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Synthesis and structure of a new iron–molybdenum–oxygen cluster with α-furoic acid

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A new hexanuclear iron–molybdate cluster containing the α-furoic acid ligand, $[\mathrm{Fe}_4^{\mathrm{III}}\mathrm{Mo}_2^{\mathrm{VI}}\mathrm{O}_{10}(\mathrm{C}_4\mathrm{H}_3\mathrm{OCOO})_4(\mathrm{DMF})_4]\cdot 2\mathrm{DMF}$, has been synthesised by a solid state reaction and characterised by X-ray crystallography, EPR, XPS and IR spectroscopy.

Solids containing Mo–O–M (M = Fe, Cu, Zn, Co or Ni) units have been widely investigated.[1–7] Examples based on Mo–O–Fe hetero-metal oxide assemblies include $[\{\mathrm{FeCl}(2,2'\text{-bpy})\}_2\mathrm{MoO}_4]$,[8] $[\{\mathrm{Fe(typy)}\}_2\mathrm{Mo}_4\mathrm{O}_{12}]$,[9] $[\{\mathrm{Fe(typor)}\}_3(\mathrm{Mo}_6\mathrm{O}_{19})_2]$[10] and $[\{\mathrm{Fe(typtrz)}\}_2\mathrm{Mo}_4\mathrm{O}_3]$.[11] Under hydrothermal conditions, they were synthesised in the presence of an organoimine such as (2,2′-bpy), (4,4′-bpy) and typtrz. However, iron molybdates containing carboxylic acid ligands are very rare. Here, we report the synthesis and structural characterization of the interesting discrete neutral iron molybdate complex $[\mathrm{Fe}_4\mathrm{Mo}_2\mathrm{O}_{10}(\mathrm{C}_4\mathrm{H}_3\mathrm{OCOO})_4(\mathrm{DMF})_4]\cdot 2\mathrm{DMF}$[10] with the α-furoic acid ligand.

Compound **1** was synthesised by a low temperature solid-state reaction. A well-ground mixture of $[\mathrm{NH}_4]_2\mathrm{MoS}_4$ (0.3 g, 1 mmol), $\mathrm{FeCl}_2\cdot 4\mathrm{H}_2\mathrm{O}$ (0.4 g, 2 mmol) and α-furoic acid (0.5 g, 4.5 mmol) was placed in a reaction tube, which was sealed and then heated at 95 °C for 18 h. The tube was cooled to room temperature, and a black solid was obtained. After extracting the product with DMF (30 ml), the deep red extract was filtered, and the filtrate was layered with $\mathrm{Pr^iOH}$ (20 ml) and allowed to stand at room temperature for about a month. Deep red cubic crystals of compound **1** were obtained (0.15 g, 35.7% yield, based on Mo). Found (%): C, 31.20; H, 3.82; N, 5.51. Calc. for $\mathrm{C}_{19}\mathrm{H}_{27}\mathrm{N}_3\mathrm{O}_{14}\mathrm{Fe}_2\mathrm{Mo}$ (%): C, 31.29; H, 3.73; N, 5.76. IR (KBr, ν/cm^{-1}): 1657 (ν_{COO}), 1014 and 929 ($\nu_{\mathrm{Mo=O}}$), 786 ($\nu_{\mathrm{Mo–O–Fe}}$), 365 ($\nu_{\mathrm{Fe–O}}$).

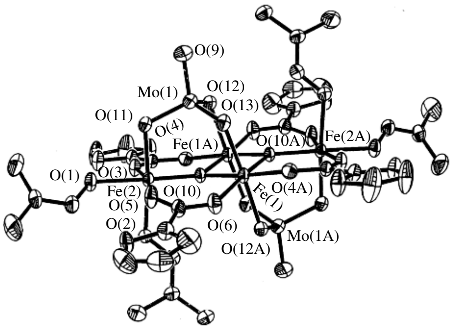

Figure 1 The molecular structure of $[\mathrm{Fe}_4^{\mathrm{III}}\mathrm{Mo}_2^{\mathrm{VI}}\mathrm{O}_{10}(\mathrm{C}_4\mathrm{H}_3\mathrm{OCOO})_4(\mathrm{DMF})_4]$.

Compound **1** is a discrete neutral cluster with two crystal solvent molecules. The multinuclear structure of $[\mathrm{Fe}_4\mathrm{Mo}_2\mathrm{O}_{10}(\mathrm{C}_4\mathrm{H}_3\mathrm{OCOO})_4(\mathrm{DMF})_4]$ is shown in Figure 1.† In each molecule unit with a crystallographic inversion centre, a crystallographically unique hexavalent molybdenum ion, Mo(1), and two trivalent iron ions, Fe(1) and Fe(2), occurred. The Mo(1) atom in a tetrahedral site is coordinated by one terminal oxygen atom [O(9)] and three μ$_2$-bridging oxygen atoms, [O(11), O(12) and O(13)]. The Mo–O$_\mathrm{t}$ distance [1.695(4) Å], as expected, is much shorter than the other three Mo–(μ$_2$-O) distances [1.777(4)–1.811(4) Å]. The O–Mo–O angles, ranging from 107.3(2) to 112.46(17)°, suggest that the coordination environment of the tetrahedral Mo centre is slightly distorted. Both Fe atoms are in an octahedral geometry and coordinated by six oxygen atoms, but the specific coordination environments are different. The Fe(1) atom is bonded to two μ$_3$-O atoms [O(10) and O(10A)], two μ$_2$-O atoms [O(13) and O(12A)] and two terminal O atoms [O(4A) and O(6)] from two α-furoic acid ligands forming octahedral $\{\mathrm{Fe(1)O}_6\}$. Whereas the Fe(2) atom is coordinated by a μ$_3$-O atom [O(10)], a μ$_2$-O atom [O(11)], two terminal O atoms [O(3) and O(5)] from two α-furoic acid ligands and two terminal O atoms [O(1) and O(2)] of DMF units, building up the octahedral $\{\mathrm{Fe(2)O}_6\}$. The Fe–(μ$_2$-O) distances are in the range 1.991(4)–2.065(4) Å. The average distance (2.053 Å) of Fe–O$_{\mathrm{DMF}}$ coordination bonds is longer than that of Fe–O$_{\mathrm{Furoic}}$ (2.025 Å) belonging to covalent bonds. The Fe(2)–(μ$_3$-O) distance, 1.884(3) Å, is significantly shorter than the Fe(1)–(μ$_3$-O) and Fe(1A)–(μ$_3$-O) distances [1.971(3) and 1.986(3) Å, repectively]. The *cis* angles [83.09(13) to 96.58(14)°] and *trans* angles [168.50(15) to 177.95(14)°] show that the octahedral coordination geometry of Fe atoms is highly distorted. The polyhedron graph of the compound is shown in Figure 2. Both octahedral coordination Fe(1) and Fe(1A) are bonded through sharing an

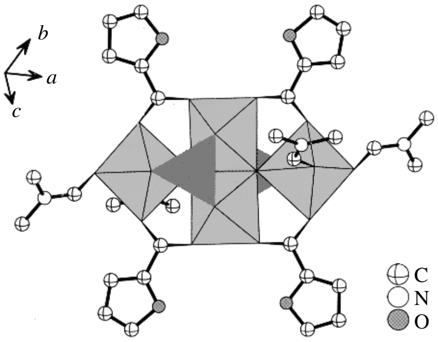

Figure 2 The polyhedral and ball-and-stick representation of the structure of compound **1**. The deep grey polyhedrons represent the MoO_4 tetrahedra, and the light grey polyhedrons represent the FeO_6 octahedra.

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† *X-ray structure data for* **1**: monoclinic, space group *C*2/*c*, a = 24.669(5), b = 15.005(3), c = 16.366(3) Å, β = 108.97(3)°, V = 5729(2) Å^3, Z = 8, d_{calc} = 1.691 g cm^{-3}, μ(MoKα) = 6.672 mm^{-1}, MoKα radiation, λ = 0.71073 Å. A deep red cubic crystal with dimensions of 0.473×0.264×0.230 mm was mounted on a glass fibre. Data collection was performed on a Rigaku R-AXIS RAPID IP diffractomerter at 293(2) K in the range $1.61 < \theta < 27.48°$ using ω and φ scan. A total of 6556 data were collected and merged to give 6556 unique reflections of which 3920 were considered to be observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined using the SHELXTL software. All the non-hydrogen atoms were refined anisotropically. Final R values (R = 0.0511, wR = 0.1407, S = 0.906) were obtained for 3920 reflections with $I > 2\sigma(I)$ and a total of 347 parameters.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 200991. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

edge [O(10) and O(10A)]. The other two distorted octahedral $\{Fe(2)O_6\}$ respectively share a corner through a μ_3-O atom with octahedral $\{Fe(1)O_6\}$ and $\{Fe(1A)O_6\}$. Tetrahedral $\{Mo(1)O_4\}$ and $\{Mo(1A)O_4\}$ units share corners through their μ_2-O atoms with three adjacent octahedral $\{FeO_6\}$ units.

The packing of the compound is shown in Figure 3. The hydrogen bond C(15)–H···O(13) (0.5 – *x*, 0.5 + *y*, 0.5 – *z*) [3.320 Å, 144.5°] occurs between μ_2-O atoms [O(13)] from the hexanuclear iron–molybdate cluster and the C(15) of α-furoic acid in the adjacent iron–molybdate cluster. The cluster units $[Fe_4Mo_2O_{10}]^{4+}$ are connected into a one-dimensional supramolecular chain along the axis *c* through the hydrogen bond.

The EPR spectra of compound **1** show a typical signal at *g* = 2.013 attributed to Fe^{III}, while no other signals appear, indicating that the oxidation state of Mo is +6. The XPS spectra show that the binding energy of $Fe_{2p^{3/2}}$ is 712.3 eV, which indicates the existence of typical Fe^{III}, and that of $Mo_{3d^{5/2}}$ is 232 eV showing the existence of Mo^{VI}. The bond valence sum calculations made using empirical parameters[12] display that the valence states of Fe(1) and Fe(2) are 2.96 and 3.03, respectively, or 5.93 for Mo, being in agreement with the above results.

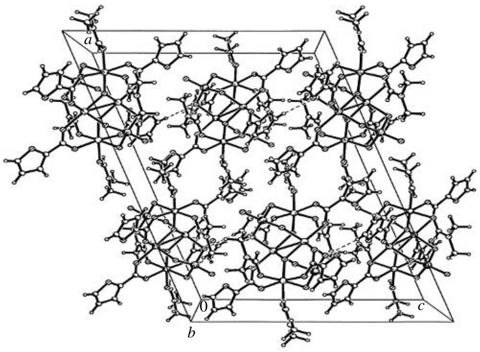

Figure 3 The packing diagram of compound **1**. Hydrogen bond: C(15)–H···O(13) 3.320 Å, 144.5° (0.5 + *x*, 0.5 – *y*, 0.5 + *z*).

It seems that sulfur atoms in MoS_4^{2-} were replaced by oxygen in air and resulted in the formation of the title compound, because pale yellow crystals of S_8 were found from the reaction system. The following reaction probably took place:

$$4Fe^{2+} + 8S^{2-} + 5O_2(g) \rightarrow 4Fe^{3+} + S_8\downarrow + 10O^{2-}$$

We once adopted CH_2Cl_2 instead of DMF to extract the product, but no good result was obtained.

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References

1 Y. Zhang, P. J. Zapf, L. M. Meyer, R. C. Haushalter and J. Zubieta, *Chem. Commun.*, 1997, 2159.
2 P. J. Zapf, C. J. Warren, R. C. Haushalter and J. Zubieta, *Chem. Commun.*, 1997, 1543.
3 D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta and R. C. Haushalter, *Angew. Chem.*, 1997, **109**, 904 (*Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 795).
4 D. Hagrman, P. J. Zapf and J. Zubieta, *Chem. Commun.*, 1998, 1283.
5 D. Hagrman, R. C. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 361.
6 D. Hagrman, C. J. Warren, R. C. Haushalter, R. S. Rarig, Jr., K. M. Johnson III, R. L. LaDuca, Jr. and J. Zubieta, *Chem. Mater.*, 1998, **10**, 3294.
7 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew Chem., Int. Ed. Engl.*, 1999, **38**, 2638.
8 P. J. Zapf, R. P. Hammond, R. C. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 1366.
9 P. J. Hagrman and J. Zubieta, *Inorg. Chem.*, 2000, **39**, 5218.
10 D. Hagrman and J. Zubieta, *Chem. Commun.*, 1998, 2005.
11 R. S. Rarig, Jr. and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 2001, 3446.
12 I. D. Brown and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192.

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