$(PPh_4)_2(ReS_4)Cu_4I_5$, a Compound with a Novel One-dimensional Polymeric Anion

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The black compound $(PPh_4)_2(ReS_4)Cu_4I_5 \cdot MeCN$, containing a polymeric heterometallic chain with very short Re–Cu distances [2.638(4)–2.712(4) Å] and the metal centres in very different formal oxidation states (VII, I), is formed by the reaction of $(PPh_4)ReS_4$ with CuI and $(PPh_4)I$, and structurally characterized by *X*-ray diffraction.

After the isolation of $[Ni(WS_4)_2]^{2-}$,[1] the first discrete thiometallato complex, the related co-ordination chemistry stimulated the interest of many research groups (ref. 1b), by virtue of its importance for bioinorganic chemistry[2] and heterogeneous catalysis.[3]

Black diamagnetic $(PPh_4)_2(ReS_4)Cu_4I_5 \cdot MeCN$ (**1**) is formed by reaction of $(PPh_4)ReS_4$[4] with CuI and $(PPh_4)I$ in MeCN under argon. Compound (**1**) was characterized by elemental analysis, IR spectroscopy, and complete *X*-ray structure analysis. The IR spectrum of (**1**) (solid, CsI pellet) shows absorptions at 488m $\nu[Re\text{–}(\mu_2\text{-}S)]$, 449m $\nu[Re\text{–}(\mu_3\text{-}S)]$, and 421m $\nu_{as}[Re\text{–}(\mu_4\text{-}S)]$ cm^{-1}. (Owing to the high mass of the Re atom and the significantly different Re–S distances the vibrations are relatively characteristic.)

The structure of the polymeric anion is shown in Figure 1.† The anion forms a polymeric chain along the crystallographic *a*

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† *Crystal data for* (**1**): $C_{50}H_{43}Cu_4I_5NP_2ReS_4$, $M = 1923.0$, orthorhombic, space group $P2_12_12_1$; $a = 7.255(1)$, $b = 25.477(5)$, $c = 30.982(5)$ Å, $U = 5726.2$ Å^3, $Z = 4$; $D_c = 2.23$ g cm^{-3}; $\mu = 65.0$ cm^{-1} for Mo-K_α radiation ($\lambda = 0.71069$ Å). The structure was solved by Patterson interpretation. Phenyl rings were refined as regular hexagons, H atoms of the acetonitrile could not be localized. $R = 0.071$ for 4431 unique reflexions [$F_0 > 3.92\sigma(F_0)$] measured on a Syntex $P2_1$ diffractometer. Absolute configuration: $\eta = 1.00(5)$ (*cf.* D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734). 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.

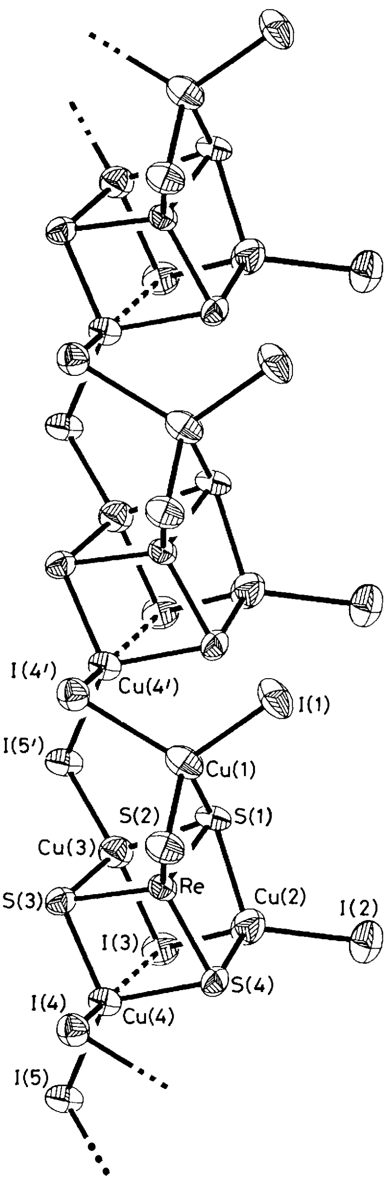

Figure 1. Structure of the polymeric chain in (**1**). Interatomic distances (Å, a prime indicates atoms translated by +1 along the crystallographic *a* axis): Re–Cu 2.638(4)—2.712(4), Re–S 2.170(7)—2.245(7), Cu–I 2.495(4)—2.773(4), Cu(4) · · · I(3) 4.075(7), Cu–S 2.292(9)—2.398(8); bond angles (°): S–Re–S 108.4(3)—110.2(3), I–Cu–I 104.9(1)—116.8(2), I–Cu–S 97.6(2)—121.6(2), S–Cu–S 100.4(3)—103.4(3), Cu–I–Cu 70.0(1)—97.8(1), Re–S–Cu 71.4(2)—74.3(3), Cu–S–Cu 82.5(3)—135.4(3).

axis and can be thought of as built up from corner-sharing of $(ReS_4)Cu_4I_5$-'units' (Figure 1) *via* I(4) and I(5), which are the corners of two CuI_2S_2 tetrahedra [bond angles 97.6(2)—121.6(2)°]. Discrete species of that type are unknown, although in principal the anion $[(ReS_4)Cu_4I_5]^{2-}$ could exist, because all atoms are co-ordinatively saturated. The edge- and corner-sharing ReS_4 tetrahedra have bond angles of 108.4(3)—110.2(3)° and the Re–Cu distances are in the range 2.638(4)—2.712(4) Å. Two Cu_2I_2 tetrahedra additionally share a common edge.

Especially interesting is the variety of the co-ordination types of the S atoms [S(2) is twofold, S(3) and S(4) are threefold co-ordinated, and S(1) has the co-ordination number 4, which is rare for sulphido ligands] and the fact that strongly distorted cubes are connected in the chain.

Though the number of ReS_4^- complexes is very small,[5] it is possible to state that the ligand shows a significantly different co-ordination chemistry compared to MoS_4^{2-} and WS_4^{2-}, which was shown recently by isolation of structurally novel complexes with the ReS_4^- ligand like $[(ReS_4)Cu_5X_7]^{3-}$ (X = Cl, Br; double cubane),[5a] or $[(ReS_4)Cu_4X_6]^{3-}$ (X = Br, I; boat structure).[5b] Among all known complexes of the type $[Cl_2Fe(MS_4)FeCl_2]^{n-}$ (M = V, Mo, W, Re), $[Cl_2Fe(ReS_4)FeCl_2]^{2-}$ is the only 13 electron cluster (see ref. 5a). This reflects the situation that the ReS_4^- ion is the strongest σ-acceptor ligand.[6]

To date, very few examples of heterometallic polymeric anions have been characterized. Known thiometallato species with, for example, a catena-structure are $(PPh_4)_2(MoS_4)Cu_4Br_4$[7] and the isostructural compounds $(PPh_4)M'(MS_4)$ (M' = Fe, Cu, Ag; M = Mo, W) with edge-sharing $M'S_4$ and MS_4 tetrahedra (ref. 3b and 8).

Compound (**1**) contains the two metal centres with very different oxidation states (VII, I) and very short distances. In spite of the closed shells of the metal centres there is certainly a strong interaction of the Cu centres with the thiometallate ligand (ref. 6).

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