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The Behavior of Cp*MoBr/Br₂ Redox Systems: The Unusual Structure of [(Cp*₂Mo₂Br₄)₂(Cp*MoBr₄)₃], a Compound Containing Mo^{III}, Mo^{IV}, and Mo^V

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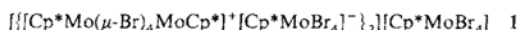
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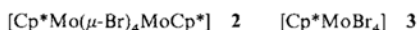
**The Behavior of Cp*MoBr/Br₂ Redox Systems:
The Unusual Structure of
[(Cp*₂Mo₂Br₄)₂(Cp*MoBr₄)₃], a Compound
Containing Mo^{III}, Mo^{IV}, and Mo^{V**}**

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Heinz-Bernhard Kraatz, Beth E. Owens-Waltermire,
Rinaldo Poli,* and Arnold L. Rheingold

There is considerable interest in the use of cyclopentadienyl transition metal complexes having one or more halo ligands as convenient starting materials for the synthesis of a large variety of organometallic compounds.^[1] Although complexes of the group 6 metals molybdenum and tungsten are well known for the III and V oxidation state, Mo^{IV} and W^{IV} complexes have received little attention. Only recently, we were able to obtain [CpMoCl₃] (Cp = η⁵-C₅H₅), an insoluble powder and presumably an oligomer^[2] In order to obtain complexes that lend themselves to structural characterization, we have moved to the more soluble Cp* complexes (Cp* = η⁵-C₅Me₅). We report here on the synthesis and highly unusual crystal structure of **1**.



This compound is novel in that it is 1) the first known tetrabromo-bridged d²-d³ dimer, 2) the first d² [Cp*MX₄]⁻ complex to be structurally characterized, and 3) the first neutral Mo^V tetrabromide to be structurally characterized. In addition, molybdenum is found in three different oxidation states in the same crystal. This is possible because of the particular redox properties of the Cp*MoBr/Br₂ system which we will describe here. Complex **2** has been prepared from **3**^[3] and sodium amalgam in toluene as a diamagnetic



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crystalline complex, which is isostructural to the neutral (d^3-d^3) complex $[\text{Cp}'\text{Mo}(\mu\text{-Br})_4\text{MoCp}']$ ($\text{Cp}' = \eta^5\text{-1-(2,5-dimethoxyphenyl)-2,3,4,5-tetraphenylcyclopentadienyl}$)^[4] and to $[(i\text{Pr})\text{CpMo}(\mu\text{-Cl})_4\text{MoCp}(i\text{Pr})]$.^[5] The unit cell of **2**^[6] contains two independent molecules, one located at an inversion center and the second one in a general position. The two crystallographically independent molecules are chemically equivalent and can be described as two four-legged piano stool structures sharing a common square face defined by the four bridging bromo ligands (Fig. 1). Complex **2** undergoes two reversible one-electron oxidations at $E = -0.30$ V and $+0.73$ V (vs. ferrocene).

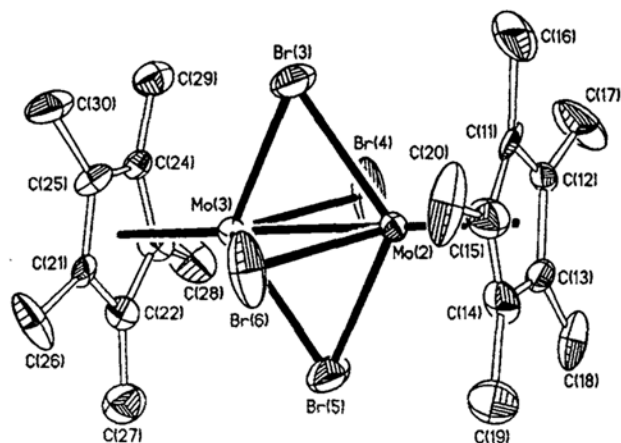
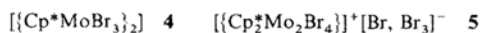


Fig. 1. Crystal structure of **2** (ORTEP plot shows the molecule in a general position). The geometry is identical to that of the molecule located at an inversion center in **2** and also to that in cation **2**⁺. Selected bond lengths [Å] and angles [°] (averaged over all chemically equivalent groups of atoms): **2**: Mo-Mo 2.643(2), Mo-Br 2.613(9); Mo-Br-Mo 60.8(3). **2**⁺: Mo-Mo 2.643(5) Mo-Br 2.64(3); Mo-Br-Mo 60.0(8).

In an attempt to prepare **4** by bromination of **2** with Br_2 (mol ratio 1:1) in benzene, we obtained a brick-red precipitate (**5**), which analyzes as $\text{Cp}^*\text{MoBr}_{3,3}$ and shows a single



broad resonance at $\delta = 4.3$ in its $^1\text{H NMR}$ spectrum in CDCl_3 . This resonance is identical to that of the product obtained upon treatment of **2** with one equivalent of AgBF_4 . Thus **5** is interpreted as being a salt of $[\text{Cp}^*\text{Mo}(\mu\text{-Br})_4\text{MoCp}^*]^+$ (**2**⁺), and its anion is presumably a 1:4 mixture of Br^- and Br_3^- . According to our electrochemical investigations and the literature,^[7] Br_2 does not have sufficient oxidizing power to produce the dication **2**²⁺ (see Fig. 2).

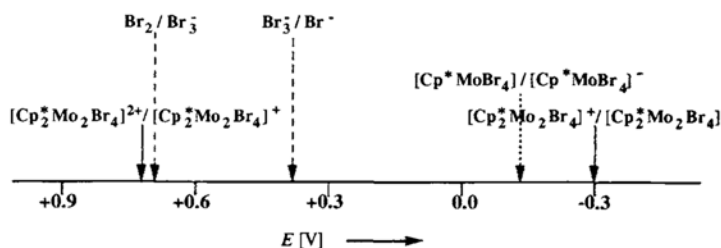


Fig. 2. Electrochemical behavior of the $[\text{Cp}^*_2\text{Mo}_2\text{Br}_4]^{2+}$, $[\text{Cp}^*\text{MoBr}_4]^+$, and $\text{Br}_2/\text{Br}_3^-$ systems.

Recrystallization of **5** from $\text{CH}_2\text{Cl}_2/n\text{-heptane}$ yielded the title compound **1** as a dark red, crystalline material, which is paramagnetic and displays two broad peaks at $\delta = 4.2$ and -19.5 in its $^1\text{H NMR}$ spectrum. The resonance at $\delta = -19.5$ is assigned to the anion $[\text{Cp}^*\text{MoBr}_4]^-$ (**3**⁻) (vide infra). The cyclic voltammogram of **1** shows, in addition to the two reversible one-electron oxidations characteristic of **2**, a reversible wave at $E = -0.14$ V (vs. ferrocene), which is due to the $[\text{Cp}^*\text{MoBr}_4]^0/[\text{Cp}^*\text{MoBr}_4]^-$ couple as shown by an independent study of **3** (Fig. 2). A comparison of the oxidation potentials in Figure 2 indicates that **1** consists of the mixed-valence cation $[\text{Cp}^*\text{Mo}(\mu\text{-Br})_4\text{MoCp}^*]^+$ and a 2:1 mixture of the anion $[\text{Cp}^*\text{MoBr}_4]^-$ and the corresponding Mo^{V} neutral analogue. This rules out the alternative formulation of **1** as a 1:1 mixture of monocation and dication for the dinuclear complex accompanied by three negatively charged mononuclear complexes.

Compound **1** crystallizes in the monoclinic space group $P2_1/m$ with two formula units per unit cell.^[8] The dinuclear monocation **2**⁺ is located in a general position, and its structure is practically identical to that of the neutral precursor **2** (Fig. 1). According to theoretical considerations,^[9] the HOMO of **2** should be nonbonding. This explains the little change in the Mo-Mo separation upon oxidation ($d(\text{Mo}-\text{Mo}): \mathbf{2} = 2.645(2)$ Å; **2**⁺ = 2.691(4) Å). This is the first direct comparison of metal-metal distances in a pair of $\{[\text{CpMX}_2]_2\}^{n+}$ complexes and experimentally confirms the theoretical predictions by Green et al.^[9] The two Mo^{IV} anions **3**⁻ and the neutral Mo^{V} complex **3** are located on mirror planes. These all have the familiar four-legged piano stool structure (Fig. 3). The bond angles are not significantly

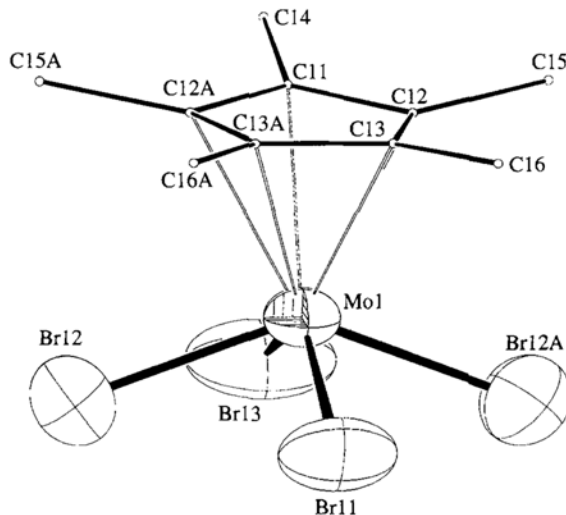


Fig. 3. Crystal structure of **3** (ORTEP). The two crystallographically independent anions **3**⁻ have identical structural parameters. Selected bond lengths [Å] and angles [°] (averaged over all chemically equivalent groups of atoms): **3**⁻: Mo-Br 2.62(4), Br-Mo-Br (cis) 81.8(4), Br-Mo-Br (trans), 136(3). **3**: Mo-Br 2.48(3), Br-Mo-Br (cis) 82.8(4), Br-Mo-Br (trans) 138(2).

different in the three mononuclear complexes; however, the Mo-Br distances at atom Mo1 are significantly shorter (average 2.48(4) Å) than those at atoms Mo4 and Mo5 (Mo4: range 2.595(6)–2.616(9) Å; Mo5: range 2.591(6)–2.721(8) Å). This reflects the stronger π acidity of the neutral d^1 complex $[\text{Cp}^*\text{MoBr}_4]$ and allows us to identify Mo1 as the central atom in **3**. An ORTEP representation of the unit

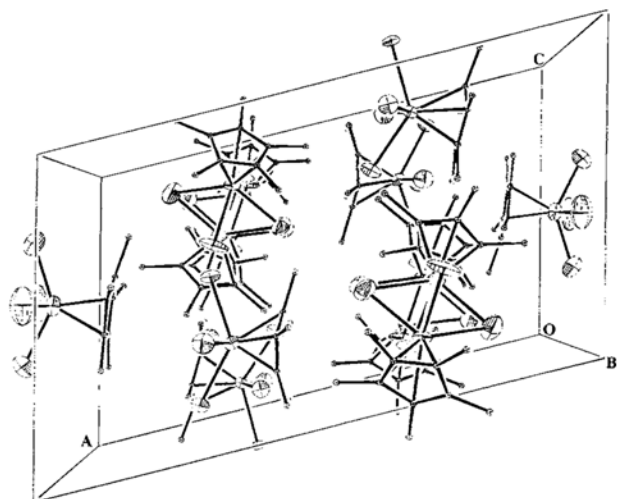
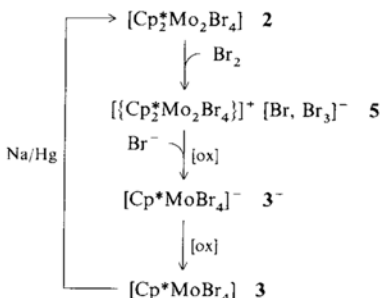


Fig. 4. Unit cell of **1** (ORTEP).

cell of **1** giving the relative orientations of all three constituents to each other is shown in Figure 4.

The formation of **1** from **2** and Br_2 can be understood in terms of their redox behaviors (see Fig. 2). Initially, Br_2 oxidizes **2** to give the benzene-insoluble salt **5**, which contains the cation 2^+ and a mixture of Br^- and Br_3^- as discussed above. During the crystallization from CH_2Cl_2 , Br^- can add to 2^+ to give the neutral adduct **2-Br**. Oxidation with Br_3^- and subsequent reaction with Br^- via the possible intermediate $[\text{Cp}^*\text{MoBr}_3]_2$ will give the paramagnetic anion 3^- (Scheme 1).



Scheme 1. [ox] = oxidation.

Any residual Br_3^- , according to the electrochemical study (Fig. 2), would be capable of oxidizing 3^- to give neutral **3**. Thus, considering the composition of compound **5**, a mixture of **2**, 3^- and **3** in a mol ratio of 1:1:2.1 should be produced in solution. But a mixture of the three components in a mol ratio of 2:2:1 is found in the crystal, presumably because a compound with this particular combination is the least soluble material in the solvent combination used for crystallization. Treatment of compound **5** with excess Br^- eventually leads to a product with a single broad ^1H NMR resonance at $\delta = -19.5$, which is attributed to 3^- in agreement with the reactions depicted in Scheme 1. Figure 2 indicates that the two neutral complexes **3** and **2** are not stable with respect to electron transfer. In fact, mixing a stoichiometric amount of **3** and **2** produces a solution that exhibits the ^1H NMR resonances of the cation 2^+ and the Mo^{IV} anion 3^- .

Currently, efforts are under way to isolate $[\{\text{Cp}^*\text{MoBr}_3\}_2]$ (**4**), which requires reaction conditions under which free bromide ion cannot exist.

Experimental Procedure

3: $[\text{Cp}^*\text{MoBr}_4]$ was prepared by a procedure similar to that described for $[\text{Cp}^*\text{MoBr}_4][3]:[\{\text{Cp}^*\text{Mo}(\text{CO})_3\}_2]$ (1.03 g, 1.62 mmol) was dissolved in CH_2Cl_2 (20 mL), and the red-orange solution was transferred by cannula to a slurry of yellow PBr_5 (2.80 g, 6.52 mmol) in CH_2Cl_2 (20 mL). Vigorous gas evolution indicated an immediate reaction. The reaction mixture was then refluxed approximately 12 h. The solution was reduced in volume to approximately 30 mL. The almost black precipitate was collected by filtration, washed with cold CH_2Cl_2 (3×5 mL) and dried under vacuum to yield 1.56 g (87%) of **3**. Correct elemental analysis (C, H, Br).

2: Compound **3** (3.427 g, 6.22 mmol) was placed in a Schlenk tube containing freshly prepared sodium amalgam (311 mg of Na, 13.5 mmol in 31 g Hg). Toluene (40 mL) was added, and the dark suspension was allowed to stir at room temperature (21°C) for about 12 h, during which the solution developed a tan brown color. The reaction mixture was filtered and the precipitate washed with toluene until the washings were colorless (4×20 mL). The combined filtrates were reduced in volume and cooled to -20°C to yield 2.18 g (90%) of **2**. ^1H NMR (200 MHz, CDCl_3 , 25°C): $\delta = 1.93(\text{s})$. Cyclic voltammogram ($\text{CH}_2\text{Cl}_2/0.1 \text{ M } n\text{Bu}_4\text{NPF}_6$, $E[\text{V}]$ vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$): -0.30 ($[\{\text{Cp}^*\text{MoBr}_2\}_2]/[\{\text{Cp}^*\text{MoBr}_2\}_2]^+$), $+0.73$ ($[\{\text{Cp}^*\text{MoBr}_2\}_2]^+ / [\{\text{Cp}^*\text{MoBr}_2\}_2]^{2+}$). Correct elemental analysis (C, H).

1: Compound **2** (538 mg, 0.69 mmol) was dissolved in benzene (10 mL). A solution of Br_2 (35 μL , 0.69 mmol) in benzene (5 mL) was added, causing the immediate formation of a red precipitate. The product was collected by filtration, washed with *n*-heptane, and dried under vacuum (381 mg). ^1H NMR (200 MHz, CDCl_3 , 25°C): $\delta = 4.3$ (br, $w_{1/2} = 120$ Hz). Recrystallization of this product from $\text{CH}_2\text{Cl}_2/n$ -heptane yielded **1** as dark red plates. ^1H NMR (200 MHz, CDCl_3 , 25°C): $\delta = 4.2$ ($w_{1/2} = 120$ Hz), -19.5 ($w_{1/2} = 137$ Hz). One of these crystals was used in the crystallographic investigation.

Reaction between **3** and **2**: To a solid mixture of **2** (17 mg; 0.022 mmol) and **3** (23 mg; 0.042 mmol) in a Schlenk tube, was added CDCl_3 (1 mL). The resulting orange-brown solution was transferred to an NMR tube (5 mm o.d.). ^1H NMR (200 MHz, CDCl_3 , 25°C): $\delta = 4.13$ ($w_{1/2} = 85$ Hz), -19.53 ($w_{1/2} = 137$ Hz).

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- [1] R. Poli, *Chem. Rev.* **1991**, *91*, 509–551.
- [2] R. Poli, M. A. Kelland, *J. Organomet. Chem.* **1991**, *419*, 127–136.
- [3] M. L. H. Green, J. D. Hubert, P. Mountford, *J. Chem. Soc. Dalton Trans.* **1990**, 3793–3800.
- [4] C. Saadeh, S. B. Colbran, D. C. Craig, A. D. Rae, *Organometallics* **1993**, *12*, 133–139.
- [5] a) M. L. H. Green, A. Izquierdo, J. J. Martin-Polo, V. S. B. Mtetwa, K. Prout, *J. Chem. Soc., Chem. Commun.* **1983**, 538–540; b) R. Poli, J. C. Gordon, J. U. Desai, A. L. Rheingold, *ibid.* **1991**, 1518–1520.
- [6] Crystal structure analysis of **2**: $\text{C}_{20}\text{H}_{30}\text{Br}_4\text{Mo}_2$, $M = 782.0$, monoclinic, $a = 8.356(1)$, $b = 32.272(5)$, $c = 13.972(2)$ Å, $\beta = 98.17(1)^\circ$, $V = 3729.3(10)$ Å³, space group $P2_1/n$, $Z = 6$, $\mu(\text{MoK}\alpha) = 73.60 \text{ cm}^{-1}$, $\rho_{\text{calcd}} = 2.088 \text{ g cm}^{-3}$, independent reflections (total reflections) 5741 (6407), 2715 reflections ($F_0 > 4\sigma(F_0)$), $R = 0.0614$ ($R_w = 0.0755$) [8].
- [7] M. Mastragostino, S. Valcher, P. Lazzari, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *126*, 189–198.
- [8] Crystal structure analysis of **1**: $\text{C}_{84}\text{H}_{137}\text{Br}_{20}\text{Mo}_7$, $M = 3416.67$, monoclinic, $a = 20.218(6)$, $b = 23.332(5)$, $c = 12.093(2)$ Å, $\beta = 104.76(2)^\circ$, $V = 5516(2)$ Å³, space group $P2_1/m$, $Z = 2$, $\mu(\text{MoK}\alpha) = 84.62 \text{ cm}^{-1}$, $\rho_{\text{calcd}} = 2.06 \text{ g cm}^{-3}$, independent reflections (total reflections) 7414 (7657), 2172 reflections ($|F_0|^2 > 3\sigma|F_0|^2$), 365 parameters refined, $R = 0.089$ ($R_w = 0.094$). The reflections were measured on an Enraf-Nonius CAD4 diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) by using the ω - 2θ scan method. The structure of **1** was solved using the TEXSAN program package. The positions of all non-hydrogen atoms were determined from difference Fourier maps. The Mo and Br atoms were refined anisotropically; the C atoms were refined isotropically. All Cp* ligands were restrained to ideal pentagons with C–C(ring) = 1.42(1) Å and C–C(Me) = 1.56 Å and the interstitial heptane molecule restrained to C–C = 1.54(2) Å (SHELX76). Some of the Cp* methyl carbon atoms refined with very a high thermal parameter, indicating fast rotation of the rings about the metal–ring axis and/or partial disorder of the rings. Further details of the crystal structure can be obtained upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.
- [9] J. C. Green, M. L. H. Green, P. Mountford, M. J. Parkinson, *J. Chem. Soc., Dalton Trans.* **1990**, 3407–3418.