The Crystal and Molecular Structure of 4,4′-(1,2-Ethanediyldinitrilo)-bis[(2,3-pentanedione)-3,3′-dioximato] (2−)N^4,$N^{4'}$,O^3,$O^{3'}$ Copper(II)

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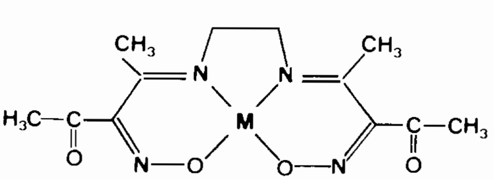
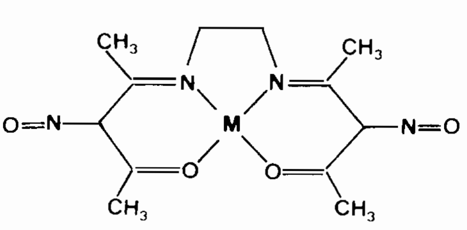
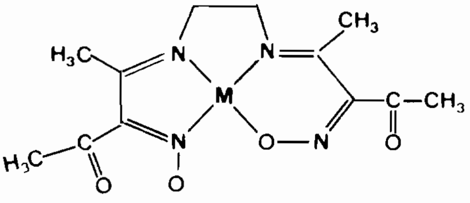
Complexes of the ligand 4,4′-(1,2-ethanediyldinitrito)-bis(2,3-pentanedione)-3,3′-dioxime, L, (also called *N,N′*-ethylenebis(isonitrosoacetylacetoneimine) or bis(4-iminopentane-2,3-dione-3-oxime)) have been of interest for some time because of the possibility of inter- and intra-molecular chelate linkage isomerism [1–6] and because the copper(III) complex of this ligand is relatively stable [7–9]. Metal complexes of L can in theory exist as a number of different isomeric forms some of which are shown in structures **I**–**IV**. A number of different forms of the copper(II) [3, 4], nickel(II) [3] and palladium(II) [3] complexes have been isolated. The infrared spectra of the isolated materials have been interpreted as indicating that the isonitroso group is coordinated to the metal ion [2] so that complexes of structure **II** have apparently not been isolated. There is conflict, however, over the assignment of structures **I**, **III** and **IV** to the isolated complexes. Both structures **I** [3] and **IV** [1, 2] have been suggested for the copper(II) complexes. One of the isolated forms of the nickel(II) complex has been shown by NMR [6] and an X-ray structural investigation [10] to have structure **III**. In recent papers concerning the copper(III) complex of this ligand both the copper(II) and copper(III) complexes have been formulated as structure **IV**. We present here an X-ray structural study which shows that in the solid the Cu(II) complex has structure **I**.



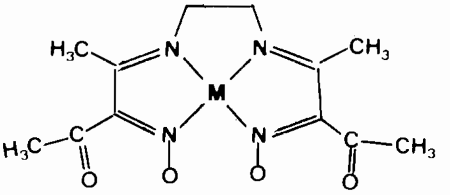
I



II



III



IV

Crystals of the title complex were obtained by reaction of bis[4,4′-(1,2-ethanediyldinitrilo)bis-2-pentanato]copper(II) [10] with ammonium acetate and sodium nitrite in a water ethanol mixture [2]. After standing for 10 days, dark brown crystals of the title complex appeared which were recrystallised from dichloromethane. The infrared spectrum of this material indicates that it is identical to the material isolated by Bose [2] and the complex described as brown–green by Ablov [4].

Crystal Data

$CuC_{12}H_{16}O_4N_4$, $M = 343.8$, crystal size 0.29 × 0.15 × 0.05 mm, monoclinic, $a = 26.5276(49)$, $b = 7.2839(10)$, $c = 7.1088(14)$ Å, $\alpha = 90°$, $\beta = 92.719(16)°$, $\gamma = 90°$, $V = 1372.1$ Å^3 (by least-squares refinement of the positions of 24 diffractometer measured reflections), $D_m = 1.67$ Mg m^{-3} (by flotation), $Z = 4$, $D_{calc} = 1.66$ Mg m^{-3}, space group $C2/c$ (from systematic absences, confirmed by solution), $F(000) = 708$. Mo Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator), $\mu = 16.8$ cm^{-1} (the crystal size precluded the need for absorption corrections). A Nicolet R3m diffractometer was used to collect 1329 reflections using the collection range $2° < 2\theta < 50°$, 1039 reflections $F > 5\sigma(F)$ were used for the refinement, $R = 0.042$, non-hydrogen atoms anisotropic, hydrogen atoms isotropic. Solved using MULTAN 77 [12] and refined using SHELX 76 [13].

A perspective view of the complex with the atom numbering scheme is shown in Fig. 1. The copper lies on a two-fold rotation axis which passes through the

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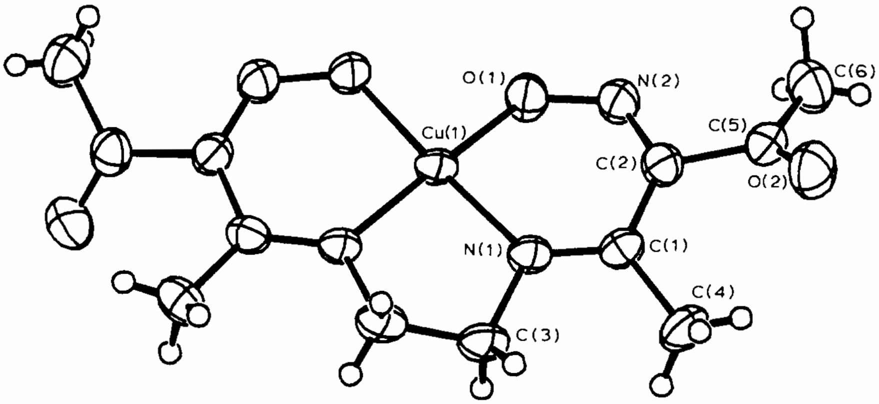

Fig. 1. A perspective view of the complex CuL showing the atomic numbering system used.

TABLE I. Bond Lengths (Å) and Angles (°)[a]

Bond lengths			
Cu-O(1)	1.892(3)	Cu-N(1)	1.922(3)
N(1)-C(1)	1.301(5)	N(1)-C(3)	1.485(5)
C(1)-C(2)	1.476(5)	C(1)-C(4)	1.494(6)
C(2)-N(2)	1.307(5)	C(2)-C(5)	1.511(5)
C(5)-C(6)	1.501(7)	C(5)-O(2)	1.209(5)
O(1)-N(2)	1.319(4)	C(3)-C(3)*	1.512(7)
Bond angles			angles
N(1)-Cu-N(1)*	87.9(1)	C(2)-C(1)-N(1)	119.1(3)
O(1)-Cu-N(1)*	173.4(1)	C(1)-C(2)-N(2)	128.5(4)
N(1)-Cu-O(1)	92.9(1)	C(5)-C(2)-N(2)	111.6(3)
C(1)-N(1)-Cu	127.4(3)	C(1)-C(2)-C(5)	119.9(3)
C(3)-N(1)-Cu	111.2(3)	C(3)*-C(3)-N(1)	110.4(5)
C(1)-N(1)-C(3)	121.1(3)	C(6)-C(5)-C(2)	118.6(4)
N(1)-C(1)-C(4)	119.4(4)	C(2)-N(2)-O(1)	122.7(3)
C(2)-C(1)-C(4)	121.3(4)	N(2)-O(1)-Cu	126.9(2)
C(2)-C(5)-O(2)	120.3(4)	O(2)-C(5)-C(6)	120.9(4)
O(1)-Cu-O(1)*	87.2(1)	N(1)-Cu-N(1)*	87.9(1)
N(2)-C(3)-C(5)	111.5(3)		

[a]Atoms designated with * are generated by the C_2 rotation axis through Cu *i.e.* by $-x, y, 0.5 - z$.

C(3)–C(3)* bond. Bond distances and angles are given in Table I. The copper is bonded to the ligand via the oxygens of the oxime groups and the two nitrogens of the ethylenediamine moiety. The complex is approximately planar; the two six-membered chelate rings are twisted slightly relative to one another so that the donor atoms are 0.11 Å above and below their mean plane which contains the copper atom. The ligand atoms in the six-membered chelate rings are almost planar (the largest dihedral angle is 13°) and the copper lies 0.24 Å out of the mean plane of this ring. Bond lengths and angles around the copper and within the ligand are very similar to those reported for the comparable part of the molecule *N*-(1-methyl-3-oxo-butyliden)-*N'*-(1-methyl-2-isonitroso-3-oxo-butyliden)ethylenediamine copper(II) [14]. The approximately planar coordination of the d^9 Cu(II) complex and the lack of interactions with other groups in the axial coordination sites probably accounts for the ease of oxidation of the compound to the d^8 Cu(III) cation which would also be planar.

Supplementary Material

Listings of the final atomic coordinates and other data relevant to the structure have been deposited with the Editor-in-Chief.

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