

## $[\text{Fe}_4\text{Te}_4(\text{SPri})_4]^{2-}$ and $[\text{Fe}_4\text{Te}_4(\text{SPri})_4]^{3-}$ , Novel $\text{Fe}_4\text{Te}_4$ Cluster Complexes in Different Metal Oxidation States and $[\text{Mn}_4\text{Te}_4(\text{TePri})_4]^{4-}$ , the First Chalcogenide Cubane Cluster containing Divalent Metal Ions

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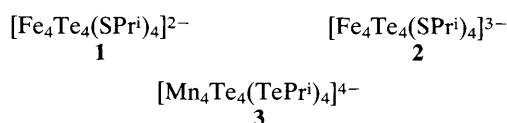
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A novel series of  $\text{M}_4\text{Te}_4$  cubane cluster complexes with average metal oxidation states ranging from +2.5 to +2.25 for  $\text{M} = \text{Fe}$  and finally reaching +2 on replacing Fe by Mn is described; the corresponding  $[\text{Mn}_4\text{Te}_4(\text{TePri})_4]^{4-}$  anion represents the first member of the mixed manganese/chalcogenide/chalcogenolate class of complexes.

In recent years synthetic iron-sulfide-thiolate complexes of general formula  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{n-}$  ( $n = 1, 2, 3$ ) have been studied extensively due to their unparalleled importance in many biological processes.<sup>1,2</sup> They can be considered as models for the active sites of *e.g.* 4Fe-4S ferredoxins and of more complex metal sulfur proteins and enzymes. A characteristic feature of these compounds is the central cubane-like  $\text{Fe}_4\text{S}_4$  cluster core. Related cage structures were found in the mixed-valent selenium and tellurium derivatives of the benzenethiolate complex, *e.g.*  $[\text{Fe}_4\text{Se}_4(\text{XPh})_4]^{n-}$  ( $\text{X} = \text{S}, n = 2;^3 \text{X} = \text{Se}, n = 2, 3;^4 \text{X} = \text{Te}, n = 3^4$ ) and  $[\text{Fe}_4\text{Te}_4(\text{XPh})_4]^{n-}$  ( $\text{X} = \text{S}, n = 2, 4;^3,4,5 \text{X} = \text{Se}, n = 3^4$  and  $\text{X} = \text{Te}, n = 3^4,6$ ) which contain Fe in the mean oxidation states of +2.5 ( $n = 2$ ) and +2.25 ( $n = 3$ ), respectively. However, more reduced cubane complexes containing divalent metal ions exclusively are still not known.

In an approach to synthesize complexes with novel coordination properties we were able to isolate  $[\text{Co}_2(\text{SPri})_5]^-$ ,<sup>7</sup>  $[\text{Fe}_2(\text{SBU}^t)_5]^-$ ,<sup>8</sup>  $[\text{Ni}_4(\text{SPri})_8]$ ,<sup>9,10</sup>  $[\text{Ni}_4(\text{SC}_6\text{H}_{11})_8]$ ,<sup>11</sup>  $[\text{Ni}_4(\text{S-Pr}^i)_8]\text{Br}$  and  $[\text{Ni}_4(\text{SPri})\text{I}]^{12}$  by using secondary and tertiary alkane thiolate ligands.  $[\text{Co}_2(\text{SPri})_8]^-$  and  $[\text{Fe}_2(\text{SBU}^t)_5]^-$  are rare examples of bitetrahedral complexes which share faces, and the Ni compounds are characterized by unprecedented cubane-like  $\text{M}_4\text{S}_8$  cages. In order to obtain a further insight into the unusual coordination properties of these and related selenium and tellurium containing ligands, we have extended our investigations to other 3d transition metals. In this paper we report the synthesis and structure of the new mixed  $\text{M}_4\text{X}_4$  cubane cluster complexes **1** and **2** containing iron in the oxidation states of +2.5 and +2.25, respectively. In addition, the novel complex **3** is described which is not only the first cubane complex with divalent metal ions but also the first manganese complex with bridging chalcogenide and terminal chalcogenolate ligands.



The anion **1** is obtained under oxidizing conditions by reaction of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NaSPri}$  with  $\text{Li}_2\text{Te}_2$  in a 1:2:1 mol ratio in MeCN and isolated as  $[\text{Ph}_4\text{P}]_2[\text{Fe}_4\text{Te}_4(\text{SPri})_4] \cdot \text{MeCN}$  **4** on addition of  $[\text{Ph}_4\text{P}]\text{Br}$ . If the oxidant  $\text{Li}_2\text{Te}_2$  is replaced by  $\text{Na}_2\text{Te}$  (mol ratio 1:4:0.75), the more

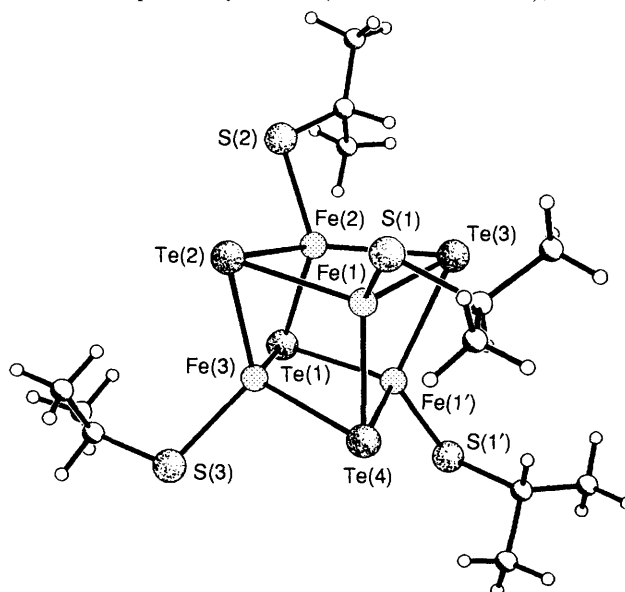
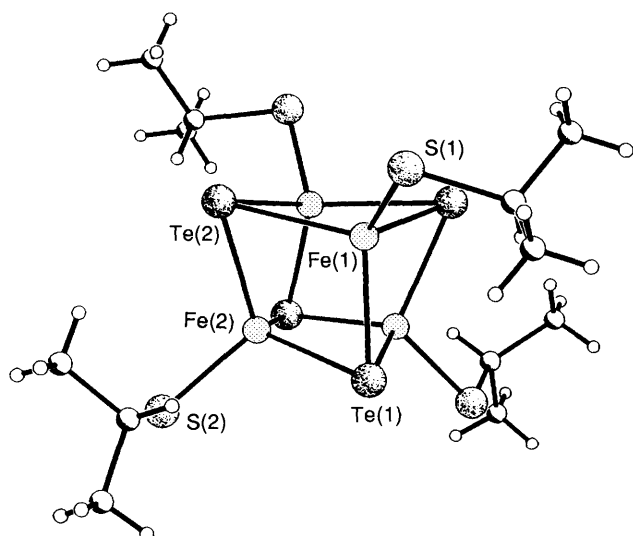


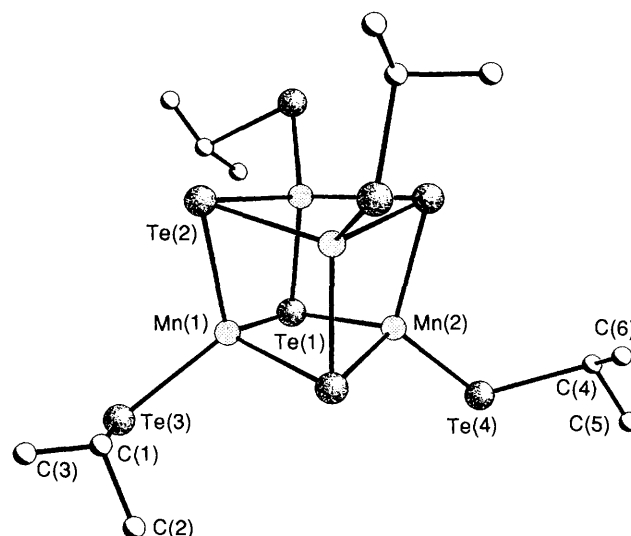
Fig. 1 Molecular structure of  $[\text{Fe}_4\text{Te}_4(\text{SPri})_4]^{2-}$

Fig. 2 Molecular structure of  $[\text{Fe}_4\text{Te}_4(\text{SPr}^i)_4]^{3-}$ 

reduced complex anion **2** can be isolated from MeCN–THF mixtures as  $[\text{Et}_4\text{N}]_3[\text{Fe}_4\text{Te}_4(\text{SPr}^i)_4]$  **5** by adding  $[\text{Et}_4\text{N}]\text{Br}$ . The structures of **4** and **5** were determined by X-ray crystallography.†

Within crystals of **4**, the complex anions **1** are distributed statistically over two interpenetrating sites which are related by a twofold rotation axis of the space group  $C2/c$ . The  $\{\text{Fe}_4\text{Te}_4\text{S}_4\}$  core portion is irregularly distorted and thus deviates significantly from the idealized  $T_d$  symmetry. A perspective view of **1** is given in Fig. 1. The  $\text{Fe}\cdots\text{Fe}$  and  $\text{Fe}\text{--}\text{Te}$  distances are unsystematically spread around their mean values of 2.808 and 2.597 Å, respectively, the individual ranges being 2.627–2.988 ( $\text{Fe}\cdots\text{Fe}$ ) and 2.512–2.670 Å ( $\text{Fe}\text{--}\text{Te}$ ). The  $\text{Fe}\text{--}\text{S}$  bond length is 2.260 Å on average.

The cluster core of **2**, however, is much more regular due to a twofold rotation axis, the average  $\text{Fe}\cdots\text{Fe}$  and  $\text{Fe}\text{--}\text{Te}$  distances being 2.815 (range 2.701–2.860) and 2.627 (range 2.602–2.663) Å, respectively. The structure is depicted in Fig. 2. Thus, on going from the oxidized **1** to the more reduced **2** cluster anion, a significant lengthening of the mean  $\text{Fe}\text{--}\text{Te}$  distances is evident as has to be expected from simple charge considerations. The same is true for the mean  $\text{Fe}\text{--}\text{S}$  bond

Fig. 3 Molecular structure of  $[\text{Mn}_4\text{Te}_4(\text{TePr}^i)_4]^{4-}$ 

lengths which approach a value of 2.287 Å in **2**. It is interesting to note that the volume of the central  $\text{Fe}_4$  tetrahedron increases only slightly on one-electron reduction.

While it is not possible to isolate a mixed iron–chalcogenide cubane cluster in the (fully reduced)  $\text{Fe}^{2+}$  state, the corresponding manganese analogue is readily accessible if  $\text{MnBr}_2$  is reacted with  $\text{NaTePr}^i$  in a 1:3 mol ratio in MeCN. The complex anion **3** thus formed can be isolated as dark red crystals of  $[\text{Me}_4\text{N}]_4[\text{Mn}_4\text{Te}_4(\text{TePr}^i)_4]\cdot\text{MeCN}$  **6** on addition of  $[\text{Me}_4\text{N}]\text{Cl}$ . The observed elimination of  $\text{Te}^{2-}$  during the reaction of  $\text{Mn}^{2+}$  with  $\text{TePr}^{i-}$  is probably coupled with metal-assisted condensational processes resulting in the formation of  $\text{Pr}^i\text{TePr}^i$ . The structure of **6** was also determined by X-ray crystallography.†

A pictorial representation of **3** is shown in Fig. 3. The complex anion is situated on a threefold axis of the cubic space group  $P2_13$  which passes through  $\text{Mn}(2)$  and  $\text{Te}(2)$ . Complex **3** contains the novel  $\text{Mn}_4\text{Te}_4$  cluster core with terminally bonded telluroate ligands which complete the tetrahedral coordination sphere around each of the manganese ions. Interestingly, the position of  $\text{Te}(4)$  (and necessarily that of the alkyl residue attached to it) is not in accordance with an overall  $C_3$  symmetry resulting in three different but equivalent positions for one of the four telluroate groups.

The mean  $\text{Mn}\text{--}\text{Te}_{\text{term}}$  bond length is 2.740 Å and thus matches exactly that of  $[\text{Mn}(\text{TePh})_4]^{2-}$ .<sup>13</sup> The  $\text{Mn}\cdots\text{Mn}$  distances are nearly identical ( $3 \times 3.275$ ,  $3 \times 3.276$  Å) and much larger than those observed in the related iron complexes **1** and **2**. They lie in the same range as analogous distances observed in complexes containing  $\text{Mn}^{2+}(\mu\text{-XR})_2\text{Mn}^{2+}$  units with chalcogenolate bridges, e.g. 3.220 Å in  $[\text{Mn}_2(\text{SET})_6]^{2-}$ ,<sup>14</sup> 3.249 Å in  $[\text{Mn}_2(\text{SPr}^i)_6]^{2-}$ <sup>15</sup> and 3.294 Å in  $[\text{Mn}_2(\text{SePr}^i)_6]^{2-}$ .<sup>15</sup> The perfect  $\text{Mn}_4$  tetrahedron finds its counterpart in a nearly regular  $\text{Te}_4$  tetrahedron ( $3 \times 4.368$ ,  $3 \times 4.392$  Å) indicating that the  $\text{Mn}_4\text{Te}_4$  core is also only slightly distorted. In fact, nine of the twelve  $\text{Mn}\text{--}\text{Te}$  distances are identical and 2.758 Å in length, the remaining ones [around  $\text{Te}(2)$ ] are only 0.022 Å longer.

Magnetic susceptibility data for a solid sample of **6** are collected in the temperature range 5.8–287.8 K (Fig. 4).‡ The effective magnetic moment per Mn atom in the tetranuclear complex varies gradually from 3.209  $\mu_B$  at 287.8 K down to 0.406  $\mu_B$  at 5.8 K. This behaviour clearly

‡ *Magnetic measurements.* Magnetic susceptibilities of a powdered sample were recorded on a Faraday-type magnetometer using a sensitive Cahn electrobalance in the temperature range 5.8–287.8 K. The applied magnetic field was  $\approx 1.2$  T.<sup>21</sup> Diamagnetic contributions are estimated to  $-986.6 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .

† *Crystal data.* Siemens P4RA four-circle diffractometer, rotating anode generator, Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), graphite monochromator, scintillation counter,  $T = 150$  K, empirical absorption corrections; direct methods, full-matrix least-squares refinements, non-hydrogen atoms anisotropic, H atoms at idealized positions for ordered groups, one common isotropic temperature factor for H within each residue, one extinction parameter, one scaling factor.

**4:**  $\text{C}_{62}\text{H}_{71}\text{NP}_2\text{S}_4\text{Fe}_4\text{Te}_4$ ,  $M = 1754.18$ , monoclinic,  $a = 17.602(3)$ ,  $b = 15.903(3)$ ,  $c = 25.623(5)$  Å,  $\beta = 108.69(2)^\circ$ ,  $V = 6793$  Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 4$ ,  $D_x = 1.714$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 2.73$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 54^\circ$ ,  $\omega$ -scan, crystal dimensions ca.  $0.42 \times 0.34 \times 0.29$  mm, 7423 unique reflections,  $R(R_w) = 0.052$  (0.046) for 4700 reflections with  $I > 2\sigma(I)$ , 402 variables.

**5:**  $\text{C}_{36}\text{H}_{88}\text{N}_3\text{S}_4\text{Fe}_4\text{Te}_4$ ,  $M = 1425.13$ , orthorhombic,  $a = 12.132(1)$ ,  $b = 24.486(3)$ ,  $c = 37.877(5)$  Å,  $V = 11251$  Å<sup>3</sup>, space group  $Fdd2$ ,  $Z = 8$ ,  $D_x = 1.683$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 3.22$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 54^\circ$ ,  $\omega$ -scan, crystal dimensions ca.  $0.51 \times 0.37 \times 0.20$  mm, 3224 unique reflections,  $R(R_w) = 0.025$  (0.030) for 3085 reflections with  $I > 2\sigma(I)$ , 235 variables.

**6:**  $\text{C}_{30}\text{H}_{79}\text{N}_5\text{Mn}_4\text{Te}_8$ ,  $M = 1750.54$ , cubic,  $a = 18.321(9)$  Å,  $V = 6150$  Å<sup>3</sup>, space group  $P2_13$ ,  $Z = 4$ ,  $D_x = 1.891$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 4.54$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 54^\circ$ ,  $\omega$ -scan, crystal dimensions ca.  $0.47 \times 0.45 \times 0.44$  mm, 2454 unique reflections,  $R(R_w) = 0.052$  (0.050) for 1856 reflections with  $I > 2\sigma(I)$ , 147 variables.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1993.

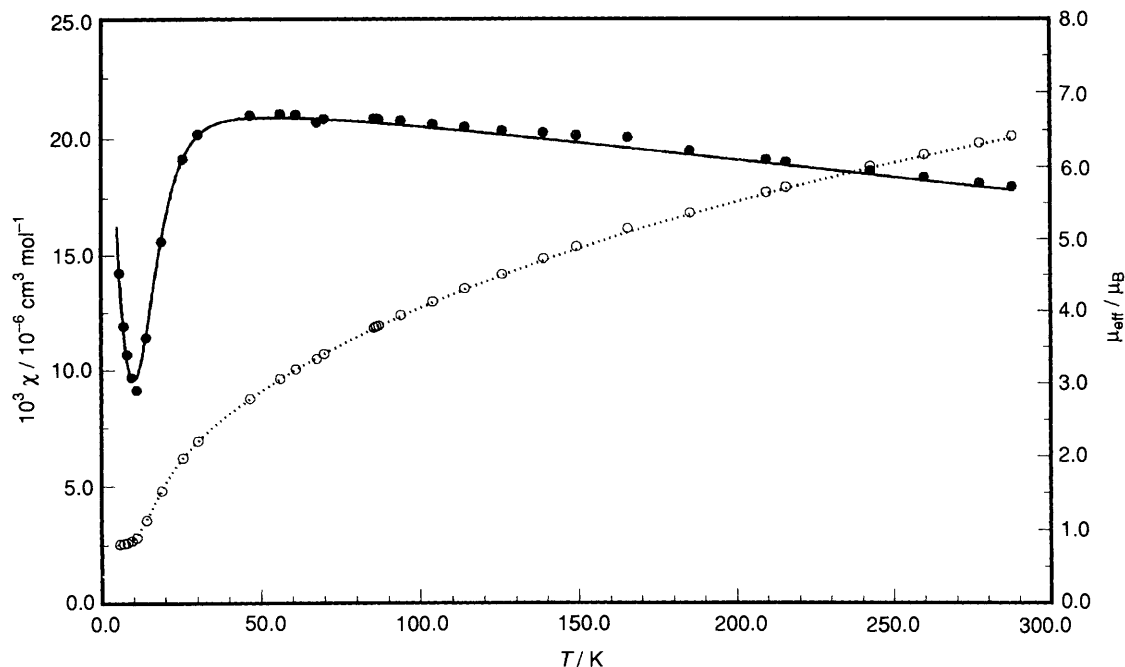


Fig. 4 Magnetic data for  $[\text{Mn}_4\text{Te}_4(\text{TePri})_4]^{4-}$ ; molar susceptibilities (—) and magnetic moments (---)

demonstrates the presence of antiferromagnetically coupled metal sites. Based on the spin Hamiltonian [eqn. (1)] the resulting eigenvalue [eqn. (2)] was used to derive an expression for the molar susceptibility of the complex.<sup>17</sup> The coupling constant converged in the curve-fitting procedure to  $J = -21.7(1) \text{ cm}^{-1}$  assuming 0.5% monomeric impurities ( $g$  fixed at 2.00). Attempts to improve the fit by reducing the symmetry of the tetrahedral exchange field clearly shows that a single one-term coupling constant is sufficient to adequately describe the magnetic behaviour of this compound.

$$H = -2J[S_1S_2 + S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4 + S_3S_4] \quad (1)$$

$$E(S_T) = -J[S_T(S_T + 1) - 4S(S + 1)] \\ (S = 5/2 \text{ and } S_T = S_1 + S_2 + S_3 + S_4)^{16} \quad (2)$$

Analysing the  $\text{Fe}_4\text{Te}_4$  cubane cores of **1** and **2**, it is evident that no systematic distortion is present in **1**, while a small compression parallel to the crystallographically imposed twofold axis is observed in **2** resulting in an idealized  $D_{2d}$  symmetry. In contrast, the  $\text{Mn}_4\text{Te}_4$  cubane core of **3** has nearly perfect  $T_d$  symmetry.

The formation of mixed metal-chalcogenide cubane cluster complexes with  $[\text{M}_4\text{X}_4]^{\pm 0}$  core oxidation levels is unexpected in the light of other spatial arrangements that permit lower formal charges per metal atom, e.g. the metal cubane cluster structure of general formula  $(\text{M}_8\text{X}_6(\text{YR})_8)^{4-18}$  or the extended adamantane type structures realized in  $[\text{Zn}_{10}\text{S}_4(\text{SPh})_{16}]^{4-19}$  and  $[\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}]^{2-20}$ . Obviously, the coordination properties of  $\text{Te}^{2-}$  ligands have to be explored more systematically, and other systematic investigations on  $\text{M}^{2+}/\text{Te}^{2-}/\text{YR}^-$  reaction systems are currently in progress.

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