Two-metal–Substrate Interactions: the Reversible Reaction of a Cu^{I} ...... Cu^{I} Complex with CO and O_2

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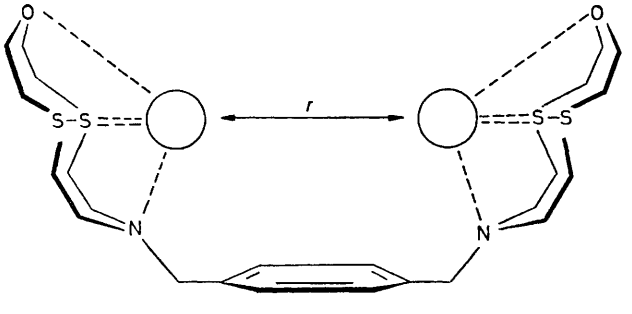
Summary The bi-metallic complex $[LCu_2]^{2+}$ ($L = C_{24}H_{40}N_2O_2S_4$) reacts reversibly with carbon monoxide and molecular oxygen.

THE preparation of complexes which contain two transition metal ions separated by distances of 3·5—6 Å, preferably without bridging ligands, would be of considerable interest. At these distances no direct interaction between the ions is expected, yet a substrate could interact simultaneously with both ions. Activation in multisite interactions has analogy in surface and cluster chemistry, and further, it seems probable such interactions may be present in several metalloprotein systems; *e.g.*, haemocyanin ($Cu^{I}\cdots O_2\cdots Cu^{I}$), hemerythrin ($Fe^{II}\cdots O_2\cdots Fe^{II}$), and perhaps nitrogenase. In view of the recent interest in cyclic polythioether–copper complexes[1] as models for certain oxidase enzymes, we report our studies on bi-metallic copper complexes.

The ligand (L), 1,4-bis-(1-oxa-4,10-dithia-7-azacyclododecan7-ylmethyl)benzene, was prepared by the usual methods,[2] and was fully characterized. Molecular models show that for the preferred ear-muff conformation (Figure) the metal ions are separated by 3·5—5 Å; the ligand provides conformational flexibility in the desired range. The ligand donor set (NOS_2) was chosen as a model for the possible copper environment in haemocyanin.[3] Accordingly, both copper(I) and copper(II) complexes were prepared.

Slow addition of L in butan-2-one to a solution of $[Cu(MeCN)_4][BF_4]$ in butan-2-one at 45 °C under argon (Cu : L = 2 : 1) gave the white crystalline complex $[LCu^{I}_2][BF_4]_2$·butan-2-one, (**1**). The diamagnetic complex was characterized by elemental analysis, and ^1H and ^{13}C n.m.r. spectroscopy. Solutions of (**1**) in $MeNO_2$ are transparent in the visible region.



FIGURE

$Cu(BF_4)_2$ [from dehydration of $Cu(BF_4)_2\cdot 6H_2O$] was combined in $MeNO_2$ with L (Cu : L = 2 : 1) at 25 °C under argon to give a dark green-blue solution. Concentration of the solution, and introduction of tetrahydrofuran (THF), gave the dark green powder $[LCu^{II}_2][BF_4]_2\cdot 2THF$, (**2**).

The complex shows normal paramagnetism (μ_{eff} *ca.* 2 B.M.) and an e.s.r. spectrum with $g_{\text{av.}} = 2{\cdot}08$. The absorption spectrum in $MeNO_2$ shows bands at 600 (ϵ *ca.* 1100) and 390 nm (ϵ *ca.* 2800) [*cf.* haemocyanin from *octopus vulgaris* with absorptions at 580 (ϵ *ca.* 500) and 347 nm (ϵ *ca.* 8900)].

A $MeNO_2$ solution of (**1**) treated with CO rapidly gave the carbonyl adduct (ν_{CO} *ca.* 2070 cm^{-1}). This complex reversibly lost CO on sweeping the solution with argon at 80 °C. Absorption of CO by (**1**) also occurred in the solid state to give the same adduct. Similarly (**1**) reacted with molecular oxygen in the solid state at 80 °C (or more slowly at 25 °C) to give a pale green powder (**3**). The e.s.r. spectrum of (**3**) yields values of $g_{\parallel}$ *ca.* 2·22 and $g_{\perp}$ at 2·05, with fine structure indicating $A_{\parallel}$ *ca.* 75 G. The reflectance spectrum of (**3**) shows broad bands centred at *ca.* 390 and 600—680 nm. On heating (**3**) *in vacuo* at 110 °C, the colour reverted to white with concomitant loss of the e.s.r. signal indicating a return to the Cu^{I} state. This oxygenation–deoxygenation sequence can be repeated several times with little noticeable decomposition in the starting material. In solution, however, the oxygenation of (**1**) is more complicated. In $MeNO_2$ solutions at 80 °C, a blue-green solution was produced with maxima at both 580 (ϵ *ca.* 300) and 680 nm (ϵ *ca.* 300). The e.s.r. spectra of such solutions (frozen) are similar to, but not identical to, those of (**2**). Moreover, reversibility of the oxygenation in such solutions has not yet been observed.

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[1] T. E. Jones, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1975, **97**, 7845; E. R. Dockal, T. E. Jones, W. F. Sokol, R. J. Engerer, D. B. Rorabacher, and L. A. Ochrymowycz, *ibid.*, 1976, **98**, 4322; M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.

[2] See D. Black and I. McLean, *Austral. J. Chem.*, 1971, **24**, 1401, for the synthesis of the NOS_2-cycle. Addition of the NOS_2-cycle to terephthaloyl chloride followed by the reduction of the resultant diamide with $BH_3{\cdot}THF$ gave L.

[3] See F. Ghiretti in 'Physiology and Biochemistry of Haemocyanins,' Academic Press, New York, 1968.