a bite of approximately 2.66 Å and are anchored to the cation by the carboxylate group at approximately 1.95 Å. In the anhydrous glycolates (Table 5), the Cu—O bond lengths in the chelate rings are equal, but usually the ring is skewed with Cu—OH or Cu—OR up to 2.5 Å. The lengths of the bonds from the Cu atom to the unidentate ligands also vary from 1.94 to 2.54 Å. Notwithstanding this, the sum of the lengths of the six bonds to the Cu atom remains close to 12.75 Å for all the CuO₆ and CuN₂O₄ chelates in Table 5. It follows that the axial and equatorial bond lengths, r_{ax} and r_{eq} , are related linearly by

$$r_{ax} = 6.37 - 2r_{eq}.$$

The distortions around the Cu atom are therefore closely circumscribed, are cooperative and may be related to the σ -donor powers of the substituted O and N atoms in the ligands and to the acceptor capacity of the copper(II). Bersuker (1984) has suggested that a linear relationship of the above type follows from the vibronic nature of the distortion of the octahedron.

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High-Resolution Neutron Study of Vitamin B₁₂ Coenzyme at 15 K: Structure Analysis and Comparison with the Structure at 279 K

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Abstract

$C_{72}H_{100}N_{18}O_{17}PCo.nH_2O$, where $n = 17–18$, $M_r = 1597$ dalton (assuming that 19 coenzyme H atoms have been exchanged for D atoms), $P2_12_1$, $a = 27.550$ (7), $b = 21.568$ (5), $c = 15.343$ (3) Å, $V = 9117$ (4) Å³, $Z = 4$, $D_x = 1.38$ (1) Mg m⁻³; Cu(220) monochromator, $\lambda_1 = 1.5446$ (5) Å, 5505 unique reflections to nominal resolution 0.98 Å, $\mu = 2.20$ cm⁻¹; Ge(115) monochromator, $\lambda_2 = 1.3169$ (3) Å, 2361 unique reflections from nominal resolution 1.02 to 0.9 Å, $\mu = 1.6$ cm⁻¹; $T = 15$ K, final $R = 0.085$ for 7378 reflections. A high-resolution and low-temperature structural study of

the vitamin B₁₂ coenzyme has been undertaken using neutrons. Details of the data collection and refinement of the low-temperature structure are described, and a comparison of the coenzyme molecule and solvent structures at 15 and 279 K made. A shrinkage of around 2% is observed in the volume of the unit cell, and the orientation of the coenzyme molecule is rotated within the unit cell by approximately 2°, about an axis almost parallel to c and close to the Co atom. Incomplete or reverse exchange between D and H atoms led to some difficulties assigning certain exchangeable H positions in the coenzyme. 56 solvent atoms have been identified from neutron difference Fourier maps.