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Heterobimetallic Clusters of Copper(I) with $[MS_4^{2-}]$ ($M = Mo, W$). Synthesis and Structural Characterization of Polymeric $(NMe_4)_2[(CuNCS)_4WS_4]$

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Reaction of $(NMe_4)_2WS_4$ with CuCl and KSCN (1 : 2 : 2) in $CH_3CN-CH_2Cl_2$ (1 : 1) produces the bimetallic sulphur anion; a crystal structure determination shows that four edges of the WS_4Cu_4 core are $-NCS-$ bridged giving a three-dimensional polymer.

Recently we reported the synthesis and characterization of a new Cu–W–S species;^{1–3} trinuclear ($n = 2$) and tetranuclear ($n = 3$) $[(CuCl)_nWS_4]^{2-}$ species were obtained, but species with $n = 4$ could not be isolated in a pure crystalline form. We have now found that other neutral Cu^I compounds such as CuSCN can be added to WS_4^{2-} to give pentanuclear ($n = 4$) complexes isolated as a polymer $[(CuNCS)_4WS_4]^\infty$.

$(NMe_4)_2WS_4$ (0.25 mmol), CuCl (0.50 mmol), and KSCN (0.50 mmol) in 50 ml of $CH_3CN-CH_2Cl_2$ (1 : 1) were stirred for 30 min in an Erlenmeyer flask. The orange–yellow solid which precipitated was filtered off. The filtrate was concentrated to ca. 25 ml by rapid evaporation under reduced pressure and ca. 15 ml of diethyl ether was added until a slight cloudiness appeared. After standing at room temperature for 2 days, red crystals were obtained, which were separated by filtration and air dried. The crystals were quantitatively analysed to establish the W : Cu ratio. The complete formula was deduced from the crystallographic results. The compound is insoluble in all usual organic solvents except dimethylformamide (DMF). The analogous compound with Mo was synthesized in a similar manner, but the microcrystalline material obtained was unsuitable for single crystal X-ray work.

The crystal structure of the polymeric anion is shown in Figure 1.† Each tungsten atom of the structure is at the centre

† Crystal data: $C_{12}H_{24}N_6Cu_4S_8W$, $M = 946$, orthorhombic, $a = 15.591(4)$, $b = 15.241(4)$, $c = 12.126(3)$ Å, $U = 2881$ Å³, space group $P2_12_1$, $F(000) = 1824$, $\mu(Cu-K\alpha) = 152$ cm⁻¹. Intensity data were collected on a Philips PW1100 four circle diffractometer with Cu- $K\alpha$ radiation. An absorption correction was applied. The structure was solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least-squares methods to an R value of 0.0408 for 3235 reflections [$2\theta < 156^\circ$ with $F_0 > 6\sigma(F_0)$]. Computer programs were those of SHELX-76 system. All atoms of the anions were refined anisotropically. One of the two crystallographically independent NMe_4^+ cations has disordered methyl groups; all atoms of the cations were assigned isotropic thermal parameters.

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, 1986.

of an essentially tetrahedral WS_4 unit in which the W–S bond lengths are all quite similar. Four copper atoms are bound symmetrically to the WS_4 core with the Cu–S bond lengths ranging from 2.272(3) to 2.327(4) Å. The WS_4Cu_4 aggregate approximates to D_{2d} symmetry. The W \cdots Cu distances

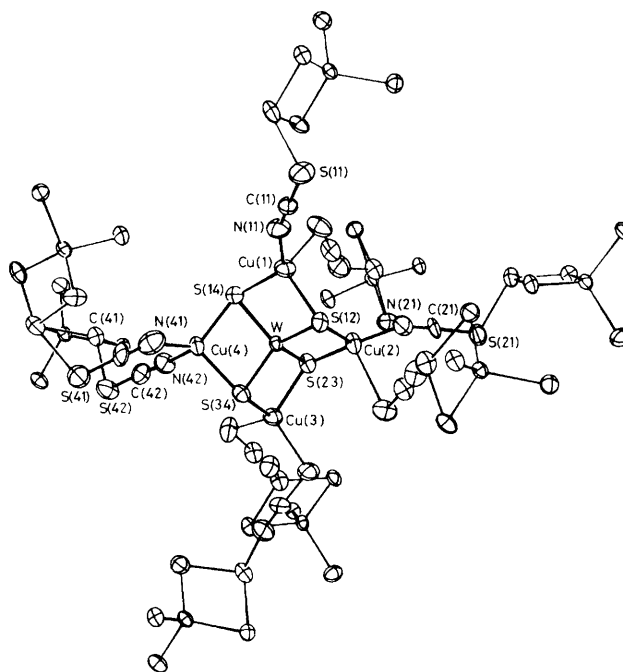


Figure 1. Perspective drawing of a part of the polymeric anion. The crystallographically independent unit with the atom labelling is indicated by thick bonds. For the sake of clarity and owing to the complexity of the polymeric network only the eight different Cu–NCS–Cu WS_4 sequences have been represented. Distances between the nearest copper atoms, 5.588(3) to 6.274(3) Å, distances between the nearest tungsten atoms, 8.4737(4) to 10.7899(7) Å.

(2.674 to 2.739 Å) are longer than the corresponding separations observed in other discrete $(\text{CuCl})_n\text{WS}_4^{2-}$ anions. The four copper atoms have different distorted tetrahedral geometries. Two copper atoms, Cu(1) and Cu(2), have their tetrahedral apices occupied by two bridging sulphur atoms, one nitrogen atom, and one sulphur atom of the two different non-symmetrically-related NCS groups, forming a CuS_3N unit. The co-ordination sphere around Cu(4) leads to a CuS_2N_2 unit (two N-bonded NCS groups and two bridging sulphur atoms) and around Cu(3) to a CuS_4 unit (two S-bonded NCS groups and two bridging sulphur atoms). These tetrahedra are mutually linked by bridging thiocyanate groups thus forming a polymeric three-dimensional anion of basic formula $[(\text{CuNCS})_4\text{WS}_4]^{2-\infty}$. The overall arrangement displays no particular directionality or layering. The 4:1 copper to M (M = Mo, W) stoichiometry is highly unusual and has only previously been observed for molybdenum.⁴

The angles around Cu(1), Cu(2), and Cu(4) [ranging from 91.8(4) to 127.4(4)°] are those of a distorted tetrahedral geometry, but interestingly the angles around Cu(3) (surrounded by only four S atoms) show only slight distortion [105.7(1) to 111.8(1)°] from tetrahedral geometry.

As expected the thiocyanate groups are nearly linear. For N-bonded groups the Cu–N–C angles are almost linear and comparable to those exhibited by complexes with Cu–NCS linkages^{5–12} except for the Cu(4)–N(41)–C(41) angle [146(1)°] which shows a significant deviation. This difference is probably due to the distance between the methyl group of the cation and the N(41) atom [C(211) ··· N(41): 3.22(5) Å] which is 0.28 Å less than the sums of their Van der Waals radii. For the S-bonded mode the Cu–S–C angles are bent with angles ranging from 91(5) to 110.5(6)°. The interatomic distances Cu–S(NCS) [2.333(4) to 2.428(5) Å] are in the range previously reported for tetrahedral copper(i) geometry while the Cu(2)–S(11) bond length [2.662(5) Å] is rather longer than expected. The Cu(2)–N(21) and Cu(1)–N(11) bond lengths compare with other copper(i)–N(NCS) bond lengths in polymeric complexes [1.92(1)–2.01(1) Å]^{5–12} while Cu(4)–N(41) and Cu(4)–N(42) are slightly longer than previously reported values.

In the i.r. spectra of the polymeric complexes, two intense bands are found for the ν_{CN} stretching mode at 2122 and 2087

cm^{-1} for both W and Mo compounds. Weak bands are found in the range 670–900 cm^{-1} and at 747, 764, 776, and 794 cm^{-1} for the W and Mo polymers respectively. These observations, together with the absence of NMe_4^+ absorption bands in this region, are consistent with their assignment as $\nu(\text{C–S})$ stretching bands for the Cu–NCS–Cu bridging mode of co-ordination.^{13,14} The absorption due to the $\delta(\text{NCS})$ deformation mode is located at 470 cm^{-1} for both compounds. Strong bands at 440 (for W) and 450 cm^{-1} (for Mo) are assigned to the bridged MS_4 group. Bands observed at 266(w), 221(w) for the W complex, and 267(w), 218(w) cm^{-1} for the Mo complex could be attributed to $\nu(\text{Cu–N})$ or $\nu(\text{Cu–S})$.

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