

A lariat-functionalized copper(II) diimine–dioxime complex

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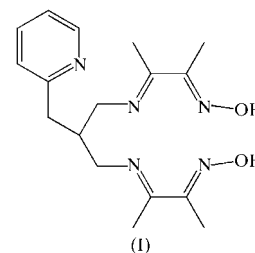
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The dimeric title copper(II) complex, diaqua-1*κ*O,2*κ*O-bis[3,9-dimethyl-6-(2-pyridylmethyl)-4,8-diazaundeca-3,8-diene-2,10-dione dioximato(1-)]-1*k*⁴N²,N⁴,N⁸,N¹⁰;1.2*k*⁵O²:N²,N⁴,N⁸,N¹⁰-dicopper(II) diperchlorate, [Cu₂(C₁₇H₂₄N₅O₂)₂](ClO₄)₂, crystallizes with one Cu atom in a square-pyramidal environment and the other Cu atom displaying a distorted octahedral coordination. In each case, the four N atoms in the core of the ligand (two imine and two oxime N atoms) form the base of the pyramid, with a water molecule at an apex. The two parts of the dimer are linked by an interaction [2.869 (2) Å] between one of the Cu atoms and one of the oxime O atoms coordinated to the second Cu atom, and also by a hydrogen bond between the apical water molecule on the second Cu atom and the pyridyl N atom from the coordination sphere of the first Cu atom. The pyridyl N atoms of the lariat arms are not coordinated to either of the Cu atoms. Thus, this potentially pentadentate ligand is only tetradentate when coordinated to Cu^{II}.

Comment

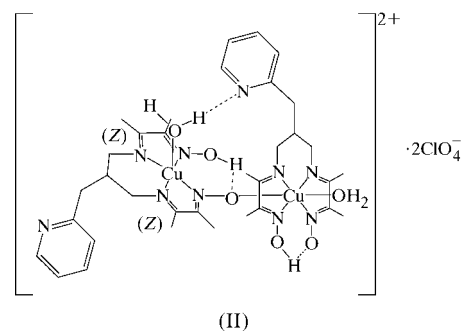
Copper-64-based radiopharmaceuticals may be of value in expanding the availability of PET (positron emission tomography) imaging to clinical facilities that do not have access to cyclotrons (McCarthy *et al.*, 1997; Smith *et al.*, 1996), but for this to occur, new ⁶⁴Cu radiopharmaceuticals must be developed. To this end, we are investigating the chemical and biological properties of lipophilic monocationic copper complexes as potential radiopharmaceuticals for the evaluation of myocardial perfusion and/or multidrug resistance in cancer using PET (Packard *et al.*, 1997, 1998). In the development of these complexes, the pyridyl-functionalized diimine–dioxime ligand (I) is of interest because of the possibility that the pyridyl moiety will bind to copper, as it

does to cobalt(III) (Gerli *et al.*, 1992), and thus enhance the *in vivo* stability of the complex. To evaluate this possibility, we synthesized the copper(II) complex, (II), of this ligand and determined its crystal structure.



The complex crystallizes as a dimer (Fig. 1); the primary Cu coordination environments (henceforth complex-1 refers to the half of the dimer consisting of Cu1 and its coordination environment, and complex-2 refers to that of Cu2) are both square pyramidal, but complex-1 (Table 1) has effective octahedral coordination completed by oxime atom O5 from complex-2 in the sixth position, with a Cu1–O5 distance of 2.869 (2) Å. There is also an O–H...N hydrogen bond (Table 2) between water atom O6 of complex-2 and pyridyl atom N5 of complex-1. The effect of this interaction is that Cu1 is only 0.112 (2) Å above the basal plane compared with a distance of 0.222 (2) Å for Cu2, where there is no sixth interaction; this distance is 0.096 Å in [Cu(PreH)(H₂O)]·ClO₄·H₂O [PreH₂ is 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime; Anderson & Packard, 1979], where there is also a sixth (weak) coordination. The dimers are linked into infinite chains along the *c* axis through O–H...N hydrogen bonds involving apical water O3 of complex-1 and pyridyl atom N10 of a *c*-glide-related complex-2.

In contrast to the Co^{III} complex of this ligand (Gerli *et al.*, 1992), in neither molecule of (II) is the pyridyl N atom coordinated to the metal. This observation is, however, consistent with the results reported for Cu^{II} complexes of pyridyl lariat derivatives of other Schiff base ligands (Adams *et al.*, 1998).



The Cu1–N_{imine} bond lengths [Cu1–N2 = 1.953 (3) Å and Cu1–N3 = 1.952 (3) Å] are somewhat shorter than those in [Cu(PreH)(H₂O)]⁺ [1.972 (7) and 1.960 (8) Å; Anderson & Packard, 1979]. The Cu1–N_{oxime} bonds lengths [Cu1–N1 = 1.960 (3) Å and Cu1–N4 = 1.944 (3) Å] are, however, similar to those observed in [Cu(PreH)(H₂O)]⁺ [1.950 (6) and 1.945 (7) Å; Anderson & Packard, 1979]. The Cu1–O_{water}

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bond [2.205 (3) Å] is significantly shorter than the value of 2.355 (7) Å observed for Cu–PreH (Anderson & Packard, 1979) and at the short end of the range of typical Cu^{II}–OH₂ bond lengths. This difference may be a consequence of the hydrogen bonds (see Table 2) between the coordinated O3 water molecule and both pyridyl atom N10 of an adjacent molecule and atom O4A of a perchlorate counter-ion; these interactions are not present in Cu–PreH. Also, in contrast to Cu–PreH, the central methylene atom C4 of complex-1 is on the opposite side of the basal plane from the axial water molecule, presumably due to steric constraints imposed by the lariat moiety and the hydrogen bonding of atom N5.

The Cu2–N_{imine} bonds are somewhat longer than those for Cu1 [Cu2–N8 = 1.962 (3) Å and Cu2–N7 = 1.964 (3) Å] and are equivalent to those observed in [Cu(PreH)(H₂O)]⁺ [1.972 (7) and 1.960 (8) Å; Anderson & Packard, 1979]. The Cu2–N_{oxime} bond lengths are also equivalent to those observed in the PreH complex; Cu2–N6 = 1.948 (3) Å and Cu2–N9 = 1.950 (3) Å in complex-2 *versus* 1.950 (6) and 1.945 (7) Å for Cu–PreH. The Cu2–O6 bond length of 2.198 (2) Å is, however, significantly shorter than the value of 2.355 (7) Å observed in Cu–PreH (Anderson & Packard, 1979) and equivalent to the value of 2.205 (3) Å observed for Cu1–O3, despite the differences in the coordination geometry between complex-1 and complex-2. As in complex-1, the difference between the Cu–O bond length in complex-2 and that in [Cu(PreH)(H₂O)]⁺ may be a consequence of the hydrogen bond that exists between apical aqua atom O6 and pyridyl atom N5, an interaction that is not present in the non-lariat complex.

Except for the presence of the pyridyl moiety, there are no significant differences between the structures of the ligands in this study and that observed for Cu–PreH (Anderson & Packard, 1979). The orientation of the pyridyl moiety is, however, different in complex-1 and complex-2, as can be seen

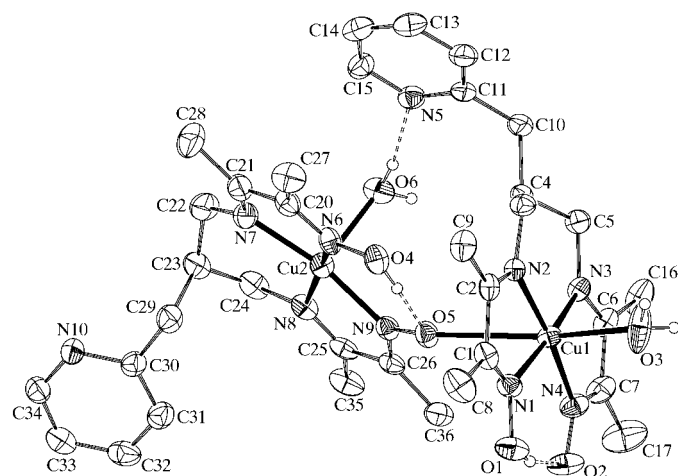


Figure 1
View of the dimer in the title compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms bonded to C atoms have been omitted for clarity

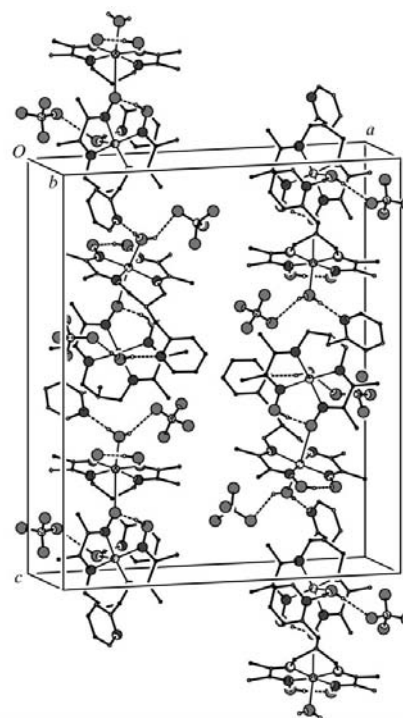


Figure 2
Packing diagram for (I), viewed down the *b* axis. Intermolecular interactions are shown with dashed lines and H atoms bonded to C atoms have been omitted for clarity.

in Fig. 1. In complex-1, the pyridyl ring is approximately perpendicular to the basal plane, while in complex-2, the pyridyl ring is roughly parallel to the basal plane.

Experimental

All commercially obtained chemicals were used without further purification. FT-IR spectra were recorded on a Bruker Vector-22 spectrometer equipped with a Pike MIRacle ATR (attenuated total reflectance) attachment. Electronic spectra were obtained with a Perkin-Elmer Lambda 40 spectrometer. Elemental analyses (CHN) were performed by Atlantic Microlabs (Norcross, Georgia, USA). ¹H NMR spectra were obtained on Varian XL-500 and 270 spectrometers. Literature procedures were followed for the preparation of 2-(2-pyridylmethyl)-1,3-propanediamine (Gerli *et al.*, 1992). The copper complex was prepared using a variation of the method used to prepare the cobalt(III) complex (Gerli *et al.*, 1992). Under a nitrogen atmosphere, 2-(2-pyridylmethyl)-1,3-propanediamine (0.165 g, 1.0 mmol) was dissolved in ethanol (1 ml) and then added slowly to a stirred solution of 2,3-butanedione monoxime (0.201 g, 2.0 mmol) in ethanol (2 ml) at room temperature. The progress of the reaction was followed using IR. After stirring for a period of 8 d, Cu(ClO₄)₂·H₂O (0.259 g, 0.70 mmol) was added (under nitrogen) to the reaction mixture. The resulting red–pink solution was stirred for another hour. Its volume was then reduced to less than 1 ml, diethyl ether (20 ml) was added, and the red precipitate was collected by filtration. The crude product was dissolved in water (5 ml), filtered through a sintered-glass filter, and the filtrate was allowed to stand at ambient temperature for 3 d to afford crystals of (II) suitable for X-ray

analysis. The red parallelepiped-shaped crystals thus obtained weighed 0.190 g (yield: 37%). Elemental analysis calculated for $C_{34}H_{52}Cl_2Cu_2N_{10}O_{14}$: C 39.93, H 5.12, N 13.69%; found: C 40.31, H 5.17, N 13.64%; IR: $\nu_{C=N}$ 1624 cm^{-1} ; UV-vis in H_2O : λ_{max} 489 nm; ϵ 145 $cm^{-1} M^{-1}$.

Crystal data

$[Cu_2(C_{17}H_{24}N_5O_2)_2](ClO_4)_2$ $D_x = 1.529 Mg m^{-3}$
 $M_r = 1022.82$ $Mo K\alpha$ radiation
 Monoclinic, $P2_1/c$ Cell parameters from 87 reflections
 $a = 21.7323 (15) \text{ \AA}$ $\theta = 2.3\text{--}17.7^\circ$
 $b = 7.8564 (5) \text{ \AA}$ $\mu = 1.15 mm^{-1}$
 $c = 26.0263 (18) \text{ \AA}$ $T = 213 (2) K$
 $\beta = 90.605 (1)^\circ$ Parallelepiped, red
 $V = 4443.4 (5) \text{ \AA}^3$ $0.20 \times 0.10 \times 0.10 mm$
 $Z = 4$

Data collection

Bruker SMART CCD diffractometer $R_{int} = 0.039$
 $0.3^\circ \omega$ scans $\theta_{max} = 27.9^\circ$
 27 348 measured reflections $h = -25 \rightarrow 27$
 9509 independent reflections $k = -10 \rightarrow 4$
 6206 reflections with $I > 2\sigma(I)$ $l = -33 \rightarrow 33$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.1179P]$
 $R[F^2 > 2\sigma(F^2)] = 0.045$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.137$ $(\Delta/\sigma)_{max} = 0.006$
 $S = 1.05$ $\Delta\rho_{max} = 0.61 e \text{ \AA}^{-3}$
 9509 reflections $\Delta\rho_{min} = -0.48 e \text{ \AA}^{-3}$
 575 parameters
 H atoms treated by a mixture of independent and constrained refinement

Table 1 Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	1.960 (3)	Cu2—N6	1.948 (3)
Cu1—N2	1.953 (3)	Cu2—N7	1.964 (3)
Cu1—N3	1.952 (3)	Cu2—N8	1.962 (3)
Cu1—N4	1.944 (3)	Cu2—N9	1.950 (3)
Cu1—O3	2.205 (3)	Cu2—O6	2.198 (2)
Cu1—O5	2.869 (2)		
N4—Cu1—N3	81.71 (12)	N6—Cu2—N9	95.42 (13)
N4—Cu1—N2	173.44 (12)	N6—Cu2—N8	166.53 (11)
N3—Cu1—N2	99.95 (11)	N9—Cu2—N8	81.17 (13)
N4—Cu1—N1	96.95 (13)	N6—Cu2—N7	81.06 (13)
N3—Cu1—N1	172.47 (12)	N9—Cu2—N7	167.51 (12)
N2—Cu1—N1	80.56 (12)	N8—Cu2—N7	99.46 (14)
N4—Cu1—O3	96.01 (13)	N6—Cu2—O6	97.53 (10)
N3—Cu1—O3	92.95 (12)	N9—Cu2—O6	97.09 (11)
N2—Cu1—O3	90.25 (12)	N8—Cu2—O6	95.82 (10)
N1—Cu1—O3	94.55 (13)	N7—Cu2—O6	95.25 (11)

Table 2 Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots O2	0.88 (4)	1.67 (4)	2.533 (4)	164 (4)
O3—H3A \cdots N10 ⁱ	0.85	1.87	2.708 (4)	169
O3—H3B \cdots O4A	0.85	2.30	2.897 (5)	127
O4—H4A \cdots O5	0.91 (6)	1.58 (6)	2.486 (4)	173 (6)
O6—H6A \cdots N5	0.85	1.93	2.775 (4)	171
O6—H6B \cdots O2B	0.85	2.22	3.062 (4)	171

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

The title complex crystallized in space group $P2_1/c$, determined by analysis of the systematic absences. The coordinates of the carbon-bound H atoms were calculated geometrically and refined as a riding model, with C—H distances in the range 0.94–0.99 \AA . Oxygen-bound H atoms were located by difference Fourier methods and allowed for as riding atoms, except for atoms H1A and H4A, which were refined isotropically.

Data collection: *ASTRO* (Bruker, 1997); cell refinement: *SMART* (Bruker, 1998); data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1662). Services for accessing these data are described at the back of the journal.

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