$[NPr^n_4]_2[(ReS_4)Cu_5I_6]$ and $[NEt_4]_2[(ReS_4)Cu_3I_4]$: Novel Low Dimensional Solids

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The compounds $[NPr^n_4]_2[(ReS_4)Cu_5I_6]$ **1** and $[NEt_4]_2[(ReS_4)Cu_3I_4]$ **2**, containing polymeric heterometallic chains and interesting structural features according to X-ray structure analyses, have been obtained by reaction of CuI with $[NPr^n_4][ReS(S_4)_2]$ in dichloromethane **1** or $[NEt_4][ReS_4]$ **2** in acetone; complexes **1** and **2** are examples of a series of compounds which prove the possibility of a stepwise 'capping' of the edges of an ReS_4 tetrahedron by a $Cu(hal/pseudohal)_x$ fragment (x = 1,2).

It is still a challenge to prepare polymeric species or low-dimensional solids containing different metals. One elegant method is the use of thiometallates as educts. The number of species of this type is still small[1] and only one is known for the $[ReS_4]^-$ anion.[2]

Black crystals of $[NPr^n_4]_2[(ReS_4)Cu_5I_6]$ **1** were obtained in 50% yield by stirring $[NPr^n_4][ReS(S_4)_2]$ (which decomposes to $[ReS_4]^-$), $[NPr^n_4]I$ and CuI in dichloromethane (2.5 h; under argon atmosphere) and leaving the filtered solution in a flask covered with a watch glass for 3–5 days. Refluxing (2.5 h) a

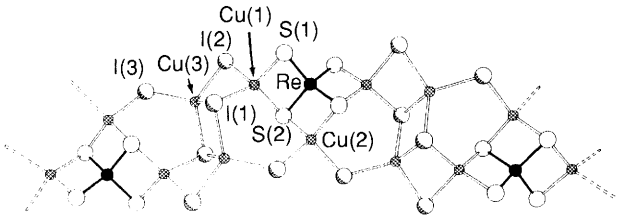

Fig. 1 Structure of the polymeric chain in $[NPr^n_4]_2[(ReS_4)Cu_5I_6]$ **1**. Interatomic distances (Å): Re···Cu 2.674(1), 2.678(2), Re–S(1) 2.148(4), Re–S(2) 2.205(2), Cu–S 2.273(3)–2.283(4), Cu(3)–I(1) 2.854(1), (others:) Cu–μ_3-I 2.659(2), 2.662(2), Cu–μ_2-I 2.592(3)–2.647(1); bond angles (°): S–Re–S 109.2(1)–109.6(2), I–Cu–I in four-membered rings 92.7(1)–103.3(1), other I–Cu–I 103.0(1)–126.8(1), I–Cu–S 107.9(1)–120.9(1), S–Cu–S 102.7(2)–104.2(1), Cu–I–Cu in four-membered rings 68.6(1)–87.3(1), (others:) Cu–I–Cu 95.8(1), 109.1(1), Re–S–Cu 73.1(1)–74.5(1), Cu–S–Cu 110.8(1).

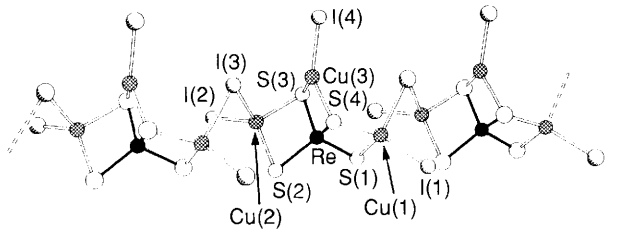

Fig. 2 Structure of the polymeric chain in $[NEt_4]_2[(ReS_4)Cu_3I_4]$ **2**. Interatomic distances (Å): Re···Cu 2.614(4)–2.685(4), Re–μ_2-S 2.158(6), 2.170(7), Re–μ_3-S 2.216(5), 2.224(6), Cu–I_{term} 2.452(4)–2.532(4), Cu–μ_2-I 2.721(4), 2.862(4), Cu(1)–S, Cu(2)–S 2.276(7)–2.316(7), Cu(3)–S 2.253(6), 2.259(6); bond angles (°): S–Re–S 106.9(2)–111.5(2), I–Cu–I 106.9(1), 108.1(1), I–Cu(1)–S, I–Cu(2)–S 100.6(2)–122.6(2), I–Cu(3)–S 123.6(2), 126.0(2), S–Cu–S 101.7(2)–107.0(2), Cu–I–Cu 89.8(1), Re–S–Cu 71.4(2)–73.8(2), Cu–S–Cu 93.6(2), 103.4(3).

mixture of $[NEt_4]I$ and CuI in acetone and stirring of the filtered mixture with $[NEt_4][ReS_4]$[3] (15 min) leads to the formation of black crystals of $[NEt_4]_2[(ReS_4)Cu_3I_4]$ **2** in 67% yield after leaving the filtered solution in a flask covered with a watch glass for 8–10 days.

Complexes **1** and **2** have been characterized by elemental analysis, IR spectroscopy† and complete X-ray structure analysis.‡ The structures of the polymeric anions in **1** and **2** are shown in Figs. 1 and 2. The most important bond lengths and angles characterizing the geometry of the building blocks, for instance the constitutional tetrahedra, are given in the legends. The IR data† allow Re–μ_2-S and Re–μ_3-S units to be distinguished easily.[4]

The anion in **1** can formally be described as an infinite double chain, composed of (strongly) distorted CuI_4 tetrahedra sharing edges or corners, whereby every sixth CuI_4 tetrahedron is replaced by a rather regular ReS_4 tetrahedron alternately in the upper and lower strand of the double chain. On the other hand in the compounds $(cat)Cu_2I_3$ (cat = Cs, Rb, NC_6H_8, SMe_3),[5] which also contain double chains, the CuI_4 tetrahedra only share edges. In **1** the 'capping' of three edges (n_e = 3) of the ReS_4 tetrahedron occurs by CuI_2 fragments.

The same value n_e is found in the polymeric anion of **2**, where the 'capping' of three edges of the ReS_4 tetrahedron by

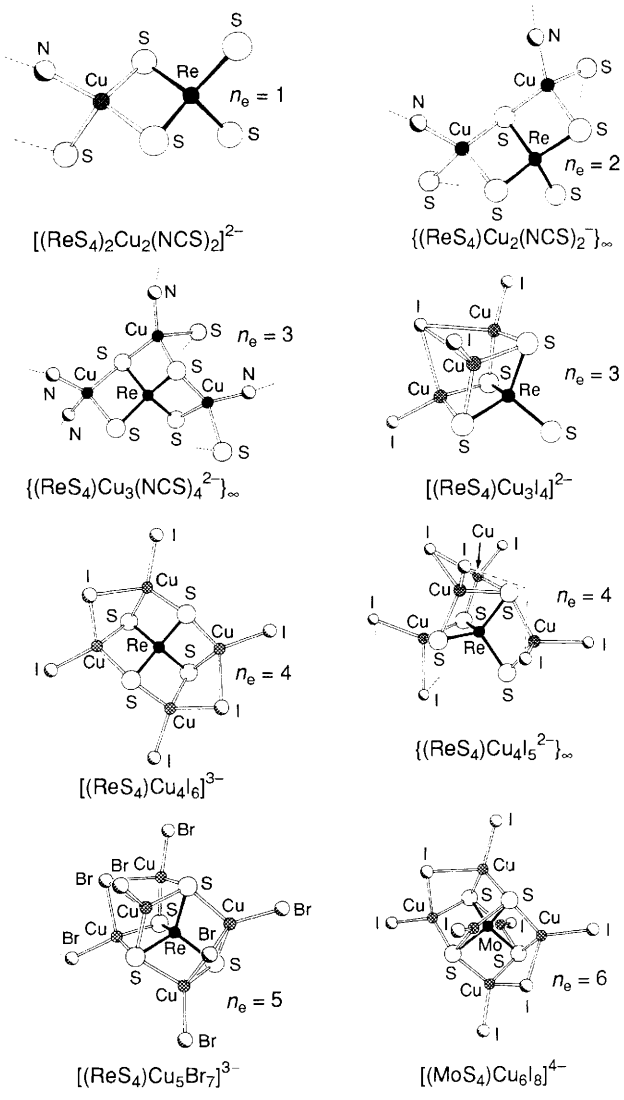

Fig. 3 Central basic structures demonstrating the stepwise 'capping' of the edges of an ReS_4 tetrahedron (n_e = number of capped edges) as found in the following compounds with their characteristic structural features of the anions mentioned in brackets: $[PPh_4]_2[(ReS_4)_2Cu_2(NCS)_2]$[7] {eight-membered $Cu(NCS)_2Cu$ ring system and two terminal $[ReS_4]^-$ ligands}; $[PPh_4][(ReS_4)Cu_2(NCS)_2]$[7] (polymeric chain containing twelve-membered ring systems); $[NEt_4]_2[(ReS_4)Cu_3(NCS)_4]$[7] (polymeric chain containing twelve- and sixteen-membered ring systems); $(cat)_2[(ReS_4)Cu_3X_4]$[3,8] {cubane-type structure; cat = NPr^n_4, X = Cl; cat = $[PPh_4]$, X = I}; $[NEt_4]_3[(ReS_4)Cu_4X_6]\cdot n CH_2Cl_2$[9] (boat structure; X = Br, n = 0.5; X = I, n = 1); $[PPh_4]_2[(ReS_4)Cu_4I_5]\cdot MeCN$[2] (polymeric chain containing cubane-type units); $[PPh_4]_2[NEt_4][(ReS_4)Cu_5X_7]$[3,10] (distorted double-cubane structure; X = Cl, Br); $[PPh_4]_4[(MoS_4)Cu_6I_8]\cdot 4Me_2CO$ {unpublished, given only for completeness as no corresponding Re compound with n_e = 6 is known; see also the structure of the compound $[(VS_4)Cu_6(PPh_3)_5Cl_3]\cdot CH_2Cl_2$[11]}.

† Selected IR data (Nujol mull) in cm^{-1} for **1**: ν[Re–(μ_2-S)] 480s; ν[Re–(μ_3-S)] 445sh, 438m; **2**: ν[Re–(μ_2-S)] 484m, 470m; ν[Re–(μ_3-S)] 447sh, 439m.

‡ *Crystal data* for **1**: $C_{24}H_{56}Cu_5I_6N_2ReS_4$, M = 1766.2, monoclinic, space group $C2/c$; a = 27.178(5), b = 13.477(2), c = 19.225(3) Å, β = 139.44(1)°, U = 4578.8(13) Å^3, Z = 4; D_c = 2.562 g cm^{-3}; μ = 9.161 mm^{-1}.

For **2**: $C_{16}H_{40}Cu_3I_4N_2ReS_4$, M = 1273.2, monoclinic, space group Cc; a = 7.220(4), b = 24.167(22), c = 19.045(14) Å, β = 97.25(5)°, U = 3297(4) Å^3, Z = 4; D_c = 2.565 g cm^{-3}; μ = 9.591 mm^{-1}.

Data were collected using a Siemens R3m/V diffractometer (Mo-Kα radiation, graphite monochromator). The structures were solved by direct methods. Full-matrix least-squares refinement converged at R values of 0.044 for 4164 unique reflexions [$F_o > 4.0\sigma(F_o)$] for **1** and 0.055 for 3810 unique reflexions [$F_o > 4.0\sigma(F_o)$] for **2**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

different CuI_x fragments (x = 1, 2) generates formally $\{(ReS_4)Cu_3I_4\}$ units, which are connected *via* Cu–I bonds thereby forming heterometallic chains. These can also be described as rather regular ReS_4 (A) and distorted CuI_2S_2 tetrahedra (B) connected in the following way: ···ABBABBA···. The ReS_4 and CuI_2S_2 tetrahedra share edges, whereas the latter are connected by corner sharing. This also corresponds to the bridging of ReS_4 units by chain type $I_{term}CuICuI_{term}$ fragments *via* the two Cu atoms. {In the interesting compound $[PPh_4]_2[(MoS_4)Cu_4Br_4]\cdot Me_2CO$[1c] the $[MoS_4]^{2-}$ anions are bridged by $Cu(\mu_2\text{-}Br)_2Cu$ units.} In this description one further edge of the ReS_4 tetrahedron in **2** is 'capped' by a CuI unit giving rise to a Cu atom in a trigonal environment.

Complexes **1** and **2** are examples of a series of compounds which prove the possibility of a stepwise 'capping' of the edges of an ReS_4 tetrahedron by a $Cu(hal/pseudohal)_x$ fragment (x = 1, 2). Using this method a variety of compounds containing the $[ReS_4]^-$ ion with very different structures (including chain type ones) due to different n_e values (1–5) can be generated (Fig. 3). The corresponding chemistry is different from that of the MS_4^{2-} (M = Mo, W) ions.

The next challenge is to replace closed shell metal centres like Cu^+ by open shell ones (like Fe^{n+}),[6] and that means varying the (important) exchange coupling.

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