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The Role of Halide Ligands in Copper(I) Carbonyl Chemistry: Synthesis of Monohalogen-bridged Dinuclear Copper(I) Carbonyls, and *X*-Ray Crystal Structure of $[Cu_2(Me_2NCH_2CH_2NMe_2)_2(CO)_2Cl](BPh_4)$

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Summary Reaction of copper(I) halides, CuX (X = Cl, Br, or I), with carbon monoxide in MeOH in the presence of *NNN'N'*-tetramethylethylenediamine (tmen) produces dinuclear copper(I) carbonyls, $[Cu_2(tmen)_2(CO)_2X]^+$, ν_{CO} *ca.* 2070 cm^{-1}; the structure of the chloro-derivative, $[Cu_2(tmen)_2(CO)_2Cl](BPh_4)$, has been determined by *X*-ray crystallography which shows that the two copper atoms in the molecule are bridged by a single halogen atom and the molecule contains a bent Cu–Cl–Cu unit with an angle of 103·0(1)°.

There are no reports in the literature on the structure of halogeno-carbonyls of group IB metals,[1,2] in particular those of copper(I), which is by far the most versatile metal to bind carbon monoxide. While the absorption of CO by copper(I) halides depends on the nature of the halogen, a definite bonding mode has not yet been proposed for the halide ligand which is believed to be present in several cases as a non-co-ordinating counter-anion.[1] We report the synthesis and structural characterisation of complexes containing the OC–Cu–X–Cu–CO framework which are relevant to both multisite copper(I)-promoted molecular activations,[3] and to carbonyl chemistry in general, where the metal atoms rarely appear in pairs with the two metal centres bridged by a single halogen atom.[4]

CuI and Cu(CO)Cl react in methanol in a carbon monoxide atmosphere with polydentate primary amines to give stable copper(I) carbonyls which do not contain halide ligands.[5] However, when in the same reaction CuX (X = Cl, Br, or I) and *NNN'N'*-tetramethylethylenediamine (tmen) are employed, the addition of $NaBPh_4$ to the carbonylated solution gives complexes (**1**), as white crystalline solids [equation (1)].† While polyamines bearing primary amino-groups give halide free copper(I) carbonyls,[5] the use of sterically hindered ligands, *e.g.* tmen, allows the halogen atom to remain in the complex. The complexes (**1**) are thermally stable and do not lose CO in the solid state. The CO stretching frequency falls in the range expected for tetraco-ordinate copper(I)[5] [ν_{CO} (Nujol): X = Cl, 2065 cm^{-1}; X = Br, 2060 cm^{-1}; and X = I, 2060 and 2070 cm^{-1}] and is independent of the nature of the halogen atom. The structure of $[Cu_2(tmen)_2(CO)_2Cl](BPh_4)$, sealed under N_2 in a Lindeman capillary tube, has been determined by *X*-ray crystallography.

$$\begin{array}{c} 2\,\mathrm{CuX} + 2\,\mathrm{tmen} + 2\,\mathrm{CO} \\ \mathrm{NaBPh_4}\ \Big\downarrow\ -\mathrm{NaX} \\ [(\mathrm{tmen})(\mathrm{CO})\mathrm{Cu{-}X{-}Cu}(\mathrm{CO})(\mathrm{tmen})](\mathrm{BPh_4}) \\ \mathbf{(1)} \end{array} \qquad (1)$$

Crystal data: $C_{38}H_{52}BClCu_2N_4O_2$, M = 770·2, triclinic, a = 14·179(2), b = 15·525(2), c = 9·399(1) Å, α = 82·49(2), β = 89·19(2), γ = 80·06(2)°, U = 2020·0 Å^3, Z = 2, D_c =

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† Satisfactory elemental analytical data were obtained for the three compounds reported.

1·266 g cm^{-3}, space group $P\bar{1}$. Intensity data ($6 < 2\theta < 140°$) were recorded on a Siemens AED computer-controlled diffractometer, with Ni-filtered Cu-K_α radiation. 7662 independent reflections were collected, 5969 of which [$I > 2\sigma(I)$] were used in the analysis. The structure was solved by heavy-atom method and refined by full-matrix least-squares techniques[6] with anisotropic thermal parameters for all non-hydrogen atoms. The final R index is 6·1%.‡

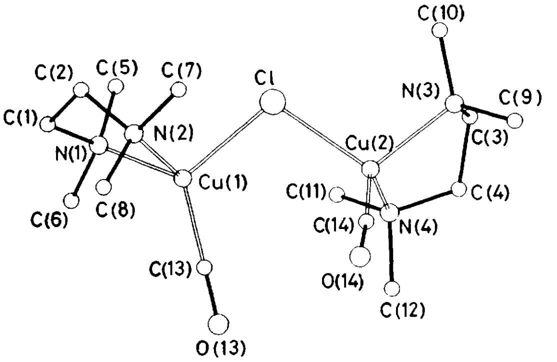

FIGURE. The structure of $[Cu_2(tmen)_2(CO)_2Cl]^+$. Bond distances are: Cu(1)–N(1), 2·081(3); Cu(1)–N(2), 2·112(3); Cu(1)–C(13), 1·786(5); C(13)–O(13), 1·134(7); Cu(1)–Cl, 2·348(2); Cu(2)–Cl, 2·308(2); Cu(2)–C(14), 1·757(5); C(14)–O(14), 1·148(7); Cu(2)–N(3), 2·104(4); Cu(2)–N(4), 2·102(3); and Cu(1) · · · Cu(2), 3·643(2) Å; bond angles are: Cu(1)–C(13)–O(13), 179·8(5); Cu(2)–C(14)–O(14), 176·4(5); and Cu(1)–Cl–Cu(2), 103·0(1)°.

The crystals are built of dinuclear cations $[Cu_2(tmen)_2(CO)_2Cl]^+$ and BPh_4^- anions. The Figure shows a view of the cation and some bond distances and angles. The two copper atoms, with pseudo-tetrahedral geometries, are bridged by a chlorine atom. The co-ordination sphere around each copper is completed by a chelating tmen and a carbon monoxide molecule. The OC–Cu–Cl–Cu–CO framework in the cation is of particular interest. Cu–C distances are short in conjunction with rather long C–O bond lengths.[5] The rather long Cu–Cl bond distances agree well with those in other double-[7] and single-[8] bridged dinuclear copper(I) complexes. These values, along with the Cu–Cl–Cu angle [103(1)°], suggest that the Cu–Cl–Cu linkage may be described simply in terms of localised electron-pair Cu–Cl σ-bonds.

A monohalogen-bridged dinuclear metallic unit was identified in $[Cr_2(CO)_{10}I]^-$, where the bridging iodide ligand can be replaced by a wide range of different ligands.[4] The relative orientation of the two CO groups is staggered with a torsion angle around the Cu–Cu of 53·2°. The Cu–Cu distance of 3·643(2) Å rules out direct metal–metal interaction.[9]

The presence of two copper(I) atoms, > 3·5 Å apart, is of considerable interest in molecular activation processes, since a substrate could interact simultaneously with both metal ions, with displacement of carbon monoxide;[2,8] similar interactions are likely to occur in some haemocyanins.[10]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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