Linear Face-sharing Trioctahedral $[Mo_3I_{12}]^{3-}$ by Spontaneous thf Loss from $[MoI_4(thf)_2]^-$: Structure, Bonding and Magnetic Properties

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Complexes $[Mo_3X_{12}]^{3-}$ (X = I, Br) assemble by spontaneous thf loss in noncoordinating solvents from $[MoX_4(thf)_2]^-$ and exhibit a linear face-shared trioctahedral structure with, at the same time, delocalized metal–metal bonding and local moment antiferromagnetic exchange interactions.

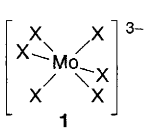
Halide complexes of molybdenum(III) adopt an octahedral coordination geometry, as in mononuclear $[MoX_6]^{3-}$ **1** and dinuclear face-shared bioctahedral $[Mo_2X_9]^{3-}$ **2**.[1] The structure of MoX_3 (X = halogen) consists of close-packed X atoms with the Mo centres filling one-third of the octahedral 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 $(\mu\text{-Br})_3Mo(\mu\text{-Br})_3$ 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 $[Mo_3Cl_{12}]^{3-}$, which was obtained from the thermal condensation of $[Mo_2Cl_9]^{2-}$ and $[MoCl_3(CO)_4]^-$, 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 $[Mo_3X_{12}]^{3-}$ (X = Br, I) ions, and the structural characterization of the iodide complex which reveals, contrary to **3**, delocalized metal–metal bonding.

A number of new *trans*-$[MoX_4(thf)_2]^-$ salts (X = Br, I) have been isolated from the reaction of $MoX_3(thf)_3$ and the desired salt of X^- in thf.† The analogous formation of *trans*-$[MoCl_4(thf)_2]^-$ from $MoCl_3(thf)_3$ 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 $[Mo_3X_{12}]^{3-}$ anions have been isolated either by this procedure or by carrying out the reaction between $MoX_3(thf)_3$ and X^- directly in CH_2Cl_2.‡

$$3[MoX_4(thf)_2]^- \xrightarrow{CH_2Cl_2} [Mo_3X_{12}]^{3-} + 6thf \quad (X = Br, I) \qquad (1)$$

The corresponding $[Mo_3Cl_{12}]^{3-}$ species cannot be obtained by this method, as only 1.5 thf moles per mole of $[MoCl_4(thf)_2]^-$ are released, presumably to give a $[Mo_2Cl_8(thf)]^{2-}$ product, a related phosphine derivative of which, $[Mo_2Cl_8PEt_3)]^{2-}$, 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 $MoX_3(thf)_3$ in non-coordinating solvents to afford edge-sharing bioctahedral $Mo_2X_6(thf)_4$ and ultimately face-sharing bioctahedral $Mo_2X_6(thf)_3$ (X = Cl, Br).[8]

The structure of $[PPh_4]_3[Mo_3I_{12}]$ has been determined by X-ray crystallography.§ The $[Mo_3I_{12}]^{3-}$ trianion (Fig. 1) clearly shows a linear face-sharing trioctahedral geometry. The only other structurally characterized dodecahalotrimetal complex[9] is $[Ru_3Cl_{12}]^{4-}$; a few related phosphine derivatives of types $[Ru_3Cl_8(PR_3)_4]^{n+}$ (n = 0, 1) and $[Ru_3Cl_6(PR_3)_6]^+$ 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°.



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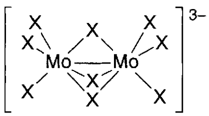

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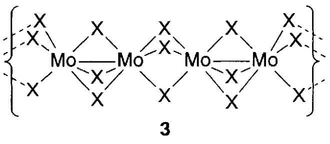

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As detailed in the classical contribution of Cotton and Ucko,[13] an ideal face-sharing bioctahedron is characterized by a M–(μ-X)–M angle of 70.53°. When a metal–metal bonding interaction is *not* present, a *much larger* angle results as a consequence 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 $[Mo_3I_{12}]^{3-}$ ion thus indicates that *metal–metal interactions are present*. This angle is smaller than those reported for the trioctahedral *metal–metal bonded* ruthenium complexes $[Ru_3Cl_{12}]^{4-}$, $[Ru_3Cl_8(PR_3)_4]^{n+}$ (n = 0,1) and $[Ru_3Cl_6(PR_3)_6]^+$ (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 $[Ru_3Cl_{12}]^{4-}$.[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 isoelectonic face-sharing bioctahedral $[Mo_2I_9]^{3-}$ [Mo–Mo, 3.07(2) Å][15] and $[Mo_2I_7(PMe_3)_2]^-$ [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 $[Ru_3Cl_{12}]^{4-}$.

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-

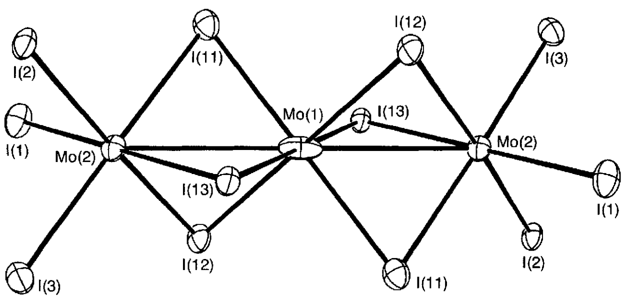


Fig. 1 An ORTEP view of the $[Mo_3I_{12}]^{3-}$ ion. Selected distances (Å) and angles (°) (averaged over chemically equivalent parameters; b = bridging, t = terminal): Mo–Mo 3.258(2), Mo(1)–I_b 2.769(10), Mo(2)–I_b 2.817(8), Mo(2)–I_t 2.752(4), I_t–Mo(2)–I_t 90.4(2), I_b– Mo(2)–I_b 88.4(5) I_b–Mo(1)–I_b 90.4(2), I_b–Mo(1)–I_b' 89.6(2), Mo(1)–I_b–Mo(2) 71.34(7)°.

tibility measurements for $[PPh_4][Mo_3I_{12}]$ show a moment reduction upon cooling, converging toward the value expected for one unpaired electron per trinuclear unit at low temperature (3.92 μ_B at 200 K, 2.38 μ_B at 1.75 K). For comparison, the magnetic moment of $[Bu^n{}_4N]_3[Mo_3Cl_{12}]$ was reported as 2.02 μ_B at 302 K.[4] In conclusion, the theoretical analysis rationalizes the experimentally verified co-existence, in $[Mo_3I_{12}]^{3-}$, of delocalized metal–metal bonding and local-moment antiferromagnetic exchange coupling. The ideal extension of the $[Mo_nX_{3n+3}]^{3-}$ 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 $[Mo_3X_{12}]^{3-}$ 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, $[Mo_3X_{11}]^{2-}$. Crystals of $[Bu_4N]_2[Mo_3I_{11}]$ 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) Å] 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 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.

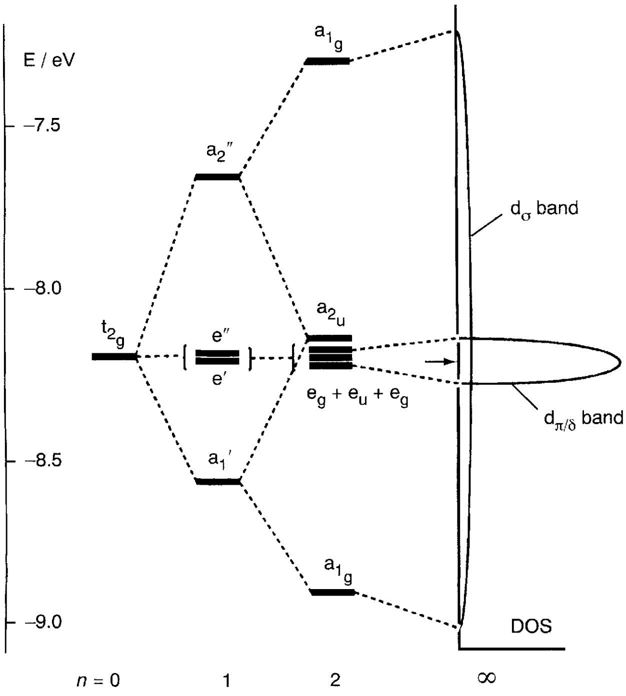
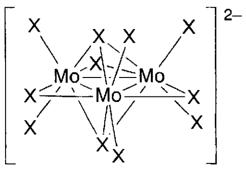


Fig. 2 MO diagram of the metal orbital region for complexes $[I_3\{Mo(\mu\text{-}I)_3\}_nMoI_3]^{3-}$ (calculated for $n = 0, 1, 2$; qualitative for $n = \infty$). The arrow indicates the Fermi level.



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Footnotes

† Stirring equimolar mixtures of $MoX_3(thf)_3$ and the desired [Cat]X {X = Br, Cat = $Bu^n{}_4N$, PPN $[(Ph_3P)_2N]$; X = I, Cat = 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 $[PPh_4][MoI_4(thf)_2]$ where obtained from $MoI_3(thf)_3$ (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.): $[MoI_4(thf)_2]^-$ δ 100 ($w_{1/2}$ = 840 Hz, α-H), 12.5 ($w_{1/2}$ = 150 Hz, β-H); $[MoBr_4(thf)_2]^-$ δ 83 ($w_{1/2}$ = 1100 Hz, α-H), 9.0 ($w_{1/2}$ = 220 Hz, β-H). However, prolonged standing of these solution led to loss of coordinated thf and formation of the $[Mo_3X_{12}]^{3-}$ 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 (X = Br, Cat = PPN; X = I, Cat = PPh_4, $Pr^n{}_4N$, $Bu^n{}_4N$, PPN). A single crystal of $[PPh_4]_3[Mo_3I_{12}]$ suitable for the X-ray analysis was grown by dissolving $[PPh_4][MoI_4(thf)_2]$ (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 $[PPh_4]_3[Mo_3I_{12}]\cdot 1.5(CH_2Cl_2)\cdot 0.5(Et_2O)$: triclinic, space group $P\bar{1}$, a = 11.385(2), b = 12.697(3), c = 16.849(2) Å, α = 76.65(2), β = 71.967(12), γ = 84.56(2)°, V = 2252.5(7) $Å^3$, Z = 1, D_c = 2.201 Mg m^{-3}, μ(Mo-Kα) = 4.703 mm^{-1}, 2θ(max) = 45.0°, scan mode = ω, λ = 0.71073 Å, T = 153 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_{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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