

X-Ray Structure of $\text{Cu}_2(\text{medpco})\text{Cl}_4$, a Complex with the Potentially Binucleating *N*-Oxide Ligand *N,N'*-Bis(2-*N,N*-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-Oxide (medpco)

Michael Antolovich, David J. Phillips,* and A. David Rae*

School of Chemistry, University of New South Wales, Kensington, NSW 2033, Australia

The complex $\text{Cu}_2(\text{medpco})\text{Cl}_4$, with the *N*-oxide ligand *N,N'*-bis(2-*N,N*-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-oxide (medpco), does not have the expected binucleated structure; X-ray analysis shows that one Cu^{II} ion occupies an ONN ligand site, and is linked by a double chloride bridge to an external Cu^{II} ion whose co-ordination is completed by two terminal chlorides.

There is considerable current interest in metal complexes of binucleating ligands, but no examples have been reported with bridging pyridine *N*-oxides.¹⁻³ We find that the potentially binucleating *N*-oxide ligand medpco [*N,N'*-bis(2-*N,N*-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-oxide] yields 1:1 complexes with Ni^{II} and Cu^{II} salts, except for the bimetallic complex $\text{Cu}_2(\text{medpco})\text{Cl}_4$, whose novel structure is reported.

The magnetic moment of $\text{Cu}_2(\text{medpco})\text{Cl}_4$ is almost invariant with temperature (μ_{eff} is 1.85 μ_{B} at 305 K, and 1.90 μ_{B} at 89 K) and this makes the expected planar *N*-oxide-bridged structure unlikely.⁴ The reflectance electronic spectrum at 89 K is detailed, with bands at 9000, 12100, and 15700 cm^{-1} suggesting that the two Cu^{II} ions are in different environments. Because of these unusual features, an X-ray structure analysis was performed† and the results are shown in

† Crystal data: $\text{C}_{15}\text{H}_{25}\text{N}_5\text{O}_3\text{Cu}_2\text{Cl}_4$, $M = 592.3$, triclinic, space group $P\bar{1}$, $a = 8.558(8)$, $b = 10.824(8)$, $c = 15.335(3)$ Å, $\alpha = 89.77(5)$, $\beta = 84.47(6)$, $\gamma = 72.42(7)^\circ$, $U = 1139.0$ Å³, $Z = 2$, $\mu(\text{Cu-K}\alpha) = 69.2$ cm^{-1} , $D_c = 1.73$ g cm^{-3} . The intensity data were collected on an Enraf-Nonius, Delft Diffractis 585 computer controlled diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056$ Å). A total of 4306 unique reflections were measured and 899 of these had $I < 3\sigma(I)$. The structure was solved by Patterson heavy atom methods and refined by a block diagonal least-squares procedure. All the hydrogen atoms were found by a difference map and the final R factor was 0.051 for 3407 contributing reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure factor table is available as Supplementary Publication No. SUP 23901 (14pp.) from the British Library Lending Division. For details of how to obtain this material, see Instructions to Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xviii.

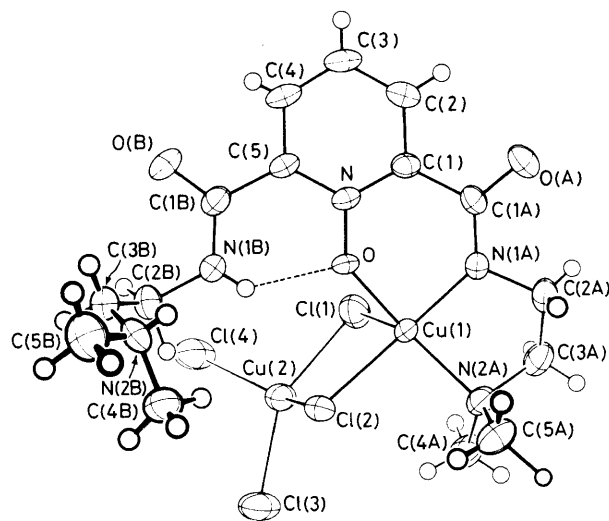


Figure 1. The molecular structure of $\text{Cu}_2(\text{medpco})\text{Cl}_4$. Principal bond lengths (Å): Cu(1)–O 1.967(3); Cu(1)–N(1A) 1.913(4); Cu(1)–N(2A) 2.051(4); Cu(1)–Cl(1) 2.634(1); Cu(1)–Cl(2) 2.306(1); Cu(2)–Cl(1) 2.265(1); Cu(2)–Cl(2) 2.389(1); Cu(2)–Cl(3) 2.193(1); Cu(2)–Cl(4) 2.197(1); Cu(1)–Cu(2) 3.454(1); N–O 1.335(4).

Figure 1 together with some important bond parameters. The ligand is not binucleating, but acts as an ONN donor to one Cu^{II} ion. This copper has a distorted square-pyramidal structure, and is linked by a double chloride bridge to the second Cu^{II} ion. The second Cu^{II} ion has a distorted tetrahedral structure completed by two terminal chlorides, and it is located well away from the second donor site in the ligand.

The co-ordinated amide nitrogen, N(1A), is trigonal, and its hydrogen has been transferred to the unco-ordinated amine nitrogen, N(2B), in a novel deprotonation by a tertiary amine within the ligand. The transferred hydrogen is involved in an intermolecular hydrogen-bond to the carbonyl oxygen, O(A'), of another molecule related by a centre of inversion, to give a dimer. The hydrogen on the unco-ordinated amide, N(1B), is hydrogen-bonded to the *N*-oxide oxygen, O, effectively blocking the second co-ordination site of the ligand. We shall examine co-ordination by deprotonated medpco, and by its amide *N*-methyl derivatives; these approaches might release both ligand sites for metal co-

ordination. The co-ordination of the metal ions, and the internal deprotonation, described here, appear to be unique for a potential binucleating ligand.

Received, 5th December 1983; Com. 1576

References

- 1 M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259.
 - 2 U. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, 1977, **23**, 31.
 - 3 S. E. Groh, *Isr. J. Chem.*, 1976/77, **15**, 277.
 - 4 D. J. Hodgson, *Prog. Inorg. Chem.*, 1975, **19**, 173.
-