$[Fe_3Cu(SPr^i)_6Cl_3]^{2-}$: a novel mixed-metal thiolate complex with a 'truncated' adamantane-like structure

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Reaction of $[Fe_2(SPr^i)_6]^{2-}$ with $FeCl_2$ and CuCl in a 1:1:1 molar ratio in hot tetrahydrofuran gives the complex anion $[Fe_3Cu(SPr^i)_6Cl_3]^{2-}$ which contains a Fe_3Cu pyramidal core; the structure, magnetic properties and the solution ^1H NMR spectrum are reported.

The chemistry of homometallic thiolate complexes has been developed to a remarkable extent in the last 20 years.[1,2] Nevertheless, there are amazingly few reports on analogous heterometallic clusters. The reason may be that these clusters are not as straightforward to stabilize as the homometallic ones because, in addition to the usual problems one has in isolating these labile complexes and crystallizing them, one is also faced with the problem of phase separation which leads to a mixture of homometallic complexes. To date, the most notable examples are $[Au_3Cu_3(SCH_2CH_2)_4]^{2-}$,[3] $[Au_2Cu_4(SCH_2CH_2)_4]^{2-}$,[3] $[Au_2Ag_4(SCH_2CH_2)_4]^{2-}$,[3] $[Cu_6In_3(SEt)_{16}]^-$,[4] $[Eu_2M_2(SPh)_8(py)_6]$ (M = Cd, Hg)[5] and $[Eu_2Zn_2(SPh)_8(thf)_6]$[5] as well as $[CuIn(ER)_4(PPh_3)_2]^6$ (E = S, Se).[6] Focussing attention onto the chemistry of heterometallic thiolate complexes is now timely because, in addition to the novel properties and structures one might encounter, they could serve as molecular precursors to high-quality ternary heterometallic solids. This was shown earlier in the case of $[CuIn(ER)_4(PPh_3)_2]$ which leads cleanly to the photovoltaic material $CuInSe_2$.[6]

Our approach towards this class of complexes is to react well defined homometallic thiolate precursors with readily available sources of the heterometal such as metal halides.

Very recently, we found that the reaction of $[NMe_4]_2[Mn_2(SPr^i)_6]^7$ with CuCl gives the remarkable anion $[Mn_4Cu_4(SPr^i)_{12}(\mu_4-S)]^{2-}$.[8] The core of this cluster consists of a distorted Mn_4Cu_4 metal cube which is stabilized with an interstitial μ_4-S ligand and edge-bridging thiolate ligands. Encouraged by this result, we started to explore the chemistry of the analogous $Fe^{2+}Cu^+$ system and discovered the novel mixed-metal cluster $[NMe_3(CH_2Ph)]_2 [Fe_3Cu(SPr^i)_6Cl_3]$ **1**. Complex **1** is best accessible by a reaction of $[Fe_2(SPr^i)_6]^{2-}$ with solid $FeCl_2$ and CuCl (molar ratio 1:1:1) in hot tetrahydrofuran and can be isolated as orange–brown crystals upon addition of $[NMe_3(CH_2Ph)]Br$.†

The structure‡ of the tetranuclear cluster **1** is shown in Fig. 1. It contains a Fe_3Cu trigonal pyramid with idealized C_{3v} symmetry. The three Fe atoms define the vertices of the basal triangular plane with Fe⋯Fe separations of 3.852 Å. The apex of the pyramid is occupied by the Cu atom (Fe⋯Cu 3.205 Å). This metal core is held together by six thiolate groups. The observed Fe–S and Cu–S distances of 2.345 Å and 2.241 Å, respectively, are similar to the corresponding bond lengths in homoleptic homometallic Fe[9] and Cu[10] thiolate clusters. In contrast to the Fe atoms which each bind to terminal Cl ligands (Fe–Cl 2.313 Å) to adopt a tetrahedral coordination [S–Fe–S(Cl) 109.3°], the Cu atom resides inside the 'upper' S_3 face and thus has a trigonal planar environment (S–Cu–S 119.9°). This is the reason why the overall shape of **1** appears to be a truncated adamantane.

Complex **1** is a structural derivative of homometallic thiolate adamantanes of the formula $[M_4(SR)_6X_4]^{2-}$ (X = halogen).[7,11,12b] The central core of these complexes is an M_4 tetrahedron of tetrahedrally coordinated metal atoms. The formal replacement of one of these metal sites with a trigonal-planar M′ centre results in the loss of one terminal ligand. At the same time, the idealized symmetry of the M_3M' core drops to C_{3v} since M′ is shifted towards the centre of the cluster. However, the symmetry of the entire cluster is C_3 rather than C_{3v}, because of the orientation of the organic groups. The cluster shows the $(3,-1,-1,-1)$ pattern§ with three axially oriented ligands within the basal Fe_3S_3 ring. The three $CuFe_2S_3$ rings have one axially disposed group each. This situation leads to a 'paddlewheel'-like arrangement of the thiolate ligands attached to Cu. The C_3 axis of the molecule thus runs through the Cu atom and the centre of the basal Fe_3 triangle.

Since **1** can be considered as an $[Fe_3(\mu-SR)_3(SR)_3Cl_3]^{3-}$ cluster which is stabilized by the incorporation of an additional Cu^+ ion, its structure is reminiscent of the trinuclear Fe clusters
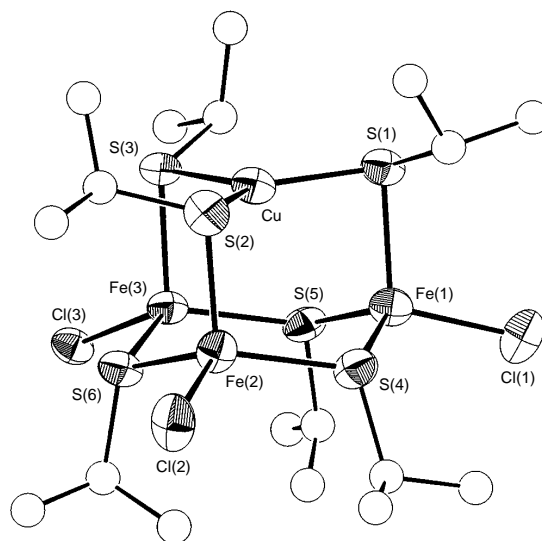

Fig. 1 ORTEP plot of $[Fe_3Cu(SPr^i)_6Cl_3]^{2-}$ with labelling scheme. Selected bond distances (Å) and angles (°): Cu–Fe(1) 3.145(3), Fe(1)–Fe(2) 3.849(3), Cu–Fe(2) 3.234(3), Fe(1)–Fe(3) 3.851(3), Cu–Fe(3) 3.235(3), Fe(2)–Fe(3) 3.857(3), Cu–S(1) 2.228(4), Cu–S(2) 2.233(4), Cu–S(3) 2.261(4), Fe(1)–Cl(1) 2.307(5), Fe(1)–S(1) 2.334(5), Fe(1)–S(4) 2.356(5), Fe(1)–S(5) 2.347(4), Fe(2)–Cl(2) 2.313(4), Fe(2)–S(2) 2.345(5), Fe(2)–S(4) 2.334(4), Fe(2)–S(6) 2.355(4), Fe(3)–Cl(3) 2.321(4), Fe(3)–S(3) 2.350(4), Fe(3)–S(5) 2.343(4), Fe(3)–S(6) 2.344(4); S(1)–Cu–S(2) 127.6(2), S(1)–Cu–S(3) 114.4(2), S(2)–Cu–S(3) 117.9(2), S(1)–Fe(1)–S(4) 109.0(2), S(1)–Fe(1)–S(5) 99.8(2), S(4)–Fe(1)–S(5) 118.9(2), S(2)–Fe(2)–S(4) 103.1(2), S(2)–Fe(2)–S(6) 102.3(2), S(4)–Fe(2)–S(6) 119.7(2), S(3)–Fe(3)–S(5) 102.4(2), S(3)–Fe(3)–S(6) 104.2(2), S(5)–Fe(3)–S(6) 119.2(2), Cu–S(1)–Fe(1) 87.1(2), Cu–S(2)–Fe(2) 89.9(2), Cu–S(3)–Fe(3) 89.1(1), Fe(1)–S(4)–Fe(2) 110.3(2), Fe(1)–S(5)–Fe(3) 110.4(2), Fe(2)–S(6)–Fe(3) 110.4(2).
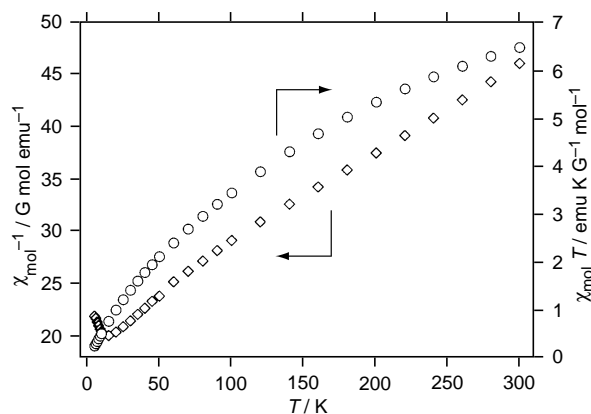
Fig 2 Magnetic data for $[NMe_3(CH_2Ph)]_2[Fe_3Cu(SPr^i)_6Cl_3]$. The suscepti-bilitiy data were recorded on a powdered sample in the temperature range 5–300 K in a 2 kG applied magnetic field.

of composition $[Fe_3(\mu\text{-}SR)_3Cl_6]^{3-}$.[12] These clusters, however, exhibit strictly planar Fe_3S_3 rings with very large Fe–S–Fe bridging angles of *ca.* 140°. To examine if this major structural difference is reflected in the magnetic properties of **1**, we measured magnetic susceptibility data for $[NMe_3(CH_2Ph)]_2$-$[Fe_3Cu(SPr^i)_6Cl_3]$ (Fig. 2). The data show antiferromagnetic exchange interactions with Curie–Weiss behaviour within the temperature range 120–300 K. The Weiss constant is calculated to be $\theta = -246$ K. The susceptibility data for $[Fe_3(\mu\text{-}SPh)_3Cl_6]^{3-}$,[12b] compare very well with the behaviour observed for **1**. Obviously, neither the presence of Cu^+ ions in **1** nor the fact that the Fe–S–Fe bridging angles in **1** are about 30° smaller than in $[Fe_3(\mu\text{-}SPh)_3Cl_6]^{3-}$, are followed by major changes in the magnetic behaviour.

The solution ^1H NMR spectrum of $[NMe_3(CH_2Ph)]_2[Fe_3$-$Cu(SPr^i)_6Cl_3]$ in CD_3CN at room temperature was recorded. Since the isotropic shift of the SC*H*Me$_2$ signal is a function of the local magnetic moment of the iron atoms, we expected two signals, one in the neighbourhood of δ 163 in the downfield region of the spectrum. This value can be calculated from the known magnetic moments[12b] and paramagnetic shifts[9b] of the CH_2 groups of $[Fe(SEt)_4]^{2-}$ and $[Fe_4(SEt)_{10}]^{2-}$. In fact, we observed one resonance at δ 161 and an additional signal at δ 87. While the first peak most probably arises from SC*H*Me$_2$ ligands bridging two paramagnetic Fe atoms **1**, that at δ 87 could tentatively be assigned to SC*H*Me$_2$ ligands bridging one diamagnetic Cu and one paramagnetic Fe atoms.

In summary, we have presented the first mixed-metal FeCu thiolate complex, with a structure reminiscent of adamantane. This cluster might act as a useful starting material to novel mixed-metal thiolates or sulfido/thiolato compounds. In particular, the synthesis of mixed-metal cubanes of the formula $[Fe_3CuE_4(SR)_3]^{2-}$ (E = S, Se, Te), in which one iron atom of the $[Fe_4E_4]$ parent cluster core is replaced by a Cu^+ ion, might be accessible by reaction of **1** with elemental chalcogen.

Footnotes

† *Synthesis of* $[NMe_3(CH_2Ph)]_2[Fe_3Cu(SCPr^i)_6Cl_3]$. To a slurry of NaSPr^i (0.59 g, 6 mmol) in 25 ml MeCN was added solid $FeCl_2$ (0.25 g, 2 mmol) and the mixture was stirred for 2 h. Then $[NMe(CH_2Ph)]Br$ (0.46 g, 2 mmol) was added and the stirring continued for 24 h. The solvent was evaporated and replaced by 25 ml of thf. Then, the mixture was filtered and the resulting solution of $[NMe_3(CH_2Ph)]_2[Fe_2(SPr^i)_6]$ was heated to its boiling point. Solid $FeCl_2$ (0.13 g, 1 mmol) and CuCl (0.10 g, 1 mmol) were added and the mixture was boiled for 20 min whereupon a small amount of a black precipitate was filtered off. The volume of the solution was reduced to *ca.* 15 ml. After stirring for 2 days at room temperature, the crude product precipitated. This material was recrystallized from MeCN–Et$_2$O (1:5) to give 0.35 g (33%) of the desired compound. More material can be recovered from the mother-liquor to give an overall yield of 60%. The single crystal used for the X-ray structure determination was obtained from a solvo-thermal reaction of $[NMe_3(CH_2Ph)]_2[Fe_2(SPr^i)_6]$ with 2 equiv. of CuCl in thf at 80 °C.

‡ *Crystal data*: $[NMe_3(CH_3Ph)]_2[Fe_3Cu(SPr^i)_6Cl_3]$, monoclinic, space group $P2_1/n$ with $a = 10.846(4)$, $b = 12.018(5)$, $c = 41.23(1)$ Å, $\beta = 94.97(2)°$, $U = 5354(3)$ Å^3, $Z = 4$, $D_c = 1.351$ g cm^{-3} and $\mu = 15.9$ cm^{-1}. Single-crystal X-ray diffraction data were collected (at −110 °C) on a Nicolet P3 four-circle diffractometer (Mo-Kα radiation) with ω-scans, $4 < 2\theta < 45°$, and 3764 reflections with $F_o^2 > 3\sigma(F_o^2)$. An empirical absorption correction (DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158) was applied as recommended. The number of variables were 477, and final R, R_w = 0.070, 0.045. The structure was solved with SHELXS86 and was refined with the TEXSAN Structure Analysis Package (Molecular Structure Corporation, 1985) of crystallographic programs. Sigma weights were used. The isopropyl group attached to S(5) is disordered over two positions. The structure of the $[NMe_3(CH_2Ph)]^+$ cations is normal and there are no bonding cation–anion contacts. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/292.

§ An adamantane-like cluster of composition $[M_4(\mu\text{-}SR)_6X_4]^{2-}$ (X = Cl, Br, I, SR) is built up of four fused M_3S_3 rings in chair conformation in which the organic group bound to the μ-S atoms can either be axially or equatorially oriented. There are four independent conformers for $M_4(\mu$-$SR)_6$ cages which are symbolized by the following orientation patterns: $(3,-2,-1,-0)$, $(2,2,2,0)$, $(3,-1,-1,-1)$ and $(2,-2,-1,-1)$. The four numbers within the parentheses represent the number of axially oriented groups in each of the four $M_3(SR)_3$ six-membered rings. The most common one is $(2,-2,-1,-1)$, while all other adamantane-like Fe thiolates known so far adopt the $(3,-2,-1,-0)$ pattern.

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