Formation and Structure of a Quadruply-iodo-bridged Complex of Dimolybdenum(III,IV), $[(Cp^*Mo)_2(\mu\text{-}I)_4]I_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and Its Reversible Oxidation and Reduction

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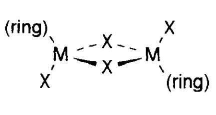
The mixed-valence quadruply-iodo-bridged $[(Cp^*Mo)_2(\mu\text{-}I)_4]I_3$ has been crystallographically characterized; its cyclic voltammogram shows reversible oxidation and reduction processes and suggests that the $[(Cp^*Mo)_2(\mu\text{-}I)_4]^{n+}$ (n = 0, 1, 2) series of complexes is isostructural.

Transition metal complexes containing only halides and one cyclopentadienyl ring per metal atom are very valuable synthons to a wide variety of other organometallic compounds.[1] In addition, they provide interesting and often intriguing examples of structure diversity, see for instance the series of group 6 $[(\text{ring})MCl_2]_2$ complexes [M = Cr, **1** (no Cr–Cr bond);[2] Mo, **2** (Mo–Mo single bond);[3] W, **3** (W–W triple bond);[4] ring = substituted cyclopentadienyl].

Among the $(\text{ring})MX_n$ systems, those of Mo^{IV} were unknown until recently when $CpMoCl_3$ ($Cp = C_5H_5$) has been produced in our laboratory as an insoluble, presumably oligomeric powder.[5] In order to produce materials amenable to a structural analysis, we have moved to the more soluble Cp* systems. These studies have resulted in the formation of the first member of the type **2** structure with a d^2–d^3 electronic configuration, $[(Cp^*Mo)_2(\mu\text{-}I)_4]I_3$. In addition, this represents



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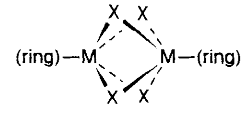

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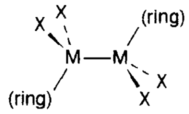

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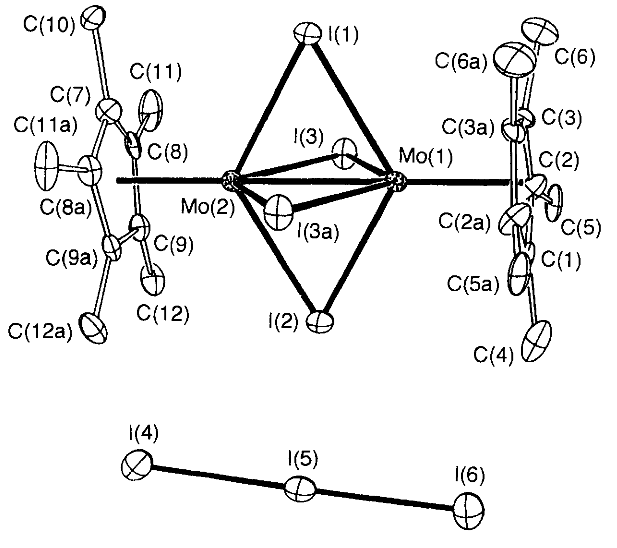

Fig. 1 Thermal ellipsoid diagram of [(Cp*Mo)$_2$(μ-I)$_4$]I$_3$ with the ions in their correct relative locations. Mo(1)–Mo(2), 2.718(3); all Mo–I, 2.78 ± 0.01; Mo(1)–CNT(1), 2.012(6); Mo(2)–CNT(2), 1.993(6); I(4)–I(5), 2.919(5); I(5)–I(6), 2.905(5) Å. Mo–I–Mo, all 58.4 ± 0.2, I(4)–I(5)–I(6), 178.7(2)°; (CNT = centre of cyclopentadienyl ring).

the first complex of any kind where two metals are bridged by four iodide ions.

The strategy utilized for the preparation of Cp*MoX$_3$ materials (X = Cl, Br, I) is shown in eqn. (1).

$$[\mathrm{Cp^*Mo(CO)_3}]_2 \xrightarrow{X_2} \mathrm{Cp^*MoX(CO)_3} \xrightarrow{X_2} \mathrm{Cp^*MoX_3(CO)_2} \xrightarrow[-2\mathrm{CO}]{\text{heat}} \mathrm{Cp^*MoX_3} \quad (1)$$

The Cp*MoX$_3$(CO)$_2$ complexes had not been previously reported,[6] but the corresponding Cp systems had been made by an identical procedure from [CpMo(CO)$_3$]$_2$, and they were described as unstable compounds, decomposing with CO loss.[7] The nature of the decomposition product(s) was not investigated.

The interaction between [Cp*Mo(CO)$_3$]$_2$ and dihalogen (I$_2$, Br$_2$, or PhI·Cl$_2$) in a 1 : 3 molar ratio at room temperature in CH$_2$Cl$_2$ (X = Cl, Br) or tetrahydrofuran (THF) (X = I) as solvent was monitored by IR spectroscopy. The intermediate Cp*MoX(CO)$_3$ was identified by the IR pattern in the CO stretching region† but not isolated. The final Cp*MoX$_3$(CO)$_2$ products precipitated directly out of solution and were identified by analysis, IR, and ^{1}H NMR spectroscopy.‡ The IR pattern in the CO stretching region for the Cp*MoX$_3$(CO)$_2$ series is identical to that of the corresponding Cp complexes,[7a] the CO stretching vibrations being red-shifted by approximately 20 cm^{-1}. The Cp*MoX$_3$(CO)$_2$ complexes appear to be thermally more stable than the corresponding Cp systems. Thermal decarbonylation in refluxing heptane or toluene provides sparingly soluble, CO-free crude crystalline materials that analyse correctly for Cp*MoX$_3$.§ An attempt to recrystallize the Cp*MoI$_3$ material by diffusion of heptane into a CH$_2$Cl$_2$ solution gave black crystals of the title compound.¶ Solutions of this compound in CH$_2$Cl$_2$ are green.

The molecule of the cation is shown in Fig. 1 and consists of two four-legged piano stools which share the common square base identified by the four bridging iodo ligands. This geometry is common to other monocyclopentadienyl halides, that is the d^2–d^2 [(η^5-C$_5$Me$_4$Et)VBr$_2$]$_2$[8] and [Cp*TaBr$_2$]$_2$,[9] and the d^3–d^3 [(η^5-C$_5$H$_4$-Pr^i)MoCl$_2$]$_2$[10] and [Cp*WCl$_2$]$_2$,[11] but this is the first time that such a structure has been observed for a mixed-valence d^2–d^3 system. According to a recent theoretical investigation,[12] the five metal electrons of the [(Cp*Mo)$_2$(μ-I)$_4$]$^+$ cation are anticipated to give rise to a strong σ bond and to leave three substantially non-bonding electrons in metal–metal combinations of δ* and δ symmetry. The metal–metal distance of 2.718(3) Å and especially the acute Mo–(μ-I)–Mo angles [average 58.4(1) Å] are strong indication of metal–metal bonding. The paramagnetism of the molecule is shown by EPR spectroscopy: the compound is EPR silent in CH$_2$Cl$_2$ at room temperature, but at 77 K a tetragonal g tensor is observed with $g_\perp = 2.14$ and $g_\parallel = 2.35$, as expected for the axial symmetry of the ion.

An electrochemical investigation of the title compound shows reversible oxidation and reduction. As Fig. 2(*a*) and (*b*) show, the compound has a complex redox behaviour with four distinct redox processes. However, only the two ones labelled A and D (at $E_{1/2} = +0.475$ and -0.381 V with respect to the ferrocene–ferricinium couple) are attributable to the cation. The processes labelled B and C are due to the I$_3^-$ anion as shown by a control experiment carried out on Bu$_4$N$^+$I$_3^-$ under the same experimental conditions [Fig. 2 (*c*)]. The shift of process C on going from (*a*)/(*b*) to (*c*) is attributable to the different concentration and counterion. Both A and D are one-electron processes as shown by the rate-independent 60 mV peak-to-peak separations and by the internal calibration with the I$_3^-$ processes. The voltammogram shows zero current in the region between processes B (oxidation of I$_3^-$ to I$_2$) and

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† IR spectra of Cp*MoX(CO)$_3$ (ν_{CO}/cm^{-1}). X = Cl (CH$_2$Cl$_2$): 2041s, 1958s, 1938m, sh. X = I (THF): 2045s, 1955s, 1934m, sh.

‡ Yield of Cp*MoX$_3$(CO)$_2$: 74% (X = Cl), 94% (X = Br), 80% (X = I). Satisfactory elemental analyses were obtained for all new compounds. IR (ν_{CO}/cm^{-1} CH$_2$Cl$_2$); X = Cl: 2087s, 2044s; X = Br: 2076s, 2041s; X = I; 2054s, 2016s. ^{1}H NMR (δ/ppm); X = Cl (CDCl$_3$): 2.18; X = Br (CD$_2$Cl$_2$): 2.19; X = I (CDCl$_3$): 2.24.

§ Yield of Cp*MoX$_3$: 60% (Cl): 45% (Br): 74% (I). See also footnote ||.

¶ *Crystal data* for [(Cp*Mo)$_2$(μ-I)$_4$]I$_3$: C$_{20}$H$_{30}$I$_7$Mo$_2$, orthorhombic, *Cmc*2, $a = 11.756(3)$, $b = 14.103(4)$, $c = 18.696(5)$ Å, $U = 3100.0(14)$ Å^3, $Z = 4$, $D_x = 2.894$ g cm^{-3}, μ(Mo-Kα) = 106.7 cm^{-1}, $T = 296$ K. Systematic absences allowed the space groups *Cmcm*, *Cmc*2 and *C*2*cm*. Since only one of the two potential structural mirror planes is aligned with the crystallographic axes, either of the non-centrosymmetric alternatives was initially preferred. Of 1148 reflections collected ($4 \leq 2\theta \leq 48°$), 976 were independent and observed ($5\sigma F_o$) and corrected for absorption. A chemically sensible and computationally stable structure was developed in *Cmc*2. All nine heavy-atoms were obtained by direct methods. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed in idealized locations. At convergence: $R(F) = 4.16\%$, $R_w(F) = 4.52\%$ $S = 1.12$, highest peak = 1.73 e Å^{-3}. The correctness of the reported enantiomer was determined by the Rogers test. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

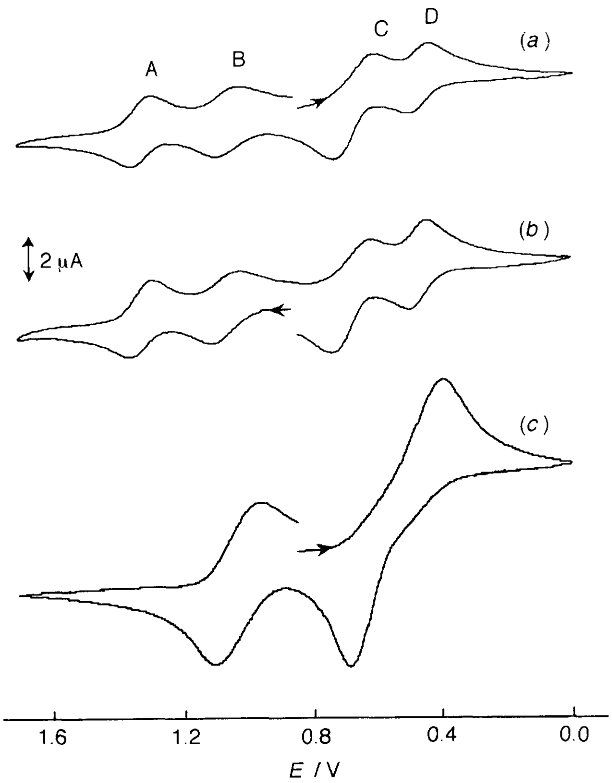

Fig. 2 Cyclic voltammetric studies of $[(Cp^*Mo)_2(\mu\text{-}I)_4]I_3$, (*a*) and (*b*); Bu_4NI_3, (*c*). Room temperature, Pt working electrode, Ag/AgCl reference electrode, CH_2Cl_2 solvent, $TBAPF_6$ supporting electrolyte.

C (reduction of I_3^- to I^-), thus process A corresponds to oxidation of the cation to $[Cp^*_2Mo_2I_4]^{2+}$, whereas D corresponds to reduction to $Cp^*_2Mo_2I_4$. The reversibility of both these processes indicates that the molecular structure of all the three $[Cp^*_2Mo_2I_4]^{n+}$ (n = 0, 1, 2) species is identical, *i.e.* of type **2**.

The synthesis, isolation and structural characterization of the oxidized and reduced complexes, $[Cp^*_2Mo_2I_4]^{n+}$ (n = 0, 2) is one of our immediate goals, since the way the metal–metal separation responds to the change in electronic structure should provide an experimental test for the bonding description given[12] for **2**. Efforts are also underway to characterize completely the Cp^*MoX_3 (X = Cl, Br, I) materials.|| The voltammograms of Fig. 2 already suggest that a Cp^*MoI_3 compound is not likely to be stable as a molecular species, since a simple rearrangement would produce the $[(Cp^*Mo)_2(\mu\text{-}I)_4]^{2+}$ ion which is able to oxidize I^- to I_2.

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|| After the submittance of this manuscript, we have obtained an X-ray structure of the chloride compound (P. E. Fanwick, Purdue University), which corresponds to $[(Cp^*Mo)_3(\mu\text{-}Cl)_5(\mu\text{-}O)][MoOCl_4]\cdot C_7H_{16}$ (calcd. for $C_{37}H_{61}Cl_9Mo_4O_2$: C, 35.81; H, 4.96%).