Synthesis and characterization of a new double-cubane Mo–Fe–S cluster compound, $[NEt_4]_3[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_3Cl_3]$

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The new double-cubane cluster compound $[NEt_4]_3[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_3Cl_3]$ is synthesized from $(NH_4)_2MoS_4$, $FeCl_3$, Fe powder, S powder, NaSPh and NEt_4Br in MeOH–DMF, its crystal structure is determined by X-ray crystallography, and results of XPS indicate a valence state of +4 for Mo.

Recently, a breakthrough in the study of the nitrogenase structure has been made with the X-ray single-crystal structure determinations of the MoFe proteins of the nitrogenases from *A. vinelandii*[1–3] and *C. Pasteurianum*[4–6] which show the FeMo cofactor to be a cluster formed from Fe_4S_3 and $MoFe_3S_3$ subunits, through two[1–4] or three[5,6] S^{2-} bridges, with homocitrate acting as a bidentate ligand coordinated to Mo. For modelling the coordination environment of Mo in FeMo-co, recent studies on Mo–Fe–S cluster compounds with polycarboxylate ligands have been reported.[7–9]

During the last decade, as a consequence of the interesting active centre structure of the FeMo protein of nitrogenase, many kinds of Mo–Fe–S cluster compounds have been synthesized and their structures and properties extensively studied.[10–17] In double-cubane-like M–Fe–S (M = Mo or W) cluster compounds with triple bridges, $[M_2Fe_6S_8(\mu\text{-}SR)_3(SR)_6]^{3-}$ and $[M_2Fe_6S_8(\mu\text{-}OR')_3(SR)_6]^{3-}$, all of the Fe atoms in the MFe_3S_4 units are bonded to the same terminal ligands.[10,11,14,15,18] We report here the synthesis and characterization of a novel double-cubane Mo–Fe–S cluster compound, $[NEt_4]_3[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_3Cl_3]$ **1**, in which Fe atoms in two cubane units link different terminal ligands, SPh and Cl.

Synthetic manipulations were carried out under anaerobic conditions. Compound **1** was obtained in 28% yield from $(NH_4)_2MoS_4$, $FeCl_3$, Fe powder, S powder, NaSPh and NEt_4Br (molar ratio: 1 : 4 : 2 : 2 : 8 : 1) in methanol–dimethylformamide. The magnetic susceptibility of **1**, which has satisfactory elemental analyses,† was measured in the solid state using a Faraday balance at 293 K, and the calculated magnetic moment (μ_{eff}) was 5.3 μ_B. The ^{57}Fe Mössbauer spectrum for **1** at ambient temperature consists of two asymmetric quadrupole doublets with average values of isomer shifts and quadrupole splittings of 0.27 (δ_1), 0.32 (δ_2) mm s^{-1}; 1.01 (Δ_1) and 0.62 mm s^{-1} (Δ_2), indicating two different kinds of Fe sites in **1**. The measurement of the X-ray photoelectron spectrum (XPS) of **1** shows binding energies for Mo $3d_{5/2}$ of 229.9 eV and for Fe $2p_{3/2}$ of 709.2 eV, suggesting valence states of +4 for Mo, and between +2 and +3 for Fe.‡

A complete X-ray structural determination§ revealed that the crystal structure of **1** consists of discrete $[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_3Cl_3]^{3-}$ cluster anions and $[NEt_4]^+$ cations. Fig. 1 shows a perspective view of the cluster anion with selected bond lengths and angles. Compound **1** is crystallographically isomorphous with $[NEt_4]_3[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_6]$ **2**[18] and $[NEt_4]_3[W_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_6]$ **3**.[19] The cluster anion contains two $MoFe_3S_4$ cubane-like units linked by three μ-methoxo groups. In each cubic unit, each Fe atom is coordinated by a half-occupied Cl atom and a half-occupied SPh group and therefore the cluster anion exhibits crystallographically imposed $3/m$ symmetry with Mo and S(2) atoms lying on the 3 axis and methoxo groups on the mirror. As far as an individual anion is concerned, the Fe atoms are bonded to the SPh groups in one $MoFe_3S_4$ unit and to terminal Cl atoms in the other unit. A comparison of important bond lengths between **1** and **2**[18] shows that Mo–O [2.147(19) Å] and Fe–S(2) [2.286(9) Å] for **1** are longer than those [2.112(5), 2.267(3) Å, respectively] for **2**, but Mo–S(1) [2.337(10) Å] and Fe–S(1) [2.240(9) Å] of **1** are shorter than those [2.354(2), 2.278(2) Å, respectively] of **2**. The remaining important bond lengths in these two cluster compounds are very similar. The ^{57}Fe Mössbauer spectra of **1** and **3** indicate that the iron atoms in **1** are not electronically equivalent but that those in **3** are nearly equivalent. The inequivalence of the atoms in **1** is probably a result of the Fe atoms in each of the two cubic units of **1** being linked to different terminal ligands.

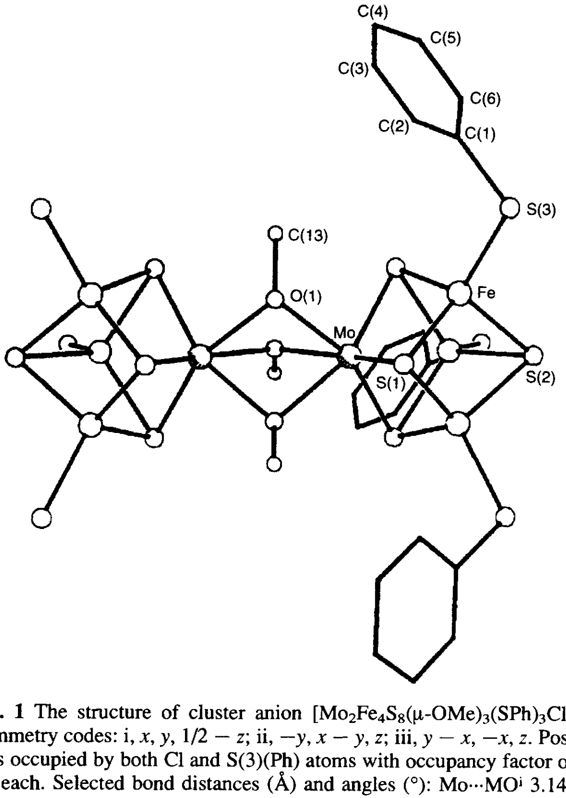

Fig. 1 The structure of cluster anion $[Mo_2Fe_4S_8(\mu\text{-}OMe)_3(SPh)_3Cl_3]^{3-}$. Symmetry codes: i, *x*, *y*, 1/2 − *z*; ii, −*y*, *x* − *y*, *z*; iii, *y* − *x*, −*x*, *z*. Position X is occupied by both Cl and S(3)(Ph) atoms with occupancy factor of 0.5 for each. Selected bond distances (Å) and angles (°): Mo···MO^{i} 3.146(7), Mo···Fe 2.726(5), Fe···Fe^{ii} 2.705(5), Mo–S(1) 2.337(10), Mo–O(1) 2.147(19), Fe–S(1) 2.240(9), Fe–S(1^{iii}) 2.259(7), Fe–S(2) 2.286(9), Fe–X 2.235(11); S(1)–Mo–S(1^{ii}) 102.5(2), S(1)–Mo–O(1) 89.3(9), S(1^{ii})–Mo–O(1) 158.6(6), S(1^{iii})–Mo–O(1) 92.2(6), O(1)–Mo–O(1^{ii}) 72.2(4), S(1)–Fe–S(1^{iii}) 108.2(4), S(1)–Fe–S(2) 104.2(3), S(1)–Fe–X 114.7(5), S(1^{iii})–Fe–S(2) 103.6(3), S(1^{iii})–Fe–X 115.9(4), S(2)–Fe–X 109.1(3).

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Footnotes

† *Anal. Calc.* for $Mo_2Fe_6Cl_3S_{11}O_3N_3C_{45}H_{84}$: Mo, 11.28; Fe, 19.70; Cl, 6.25; S, 20.73; N, 2.47; C, 31.77; H, 4.99. Found: Mo, 11.02; Fe, 19.37; Cl, 5.99; S, 20.40; N, 2.58; C, 31.97; H, 5.14%.

‡ Binding energies (eV) of standard samples: $C_4H_4Fe(C_5H_5)$, Fe $2p_{3/2}$ 708.1; Fe_2O_3, Fe $2p_{3/2}$ 710.7; Mo compounds with valence of +4, Mo $3d_{5/2}$ 229.9–229.2.

§ *Crystal data* for $[NEt_4]_3[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SPh)_3Cl_3]$: M = 1701.31, hexagonal, space group $P6_3/m$, a = 16.884(5), c = 15.746(6) Å, U = 3887(3) Å^3, Z = 2, D_c = 1.31 g cm^{-3}, scan mode ω, 2θ range 3–50°, μ(Mo-Kα) = 18.0 cm^{-1}, R = 0.089 (R_w = 0.086) from 705 reflections $[I > 3\sigma(I)]$ and 103 parameters.

The crystal was sealed in a glass capillary. Data were collected at room temperature on a Nicolet R3m/E four-circle diffractometer using graphite-monochromated Mo-Kα radiation. The data were corrected for absorption. The coordinates of Mo, Fe and S atoms were obtained by direct methods and the remaining non-hydrogen atoms were located on the difference Fourier map. The carbon atoms in the phenyl group showed large thermal parameters indicating disorder, and partial occupancy. The occupancy factors were estimated at 0.5 on the basis of their electron densities. All non-hydrogen atoms were refined anisotropically except for those of the disordered phenyl ring, which were refined isotropically as a rigid hexagon with C–C bond lengths constrained to 1.39 Å. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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