SHORT PAPER

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Study on the reaction of the anionic copper selenolate complex $[Me_4N]_2[Cu_4(SePh)_6]$ with CS_2 in solvents; the crystal structure of a polymeric complex $[CuS_2COMe]_n$(I)[†]

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The anionic copper selenolate complex $[Me_4N]_2[Cu_4(SePh)_6]$ reacted with CS_2 in solvents CH_3CN/CH_3OH or DMF/CH_3OH producing an uncharged two-dimensional layer polymeric complex $[Cu(S_2COMe)]_n$ (I) and a mononuclear complex $[Cu(S_2CNMe_2)_2]$ (II), respectively. The crystal structure of (I) is reported.

The insertion reaction of carbon disulfide into M–S bonds (M = Cu, Ag, Cd) has been investigated extensively by us.[1] We have found that uncharged silver or copper thiolate complexes can react readily with CS_2 in the presence of PPh_3 to give mononuclear insertion products.

$$(MSR)_n + PPh_3 + CS_2 \rightleftharpoons (PPh_3)_2M(S_2CSR) \qquad (M = Cu, Ag; R = aryl, alkyl)$$

Further investigation showed that some insertion products of this type could easily react with various solvents such as alkyl halides, alcohols, ethers and DMF to form unexpected metal cluster complexes. By applying this method, we have synthesized a series of cluster complexes with amazing structures, including $Cu_{14}(\mu_2\text{–}S)(SPh)_{12}(PPh_3)_6$,[2] $[Ag_{14}(\mu_6\text{–}S)(SPh)_{12}(PPh_3)_8]\cdot 4CH_3OH\cdot 13H_2O$[3], $[Ag_5I_6]_n[PPh_3CH_2I]_n$[4] and so on.

Recently we studied the reactions of anionic copper or silver thiolate or selenolate complexes $[Me_4N]_2[M_4(EPh)_6]$ (M = Cu, Ag; E = S, Se) with CS_2 in solvents (CH_3CN/CH_3OH or DMF/ CH_3OH) in the presence or the absence of sulfur. We have found that the above reaction in the presence of a small amount of S produced complexes with perthiocarbonate ligand.[5] Thus, the anionic complex $[Me_4N]_2[Cu_4(SePh_6)]$ reacted with CS_2 in DMF/ C_2H_5OH in the presence of a small amount of S producing a two-dimensional layer polymeric anionic complex $[Me_4N]_{2n}[Cu_2(CS_4)_2]_n$;[5] while the same reaction in CH_3CN/CH_3OH produced tetranuclear copper cluster anionic complex $[Me_4N]_2[Cu_4(CS_4)_4]$.[5]

However, when the anionic copper selenolate compex reacted with CS_2 in solvents in the absence of S, quite different products resulted. The solvents reacted with CS_2 to form new ligands. The anionic copper selenolate complex $[Me_4N]_2[Cu_4(SePh_6)]$ reacted with CS_2 in CH_3CN/CH_3OH or DMF/ CH_3OH to form an uncharged two-dimensional layer polymeric complex $[Cu(S_2COMe)]_n$ (I) and a mononuclear complex $[Cu(S_2CNMe_2)_2]$ (II), respectively. The reactions can be illuminated by following chemical equations:

$$[Me_4N]_2[Cu_4(SePh)_6] + CS_2 \xrightarrow{CH_3CN/CH_3OH} [Cu(S_2COMe)]_n \qquad (I)$$

$$[Me_4N]_2[Cu_4(SePh)_6] + CS_2 \xrightarrow{DMF/\ CH_3OH} [Cu(S_2CNMe_2)_2] \qquad (II)$$

The crystal structures of (I) and (II) have been determined. The structure of (II) is the same as that reported by L. V. Shirshova [6] using a different formation method. Herein we report the formations of the two complexes and the crystal structure of the complex (I).

The X-ray crystal structure determination indicates that the complex (I) is an uncharged two-dimensional layer polymeric complex, in which the new ligand CH_3OCS_2– bridges Cu(I) atoms. A layer structure of (I) is shown in Fig.1. The packing arrangement in the unit cell of (I) is shown in Fig.2.

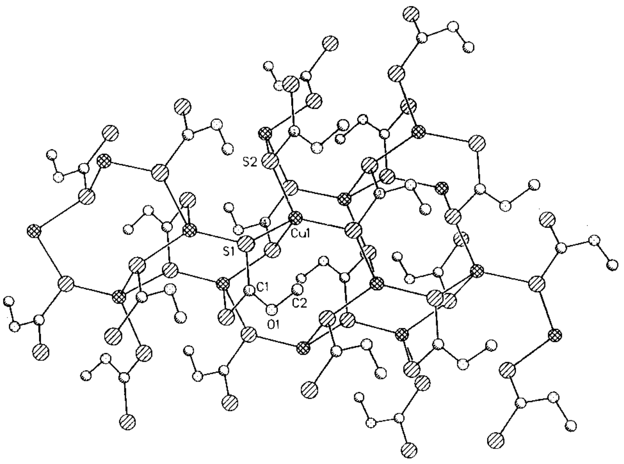

Fig. 1 A layer structure of the polymeric complex $[CuS_2COMe]_n$(I).

The building unit of the polymeric complex (I) is $[Cu(S_2COMe)]$. Each sulfur atom in the bidentate ligand CH_3OCS_2– bridges two copper atoms. The sulfur atom in one of the two C–S bonds (the C–S bond length is 1.699Å) coordinates to two Cu atoms, the Cu–S bond lengths are 2.291Å and 2.636Å, respectively. The bond angle of Cu–S–Cu is 105.46°. The S atom in another C–S bond (the length is 1.696Å) coordinates to other Cu atoms, the Cu–S bond lengths are 2.291Å and 2.305Å, respectively. The bond angle of Cu–S–Cu is 117.96°.

The coordination geometry of the Cu atoms is a distorted tetrahedron, composed of four S atoms from four ligands. The S…S distances average 3.822Å (3.588–4.013Å). The Cu–S–Cu mean bond angle is 107.82° (93.11–122.24°). Alternate Cu and S atoms form a "chair-form" eight-membered ring. The Cu atom locates at the centre of four eight-membered rings. The eight-membered rings share edges to form a two-dimensional non-planar layer polymer. The Cu atoms of one layer are on two planes with the distance between them 2.202Å. The groups CH_3O^- are on both sides of the layer. The layers are separated by the distance 10.021Å. They are packed together by Van der Waals forces.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

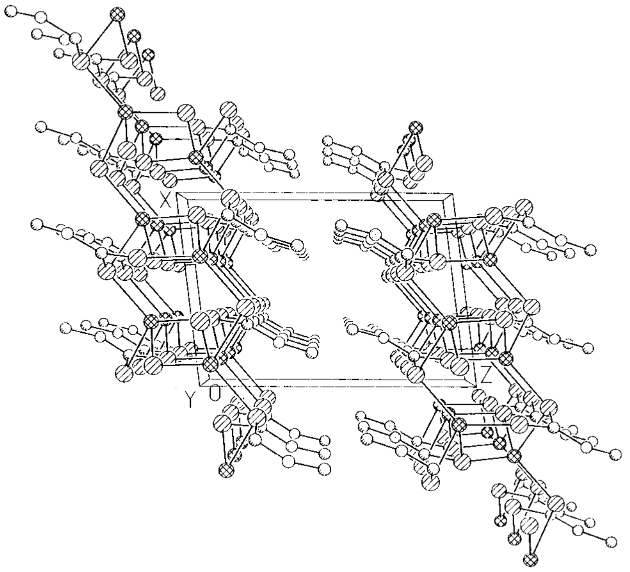

Fig. 2 The packing arrangement in the unit cell of $[CuS_2COMe]_n$(I).

In both (I) and (II), the new ligands were formed by the reactions of CS_2 with solvents (CH_3OH or DMF):

$$CS_2 + CH_3O^- \rightleftharpoons [CH_3OCS_2]^-$$

$$CS_2 + Me_2NCOH + e \rightleftharpoons [Me_2NCS_2]^-$$

The formation of complex (II) involves a redox reaction, copper(I) is oxidized to copper(II)

$$[Cu(SePh)_6]^{2-} + [Me_2NCS_2]^- \rightleftharpoons [Cu(S_2CNMe_2)_2]\ (II) + e$$

Similar reactions of CS_2 and solvents have occurred in our previous research works.[7,8] The ligand CH_3OCS_2- in the polymeric complex $[S_4(Cd_{17}(SPh)_{24}(CH_3OCS_2)_{4/2}]_n \cdot nCH_3OH$ is also formed by the reaction of CS_2 with CH_3OH.[7] In that case, the bidentate donor ligand connects two 17-nuclear units through two sulfur atoms. The S–C–S bond angle is 126.0° and the mean C–S bond length is 1.662Å. In the ligand of the present complex (I), the S–C–S bond angle is 125° and the C–S mean bond length is 1.698Å.

We are also studying the reactions of anionic silver thiolate or selenolate complexes $[Me_4N]_2[Ag_4(EPh)_6]$(E = S, Se) and $[Me_4N]_2[Ag_5(SPh)_7]$ with CS_2 in various solvents.

Experimental

Synthesis: All reactions were carried out under a dinitrogen atmosphere using standard Schlenk technique. The anionic complex $[Me_4N]_2[Cu_4(SePh)_6]$ was prepared by our previously reported method.[9] Carbon disulfide was treated by $KMnO_4$, Hg and $HgSO_4$ to remove sulfur, then dried and distilled under N_2. All solvents were dried and distilled under N_2.

Preparation of complex (I): To a yellow solution of $[Me_4N]_2[Cu_4(SePh)_6]$ (10mg) in CH_3CN (one ml) was added CS_2 (0.3 ml). The resulting solution turned orange. Some brown-black, block-shaped crystals of (I) formed by slow diffusion of CH_3OH into the above orange solution after several days. They are air-stable at room temperature.

IR (Perkin-Elmer 983G spectrometer, KBr, 200-4000cm^{-1}): 3023w, 2991w, 2939w, 2831w, 2041w, 1431s, 1212s, 1163s, 1140m, 1100w, 1078w, 1018s, 954m, 605w, 547w, 469m, 331w.

Preparation of complex (II): To a yellow solution of $[Me_4N]_2[Cu_4(SePh)_6]$ (10mg) in DMF (1ml) was added CS_2 (0.3ml). The resulting solution turned dark. Some black, rectangular crystals of (II) formed by slow diffusion of CH_3OH into the above dark solution after one month.

Crystal structure determination: Crystal data for complex (I): $[C_2H_3CuOS_2]_n$, brown-black crystal, monoclinic, space group $P2_1/a$, a=7.229(4), b=6.018(3), c=10.021(6)Å, β=96.76(5)° V=432.9(4)Å^3, Z=4, Dc=2.619gcm^{-3}, μ (Mo–K α)=5.822mm^{-1}, $F(000)$=336. The intensity data were collected on a Rigaku AFC6S diffractometer with Mo–Kα radiation (λ=0.71069 Å) and ω–2 θ scan technique at room temperature. The structure was solved by a direct method and subsequent Fourier different technique using the SHELX-97 program. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The final R value was 0.0354 based on 721 observed reflections. The estimated standard deviation for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: bond lengths 0.0013–0.005 Å, bond angles 0.04–0.3.

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