Assembly based on μ_4-bridging thiolate: a new type of polymeric silver(I) complex having a one dimensional chain structure

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The polymeric silver(I)–thiolate complex $[\{Ag_8(\mu_4\text{-}SC_2H_4NH_3)_6Cl_6\}Cl_2]_n$ has been prepared from the assembling reaction of silver chloride and 2-mercaptoethylamine hydrochloride in DMF; X-ray diffraction analysis shows the complex has a one dimensional chain structure and all the sulfur atoms of the thiolates exhibit μ_4 bonding bridging four silver(I) centers.

Thiolates are a subject of great interest in the chemistry of transition-metal complexes.[1–4] Dithiolates acting as μ_2 or μ_3 bridging ligands have been used to link metal ions such as Cu^I or Ag^I giving rise to complexes with infinite-chain structures.[5–8] Simple monothiolate ligands acting as μ_2 or μ_3 bridges are very common in transition metal chemistry,[8,9] however, those acting as μ_4 bridges and linking metal atoms to form polymeric complexes in one infinite chain or in network structures are unknown.[10] Recently, we have explored ways to design syntheses of polymeric complexes with chain structures by using coinage metal ions and dithiolate ligands.[11] By changing from dithiolate to monothiolate bridging ligands, we obtained a new type of polymeric silver(I) complex having a one dimensional chain structure and metal–metal interactions in which the thiolates show μ_4 bridging linking four Ag^I centers.

We have found that it is possible to use this simple monothiolate ligand to generate an unusual one dimensional molecular component of ligand bridged Ag^I ions.

By very slowly mixing a DMF solution of AgCl and NEt_4Cl and a DMF solution of 2-mercaptoethylamine hydrogen chloride in an H-tube at room temperature, a large quantity of colorless prismatic crystals deposited.‡ Clearly, the synthesis of the polymeric silver(I) 2-mercaptoethylamine complex can be approached from the controlled assembling reaction of $[AgCl_2]^-$ and $HSC_2H_4NH_2{\cdot}HCl$ in DMF [eqn. (1)]. In this

$$8n[NEt_4][AgCl_2] + 8nHSC_2H_4NH_2{\bullet}HCl \longrightarrow \underset{\mathbf{1}}{[\{Ag_8(\mu_4\text{–}SC_2H_4NH_3)_6Cl_6\}Cl_2]_n} + 8n[NEt_4]Cl + 2nHSC_2H_4NH_2{\bullet}HCl \quad (1)$$

reaction, one mole of HCl is liberated for each Ag^+ added and shows the zwitterion $^-SC_2H_4NH_3^+$ acts as a ligand to form the complex. A crystallographic analysis reveals that the complex is a polymer and the octanuclear cation $[Ag_8(SC_2H_4NH_3)_6Cl_6]^{2+}$ constitutes the building-block unit. The octanuclear units, possessing a crystallographic mirror plane through Ag(1), Ag(3) and S(2) (Fig. 1), are bound by Ag–S and Ag–Ag interactions to form a one dimensional chain structure along the *b* axis and the chains are linked by hydrogen bonds in the crystal (Fig. 2). Two types of coordination environments for Ag^I ions are present: six Ag^I ions have a distorted tetrahedral S_3Cl coordination environment, generated by the sulfur atoms of the zwitterions and terminal chloride; the other two are trigonal planar with an S_3 coordination environment from the sulfur atoms of the zwitterion. All six zwitterions $^-SC_2H_4NH_3^+$ exhibit μ_4 bridge linking four metal centers. The occurrence of μ_4 bridging coordination of thiolate ligands in transition metal chemistry is very limited.[10] This is the first example of an $Ag_4(\mu_4\text{-}S)$ bridge coordination mode for thiolate found in silver(I) chemistry and the third example of a $M_4(\mu_4\text{-}S)$ bridge coordination mode of the zwitterion found in transition metal thiolate chemistry (the other examples being $[Cu_{13}Cl_{13}(SC_2H_4NH_3)_6]$[10a] and $[\{Cu_8Cl_6(SC_2H_4NH_3)_6\}Cl_2]_n$[10b]). The coordination geometry of all the sulfur atoms is a highly distorted square pyramidal $CSAg_4$ unit with one carbon atom at the apex and four silver atoms in the equatorial plane. The four Ag–S bonds in the μ_4-$S(1)Ag_4$ unit are all similar in length [2.577(5), 2.583(5), 2.611(5), 2.690(5) Å], while those in the μ_4-$S(2)Ag_4$ unit are non-equivalent, one shorter at 2.440(7) Å, two at 2.626(4) Å and one longer at 2.917(7) Å. The average Ag–S bond distance [2.634(7) Å] is much longer than that [2.248 Å] in $[Cu_{13}Cl_{13}(SC_2H_4NH_3)_6]$[10a] and slightly longer than those for Ag^I–SR involving three- or four-coordinate silver (2.40–2.55 Å).[3,4] The Ag–Ag separations range from 2.976(2) to 3.046(3) Å with an average value of 3.003 Å. All are best considered as non-bonding,[3] although the values are very similar to those present in metallic silver (2.88 Å).[12] The average Ag–Cl bond distance [2.489(5) Å] is slightly longer than that (2.448 Å) in $[Cu_{13}Cl_{13}(SC_2H_4NH_3)_6]$[10a] and lies in the normal range for Ag^I–Cl bonds.[4] Two Cl^- are not coordinated to silver atoms, but are bonded to NH_3^+ *via* a strong hydrogen bond N–H···Cl (N···Cl= 3.20 Å) in the crystal.

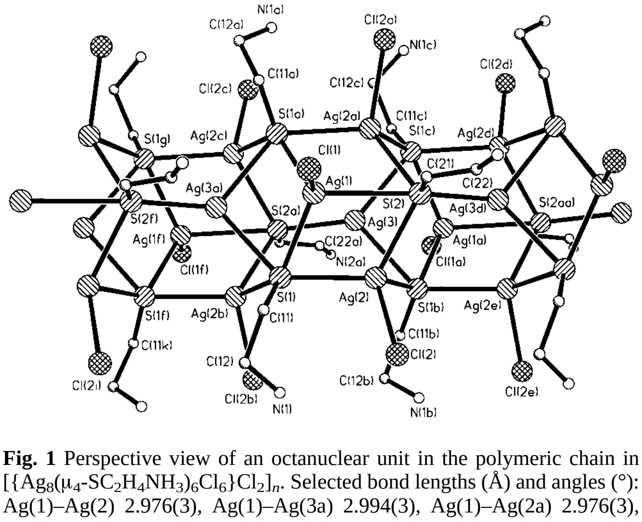

Fig. 1 Perspective view of an octanuclear unit in the polymeric chain in $[\{Ag_8(\mu_4\text{-}SC_2H_4NH_3)_6Cl_6\}Cl_2]_n$. Selected bond lengths (Å) and angles (°): Ag(1)–Ag(2) 2.976(3), Ag(1)–Ag(3a) 2.994(3), Ag(1)–Ag(2a) 2.976(3), Ag(2)–Ag(3) 3.046(3), Ag(3)–Ag(1a) 2.994(3), Ag(3)–Ag(2a) 3.046(3), Ag(1)–S(1) 2.577(5), Ag(1)–S(2) 2.917(7), Ag(1)–Cl(1) 2.464(7), Ag(1)–S(1a) 2.577(5), Ag(2)–S(1) 2.611(5), Ag(2)–S(2) 2.626(4), Ag(2)–Cl(2) 2.514(5), Ag(2)–S(1b) 2.583(5), Ag(3)–S(1b) 2.690(5), Ag(3)–S(1c) 2.690(5), Ag(3)–S(2a) 2.440(7); C(11)–S(1)–Ag(1) 104.1(6), C(11)–S(1)–Ag(2) 103.8(7), C(11)–S(1)–Ag(2b) 119.5(6), C(11)–S(1)–Ag(3a) 110.3(6), Ag(1)–S(1)–Ag(2) 70.0(1), Ag(1)–S(1)–Ag(3a) 69.2(1), Ag(2)–S(1)–Ag(2b) 119.7(1), Ag(2b)–S(1)–Ag(3a) 70.5(1), C(21)–S(2)–Ag(1) 94.1(13), C(21)–S(2)–Ag(2) 114.6(6); C(21)–S(2)–Ag(2a) 114.6(6), C(21)–S(2)–Ag(3d) 101.3(13), Ag(1)–S(2)–Ag(2) 64.7(1), Ag(1)–S(2)–Ag(2a) 64.7(1), Ag(2)–S(2)–Ag(3d) 108.1(2), Ag(2a)–S(2)–Ag(3d) 108.1(2).

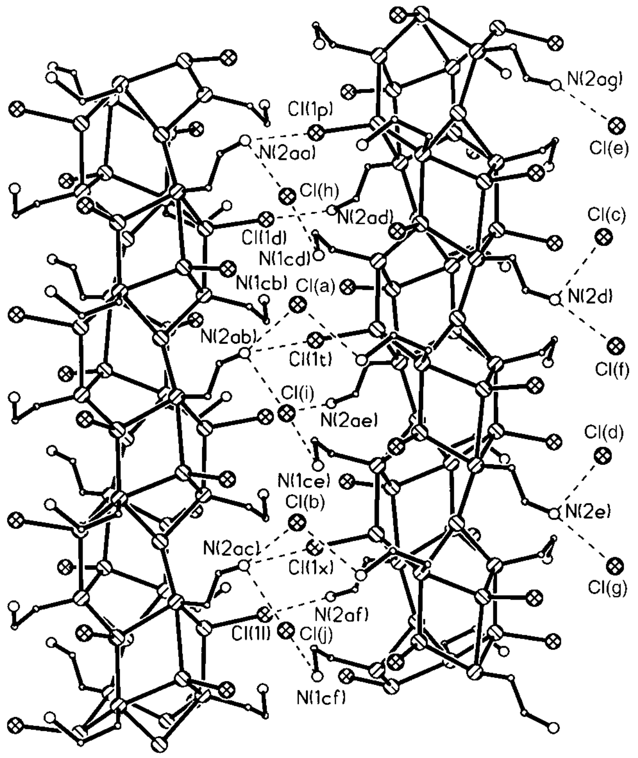

Fig. 2 View of the one dimensional chains and hydrogen bonds between the chains running along the *b* axis in $[\{Ag_8(\mu_4\text{-}SC_2H_4NH_3)_6Cl_6\}Cl_2]_n$

The IR spectrum of the complex exhibit a shift of the C–S stretching band from 659 cm^{-1} for the free mercaptoethylamine to 644 cm^{-1} upon coordination. The C–H and N–H stretching bands are complicated and occur between 2798 and 3162 cm^{-1} for the complex.

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Notes and References

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‡ *Crystal data*: crystal dimensions 0.12 × 0.15 × 0.30 mm, $C_{12}H_{42}N_6Ag_8S_6Cl_8$, M = 1609.4, orthorhombic, space group *Pnma*, a = 7.831(1), b = 15.180(1), c = 16.410(1) Å, U = 1951.1(4) Å^3, Z = 2. D_c = 2.743 g cm^{-3}. 5955 intensity data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation at room temperature, of which 1471 (R_{int} = 0.0492) are independent. $R(R_w)$ = 0.082 (0.090) for 1178 reflections with $I \geqslant 2.0\sigma(F_o)$ and 103 refined parameters. $\Delta\rho_{max}$ = 1.44 e Å^{-3} near the silver atoms. CCDC 182/871.

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