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Synthetic Routes to $[Fe_2X_2(X_5)_2]^{2-}$ Anions (X = S, Se).
Structure and Properties of $[Fe_2Se_2(Se_5)_2]^{2-}$, a Complex with Selenido and Pentaselenido Ligands

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Several isolated binary transition-metal–sulfur complexes containing polysulfido ligands, S_x^{2-}, with $x > 2$ have been structurally characterized, *e.g.* $[Fe_2S_2(S_5)_2]^{2-}$ [1], $[M(S_4)_2]^{2-}$ (M = Ni, Pd) [2], $[Cu_3(S_6)_3]^{3-}$ [3], $[Cu_4(S_4)_{3-x}(S_5)_x]^{2-}$ (x = 0–2) [4], $[Cu_6(S_4)_3(S_5)]^{2-}$ [5], $[MoS(S_4)_2]^{2-}$ [6], $[Mo_2S_4(S_2)(S_4)]^{2-}$ [7], $[Pt(S_5)_3]^{2-}$ [8], $[Au(S_9)]^-$ [9], and $[Hg(S_6)_2]^{2-}$ [10]. One possible method in the synthesis of M/S_x complexes is the use of polymeric or complex compounds with metal atoms already bonded to sulfur as starting materials. As an example $[Fe_2S_2(S_5)_2]^{2-}$ is prepared from $[Fe(SPh)_4]^{2-}$ by reaction with $PhCH_2SSSCH_2Ph$ [1]. This dimeric complex contains a planar $[Fe_2S_2]^{2+}$ core similar to the inorganic portion of oxidized [2Fe–2S] protein centers. The existence of analogous selenium fragments, $[Fe_2Se_2]^{2+}$, as well as of the $[Fe_4Se_4]^{2+}$ and $[Fe_6Se_9]^{2-}$ cluster cores has been demonstrated by the structural characterizations of $[Fe_2Se_2(SC_6H_4\text{-}p\text{-}Me)_4]^{2-}$ [11], $[Fe_4Se_4(SPh)_4]^{2-}$ [12], and $[Fe_6Se_9(SMe)_2]^{4-}$ [13], respectively. In contrast to selenide little work has been done to introduce polyselenido ligands to transition-metal complexes. Here we report the preparation and selected spectroscopic properties of $[Fe_2X_2(X_5)_2]^{2-}$ complexes (X = S: **1**, X = Se: **2**) and the X-ray structure of $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$.

Besides the literature method mentioned above the following reactions can be used for the preparation of **1**:

(i) A solution of **1** is obtained when the dark precipitation formed by the reaction of $FeCl_3$ with 3 equivalents of $(p\text{-Me-}C_6H_4)_2PS_2^-$ in methanol is treated with Na_2S_4.

(ii) In acetonitrile $FeCl_3$ reacts with $Et_2NPS(SH)_2$ in a 1:2 mol ratio to form a soluble complex whose electronic spectrum indicates a $Fe^{III}ClS_4$ coordination unit similar to that found in the structurally characterized complex $[FeCl\{S_2PS(OMe)\}_2]^{2-}$ [14]. Treatment of this solution with elemental sulfur and pyridine results in the formation of **1**.

(iii) The reaction of $FeCl_3$ or $FeCl_2$ with elemental sulfur and CaH_2 in dimethylformamide (DMF) at 70 °C yields **1**. The complex is also obtained from $FeCl_2$ and elemental sulfur using sodium instead of CaH_2.

In each case the Ph_4P^+ salt of **1** has been identified by elemental analysis, the characteristic UV/Vis spectrum of **1** and/or X-ray structure determination.

The reaction with sodium described under (iii) proceeds in an analogous way with selenium instead of sulfur:

$$2FeCl_2 + 12X + 6Na \xrightarrow[70\,^{\circ}C]{DMF} Na_2[Fe_2X_2(X_5)_2] + 4NaCl$$

(X = S or Se)

Under an atmosphere of pure nitrogen 1.27 g (10 mmol) of $FeCl_2$, 4.7 g (60 mmol) of powdered black selenium, and 0.69 g (30 mmol) of sodium in 50 ml of DMF were stirred at 70 °C for 6 hours. After cooling, 50 ml of methanol were added to the deep-brown reaction mixture. The solution was filtered, and the filtrate treated with 4.2 g (10 mmol) of Ph_4PBr. After 2 days the black crystalline $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$ is collected, washed with methanol and dried *in vacuo*; yield: 3.3 g (38%). In a similar manner $(Ph_4P)_2[Fe_2S_2(S_5)_2]$ can be prepared in 49% yield.

Crystals of $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$ are monoclinic, space group C2/c with a = 21.451(5), b = 16.076(4), c = 16.244(4) Å, β = 103.63(2)°, V = 5443.9 Å^3, Z = 4, D_x = 2.121 g cm^{-3}, and μ = 92.7 cm^{-1}. Single crystal X-ray diffraction data were collected on a Syntex $P2_1$ four-circle diffratometer (MoKα radiation, scintillation counter, $4° < 2\theta < 54°$, θ–2θ scan, 5984 independent reflections, 3617 with $I > 1.96\ \sigma(I)$, empirical absorption correction). During data collection the crystal was cooled to −133 °C by a stream of cold nitrogen.

The structure was solved and successfully refined in the space group C2/c. The positions of the Fe and Se atoms were provided by direct methods. Repeated least-squares refinements and difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Final full-matrix least-squares refinements with anisotropic thermal vibrations of the Fe, Se, and P atoms, isotropic temperature factors of the C atoms and all H atoms fixed at their idealized positions converged to R (R_w) = 0.072 (0.054). In crystals of $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$ discrete anions **2** are separated by tetraphenylphosphonium cations. The cation features the expected structural properties and calls for no special comment.

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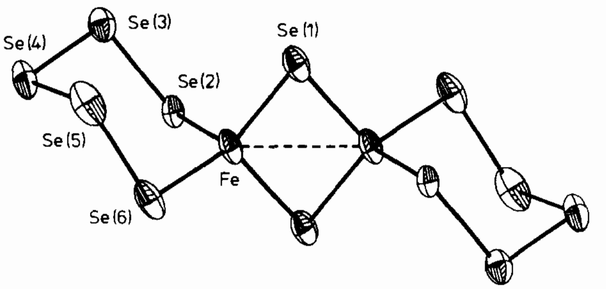

Fig. 1. Thermal ellipsoid plot (50% probability) of the $[Fe_2Se_2(Se_5)_2]^{2-}$ anion. Bond lengths [Å] and angles [°] with standard deviations in parenthesis: Fe–Fe' 2.787(2), Fe–Se(1) 2.329(2), Fe–Se(1') 2.317(2), Fe–Se(2) 2.428(2), Fe–Se(6) 2.421(2), Se(2)–Se(3) 2.345(2), Se(3)–Se(4) 2.318(2), Se(4)–Se(5) 2.337(2), Se(5)–Se(6) 2.347(2); Se(1)–Fe–Se(1') 106.27(8), Se(1)–Fe–Se(2) 114.95(8), Se(1)–Fe–Se(6) 115.18(8), Se(1')–Fe–Se(2) 102.93(7), Se(1')–Fe–Se(6) 107.93(8), Se(2)–Fe–Se(6) 108.61(7), Fe–Se(1)–Fe' 73.73(7), Fe–Se(2)–Se(3) 102.86(6), Se(2)–Se(3)–Se(4) 104.05(6), Se(3)–Se(4)–Se(5) 103.35(7), Se(4)–Se(5)–Se(6) 104.27(7), Fe–Se(6)–Se(5) 97.35(7). The primed atoms are related to the unprimed ones by the symmetry transformation –x, –y, –z. Listings of all bond lengths and valence angles as well as of observed and calculated structure factors have been deposited together with final atomic parameters with the Editor.

The anion 2 is shown in Fig. 1; bond lengths and angles are given in the caption. The complex possesses idealized C_{2h} symmetry and crystallographically imposed C_i symmetry which gives rise to the exact planarity of the central $Fe_2(\mu_2\text{-}Se)_2$ rhomb. Due to a significant shift of the $Fe-(\mu_2\text{-}X)$ bond lengths towards larger values on going from X = S (2.192 Å in 1) to X = Se (2.323 Å in 2), the Fe•••Fe distance in 2 (2.787(2) Å) is 0.086 Å longer than the corresponding distance in 1, but is still in the range where direct Fe•••Fe interactions are possible. The lengthening of the $Fe-(\mu_2\text{-}X)$ bond is accompanied by a simultaneous reduction of the $Fe-(\mu_2\text{-}X)-Fe$ angle (76.1(1)° in 1 and 73.73(7)° in 2, respectively). The Fe atoms of 2 are each tetrahedrally coordinated by two μ_2-Se atoms and two Se atoms of a Se_5^{2-} chelate ligand with Se–Fe–Se angles ranging from 102.93(7)° to 115.18(8)°. 2 can be described as a spiro-tricyclic system composed of the central four-membered $Fe_2(\mu_2\text{-}Se)_2$ cycle and two six-membered $FeSe_5$ chelate rings. From a structural point of view the $FeSe_5$ rings may be regarded as metal-substituted Se_6 molecules. Both $FeSe_5$ and Se_6 exist in the chair conformation with dihedral angles of 72.3° (range: 66.8 to 80.5°) and 76.2(4)°, respectively [15]. The averaged Se–Se bond length in 2 (2.337 Å) is the same, within the limits of experimental error, as in the three monoclinic modifications of selenium (from 2.334 to 2.337 Å, Se_8 molecules) [16] and is only slightly smaller than the Se–Se bond lengths reported for rhombohedral (2.356(9) Å, Se_6 molecules) [15] and trigonal selenium (2.373(5) Å, Se_∞ chains) [17]. In addition, the averaged bond angle at Se is 102.38° for the $FeSe_5$ group compared to 101.1(3)° for Se_6.

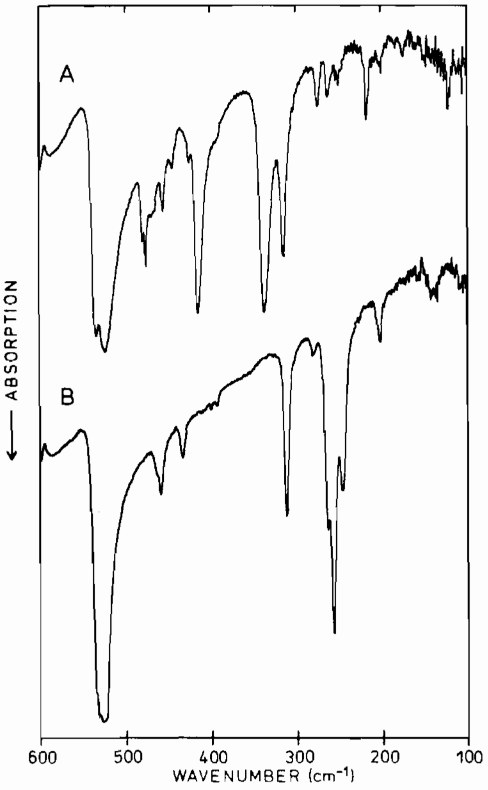

Fig. 2. FT IR spectra of polycrystalline (A) $(Ph_4P)_2[Fe_2S_2(S_5)_2]$ and (B) $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$.

In Figure 2 the infrared spectra of the Ph_4P^+ salts of 1 and 2 are shown (Bruker IFS-114 FT-IR-spectrometer, nujol suspensions between polyethylene plates). The strong absorptions near 530 cm^{-1} are caused by the Ph_4P^+ cations. $(Ph_4P)_2[Fe_2S_2(S_5)_2]$ has three bands at 414, 338 and 315 cm^{-1} that are assigned to Fe–S stretching vibrations on the basis of vibrational assignments for other [2Fe–2S] species [18]. A band at 474 cm^{-1} is probably due to a S–S vibration. S–S modes at similar IR frequencies have been observed for MS_4 and MS_5 chelate rings [19] and for S_6 [20]. Fe–Se vibrations of $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$ occur at 312 cm^{-1} and in the 250 cm^{-1} region where three bands at 264, 258 and 247 cm^{-1} are observed. The two bands of lower intensity (264 and 247 cm^{-1}) are also possible candidates for Se–Se vibrations. In the IR spectrum of Se_6 an absorption band at 253 cm^{-1} is found [21].

The electronic spectrum of $(Ph_4P)_2[Fe_2Se_2(Se_5)_2]$ in DMF solution (absorption maxima at 312(sh), 386(sh), 415(sh), 498, and 670(sh) nm) resembles that of the sulfur homolog. Corresponding bands are red-shifted.

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