

A Novel Type of Tetranuclear Copper(II) Cluster, containing Deprotonated 3-(Pyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazole (Hppt) as a Diatomic Bridging Ligand. Preparation, Magnetism, and X-Ray Crystal Structure of $[\text{Cu}(\mu\text{-ppt})(\text{H}_2\text{O})]_4(\text{NO}_3)_4(\text{H}_2\text{O})_{12}$

Rob Prins, Rudolf A. G. de Graaff, Jaap G. Haasnoot,* Cees Vader, and Jan Reedijk

Gorlaeus Laboratories, Department of Chemistry, State University Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

The title compound, characterized by means of an X-ray structure analysis, represents the first example of a tetranuclear co-ordination compound with only diatomic bridges.

Recently the synthesis, structure, and magnetic properties of a series of dinuclear copper(II) compounds have been reported, introducing the 3,5-di(pyridin-2-yl)-1,2,4-triazolato anion as a dinucleating bridging ligand.^{1,2} To investigate the correlation between the magnetic exchange mechanism, structural features, and ligand properties more thoroughly, a related ligand, 3-(pyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazole (Hppt), was synthesized by the method described by Browne.³ This ligand, with which dinuclear co-ordination compounds could be synthesized,⁴ also yielded, surprisingly, a novel type of tetranuclear copper(II) compound, representing the first example of a new class of tetrameric co-ordination compounds.

Tetranuclear copper(II) co-ordination compounds show a variety of structures. Well known examples are the clusters having the metal ions in a tetrahedral arrangement bridged over the edges by halide ions and by an oxygen atom in the centre of the tetrahedron.⁵⁻¹⁰ More recently tetranuclear compounds of the cubane type have been studied extensively, structurally as well as with respect to their magnetic properties, by Haase and others.¹¹⁻¹⁵ Both types of clusters are schematically depicted in Figure 1. The common feature characterizing the tetranuclear compounds studied so far is the fact that monoatomic bridges interconnect the metal ions.

Although tetranuclear structures containing diatomic ligand bridges are known,¹⁶ the title compound represents, to the best of our knowledge, the first example of a regular

tetranuclear copper compound containing only diatomic bridges. The ligand Hppt was synthesized starting from 2-cyanopyridine and pyrazine-2-carboxylic acid. The title compound was synthesized by adding a slurry of Hppt in water to a stirred aqueous solution of an equimolar amount of

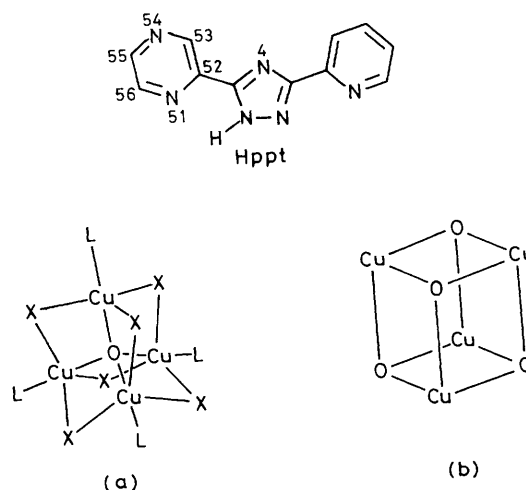


Figure 1. (a) Halide bridged type clusters (X = halide ion, L = ligand); (b) cubane type clusters.

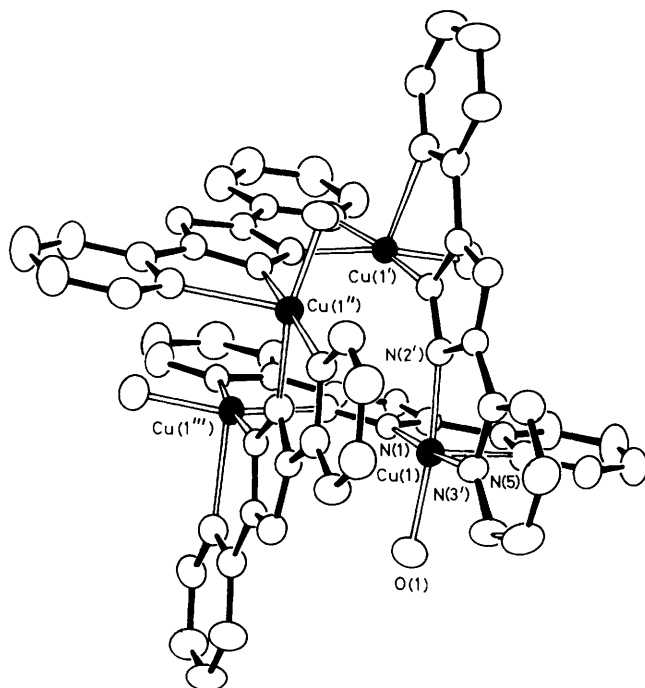


Figure 2. Projection of the structure of the $[\text{Cu}(\mu\text{-C}_{11}\text{N}_6\text{H}_7)(\text{H}_2\text{O})]_4^{4+}$ cation. Selected bond distances and angles are Cu–Cu' (Cu''), Cu'–Cu'' and Cu''–Cu''' 4.2686(4), Cu–Cu' and Cu'–Cu'' 4.3195(5), Cu(1)–N(1) 2.004(2), Cu(1)–N(5) 2.289(2), Cu(1)–O(1) 1.951(2), Cu(1)–N(2') 1.969(2), Cu(1)–N(3') 2.040(2) Å; N(1)–Cu(1)–N(2') 93.8(1), N(2')–Cu(1)–N(3') 80.0(1), N(1)–Cu(1)–O(1) 92.0(1), N(3')–Cu(1)–O(1) 93.7(1), N(1)–Cu(1)–N(5) 76.6(1), N(2')–Cu(1)–N(5) 99.0(1), N(3')–Cu(1)–N(5) 105.9(1), N(5)–Cu(1)–O(1) 92.8(1)°. Atoms marked ', ', or ''' are generated by symmetry operations: ' = $y-3/4, 3/4-x, 3/4-z$; '' = $-x, 3/2-y, z$; ''' = $3/4-y, 3/4+x, 3/4-z$.

copper(II) nitrate. The resulting clear green solution was filtered; after several hours, dark green crystals separated.

The molecular structure of the tetranuclear unit,[†] as shown in Figure 2, consists of four copper ions at the vertices of a slightly distorted tetrahedron, four deprotonated ligand molecules (ppt) bridging the edges of the tetrahedron, and four co-ordinated water molecules. The co-ordination geometry around the copper ions is distorted square pyramidal, with a basal plane consisting of three ligand nitrogen atoms and one oxygen atom from the co-ordinated water molecule. A ligand nitrogen atom completes the co-ordination geometry at the apical position of the pyramid. The tetranuclear unit has two different copper–copper distances: *i.e.*, copper ions that are bridged by a ligand molecule [4.2686(4) Å], and copper

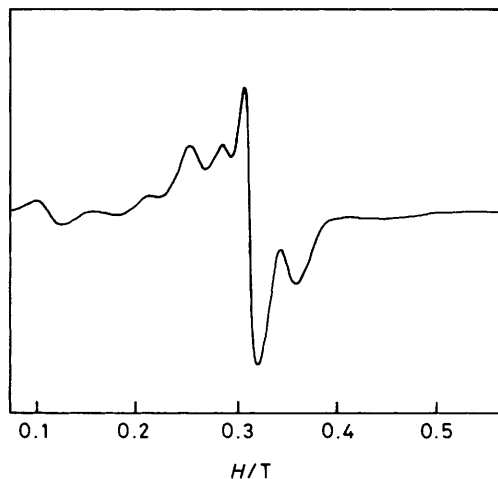


Figure 3. X-Band powder e.s.r. spectrum of $[\text{Cu}(\mu\text{-C}_{11}\text{N}_6\text{H}_7)(\text{H}_2\text{O})]_4(\text{NO}_3)_4(\text{H}_2\text{O})_{12}$ at 77 K (frequency 9.196 GHz; Varian E-3 spectrometer).

ions lacking the ligand bridge [4.3195(5) Å]. The tetranuclear units are interconnected *via* the triazole N-4 by a complicated network of hydrogen bonds. In comparison with cubane-type clusters, this structure lacks the four additional groups completing the 'cubic' structure.

The magnetic properties of this compound appear to be interesting as suggested by the powder e.s.r. spectrum (Figure 3). The several signals below 0.2 T strongly suggest a spin state >1 . With respect to the compatibility of this compound with those already reported^{11–15} the magnetic properties can best be described using a four-centre exchange-coupled model. Preliminary susceptibility data indicate a μ_{eff} value of 1.8 μ_{B} at room temperature and a maximum in the susceptibility at about 12 K. It is assumed that two different coupling constants will be required to characterize fully the magnetic behaviour of the compound.

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References

- 1 A. Bencini, D. Gatteschi, C. Zanchini, J. G. Haasnoot, R. Prins, and J. Reedijk, *Inorg. Chem.*, 1985, **24**, 2812.
- 2 R. Prins, P. J. M. W. L. Birker, J. G. Haasnoot, G. C. Verschoor, and J. Reedijk, *Inorg. Chem.*, 1985, **24**, 4128.
- 3 E. J. Browne, *Aust. J. Chem.*, 1975, **28**, 2543, and references therein.
- 4 C. Vader, J. G. Haasnoot, R. Prins, J. Reedijk, and M. Biagini-Cingi, to be published.
- 5 R. F. Drake, V. H. Crawford, and W. E. Hatfield, *J. Chem. Phys.*, 1974, **60**, 4525.
- 6 D. H. Jones, J. R. Sams, and R. C. Thompson, *J. Chem. Phys.*, 1983, **79**, 3877.
- 7 B. T. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, 1967, **1**, 209.
- 8 J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495.
- 9 J. A. Bertrand and J. A. Kelley, *Inorg. Chem.*, 1969, **9**, 1982.
- 10 N. S. Gill and M. Sterns, *Inorg. Chem.*, 1970, **9**, 1619.
- 11 L. Schwabe and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1985, 1909.
- 12 L. Schwabe and W. Haase, *Z. Naturforsch., Teil A*, 1985, **40**, 229.
- 13 L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1980, 875.
- 14 L. Laurent, J. Bonnet, F. Nepveu, H. Astheimer, L. Walz, and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1982, 2433.
- 15 L. Merz, Dissertation, Technische Hochschule Darmstadt, 1980.
- 16 R. W. M. ten Hoedt, F. B. Hulsbergen, G. C. Verschoor, and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2369.
- 17 J. Waser, *Acta Crystallogr.*, 1963, **16**, 1091.

[†] Crystal data: $\text{C}_{11}\text{H}_{15}\text{Cu}_4\text{N}_6\text{O}_7$ at 298 K, $M_r = 420.83$, tetragonal, space group $I4_1/a$, $a = 18.868(3)$, $c = 18.936(2)$ Å, $D_c = 1.66(1)$ g cm⁻³, $Z = 16$, $F(000) = 3445$. The structure was solved by direct methods and by difference Fourier techniques using 3119 unique intensities were collected on an Enraf-Nonius CAD-4 automated diffractometer using Mo- K_α radiation [$\lambda(\alpha_1) = 0.70930$ Å] for $4 < 2\theta < 55^\circ$, and refined by least squares methods. The hydrogen atoms of the water molecules were refined with Wasser constraints¹⁷ [O–H = 0.89(4) Å; \angle H–O–H = 104.5 (1.0)°]. All hydrogen atoms were refined with isotropic thermal parameters, while the remaining atoms were refined with anisotropic thermal parameters. Final refinement converged to $R = 0.0337$ ($R_w = 0.0470$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.