Synthesis, *X*-Ray Structure, and Chemical Properties of $[Cu_8(dmpz)_8(OH)_8]$ (Hdmpz = 3,5-dimethylpyrazole). First Example of a Copper Complex containing a Planar Ring of Eight Metal Atoms

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Reaction of the polymeric copper(I)–3,5-dimethylpyrazolate, $[Cu(dmpz)]_n$, with molecular dioxygen gives the octameric copper(II) complex, $[Cu_8(dmpz)_8(OH)_8]$, whose spectroscopic and chemical properties, and *X*-ray structure analysis are reported.

Metal-assisted reactions of dioxygen are important processes and there is increasing interest in their products and mechanisms.[1] The polymeric copper(I)–3,5-dimethylpyrazolate complex, $[Cu(dmpz)]_n$ (**1**), has been known since 1971,[2] but little attention has been devoted to its chemical properties. We have recently studied its reactions with neutral ligands such as 1,10-phenanthroline[3] and cyclohexyl isocyanide.[4] We report here the results of the reaction of (**1**) with molecular dioxygen.

When suspensions of (**1**) in wet CH_2Cl_2, pyridine, or nitrobenzene are treated with O_2 under atmospheric pressure at room temperature, a blue solution is obtained, from which the unexpected blue octameric copper(II)–hydroxo complex, $[Cu_8(dmpz)_8(OH)_8]$ (**2**) is obtained in quantitative yield, decomp. > 160 °C.[†] Its IR spectrum (Nujol mull or KBr

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[†] Satisfactory elemental analyses were obtained for $[Cu_8(dmpz)_8(OH)_8]\cdot 2C_5H_5N$ ($C_{50}H_{74}Cu_8N_{18}O_8$) after removal of water at 10^{-1} Torr and 25 °C; λ_{max} (CH_2Cl_2) 542 nm (ε 645.3 l mol^{-1} cm^{-1}).

pellets) exhibits absorptions which confirmed the presence of bridging OH groups [ν(OH) 3637s and 3598s cm^{-1}].[5,6] Moreover, two bands at 3392s,br and 898vs cm^{-1} are present. On the basis of the literature data,[7] we assign these absorptions to ν(OH) and libration of clathrated water molecules (*vide infra*). On treatment with D_2O, the above bands shift to 2673s, 2645s, 2532m,br, and 647m cm^{-1}; isotopic shifts are in agreement with analogous results already published.[5,8]

The magnetic moment of complex (**2**) gave a value of about 2.0 μ_B per octameric unit, indicating strong exchange coupling between the eight metal centres. Moreover, its EPR spectra, recorded at room and liquid nitrogen temperatures, showed only a very weak signal at *ca.* 3000 G (1 G = 10^{-4} T). A detailed study of the magnetic behaviour of complex (**2**) is in progress and the results will be included in a forthcoming paper.

When (**2**) is treated with methanol or propanol, a green insoluble product is obtained, whose spectroscopic properties can be interpreted in terms of the formation of $[Cu_8(dmpz)_8(OR)_8]$ [(**3a**), R = Me; (**3b**), R = Pr^n]. Complexes (**3a**) and (**3b**) are easily converted into (**2**) by exposure to moisture.

$[Cu(dmpz)]_n$
(**1**)

$[Cu_8(dmpz)_8(OR)_8]$
(**2**) R = H
(**3a**) R = Me
(**3b**) R = Pr^n

Complex (**2**) oxidizes PPh_3 to $Ph_3P{=}O$ in pyridine or toluene under N_2 at 60 °C, four moles of triphenylphosphine oxide per mole of (**2**) always being formed and the polymeric $[Cu(dmpz)]_n$ was recovered as the final product. When the same reaction is carried out under O_2 in pyridine at 60 °C, PPh_3 is catalytically converted into $Ph_3P{=}O$. Analogously, CO is catalytically oxidized to CO_2. Preliminary investigations show that oxidations take place also when cyclohexyl isocyanide, aromatic amines, or $(PhCH_2)_2NH$ are treated with (**2**), cyclohexyl isocyanate, azobenzenes, and $PhCH_2N{=}CHPh$, respectively, being formed. Pyridine is necessary as a solvent for catalytic reactions.

The reaction of (**2**) with PPh_3 under N_2 seems to suggest the presence, in solution, of tautomeric species of general formula $[Cu_8(dmpz)_8(O)_x(OH)_{8-2x}(H_2O)_x]$ (x = 1—4). Evidence of two 'frozen' tautomers in the solid state, $[Cu_2L_2(OH)_2]$ and $[Cu_2L_2(O)(H_2O)]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), has been recently claimed.[5]

Single-crystal *X*-ray diffraction‡ showed that $[Cu_8(dmpz)_8(OH)_8]$ consists of a discrete molecule of toroidal shape (Figure 1), containing a ring of eight monomeric units (Figure 2). Each molecule lies on a crystallographic mirror plane and possesses idealized D_{4d} symmetry, with an eight-fold rotary inversion S_8 axis normal to the plane of the perspective view of Figure 1, and is topologically equivalent to cyclo-octane. Each of the copper(II) atoms, approximately located at the vertices of a regular octagon, is connected to two hydroxo and two dmpz groups, with almost square-planar co-ordination geometry (*trans*-isomer). $[Cu_8(dmpz)_8(OH)_8]$ is the first example of a discrete molecule containing a planar system of eight copper atoms [maximum deviation from the least-squares plane 0.014(3) Å]; similar regular polygons have been found in $[V_8O_8(OMe)_{16}(C_2O_4)]^{2-}$ [9] and $[Mo_8O_{16}(OR)_8(C_2O_4)]^{2-}$ (R = Me or Et),[10] while for copper only Cu_5 pentagons $[Cu_5I_7]^{2-}$ [11] and $Cu_5(mes)_5$,[12] mes = μ-(2,4,6-trimethyl)phenyl] and the hexameric $[Cu(C_8H_7O_3)]_6$ ($C_8H_7O_3$ = $PhOCH_2CO_2^-$)[13] are known; an octameric copper derivative, $[Cu_8(urid)_8]^{8-}$ (H_3urid = uridine), with distorted antiprismatic geometry was also reported.[14] All ligands bridge Cu^{II} pairs, having average non-bonding distance of 3.237 Å, which, owing to the presence of the dmpz groups, is significantly longer than those found within the Cu–OH–Cu–OH systems of ref. 15a,f (2.89—3.00 Å).

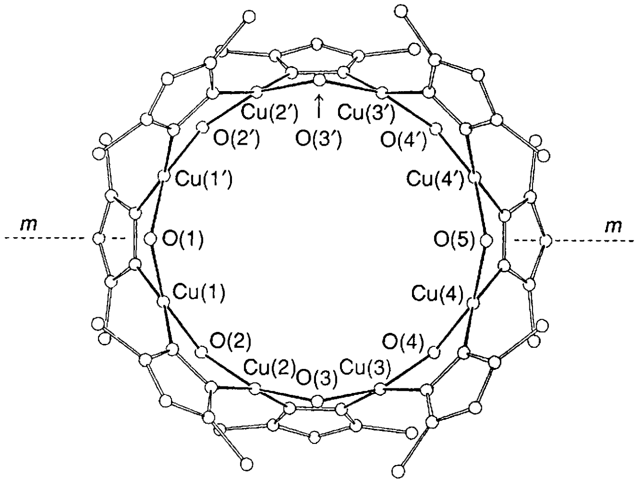

Figure 1. ORTEP drawing of the octameric $[Cu_8(dmpz)_8(OH)_8]$ molecule with partial labelling scheme; for clarity all atoms have been given an isotropic thermal parameter of 0.5 Å^2 and hydrogen atoms have been removed; relevant bond lengths are: Cu · · · Cu 3.237 (mean) Å, min 3.213(3), max 3.268(2) Å; Cu–O 1.921 (mean) Å, min 1.911(8), max 1.943(7) Å; Cu–N 1.967 (mean) Å, min 1.946(9), max 1.984(9) Å; N–N 1.35 (mean) Å, min 1.29(2), max 1.39(1) Å. The superscript refers to the $x, \frac{1}{2} - y, z$ symmetry operation.

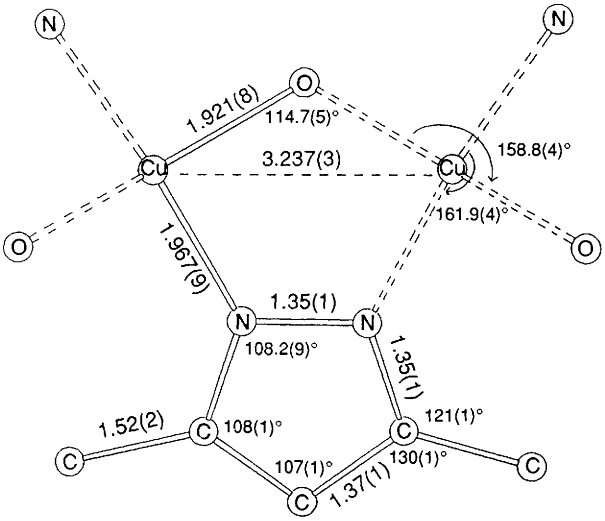

Figure 2. ORTEP view of the repeating [Cu(dmpz)(OH)] monomeric unit; the H atom of the bridging hydroxo ligand is not shown nor was it located. The values in parentheses are the typical standard deviations of the single values.

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‡ *Crystal data* for $C_{52}H_{74}Cu_8N_{18}O_{12}$: M = 1651.6, monoclinic, space group $P2_1/m$ (No. 11), a = 10.229(3), b = 27.217(2), c = 14.532(1) Å, β = 98.51(1)°, U = 4001(2) Å^3, $F(000)$ = 1680, Z = 2, D_c = 1.371 g cm^{-3}, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 21.47 cm^{-1}; current R value 0.071 for 2188 absorption-corrected reflections with $I > 3\sigma(I)$. Four ordered nitrobenzene molecules are present in the unit cell between the $[Cu_8(dmpz)_8(OH)_8]$ molecules; the three-dimensional stack of the cyclic octameric units generates infinite channels along the crystallographic a axis. 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.

However, the ligand stereochemistry around each Cu atom is tetrahedrally distorted, the oxygen atoms being in an inner position in the molecular core relative to the nitrogen atoms of the dmpz ligands, the average angles between *trans*-ligands being O–Cu–O 158.8° and N–Cu–N 161.9°.

The metallacycles $\overline{\text{Cu–O–Cu–N–N}}$ are not planar but show an envelope conformation with the oxygen atoms out of the Cu_2N_2 planes by about 0.7 Å. A similar stereochemistry of the five-membered ring was previously found in the copper derivatives of ref. 16a,e.

The internal cavity of the octameric unit, similar to that found in calixarenes,[17] after subtraction of the van der Waals radii, has a diameter of about 6 Å and may contain water or other guest molecules; similar cavities in $[Cu_8(urid)_8]^{8-}$ [14] and in $[M_8O_{8x}(OR)_{8(3-x)}]$ ($M = V, x = 1, R = Me$[9] and $M = Mo, x = 2$, R = Me or Et[10]) contain, in fact, ordered ions, such as $[Na(H_2O)_6]^+$ and $C_2O_4{}^{2-}$, respectively. In the present case, several peaks, not exceeding 1.6 e/Å^3, were localized inside the cavity (mostly on the mirror plane) in the last difference Fourier map, but could not be related to any ordered model nor could any disorder be rationalized; therefore, their contribution was omitted from structure factors calculations, resulting in the final (poor) agreement factor of $R = 0.071$.

On the basis of the toroidal shape of the title compound, steric effects on the chemical reactivity are expected; in fact, preliminary results for reactions of (**2**) with different aliphatic alcohols show a significant trend; similar effects on oxidative reactions are presently under investigation.

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References

1 M. A. El-Sayed, A. Abu-Ragabah, G. Davies, and A. El-Toukhy, *Inorg. Chem.*, 1989, **28**, 1909, and references therein.

2 C. B. Singh, S. Satpathy, and B. Sahoo, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1313.

3 G. A. Ardizzoia, G. La Monica, M. Angaroni, and F. Cariati, *Inorg. Chim. Acta*, 1989, **158**, 159.

4 G. A. Ardizzoia, M. Angaroni, G. La Monica, N. Masciocchi, and M. Moret, *J. Chem. Soc., Dalton Trans.*, 1990, in the press.

5 P. Chaudhuri, D. Ventur, K. Wieghardt, E. M. Peters, K. Peters, and A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 58.

6 L. H. Jones, *J. Chem. Phys.*, 1954, **22**, 217.

7 D. M. Adams and P. J. Cook, *J. Chem. Soc. (A)*, 1971, 2801.

8 (a) M. Falk and O. Knop, *Can. J. Chem.*, 1977, **55**, 1736; (b) G. H. Thomas, M. Falk, and O. Knop, *ibid.*, 1974, **52**, 1029.

9 Q. Chen, S. Liu, and J. Zubieta, *Inorg. Chem.*, 1989, **28**, 4434.

10 Q. Chen, S. Liu, and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1987, **27**, 1724.

11 H. Hartl and F. Mahdjour-Hassan-Abadi, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 378.

12 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1983, 1156.

13 J. R. Carruthers, K. Prout, and F. J. C. Rossotti, *Acta Crystallogr., Sect. B*, 1975, **31**, 2044.

14 J. Galy, A. Mosset, I. Grenthe, I. Puigdomènech, B. Sjöberg, and F. Hultén, *J. Am. Chem. Soc.*, 1987, **109**, 380.

15 (a) T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Crystallogr., Sect. B*, 1970, **26**, 2096; (b) D. L. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1974, **13**, 1013; (c) E. D. Estes, W. E. Hatfield, and D. J. Hodgson, *ibid.*, 1974, **13**, 1654; (d) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *ibid.*, 1972, **11**, 2216; (e) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 1970, 904; (f) B. N. Figgis, R. Mason, A. R. P. Smith, J. N. Varghese, and G. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 703.

16 (a) G. Marongiu and E. C. Lingafelter, *Acta Crystallogr., Sect. B*, 1982, **38**, 620; (b) L. K. Thompson, *Can. J. Chem.*, 1983, **61**, 57; (c) L. K. Thompson, A. W. Hanson, and B. S. Ravaswamy, *Inorg. Chem.*, 1984, **23**, 2459; (d) S. K. Mandal, T. C. Woon, L. K. Thompson, M. J. Newlands, and E. G. Gabe, *Aust. J. Chem.*, 1986, **39**, 1007; (e) L. K. Thompson, F. L. Lee, and E. G. Gabe, *Inorg. Chem.*, 1988, **27**, 39.

17 See for example: I. Tabushi and K. Yamamura, *Top. Curr. Chem.*, 1983, **113**, 145; Y. Murakami, *ibid.*, 1983, **115**, 107, and references therein.