

[NBnMe₃]₂[Fe₂Cu₄(SePrⁱ)₈Cl₂] and [NBnMe₃]₂[Fe₃Cu(SePrⁱ)₆Cl₃], novel heterometallic chalcogenolate complexes with dodecahedral and octahedral selenium cages

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[Fe₂Cu₄(SePrⁱ)₈Cl₂]²⁻, an unprecedented hexanuclear mixed iron–copper–selenolate cage complex containing a dodecahedral selenium framework and [Fe₃Cu(SePrⁱ)₆Cl₃]²⁻, a related tetranuclear complex anion with an octahedral selenium arrangement, are described.

The chemistry of transition-metal chalcogenolate complexes continues to attract widespread attention owing to their role as synthetic analogues for the active sites of various metalloproteins such as alcohol dehydrogenase, ferredoxins, blue copper proteins or nitrogenases.^{1,2} In a broader context, they display a large variety of stoichiometries and structures which have no parallels in other species. In contrast to the large number of homometallic bi- and poly-nuclear chalcogenolate complexes known so far, complexes containing different kinds of metal atoms are comparatively rare. They include [Au₃Cu₃(SCH₂CH₂S)₄]²⁻,³ [Au₄Cu₂(SCH₂CH₂S)₄]²⁻,³ [Au₂Ag₂(SCH₂CH₂S)₄]²⁻,³ [Cu₆In₃(SEt)₁₆]⁻,⁴ [Eu₂M₂(SPh)₈(py)₆] (M = Cd, Hg),⁵ [Eu₂Zn₂(SPh)₈(thf)₆],⁵ [CuIn(ER)₄(PPh₃)₂] (E = S, Se)⁶ and [(PPh₃)₂Cu₂M(EC₆H₄Me)₆].^{7,8} (M = Mo, W; E = S, Se)

Recently, we synthesized novel heterometallic thiolate complexes by reacting homometallic thiolate precursors with simple copper halides. The octanuclear complex anion [Mn₄Cu₄S(SPrⁱ)₁₂]²⁻⁹ is accessible by reaction of [Mn₂(SPrⁱ)₆]²⁻¹⁰ with CuCl. The mixed sulfide–thiolate compound contains a central Cu₄Mn₄ metal cube defined by interpenetrating copper and manganese tetrahedra which is stabilised by an interstitial sulfide ion and edge-bridging thiolate groups. In the case of [Fe₃Cu(SPrⁱ)₆Cl₃]²⁻,¹¹ [Fe₂(SPrⁱ)₆]²⁻ was used as the thiolate precursor. The mixed iron–copper complex has a truncated adamantane-type structure which can be derived from the structure of the parent homometallic complex of the general formula [Fe₄(SR)₆X₄]²⁻ (X = Cl, Br, I, ER)¹² by replacement of a {FeX}⁺ unit by Cu⁺. Following this methodical approach, the chemistry of selenolate precursors under similar reaction conditions has also been investigated. In this paper, the complex anions [Fe₃Cu(SePrⁱ)₆Cl₃]²⁻ **2** and [Fe₂Cu₄(SePrⁱ)₈Cl₂]²⁻ **4** are described, which represent the first structurally characterized selenolate complexes containing different transition metals ions.

Both complex anions are formed in the reaction of [NBnMe₃]₂[Fe₂(SePrⁱ)₆] with FeCl₂ and CuCl in acetonitrile simultaneously and were isolated as their corresponding [NBnMe₃]⁺ salts **1** and **3** in form of light brown (**1**) or red (**3**) solids.† The structures of **1** and **3** were determined by X-ray crystallography.‡

Crystals of **1** are composed of isolated complex anions **2** and [NBnMe₃]⁺ counter cations. They are isotopic with the corresponding sulfur derivative [NBnMe₃]₂[Fe₃Cu(SPrⁱ)₆Cl₃] whose structural properties have already been discussed.¹¹ The structure of **2** is depicted in Fig. 1.

The Fe₃Cu framework of **2** is a trigonal pyramid with edges completely bridged by selenolate groups. The iron and three selenium atoms, Se(4), Se(5) and Se(6), define a compressed trigonal prism with homoatomic triangular and heteroatomic

prismatic faces. The copper atom does not reside exactly within the triangular selenium face, but is shifted by 0.067 Å towards the Fe atoms (mean Cu–Fe 3.351 Å). The mean Fe–Fe and Se–Se distances within the Fe₃Se₃ prism are 4.051 and 4.066 Å, respectively, whereas the Fe–Se distances are much smaller (mean value 2.471 Å).

The complete set of selenium atoms are arranged in a distorted octahedral fashion. With edge lengths of 4.322 Å the triangle Se(1)–Se(2)–Se(3) is significantly larger than the opposite one [Se(4)–Se(5)–Se(6), mean edge length 4.066 Å]. The first triangle is neither capped by a {FeCl}⁺ unit nor centered by Cu⁺. The triangles Se(1)–Se(3)–Se(4), Se(1)–Se(2)–Se(5) and Se(2)–Se(3)–Se(6) are capped by {FeCl}⁺ units, achieving an idealised C₃ symmetry of **2**. Each iron atom has a distorted pseudo-tetrahedral FeSe₃Cl coordination with selenium atoms in metal bridging positions and a terminal chloride ligand. The average Fe–Se distance of 2.471 Å is very close to the value of 2.463 Å found in [Fe₂(SePrⁱ)₆]²⁻.¹³

The complete anionic entity **2** can also be considered as being composed of the complex anion [Fe₃(SePrⁱ)₆Cl₃]³⁻ and a Cu⁺ cation which is probably needed to stabilise the structure.

Trigonal-planar CuSe₃ as well as pseudo-tetrahedral FeSe₃Cl coordination sites related to those observed in **2** are also characteristic constituents of the hexanuclear complex anion **4** (Fig. 2).

In contrast to **2** which contains an octahedral selenium framework, the selenium atoms in **4** define a triangulated dodecahedron. This dodecahedron [Fig. 3(a)] is composed of two interpenetrating tetrahedra, a compressed one consisting of Se(1), Se(4), Se(7) and Se(8) (atom type A) and an elongated one consisting of Se(2), Se(3), Se(5) and Se(6) (atom type B). The Cu atoms occupy one of the two tetrahedral sets of four triangular faces of the dodecahedron which are defined by one B and two A type selenium atoms. One half of the four triangular faces defined by one A and two B type selenium atoms are capped by {FeCl}⁺ units.

From another point of view, the Cu atoms bridge the four short edges of the compressed tetrahedral substructure defined

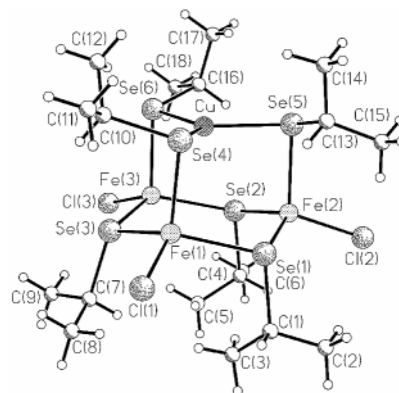


Fig. 1 [Fe₃Cu(SePrⁱ)₆Cl₃]²⁻: molecular structure with atomic labels.

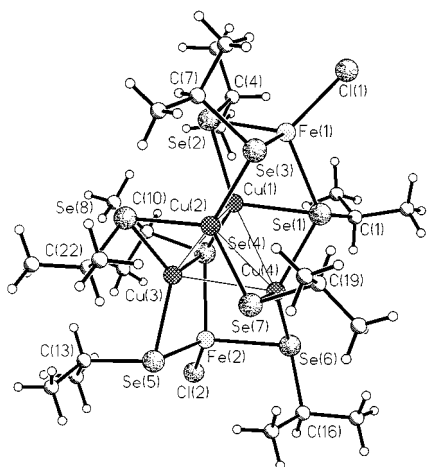


Fig. 2 $[\text{Fe}_2\text{Cu}_4(\text{SePr})_8\text{Cl}_2]^{2-}$: molecular structure with atomic labels.

by the four A type selenium atoms and form an additional bond each to a B type selenium atom of the elongated tetrahedral substructure.

The Cu–Cu distances range from 2.656(6) to 2.988(8) Å, whereas the Fe(1)–Cu(1) and Fe(2)–Cu(2) distances are 2.748(7) and 2.853(8) Å, respectively. The mean Fe–Se distance is 2.469 Å. This value is very close to the values of 2.471 Å found in **2** and 2.463 Å found in $[\text{Fe}_2(\text{SePr})_6]^{2-}$.¹³

The remarkable condensation principle observed here, for the first time, leads to two novel μ_3 -selenolate bridges which connect two different metal types (Cu₂Fe). In addition, four heterometallic μ -selenolate bridges (CuFe) are also present. The two Cl[−] ions are non-bridging in nature and expand the ligand spheres of the Fe atoms towards slightly distorted FeSe₃Cl tetrahedra.

The complex anion **4** can formally be expanded by introducing two further {FeCl}⁺ groups capping the remaining two triangular faces defined by one A and two B type selenium atoms [Se(2), Se(3), Se(8) and Se(5), Se(6), Se(7)]. The structure of the corresponding hypothetical electroneutral $[\text{Fe}_4\text{Cu}_4(\text{SePr})_8\text{Cl}_4]$ molecule is shown in Fig. 3(b) (the additional {FeCl}⁺ groups are drawn with open bonds). This complex contains two $\{\text{Fe}_2(\mu\text{-SePr})_2(\text{SePr})_2\text{Cl}_2\}$ subunits whose structural properties are very similar to those observed in the binuclear complexes of general formula $[\text{Fe}_2(\mu\text{-SR})_2(\text{SR})_4]^{2-}$ (R = Me, Et, Prⁱ, *c*-C₆H₁₁, Buⁿ).¹⁴ These subunits are linked with the central Cu₄ tetrahedron *via* selenolate bridges. Further expansion of the metal–selenium cage by adding Cu⁺ ions or {FeCl}⁺ subunits to the metal-free triangular faces of the selenium dodecahedron defined by one A and two B type atoms is not possible owing to strong repulsions.

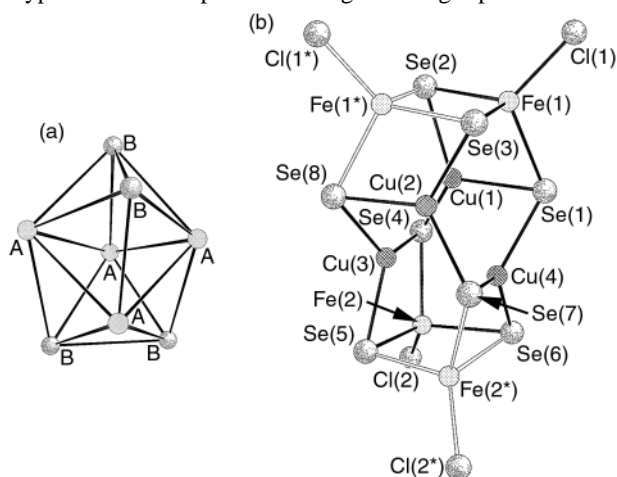


Fig. 3 (a) The triangulated Se₈ dodecahedron of $[\text{Fe}_2\text{Cu}_4(\text{SePr})_8\text{Cl}_2]^{2-}$ showing the tetrahedral substructures defined by A and B type selenium atoms. (b) Structure of the hypothetical complex $[\text{Fe}_4\text{Cu}_4(\text{SePr})_8\text{Cl}_4]$ (alkyl groups omitted, additional atoms marked with asterisk).

In summary, we have prepared and structurally characterised the first mixed-metal iron–copper–selenolate complexes containing octahedral (**2**) and novel triangulated dodecahedral (**4**) selenium frameworks.

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Notes and references

To a solution of $[\text{NBnMe}_3]_2[\text{Fe}_2(\text{SePr})_6]$ (2.86 g, 2.5 mmol) in MeCN (40 ml) was added 0.32 g of FeCl₂ (2.5 mmol) followed by addition of 0.25 g of CuCl (2.5 mmol) under stirring. The solution changed from black–brown to orange–brown, the suspension was stirred for 24 h, and the black residue was filtered off. The filtrate was reduced in volume (*ca.* 20 ml). Dark red platelets of **1** and light brown columns of **2** were obtained in a 9:1 molar ratio after diffusion of *ca.* 20 ml of diethyl ether into the solution.

‡ *Crystal data.* Siemens P4RA four circle diffractometer, rotating anode generator, Mo-K α radiation ($\lambda = 0.71073$ Å), graphite monochromator, scintillation counter, $T = 150$ K, empirical absorption correction; direct methods, full-matrix least-squares refinement, non-hydrogen atoms anisotropic unless otherwise stated, H atoms at idealised positions, one common isotropic temperature factor for H within each organic residue, one extinction parameter, one scaling factor.

1: C₃₈H₇₄N₂Cl₃Fe₃CuSe₆, $M = 1144.45$, monoclinic, $a = 10.890(3)$, $b = 12.191(3)$, $c = 41.782(9)$ Å, $\beta = 96.39(2)^\circ$, $V = 5512.52$ Å³, space group $P2_1/n$, $Z = 4$, $D_c = 1.651$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 5.29$ mm^{−1}, transmission range 0.981–0.688, $2\theta_{\text{max}} = 48^\circ$, ω scan, crystal dimensions *ca.* 0.52 × 0.21 × 0.13 mm, 8558 unique reflections, $R(F) = 0.0662$ for 4798 reflections with $I > 2\sigma(I)$, $wR(F^2) = 0.1837$ for all data, 488 variables.

2: C₄₄H₈₈N₂Cl₂Fe₂Cu₄Se₈, $M = 1713.60$, monoclinic, $a = 14.832(2)$, $b = 16.450(3)$, $c = 26.524(4)$ Å, $\beta = 105.29(1)^\circ$, $V = 6242.43$ Å³, space group Cc , $Z = 4$, $D_c = 1.823$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 6.57$ mm^{−1}, transmission range 0.997–0.484, $2\theta_{\text{max}} = 54^\circ$, ω scan, crystal dimensions *ca.* 0.45 × 0.21 × 0.11 mm, 4815 unique reflections, $R(F) = 0.0714$ for 3187 reflections with $I > 2\sigma(I)$, $wR(F^2) = 0.188$ for all data, 372 variables; isopropyl groups and counter cations isotropic, one common C–C distance within the isopropyl groups [1.475(7) Å], one common N–C distance within the counter cations [1.491(7) Å], phenyl groups with idealised geometries.

CCDC 182/1384. See <http://www.rsc.org/suppdata/cc/1999/1995/> for crystallographic files in .cif format.

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