The Molecular Structure of Tetrakis-[1,3-dimethyltriazenocopper(I)]

By J. E. O'CONNOR, G. A. JANUSONIS, and E. R. COREY*
(*Department of Chemistry, University of Cincinnati, Cincinnati, Ohio* 45221)

MANY metal complexes of 1,3-dimethyltriazene have been prepared[1] but no *X*-ray diffraction studies of these complexes have been reported. This structural investigation of 1,3-dimethyltriazenocopper(I) has revealed a novel arrangement of four dimethyltriazeno-ligands bonded to four copper atoms to form a sixteen-membered folded-ring systen with metal–nitrogen and nitrogen–nitrogen bonding.

Structural studies of the related 1,3-diphenyltriazeno-ligand have shown that two of these ligands can co-ordinate to two metal atoms, forming an eight-membered ring as in the 1,3-diphenyltriazenocopper(I) dimer,[2] or a single ligand can co-ordinate to one metal atom, forming a strained four-membered ring as in 1,3-diphenyltriazenocobalt(III).[3]

Needle-like yellow crystals of 1,3-dimethyltriazenocopper(I) were supplied by Dr. F. E. Brinckman. A single crystal was obtained by recrystallization from ligroin (b.p. 60—90°). Crystals of [Cu(MeNNNMe)]$_4$ belong to the monoclinic system with unit cell parameters $a = 12{\cdot}93 \pm 0{\cdot}02$, $b = 12{\cdot}22 \pm 0{\cdot}02$, $c = 24{\cdot}54 \pm 0{\cdot}04$ Å, and $\beta = 94°08' \pm 30'$, $D_m = 1{\cdot}86 \equiv D_c$ for $Z = 8$. Systematic extinctions of hkl reflections for $h + l$ odd, $h0l$ reflections for l odd and $0k0$ reflections for k odd indicate the space group $B2_1/c$. Multiple-film equi-inclination data were collected for the reciprocal levels $0kl$ to $12kl$ with Zr-filtered Mo-K_α radiation (λ 0·7107 Å). The intensities of 1178 independent diffraction maxima were estimated visually and were corrected for Lorentz-polarization effects. The positions of the four copper atoms were determined from a Patterson synthesis and all other non-hydrogen atoms were located from an electron-density difference-map based on phases from the heavy atoms. Full matrix isotropic least squares refinement has yielded a discrepancy index $R = 12{\cdot}8$.

The molecular configuration of [Cu(MeNNNMe)]$_4$ is shown in the Figure and is similar to one of the structures postulated on the basis of n.m.r. studies by Brinckman *et al.*[1] The four copper atoms are

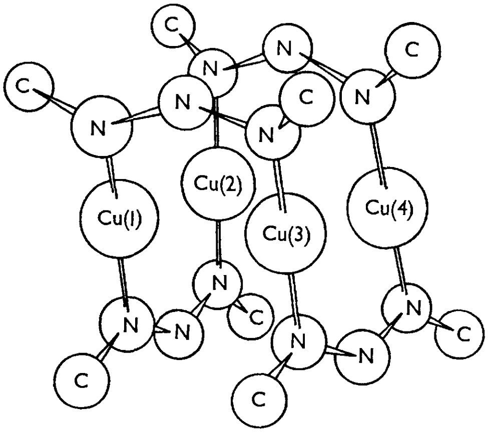

FIGURE. *The molecular configuration of* [Cu(MeNNNMe)]$_4$

TABLE. *Interatomic distances and angles**

Cu(1)–Cu(2)	2·67 (1) Å	Cu(4)–Cu(2)	2·64 (1) Å
Cu(1)–Cu(3)	2·66 (1)	Cu(4)–Cu(3)	2·68 (1)
Cu(1)–Cu(4)	4·42 (1)	Cu(2)–Cu(3)	2·97 (1)
Cu–N(av.)	1·87 (3)	N–N (av.)	1·29 (4)
N–C (av.)	1·50 (6)		
Cu(1)–Cu(2)–Cu(4)	112·5° (4)	Cu(2)–Cu(1)–Cu(3)	67·6 (3)
Cu(1)–Cu(3)–Cu(4)	111·7 (4)	Cu(2)–Cu(4)–Cu(3)	67·8 (3)
N–Cu–N (av.)	172·5 (1·5)	N–N–N (av.)	116·0 (3)

* Estimated standard deviations in the least significant figures are given in parentheses.

located in a diamond-shaped arrangement with an average distance of 2·66 Å between nearest copper atoms (Table). The Cu–N bond distances range from 1·82—1·91 ± 0·03 Å N–N from 1·23—1·37 ± 0·04$_5$ Å; and N–C from 1·39—1·61 ± 0·06 Å. Each copper atom is approximately linearly co-ordinated with an average N–Cu–N angle of 172·5° (range: 171—176 ± 1·5°). The average value of 116° for the N–N–N angles (range: 112—121 ± 3°) is larger than the 105° angles observed for the strained chelate rings in 1,3-diphenyltriazenocobalt(III)[3] but is the same as the N–N–N angle observed in the 1,3-diphenyltriazencopper(I) dimer.[2] The N–N distances are equivalent within the accuracy of the structural results and support delocalization in the triazeno-ligands. The idealized point-group symmetry of the non-hydrogen atoms in [Cu(MeNNNMe)]$_4$ is D_2(222). It appears that the square arrangement of copper atoms and ligands (D_{2d}, $\bar{4}2m$) is not realized because interactions between adjacent methyl-groups prevent this more symmetrical molecular configuration.

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[1] F. E. Brinckamn, H. S. Hain, and R. A. Robb, *Inorg. Chem.*, 1965, **4**, 936.

[2] I. D. Brown and J. D. Dunitz, *Acta. Cryst.*, 1961, **14**, 480.

[3] M. Corbett and B. F. Hoskins, *J. Amer. Chem. Soc.*, 1967, **89**, 1530.