

Crystal and Molecular Structure of $[\text{Cu}(\text{NO}_3)_2(\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2)_2]\text{H}_2\text{O}$, a Structure Containing an Unusual Zwitterion of Pyridoxamine and a Symmetric Nitrate–Oxygen Bridge

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Summary A single crystal structure determination of $[\text{Cu}(\text{NO}_3)_2(\text{pm})_2]\text{H}_2\text{O}$ has established that copper is chelated to two pyridoxamine (pm) zwitterions through the amino groups and phenolate oxygen atoms, that the protons lost from the phenolic groups have been used to protonate the pyridine ring nitrogen atoms, and that the $\text{Cu}(\text{pm})_2$ units are bridged by a single oxygen atom from one of the nitrate groups.

groups are both engaged in hydrogen bonding, the former to a water molecule O(11) and the latter to an oxygen atom O(10) in the unco-ordinated nitrate group. The $\text{N}(1) \cdots \text{O}(11)$ and $\text{N}(3) \cdots \text{O}(10)$ distances are 2.74 and 2.80 Å, respectively, and the $\text{N}(1)\text{--H}(1) \cdots \text{O}(11)$ and $\text{N}(3)\text{--H}(13) \cdots \text{O}(10)$ angles are 173 and 147°, respectively.

PYRIDOXAMINE (pm, **1**) and pyridoxal are compounds which exhibit vitamin B₆ activity. Enzymes for which vitamin B₆ is a cofactor are responsible for transamination, decarboxylation, racemization, and other reactions of amino-acids.¹ It is possible to mimic the enzymic reactions by using systems containing pyridoxal (or pyridoxamine), an amino-acid (or α -keto-acid), and a metal ion. The reaction proceeds *via* Schiff base formation, and one of the possible roles of the metal ion is that it acts as a template for the Schiff base reaction.¹ The crystal structures of several metal-pyridoxylidene Schiff base complexes have been determined² but the present paper is the first to provide detailed structural information for a metal complex with pyridoxamine itself.

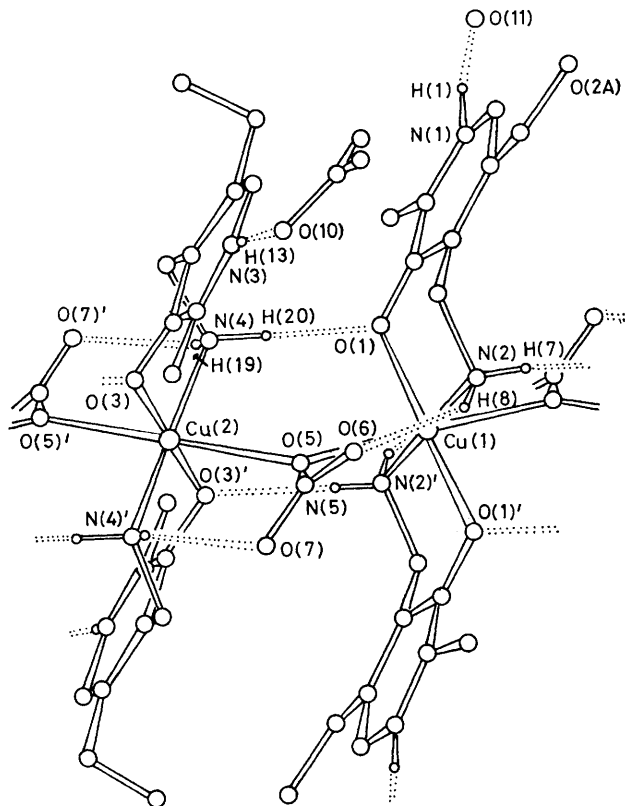


FIGURE. Part of the molecular structure of $[\text{Cu}(\text{pm})_2(\text{NO}_3)_2]\text{H}_2\text{O}$, showing the linking of the $\text{Cu}(\text{pm})_2$ units by the bridging nitrate group. Primed atoms are related to unprimed ones by a crystallographic centre of symmetry. Most of the hydrogen atoms have been omitted for clarity. One of the CH_2OH groups shows disorder in the oxygen position, and only one of the two O(2) positions is shown. Hydrogen bonds are indicated by dotted lines. Some distances are $\text{Cu}(1)\text{--O}(1)$, 1.986; $\text{Cu}(1)\text{--N}(2)$, 2.008; $\text{Cu}(1)\text{--O}(5)$, 2.466; $\text{Cu}(2)\text{--O}(3)$, 1.974; $\text{Cu}(2)\text{--N}(4)$, 1.993; $\text{Cu}(2)\text{--O}(5)$, 2.560 Å; $\text{Cu}(1) \cdots \text{Cu}(2)$, 4.284 Å.

Evaporation of an equimolar solution of pm and $\text{Cu}(\text{NO}_3)_2$ in water yielded dark green crystals of $[\text{Cu}(\text{pm})_2(\text{NO}_3)_2]\text{H}_2\text{O}$. The crystals are triclinic, space group $P\bar{1}$, $a = 14.248(2)$, $b = 8.568(1)$, $c = 9.319(1)$ Å, $\alpha = 94.08(1)$, $\beta = 89.73(1)$, $\gamma = 99.13(1)^\circ$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 10.90 \text{ cm}^{-1}$. The structure was solved by Patterson techniques from data collected on a Picker 4-circle diffractometer to $2\theta_{\text{max}} = 45^\circ$. All atoms, including hydrogens, have been located. For the 2285 independent reflections with $F \geq 3\sigma(F)$, $R = 0.0628$.†

There are some interesting features of the co-ordination of pm (Figure). Pm is believed to exist normally as the zwitterion (**2**),³ in which form it is incapable of chelation since the amino-group is protonated. However, copper is indeed chelated through the amino and phenolic groups, showing that the zwitterion (**2**) either has been converted into (**1**) or has formed a new zwitterion (**3**). That the new zwitterion (**3**) is formed is shown unequivocally from the hydrogen positions; there are protons [H(1) and H(13)] on the pyridine nitrogen atoms, but none on the phenolate oxygen atoms. The pyridinium $\text{N}(1)\text{--H}(1)$ and $\text{N}(3)\text{--H}(13)$

The nitrate group bridges the two independent copper atoms through a single oxygen atom. Only three other structures are known where this type of bridging occurs: $[\text{Cu}(\text{NO}_3)_2(\text{py})_2]\cdot\text{py}$ (py = pyridine),⁴ $[\text{Ag}\{\text{P}(\text{OMe})_3\}_2\text{NO}_3]_2$,⁵

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

and α -Cu(NO₃)₂.⁶ All these are characterized by 'bending' of the nitrate group towards one of the metal atoms so that there is an additional interaction between a nonbridging oxygen and a metal atom. The additional interaction may be either very weak^{4,5} or strong.⁶ The net result is that the metal atom undergoing the additional bonding is very close to the plane of the nitrate group whilst the other metal atom in the bridged unit is much further removed from the plane.

In the present structure, the nitrate is not bent towards one of the copper atoms, but rather is twisted by almost 45° about the O(5)–N(5) bond so that the Cu(1) and Cu(2) atoms are located almost 1.5 Å from the nitrate plane, on opposite sides. Additional bonding by the nonbridging oxygens does not occur: the Cu(1)–O(6) and Cu(2)–O(7) distances are *ca.* 3.5 Å. The twisting is quite surprising since the copper atoms should be in the same plane as the nitrate group for maximum overlap of the O(5) lone pairs with the Cu(1) and Cu(2) orbitals. [The O(5) atom is assumed to be *sp*²-hybridized, in keeping with the N(5)–O(5) bond distance of

1.22 Å and the Cu(1)–O(5)–Cu(2) angle of 116.9°.] This twisting is apparently a result of hydrogen bonding. If the nitrate group were coplanar with the Cu(1)–O(5)–Cu(2) group, the O(6) and O(7) atoms would not be able to interact with the N(2)–H(8) and N(4)–H(19) groups. Twisting allows the formation of two hydrogen bonds: the N(2)···O(6) and N(4')···O(7) distances are 2.91 and 2.94 Å, respectively, and the N(2)–H(8)···O(6) and N(4')–H(19')···O(7) angles are 140 and 129°, respectively.

The two independent copper atoms are located on centres of symmetry at (0,0,0) and 0,½,0). Each lies at the centre of a tetragonally distorted octahedron with four short and two long copper–ligand distances (Figure). This distortion is the type usually observed when Jahn–Teller effects are operative in octahedral complexes.⁷

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