A Novel Macrocyclic Binuclear Copper(II) Complex Exhibiting a Metal–Metal Interaction

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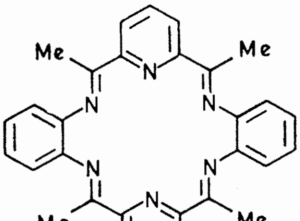
Summary The reaction between 2,6-diacetylpyridine and *o*-phenylenediamine yields a hexadentate macrocyclic ligand that forms a binuclear copper(II) complex exhibiting a metal–metal interaction.

WITHIN the past eight to ten years that branch of co-ordination chemistry involving the synthesis of transition-metal complexes with macrocyclic ligands has grown markedly,[1] as has the interest in the synthesis and study of compounds containing metal–metal bonds.[2] We now report what we believe to be the first example of a complex containing two metal ions brought into juxtaposition by a macrocyclic ligand so as to promote metal–metal interaction.



(I)

The ligand 6,12,19,25-tetramethyl-7,11:20,24-dinitrilo-dibenzo[*b*,*m*][1,4,12,15]tetra-azacyclodocosine (tmcd) (I) is obtained as bright-yellow microcrystalline needles from the acid-catalysed Schiff base condensation of 2,6-diacetylpyridine with *o*-phenylenediamine in n-butanol. The macrocyclic ligand is obtained in good yield (40—45%) and high purity provided that dilute reactant solutions and catalytic amounts of sulphuric acid are used in the synthesis. The ligand can be sublimed without decomposition at 300°/1 mm. It was characterized by its elemental analysis and mass spectrum, *m/e* 471.

The binuclear copper(II) complex of the ligand was prepared both by the direct reaction of hydrated copper(II) nitrate with the free base in absolute ethanol and by the "template" (*in situ*) method in absolute methanol. Analytical, i.r., magnetic susceptibility, and m.s. data indicate that the two methods yield the same product.

Conductance data and the i.r. spectrum of the complex support its formulation as $[Cu_2(tmcd)](NO_3)_4$. An intense unsplit absorption at 1390 cm^{-1} observed both in the KBr pellet and Kel-F oil mull spectra is assigned to the asymmetric N–O stretching vibration of the nitrate ion, and is characteristic of unco-ordinated nitrate.[3] A plethora of ligand absorptions prevented assignment of other i.r.-active nitrate absorptions. The pyridyl groups are co-ordinated in an equivalent manner as reflected by the absence of multiple absorptions in the 1600 and 400 cm^{-1} regions.

The near i.r., visible, and u.v. spectrum of $[Cu_2(tmcd)](NO_3)_4$ is distinguished by a strong absorption starting in the near i.r. region and continuing into the u.v. region. This strong absorption gives rise to the characteristic dark-brown to black colour of the complex. It also precluded the observation of any characteristic copper *d–d* transitions.

A Framework Molecular Model of $[Cu_2(tmcd)](NO_3)_4$ indicated that the copper–copper distance should approximate that found in the acetate dimer, 2·64 Å.[3] On this basis an equivalent magnetic interaction was expected.[4] Although the magnetic moment of the complex is 1·80 B.M. at ambient temperature, the moment falls to 1·40 B.M. at 96·8K; the magnetic susceptibility data, obtained between 393·6 and 96·8K, follow the Curie–Weiss law reasonably well down to *ca.* 150K, below which an increasing positive deviation is noted. The straight line portion of the plot yields a Weiss constant of *ca.* 32°. These data are taken to be an indication of a weak metal–metal interaction. Further support for this conclusion is found in the narrowing of the e.s.r. resonance as the temperature is decreased both for a solid sample and for a solution sample of the complex. It is interesting to note that a rejection of metal–metal bonding would lead to the very unusual co-ordination number of three for copper(II).

We could not obtain sufficiently low temperatures to determine a Neel temperature experimentally. However, one was estimated using the "Bleany–Bowers" equation.[5] By substituting a g value of 2·11 (determined from the e.s.r. spectrum of the complex) and a value for the exchange integral, J, of 23 cm^{-1} (calculated from the experimentally-obtained molar susceptibilities) a Neel temperature of *ca.* 50K is predicted.

Travis and Busch[6] have recently reported the synthesis of two binuclear nickel(II) complexes of an octadentate thioether macrocyclic ligand, the first examples of a macrocyclic ligand sufficiently large to circumscribe two metal ions. In this case, however, no evidence for a metal–metal interaction is reported.

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[1] D. H. Busch, *Helv. Chim. Acta., Fasciculus Extraordinorius,* Alfred Werner, 1967, M4; N. F. Curtis, *Coordination Chem. Rev.*, 1968, **3**, 3.

[2] P. W. Ball, *Coordination Chem. Rev.*, 1969, **4**, 361.

[3] C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 1960, 613.

[4] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 1956, 3637.

[5] B. Bleany and K. D. Bowers, *Proc. Roy. Soc.*, 1952, 451.

[6] K. Travis and D. H. Busch, *Chem. Comm.*, 1970, 1041.