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Linear Face-sharing Trioctahedral $[\text{Mo}_3\text{I}_{12}]^{3-}$ by Spontaneous thf Loss from $[\text{MoI}_4(\text{thf})_2]^-$: Structure, Bonding and Magnetic Properties

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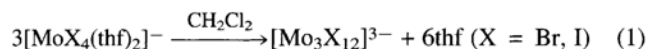
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Complexes $[\text{Mo}_3\text{X}_{12}]^{3-}$ ($\text{X} = \text{I}, \text{Br}$) assemble by spontaneous thf loss in noncoordinating solvents from $[\text{MoX}_4(\text{thf})_2]^-$ and exhibit a linear face-shared trioctahedral structure with, at the same time, delocalized metal–metal bonding and local moment antiferromagnetic exchange interactions.

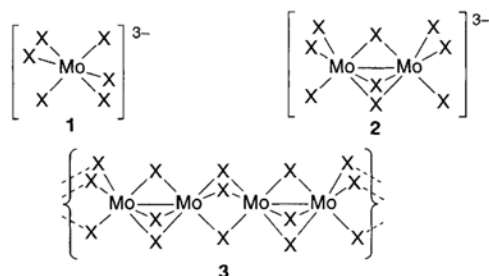
Halide complexes of molybdenum(III) adopt an octahedral coordination geometry, as in mononuclear $[\text{MoX}_6]^{3-}$ **1** and dinuclear face-shared bioctahedral $[\text{Mo}_2\text{X}_9]^{3-}$ **2**.¹ The structure of MoX_3 ($\text{X} = \text{halogen}$) consists of close-packed X atoms with the Mo centres filling one-third of the octahedral holes, in such a way that metal–metal bonded face-shared Mo_2X_9 bioctahedra are present.^{2,3} For instance, the structure of MoBr_3 **3** consists of one-dimensional $(\mu\text{-Br})_3\text{Mo}(\mu\text{-Br})_3$ stacks with alternating Mo–Mo bonding and nonbonding contacts.³ The ions **1** and **2** can be thought of as fragments of the extended structure **3**. The only reported larger fragment of this structure is $[\text{Mo}_3\text{Cl}_{12}]^{3-}$, which was obtained from the thermal condensation of $[\text{Mo}_2\text{Cl}_9]^{2-}$ and $[\text{MoCl}_3(\text{CO})_4]^-$, but was not investigated crystallographically, nor was its electronic structure described.⁴ Here we report the preparation, by a novel synthetic method, and preliminary studies of the $[\text{Mo}_3\text{X}_{12}]^{3-}$ ($\text{X} = \text{Br}, \text{I}$) ions, and the structural characterization of the iodide complex which reveals, contrary to **3**, delocalized metal–metal bonding.

A number of new *trans*- $[\text{MoX}_4(\text{thf})_2]^-$ salts ($\text{X} = \text{Br}, \text{I}$) have been isolated from the reaction of $\text{MoX}_3(\text{thf})_3$ and the desired salt of X^- in thf.[†] The analogous formation of *trans*- $[\text{MoCl}_4(\text{thf})_2]^-$ from $\text{MoCl}_3(\text{thf})_3$ and Cl^- has been previously reported.^{5,6} These compounds are stable in the solid state and in thf, but dissolution in dichloromethane or chloroform results in a smooth and quantitative loss of the thf ligands, as established by ¹H NMR integration of free thf against the internal reference of the diamagnetic cation resonances [eqn. (1)]. Salts of the $[\text{Mo}_3\text{X}_{12}]^{3-}$ anions have been isolated either by this procedure or by carrying out the reaction between $\text{MoX}_3(\text{thf})_3$ and X^- directly in CH_2Cl_2 .[‡]



The corresponding $[\text{Mo}_3\text{Cl}_{12}]^{3-}$ species cannot be obtained by this method, as only 1.5 thf moles per mole of $[\text{MoCl}_4(\text{thf})_2]^-$ are released, presumably to give a $[\text{Mo}_2\text{Cl}_8(\text{thf})]^{2-}$ product, a related phosphine derivative of which, $[\text{Mo}_2\text{Cl}_8\text{PEt}_3]^{2-}$, has been recently described.⁷ This process of thf replacement by a bridging halide is reminiscent of, but proceeds further with respect to, the thf loss from $\text{MoX}_3(\text{thf})_3$ in non-coordinating solvents to afford edge-sharing bioctahedral $\text{Mo}_2\text{X}_6(\text{thf})_4$ and ultimately face-sharing bioctahedral $\text{Mo}_2\text{X}_6(\text{thf})_3$ ($\text{X} = \text{Cl}, \text{Br}$).⁸

The structure of $[\text{PPh}_4]_3[\text{Mo}_3\text{I}_{12}]$ has been determined by X-ray crystallography.[§] The $[\text{Mo}_3\text{I}_{12}]^{3-}$ trianion (Fig. 1) clearly shows a linear face-sharing trioctahedral geometry. The only



other structurally characterized dodecahalotrimetal complex⁹ is $[\text{Ru}_3\text{Cl}_{12}]^{4-}$; a few related phosphine derivatives of types $[\text{Ru}_3\text{Cl}_8(\text{PR}_3)_4]^{n+}$ ($n = 0, 1$) and $[\text{Ru}_3\text{Cl}_6(\text{PR}_3)_6]^+$ have also been reported.^{10–12} The central metal atom resides on a crystallographic inversion centre. The coordination geometry around each metal atom is very little distorted from ideal octahedral, all *cis* I–Mo–I angles being in the narrow range 88.4–91.4°.

As detailed in the classical contribution of Cotton and Ucko,¹³ an ideal face-sharing bioctahedron is characterized by a $\text{M}-(\mu\text{-X})\text{-M}$ angle of 70.53°. When a metal–metal bonding interaction is *not* present, a *much larger* angle results as a consequence of the repulsive interaction (angles greater than 80° are typically found for molecules having no metal–metal bond).¹³ The average Mo–I–Mo angle of 71.34(7)° in the $[\text{Mo}_3\text{I}_{12}]^{3-}$ ion thus indicates that *metal–metal interactions are present*. This angle is smaller than those reported for the trioctahedral *metal–metal bonded* ruthenium complexes $[\text{Ru}_3\text{Cl}_{12}]^{4-}$, $[\text{Ru}_3\text{Cl}_8(\text{PR}_3)_4]^{n+}$ ($n = 0, 1$) and $[\text{Ru}_3\text{Cl}_6(\text{PR}_3)_6]^+$ (in the range 72–75°).^{9–12} The presence of a metal–metal interaction is also consistent with theoretical analyses of this structural type. The results of our calculations at the extended Huckel level (Fig. 2) match those previously reported for $[\text{Ru}_3\text{Cl}_{12}]^{4-}$.¹⁴ Whereas two of the three pseudo- t_{2g} orbitals per Mo atom (of π/δ symmetry with respect to the Mo–Mo–Mo axis) lead to minimal overlap and remain substantially localized on the respective metal centres, the third orbital (of σ symmetry) allows the formation of a bonding combination (a_{1g}), whose occupation leads to delocalized metal–metal bonding (bond order 1/2 per Mo–Mo bond). Indeed, the Mo–Mo distance in this trinuclear ion [3.258(2) Å] is only slightly longer than the corresponding distances found in the isoelectronic face-sharing bioctahedral $[\text{Mo}_2\text{I}_9]^{3-}$ [Mo–Mo, 3.07(2) Å]¹⁵ and $[\text{Mo}_2\text{I}_7(\text{PMe}_3)_2]^-$ [3.022(1) Å]¹⁶ where the Mo–Mo bond order is 1. The other seven electrons occupy the central manifold of non-bonding orbitals ($2e_g + e_u + a_{2u}$), whereas this manifold is completely filled up in $[\text{Ru}_3\text{Cl}_{12}]^{4-}$.

According to our calculations, the ground state configuration is $(e_g)^4(e_u)^3$, corresponding to a spin doublet state, but other states with a greater number of unpaired electrons should be close in energy. Indeed, variable temperature magnetic suscep-

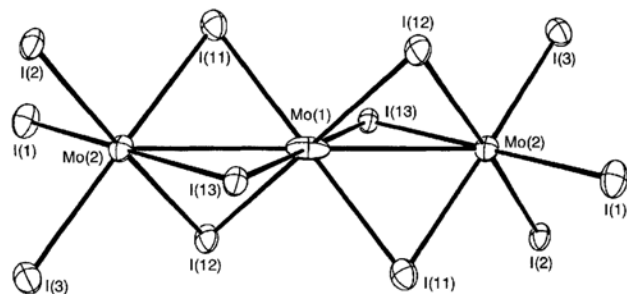


Fig. 1 An ORTEP view of the $[\text{Mo}_3\text{I}_{12}]^{3-}$ ion. Selected distances (Å) and angles (°) (averaged over chemically equivalent parameters; b = bridging, t = terminal): Mo–Mo 3.258(2), Mo(1)–I_b 2.769(10), Mo(2)–I_b 2.817(8), Mo(2)–I_t 2.752(4), I_t–Mo(2)–I_t 90.4(2), I_b–Mo(2)–I_b 88.4(5), I_b–Mo(1)–I_b 90.4(2), I_b–Mo(1)–I_{b'} 89.6(2), Mo(1)–I_b–Mo(2) 71.34(7)°.

tibility measurements for $[\text{PPh}_4][\text{Mo}_3\text{I}_{12}]$ show a moment reduction upon cooling, converging toward the value expected for one unpaired electron per trinuclear unit at low temperature ($3.92 \mu_B$ at 200 K, $2.38 \mu_B$ at 1.75 K). For comparison, the magnetic moment of $[\text{Bu}^n_4\text{N}]_3[\text{Mo}_3\text{Cl}_{12}]$ was reported as $2.02 \mu_B$ at 302 K.⁴ In conclusion, the theoretical analysis rationalizes the experimentally verified co-existence, in $[\text{Mo}_3\text{I}_{12}]^{3-}$, of delocalized metal-metal bonding and local-moment anti-ferromagnetic exchange coupling. The ideal extension of the $[\text{Mo}_n\text{X}_{3n+3}]^{3-}$ chain to $n = \infty$ would be expected to develop a half-filled d_σ band (Fig. 2), and the experimentally observed structure of MoBr_3 **3**³ can be viewed as a Peierls-distorted modification of such ideal structure.

Preliminary investigations of the chemistry of $[\text{Mo}_3\text{X}_{12}]^{3-}$ have been carried out. Standing in dilute solutions at room temperature leads to the slow release of X^- in an equilibrium process and affords a new type of trinuclear cluster, $[\text{Mo}_3\text{X}_{11}]^{2-}$. Crystals of $[\text{Bu}_4\text{N}]_2[\text{Mo}_3\text{I}_{11}]$ were slowly grown from CH_2Cl_2 -heptane, but disorder problems prevented a satisfactory refinement of the structure. However, the geometry of the ion is established as a triangular cluster of molecular D_{3h} symmetry with strong [av. $2.70(3) \text{ \AA}$] metal-metal interactions, as represented in **4**.

In conclusion, this work has shown: (i) a new strategy for the synthesis of linear face-sharing Mo^{III} trioctahedra and the first report of the bromide and iodide members of this class; (ii) the first structural characterization for these trinuclear Mo species, showing the presence of a metal-metal interaction in agreement

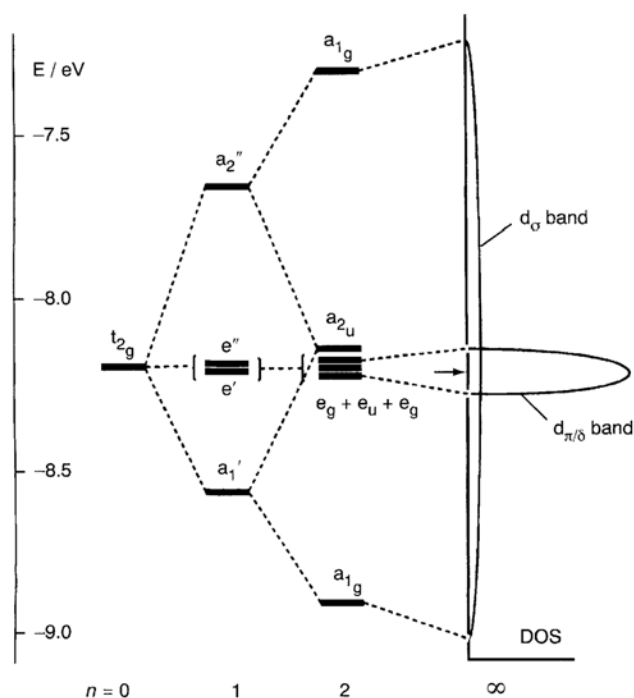
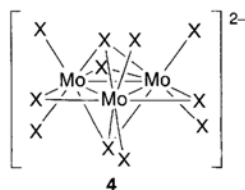


Fig. 2 MO diagram of the metal orbital region for complexes $[\text{I}_3\{\text{Mo}(\mu-1)_3\}_n\text{MoI}_3]^{3-}$ (calculated for $n = 0, 1, 2$; qualitative for $n = \infty$). The arrow indicates the Fermi level.



with the theoretical prediction of bonds of order 0.5; (iii) the magnetic properties of these complexes, again consistent with the theoretical model for the electronic structure.

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Footnotes

† Stirring equimolar mixtures of $\text{MoX}_3(\text{thf})_3$ and the desired $[\text{Cat}]\text{X}$ ($\text{X} = \text{Br}$, $\text{Cat} = \text{Bu}^n_4\text{N}$, $\text{PPN}[(\text{Ph}_3\text{P})_2\text{N}]$; $\text{X} = \text{I}$, $\text{Cat} = \text{PPh}_4$, Pr^n_4N , Bu^n_4N , PPN) in thf at room temp. overnight yielded the products, which were filtered, washed and dried under vacuum (50–80%). As a representative example, 582 mg (73%) of $[\text{PPh}_4][\text{Mo}_4(\text{thf})_2]^-$ were obtained from $\text{MoI}_3(\text{thf})_3$ (507 mg, 0.73 mmol) and PPh_4I (341 mg, 0.73 mmol) in 20 cm^3 of thf . Satisfactory C, H analyses were obtained for all compounds. Paramagnetically shifted ^1H NMR resonances are observed for the coordinated thf ligands (CDCl_3 , room temp.): $[\text{Mo}_4(\text{thf})_2]^-$ δ 100 ($w_{1/2} = 840 \text{ Hz}$, $\alpha\text{-H}$), 12.5 ($w_{1/2} = 150 \text{ Hz}$, $\beta\text{-H}$); $[\text{MoBr}_4(\text{thf})_2]^-$ δ 83 ($w_{1/2} = 1100 \text{ Hz}$, $\alpha\text{-H}$), 9.0 ($w_{1/2} = 220 \text{ Hz}$, $\beta\text{-H}$). However, prolonged standing of these solution led to loss of coordinated thf and formation of the $[\text{Mo}_3\text{X}_{12}]^{3-}$ salts, see text.

‡ Depending on the nature of X and the cation, the product either precipitated directly, or was recovered by addition of a nonsolvent (toluene, heptane or diethyl ether) or by cooling to low temperature. Satisfactory C, H analyses were obtained for all compounds ($\text{X} = \text{Br}$, $\text{Cat} = \text{PPN}$; $\text{X} = \text{I}$, $\text{Cat} = \text{PPh}_4$, Pr^n_4N , Bu^n_4N , PPN). A single crystal of $[\text{PPh}_4]_3[\text{Mo}_3\text{I}_{12}]$ suitable for the X-ray analysis was grown by dissolving $[\text{PPh}_4][\text{Mo}_4(\text{thf})_2]$ (230 mg, 0.21 mmol) and PPh_4I (105 mg, 0.22 mmol) in CH_2Cl_2 (5 cm^3) and carefully layering the resulting solution with diethyl ether (5 cm^3). The solvent diffusion was allowed to occur at -20°C .

§ Crystal data for $[\text{PPh}_4]_3[\text{Mo}_3\text{I}_{12}] \cdot 1.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{Et}_2\text{O})$: triclinic, space group $P\bar{1}$, $a = 11.385(2)$, $b = 12.697(3)$, $c = 16.849(2) \text{ \AA}$, $\alpha = 76.65(2)$, $\beta = 71.967(12)$, $\gamma = 84.56(2)^\circ$, $V = 2252.5(7) \text{ \AA}^3$, $Z = 1$, $D_c = 2.201 \text{ Mg m}^{-3}$, $\mu(\text{Mo-K}\alpha) = 4.703 \text{ mm}^{-1}$, $2\theta(\text{max}) = 45.0^\circ$, scan mode = ω , $\lambda = 0.71073 \text{ \AA}$, $T = 153 \text{ K}$, $R = 0.0574$, $R_w = 0.1236$ for 431 parameters and 3957 data with $I > 2\sigma(I)$ (6177 measured reflections, of which 5871 independent, $R_{\text{int}} = 0.065$). 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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