A Heteropolyoxomolybdenum(VI)iron(III) Cation. Synthesis and Crystal Structure of $[(LFe^{III})_3Mo^{VI}_4O_{14}(\mu\text{-}OMe)_3](ClO_4)_2$ (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane)

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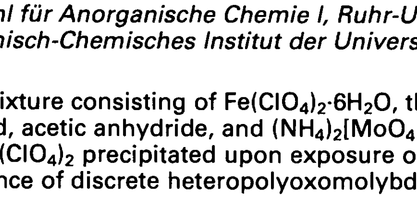
From a mixture consisting of $Fe(ClO_4)_2{\cdot}6H_2O$, the cyclic amine *N,N',N''*-trimethyl-1,4,7-triazacyclononane, glacial acetic acid, acetic anhydride, and $(NH_4)_2[MoO_4]{\cdot}4H_2O$ in methanol, red-orange crystals of $[(LFe)_3Mo_4O_{14}(\mu\text{-}OMe)_3](ClO_4)_2$ precipitated upon exposure of the solution to air; characterization by *X*-ray crystallography showed the presence of discrete heteropolyoxomolybdenum(VI)iron(III) dications and perchlorate anions.

The derivative chemistry of heteropolyanions of molybdenum(VI) has in recent years rapidly developed and a number of very unusual large anions of this type have been characterized by *X*-ray crystallography.[1] Replacement of peripheral metal–oxygen groups by other metal–ligand complexes[2] or the successful attachment of low-valent organometallic fragments[3] to such polyanions has opened up new areas of inorganic chemistry. The vast majority of these complexes are anions. Here we report the synthesis and structure of a *cationic* heteropolyoxomolybdenum(VI)iron(III) complex, which also contains methoxy bridging groups.[4]

A mixture of $Fe(ClO_4)_2{\cdot}6H_2O$ (0.36 g), *N,N',N''*-trimethyl-1,4,7-triazacyclononane (L) (0.51 g), and anhydrous sodium acetate (0.25 g) in methanol (6 ml) was stirred at 20 °C under argon for 2 h. After addition of $(NH_4)_2[MoO_4]{\cdot}4H_2O$ (0.4 g) and stirring for a further 3 h the resulting deep brown suspension was exposed to air (5 min) and filtered. From the now yellow-brown filtrate, kept in a closed vessel for a few hours, yellow crystals of $[LFe^{III}(\mu\text{-}MoO_4)_3Fe^{III}L]$ (**1**) precipitated (0.48 g). In the i.r. spectrum (KBr disc) four bands at 920sh, 880s, 815s, and 765s cm^{-1} are indicative of bidentate, bridging $[MoO_4]^{2-}$ groups (C_{2v} symmetry).[5] Complex (**1**) is soluble in organic solvents (acetone, ethanol) but not in water. We propose that it has the structure shown.[8] Temperature-dependent magnetic susceptibility measurements (90—293 K) of a powdered sample of (**1**) indicate the presence of weakly antiferromagnetically coupled high-spin iron(III) centres. The data were readily fitted using an isotropic Heisenberg model $H = -2J{\cdot}S_1{\cdot}S_2$ ($S_1 = S_2 = 5/2$) and $g = 1.9$ (temperature-independent paramagnetism = 0). The exchange coupling constant J was found to be $-3(1)\ cm^{-1}$.



(1)

Red-orange crystals of $[(LFe)_3Mo_4O_{14}(\mu\text{-}OMe)_3](ClO_4)_2$ (**2**) were obtained from a mixture of $Fe(ClO_4)_2{\cdot}6H_2O$ (0.25 g), the ligand (0.34 g), glacial acetic acid (0.2 ml), and acetic anhydride (0.3 ml) in methanol (50 ml), which was stirred for 30 min under argon at 20 °C and then $(NH_4)_2[MoO_4]{\cdot}4H_2O$ (0.27 g) added; the stirring was then continued for 4 h. The resulting red-brown suspension was filtered in the presence of air. From the clear solution, kept in a closed vessel,

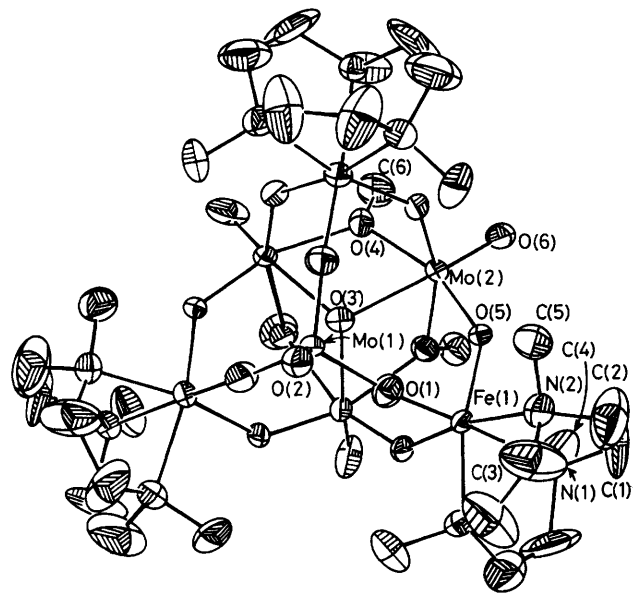


Figure 1. Perspective view of the cation $[(LFe)_3Mo_4O_{14}(\mu\text{-}OMe)_3]^{2+}$ looking down the crystallographic C_3 axis [O(2), Mo(1), O(3) are located on this axis]. Selected bond distances (Å) and angles (°): Mo(1)–O(1) 1.736(6); Mo(1)–O(2) 1.62(2); Mo(2)–(3) 2.115(6); Mo(2)–O(4) 2.127(6); Mo(2)–O(5) 1.821(7); Mo(2)–O(6) 1.714(9); Fe(1)–O(1) 1.995(7); Fe(1)–O(5) 1.911(7); Fe(1)–N(1) 2.24(1); Fe(1)–N(2) 2.22(1): O(4)–C(6) 1.46(2); Mo(2) · · · Mo(2′) 3.384(2); Fe(1) · · · Mo(2) 3.475(3); Fe(1) · · · Mo(1) 3.633(2); Fe(1)–O(5)–Mo(2) 137.2(2); Fe(1)–O(1)–Mo(1) 153.7(3); Mo(2)–O(4)–Mo(2′) 105.4(1); Mo(2)–O(3)–Mo(2) 106.3(1).

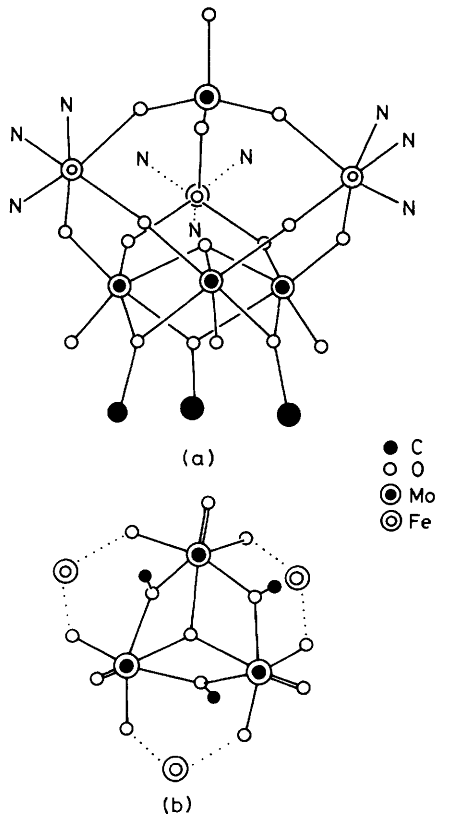


Figure 2. (a) Perspective view of the core of the complex cation omitting the atoms of the cyclic amine. (b) Schematic representation of the central $Mo_3O_9(\mu\text{-}OMe)_3$ core.

red-orange crystals of (**2**) suitable for *X*-ray crystallography were obtained (0.14 g).†

Figure 1 shows the complete dication in (**2**), which has crystallographically imposed C_{3v} symmetry. It consists of three high-spin iron(III) and four molybdenum(VI) centres. It may be described as being composed of three LFe^{III} units which are each co-ordinated *via* three μ_2-oxo bridges[6] to a $Mo_4O_{14}(\mu\text{-}OMe)_3$ core (Figure 2a) yielding three distorted octahedral *fac*-FeN_3O_3 polyhedra. One bridging μ_3-$[MoO_4]^{2-}$ anion, which also possesses C_{3v} symmetry, is bound to the three Fe^{III} centres, and each of the Fe^{III} ions is, in addition, co-ordinated in a bidentate manner to a central $Mo_3O_{10}(\mu\text{-}OMe)_3$ unit (Figure 2b). In this central $Mo_3O_{10}(\mu\text{-}OMe)_3$ moiety the molybdenum(VI) centres are six-co-ordinate; the Mo^{VI} ions are connected by one μ_3-oxo bridge [O(3)] and three μ_2-methoxy bridges [O(5)]. Each Mo^{VI} ion has one terminal oxo ligand [Mo(2)=O(6) 1.714(9) Å].

A few isopolymolybdates containing bridging methoxy groups have been described recently;[4] the geometry of the Mo(μ-OMe)Mo segment in (**2**) is very similar to that in those. The arrangement of the latter trinuclear part is reminiscent of the well characterized complexes containing the $\{Mo_3O_4\}^{4+}$ moiety,[7] but lacking the direct Mo–Mo metal bonding owing to the absence of d valence electrons of the Mo^{VI} ions [Mo(2) · · · Mo(2′) 3.384 Å]. The ClO_4 anions in crystals of (**2**) were found to be severely disordered.

The effective magnetic moment of (**2**) was found to be slightly temperature-dependent: $\mu_{eff.}$ (293 K) = 5.53 μ_B/Fe and 5.17 μ_B at 120 K indicating weak antiferromagnetic coupling of the Fe^{III} centres.

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References

1 M. T. Pope, 'Heteropoly and Isopoly Oxometalates,' in Inorganic Chemistry Concepts No. 8, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1983; V. W. Day and W. G. Klemperer, *Science*, 1985, **22**, 533.

2 A. Komura, M. Hayashi, and H. Imanaga, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 87; R. K. C. Ho and W. G. Klemperer, *J. Am. Chem. Soc.*, 1978, **100**, 6772; W. H. Knoth, *J. Am. Chem. Soc.*, 1979, **101**, 759.

3 C. J. Besecker, V. W. Day, W. G. Klemperer, and M. R. Thompson, *Inorg. Chem.*, 1985, **24**, 44.

4 Structurally characterized methoxy-bridged isopolyoxomolybdates are: $Na_4[Mo_8O_{24}(OMe)_4]\cdot MeOH$: E. M. McCarron, III, and R. L. Harlow, I, *J. Am. Chem. Soc.*, 1983, **105**, 6179; $[NBu^n{}_4]_2$-$[Mo_4O_8(OMe)_2(NNPh)_4]$: T. C. Hsieh and J. A. Zubieta, *Polyhedron*, 1986, **5**, 305.

5 R. Coomber and W. P. Griffith, *J. Chem. Soc* (*A*), 1968, 1128.

6 The preparation of a neutral heterobinuclear oxo-bridged Mo^V–Fe^{III} complex has recently been described: R. L. Elliot, P. J. Nichols, and B. O. West, *Austr. J. Chem.*, 1986, **39**, 975.

7 A. Müller, R. Jostes, and F. A. Cotton, *Angew. Chem.*, 1980, **92**, 921; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 875.

8 Since we submitted this work for publication, this structure type has been confirmed by *X*-ray crystallography for the analogous $[LFe(\mu\text{-}CrO_4)_3FeL]$ complex. For (**1**) satisfactory elemental analysis has been obtained, and, in addition, its molecular weight has been determined in an acetone solution to be 940 ± 20.

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† *Crystal data:* $C_{30}H_{72}Cl_2Fe_3O_{25}Mo_4N_9$, hexagonal, space group *P*6_3*mc* (C^4_{6v}, No. 186), $a = 15.697(7)$, $c = 14.255(8)$ Å; $U = 3041.8$ Å^3, $Z = 2$, $R = 0.054$ for 1284 observed [$I \geqslant 2.5\sigma(I)$] diffractometer-collected reflections (Mo-K_α-radiation, 293 K). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.