Synthesis and X-Ray Structure of Bis(diethyldithiocarbamato)(μ-dichloro)-dicopper(II), $Cu_2(Et_2dtc)_2Cl_2$, and the X-ray Structure of $Cu_3(Et_2dtc)_2Cl_3$, an Unusual Mixed Valence Cu^{II}/Cu^{I} Reduction Product

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Summary The preparation and crystal structure of the dimeric chloro-bridged copper(II) dithiocarbamate complex, $Cu_2(Et_2dtc)_2Cl_2$, are described, together with the crystal structure of a related minor product, $Cu_3(Et_2dtc)_2Cl_3$, which proves to be an unusual mixed valence Cu^{II}/Cu^{I} polymer.

We are examining the possibility of the systematic synthesis of polynuclear metal complexes which exhibit magnetic exchange by using co-ordinatively unsaturated metal dithiocarbamate species such as $[Co(R_2dtc)_2]^+$ and $[Cu(R_2dtc)]^+$.[1] As a possible precursor to this latter species, we have prepared and structurally characterised the polynuclear complex $Cu_2(Et_2dtc)_2Cl_2$, (I).

$Cu(Et_2dtc)_2$ (0·89 g) in benzene (150 ml) and $CuCl_2 \cdot 2H_2O$ (0·43 g) in EtOH (50 ml) react smoothly at reflux temperature to afford dark crystals of (I) of empirical formula $Cu(Et_2dtc)Cl$,† which could not be recrystallised without decomposition.

Golding *et al.*[2] have reported that copper bromide, in a similar reaction in chloroform at room temperature, is reduced, yielding mixed valence complexes of the type $Cu(R_2dtc)_2(CuBr)_n$, $n = 4, 6$. The crystal structures show that these complexes consist of individual $Cu(R_2dtc)_2$ molecules linked *via* bridging ligand sulphur atoms to polymeric CuBr chains and are fundamentally different to the complexes described below.

Crystals of (I) are monoclinic, $a = 11{\cdot}203(1)$, $b = 18{\cdot}989(2)$, $c = 9{\cdot}043(2)$ Å, $\beta = 98{\cdot}83(1)^\circ$, space group $P2_1/n$, $D_m = 1{\cdot}74$, $D_c = 1{\cdot}73\ \mathrm{g\ cm^{-3}}$ for $Z = 4$. Intensity data

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† Satisfactory elemental analyses were obtained for this compound.

were collected on a Picker FACS-I diffractometer using graphite crystal monochromated Cu-K_α radiation. The structure was solved using the MULTAN direct methods programme and refined by block-diagonal least-squares on 2204 reflections with $I \geqslant 3\sigma(I)$ which had been corrected for absorption ($\mu = 92{\cdot}1\ \mathrm{cm}^{-1}$) to a current R factor of 0·061. The molecular structure is shown in Figure 1.

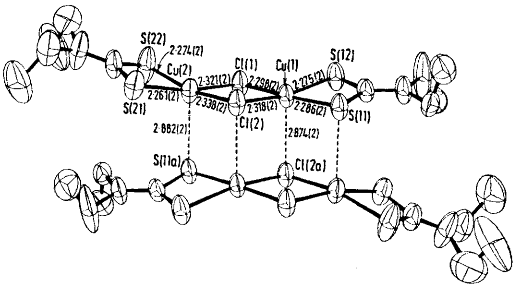

FIGURE 1. The structure of $Cu_2(Et_2dtc)_2Cl_2$.

The complex consists of symmetrical chlorobridged dimers, $Cu_2(Et_2dtc)_2Cl_2$, weakly associated through inter molecular Cu–Cl (2·874 Å) and Cu–S (2·882 Å) interactions to form discrete centrosymmetric tetrameric units. The Cu(1)–Cu(2) distance is 3·348(1) Å. Each copper atom is essentially five-co-ordinate (square-based pyramid) as is also found in the structure of the parent $Cu(Et_2dtc)_2$.[3]

X-ray examination of a number of crystals from the bulk sample of (I) fortuitously revealed one crystal of different cell dimensions. Subsequent structural analysis has shown the composition of this crystal to be $Cu_3(Et_2dtc)_2Cl_3$, (II). The crystal was monoclinic, $a = 12{\cdot}401(1)$, $b = 15{\cdot}733(1)$, $c = 11{\cdot}564(1)$ Å, $\beta = 101{\cdot}50(1)°$, space group $P2_1/n$ with $Z = 4$. At present, refinement has reached an R value of 0·036 for 2959 independent, absorption corrected ($\mu = 100{\cdot}54\ \mathrm{cm}^{-1}$) observed reflections.

This complex (Figure 2) is polymeric with centrosymmetric $Cu_2(Et_2dtc)_2Cl_2$ dimers and centrosymmetric $Cu_4(Et_2dtc)_2Cl_4$ molecules linked by Cu–S bonds in an alternating linear sequence. The geometry of the dimeric fragment is very similar to that observed in (I). The tetrameric unit, however, is a novel mixed valence Cu^{II}/Cu^{I} cluster. Cu(3) has a typical elongated, square-pyramidal stereochemistry of the d^9 Cu^{II} species,[3] [*cf.*, copper stereochemistry in structure (I)], whereas the tetrahedral geometry around Cu(2) is well-defined and consistent with the d^{10} Cu^{I} configuration.

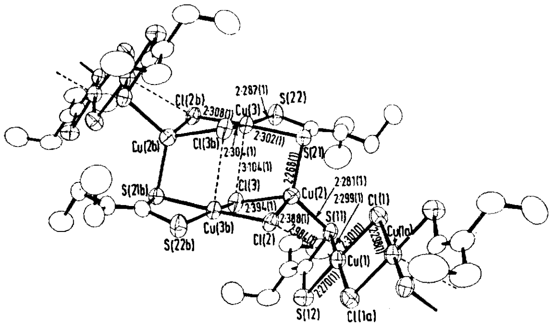

FIGURE 2. The structure of polymeric $Cu_3(Et_2dtc)_2Cl_3$.

The formation of this mixed valence tetrameric unit from complex (I) is easily visualised. The reduction of two centrosymmetrically related copper atoms in the tetrameric unit of (I), perhaps with concomitant oxidation and loss of the terminal $[Et_2dtc]^-$ ligands co-ordinated to these copper atoms, allows the closer approach of Cu(2) to S(21) (*cf.*, Figures 1 and 2). The tetrahedral co-ordination geometry of Cu(2) is completed by co-ordination of a ligand sulphur atom of a $Cu_2(Et_2dtc)_2Cl_2$ dimer. The copper–copper distances are Cu(1)–Cu(1)^a, 3·267(1); Cu(1)–Cu(2), 3·100(1); Cu(2)–Cu(3), 3·239(1); Cu(2)–Cu(3)^b, 3·171(1) Å.

Further studies are being undertaken to isolate and characterise other minor reduction products and to establish synthetic routes to unusual and interesting complexes such as (II) which possess the possibility of exhibiting anisotropic electrical and magnetic properties.

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