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Synthesis and structure of an unprecedented high-symmetry $[Fe_4S_4Cl_4]$ cubane-type unit in supramolecular $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4][Fe_4S_4Cl_4]$†

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The reduction of SCN^- ions with iron containing zirconium chloride clusters in the presence of 18-crown-6 gives crystals of $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4][Fe_4S_4Cl_4]$ which contain $[Fe_4S_4Cl_4]$ cubane-type clusters with full T_d symmetry, as well as supramolecular $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4]$ complex cations.

The chemistry of iron–sulfur clusters has attracted much scientific interest due to the occurrence of such structural units in biological systems like ferrodoxines, high potential iron proteins, nitrogenases, and others.[1–5] For the class of cubane-type $[Fe_4S_4]$ clusters which are believed to be involved in biological electron transfer processes, synthetic investigations have revealed a large number of compounds with the general formula $[Fe_4E_4X_4]^{n-}$ with E = S, Se or Te; X = SR (R = organic group), SH, OR, NO, Cl, Br, I; $n = -1, -2$, or -3.[1,2,6] They all contain cubane-type iron–sulfur cores which can be described as a tetrahedron of iron atoms, superimposed by a larger tetrahedron of chalcogen (E) atoms such that the E atoms are triply bridging the faces of the Fe tetrahedron. The tetrahedral coordination environment of each Fe atom is completed by an additional ligand X, bonded at each exo position of the Fe tetrahedron. The symmetry of the metal–chalcogen core of all the so far characterised molecular examples deviates significantly from the ideal T_d case. The core is usually compressed or elongated in one direction leaving an overall D_{2d} symmetry. This observation holds so far for all structurally characterised cubane-type iron–sulfur clusters, including those with $[Fe_4S_4Cl_4]^{2-}$ cores. The latter have been described with $[Et_4N]^+$, $[Pr^n{}_4N]^+$, $[Fe^{II}(MeCN)_2\ (POMe)_3]^{2+}$ and $[Ph_4P]^+$ counter cations.[10,13–15] This deviation from ideal symmetry has been discussed in terms of crystal packing and Jahn–Teller type electronic effects.[7,8]

Here we present the synthesis and structure of $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4][Fe_4S_4Cl_4]$ **1** which contains the $[Fe_4S_4Cl_4]^{2-}$ cluster **2** of T_d symmetry as well as the uncommon $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4]^{2+}$ complex cation **3**. **1** was an unexpected product from the reaction of $K[(Zr_6Fe)Cl_{15}]$[9] with KSCN in MeCN, to which 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was added. In a typical synthesis, 20 mg (0.017 mmol) $K[(Zr_6Fe)Cl_{15}]$, 10 mg (0.102 mmol) KSCN, and 31 mg (0.12 mmol) 18-crown-6 were dissolved in 5 ml thoroughly dried acetonitrile. The initially dark blue solution loses its colour within *ca.* 3 h. Diisopropyl ether was slowly added by diffusion and after 4 weeks **1** was isolated as a black, crystalline material (yield 3.1 mg; 76% with respect to the cluster starting material). Apparently, the Zr-cluster becomes oxidised in solution, thereby releasing Fe cations, whereas the SCN^- ions are reduced, leaving S^{2-} ions. In a further reaction step the $[Fe_4S_4Cl_4]^{2-}$ cluster anions are formed. The structure of **1** was determined by single-crystal X-ray crystallography.‡

Within crystals of **1** the three symmetry independent atoms of the $[Fe_4S_4Cl_4]^{2-}$ cubane-type complex anion are located on 16e Wyckoff-sites (x,x,x) of the cubic space group $F23$ nearby the 4d site such that with the symmetry elements present, molecular units with full T_d symmetry are formed, even though the point symmetry of the 4d site does not imply full T_d symmetry (23 instead of $\bar{4}$ symmetry). This is shown by the equivalence of all the twelve Fe–S bonds [with a length of 2.294(2) Å] and Fe–Fe–Fe angles of exactly 60°. An ORTEP plot of the structure of **2** is shown in Fig. 1. The Fe–S, Fe–Cl, and Fe–Fe distances compare well with the average values of the $[Fe_4S_4Cl_4]^{2-}$ clusters in other compounds with different cations.[10] Because of the equivalence of all the Fe atoms in **2** the charge is delocalized completely with a net charge of +2.5 on each metal atom.

In crystals of **1** the central iron atom of the $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4]^{2+}$ complex cation is located on the 4c Wyckoff site of the space group $F23$. Similar to the cluster anion on the 4d site the supramolecular entity also shows full T_d symmetry. The molecular structure of **3** is shown in Fig. 2. Compound **3** is composed of a central $[FeCl_4]^{2-}$ tetrahedron (with perfect tetrahedral Cl–Fe–Cl angles of 109.5°) and Fe–Cl distances of 2.260(4) Å. Above each triangular face of the tetrahedron a potassium cation is located which is encapsulated within a 18-crown-6 molecule. Comparable supramolecular complex cations are found so far only in a series of thallium compounds with the general formula $[A_4(MX_4)(C_{12}H_{24}O_6)_4][TlX_4]_2$ with A

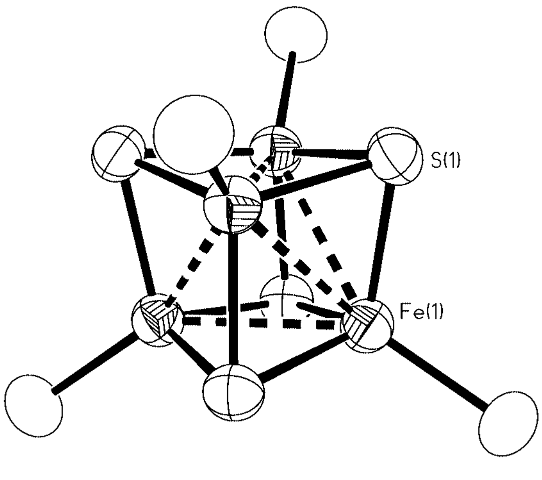

Fig. 1 Molecular structure of the $[Fe_4S_4Cl_4]^{2-}$ cluster anion **2** in crystals of **1** showing the atom labelling scheme (50% thermal probability ellipsoids). Important atom distances (Å): Fe(1)–S(1) 2.294(2), Fe(1)–Cl(1) 2.222(3), Fe(1)–Fe(1) 2.790(2); angles (°): Fe(1)–Fe(1)–Fe(1) 60, Fe(1)–S(1)–Fe(1) 74.92(8), Fe(1)–Fe(1)–Cl(1) 144.7, S(1)–Fe(1)–S(1) 103.25(6), S(1)–Fe(1)–Cl(1) 115.14(5).

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† Electronic supplementary information (ESI) available: Fig. S1: packing diagram of the molecular units in crystals of **1**. Fig. S2: structure of the supramolecular cation **3** in crystals of **1**. See http://www.rsc.org/suppdata/cc/b1/b103871k/

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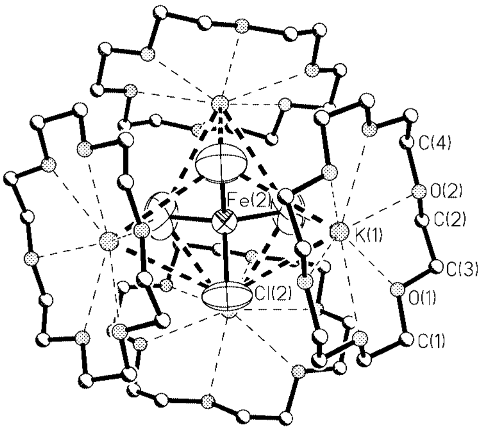

Fig. 2 Structure of the supramolecular $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4]^{2+}$ complex cation **3** in crystals of **1** with atom labelling scheme (50% thermal probability ellipsoids for the central $FeCl_4$ moiety), without hydrogen atoms. Important atom distances (Å): Fe(2)–Cl(2) 2.260(4), Fe(2)–K(1) 3.777(3), Cl(2)–K(1) 3.699(3), average distances (Å): K(1)–O 2.890, C–O 1.44, C–C 1.41; angles (°): Cl(2)–Fe(2)–Cl(2) 109.5, Cl(2)–K(1)–Cl(2) 59.8(1).

= Tl, K, Rb, Ba, NH_4; M = Cu, Mn, Zn; and X = Cl, Br which all crystallise in the same cubic space group *F*23.[11,12]

The recognition of a molecular $[Fe_4S_4Cl_4]^{2-}$ cubane-type cluster with full T_d symmetry, as reported here demonstrates clearly that intramolecular electronic Jahn–Teller type effects are not responsible for the symmetry reduction as observed in many other examples of compounds with such clusters. Rather the lattice symmetry which is, besides other factors, also affected by the local symmetry of the counter cation determines the cluster symmetry.

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Notes and references

‡ *Crystal data*: $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4][Fe_4S_4Cl_4]$: M = 1904.74, cubic, a = 21.241(2) Å, U = 9583(4) Å^3, T = 293(2) K, space group *F*23 (no. 196), Z = 4, μ(Mo-Kα) = 1.277 mm^{-1}, 23259 reflections collected, 1973 unique (R_{int} = 0.093) which were used in all calculations, two constraints, $R1(F)$ = 0.0645, $wR2(F^2)$ = 0.1750.

All thermal ellipsoids of the atoms of the 18-crown-6 molecules are elongated tangentially to the three-fold axis which cuts through the enclosed K cation, indicating that these almost flat molecules have some rotational freedom within the crystals. A thermal ellipsoid plot of the $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4]$ cation in crystals of $[K_4(FeCl_4)(C_{12}H_{24}O_6)_4][Fe_4S_4Cl_4]$ is given as ESI.†

CCDC reference number 162244. See http://www.rsc.org/suppdata/cc/b1/b103871k/ for crystallographic data in CIF or other electronic format.

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