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Metal–metal bond energy in a binuclear molybdenum(III) aqua complex

Alexander A. Proyavkin, Ilia A. Dementiev, Andrei O. Kozin, Yuri V. Kondratiev and Dimitry V. Korolkov*

Department of Chemistry, St. Petersburg State University, 198504 St. Petersburg, Russian Federation.
Fax: +7 812 428 6739; e-mail: koral@DK8181.spb.edu

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The enthalpies of oxidation of mononuclear $[Mo(H_2O)_6]^{3+}$ and binuclear $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ complexes in aqueous solutions were determined by calorimetric titration, and the metal–metal bond energy was estimated.

The stability and reactivity of cluster compounds of heavy transition metals depend on the energy of metal–metal bonds in these complexes. In polynuclear oxo and hydroxo aqua complexes of molybdenum in various oxidation states with both terminal and bridging oxo and hydroxo ligands, this energetic characteristic plays an important role because molybdenum compounds are the constituents of biologically active substances. Up to date there are only theoretical estimations,[1–4] and experimental proof is required. We obtained experimental data for the molybdenum(III) complex $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ with two bridging hydroxo groups. To determine the metal-metal bond energy, we used the enthalpies of reactions of this and related complexes in acidic aqueous solutions.

The enthalpies of reactions were determined by the calorimetry of dissolution and differential calorimetric titration with the continuous introduction of a titrant.

Heat effects were studied on a Calvet type microcalorimeter.[5,6] Both portion and continuous titrant introduction in one or two calorimetric cells can be performed in this differential diathermic calorimeter. The enthalpies of reactions were calculated by the numerical integration of fragments of differential curves obtained. All compounds were synthesised and identified by well-known methods;[7] the molybdenum content was determined by potentiometric titration with potassium dichromate; the ethylenediaminetetraacetate anion was determined by titration with bismuth(III) nitrate.

In order to find the metal-metal bond energy, we determined the enthalpies of oxidation of mononuclear $[Mo(H_2O)_6]^{3+}$ and binuclear $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ complexes by iron(III) sulfate in an acidic aqueous solution. The binuclear molybdenum(V) complex $[Mo_2O_4(H_2O)_6]^{2+}$ is the product of reactions (1) and (2).

$$2[Mo(H_2O)_6]^{3+} + 4Fe^{3+} = [Mo_2O_4(H_2O)_6]^{2+} + 4Fe^{2+} + 2H_2O + 8H^+ \quad (1)$$

$$[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 4Fe^{3+} = [Mo_2O_4(H_2O)_6]^{2+} + 4Fe^{2+} + 6H^+ \quad (2)$$

Enthalpy of reaction (1). A solution of the mononuclear complex $[Mo(H_2O)_6]^{3+}$ was obtained by the dissolution of K_3MoCl_6 in a 2.5 M aqueous solution of toluene-4-sulfonic acid (HPTS)

$$[MoCl_6]^{3-} + 6H_2O = [Mo(H_2O)_6]^{3+} + 6Cl^- \quad (3)$$

When reaction (3) was completed, an absorption band at 520 nm (electronic absorption spectrum) characteristic of the complex anion $[MoCl_6]^{3-}$ disappeared, and a band at 400 nm characteristic of the complex cation $[Mo(H_2O)_6]^{3+}$ was observed.[8] Calorimetric titration of a $[Mo(H_2O)_6]^{3+}$ solution with a $Fe_2(SO_4)_3$ solution in 2.5 M HPTS resulted in exothermic reaction (1), which was completed at a Fe^{III}:Mo^{III} molar ratio of 2:1. This is in a good agreement with the results of potentiometric titration and with changes in the spectral characteristics of the reaction mixture. The enthalpy of reaction (1) is $\Delta H^0_{298}(1) = -144\pm4$ kJ (Table 1).

Table 1 Enthalpies of reactions.

Reaction	ΔH^0_{298}/kJ
(1)[a]	–144±4
(2)[b]	–92±4
(3)	—
(4)[a]	–19±1
(5)[a]	+44±1
(6)[a]	–31±1
(7)[a]	–60±1
(8)[b]	–52±8

[a]Value was obtained in a calorimetric experiment. [b]Value was obtained by thermochemical calculations from experimental data.

Enthalpy of reaction (2). To determine the enthalpy of reaction (2), we obtained the enthalpies of the following reactions (Table 1):

dissolution of $Na_2[Mo_2O_4(edta)]\cdot H_2O$ in 2.5 M HPTS:

$$[Mo_2O_4(edta)]^{2-} + 4H^+ + 6H_2O = [Mo_2O_4(H_2O)_6]^{2+} + H_4edta, \quad (4)$$

oxidation of $Na_2[Mo_2O_4(edta)]\cdot H_2O$ by $Fe_2(SO_4)_3$ in 2.5 M HPTS:

$$[Mo_2O_4(edta)]^{2-} + 2Fe^{3+} + 8H_2O = 2[Mo(OH)_6] + 2Fe^{2+} + H_4edta, \quad (5)$$

dissolution of $K[Mo_2(OH)_2(ac)(edta)]\cdot 2H_2O$ in 2.5 M HPTS:

$$[Mo_2(OH)_2(ac)(edta)]^- + 5H^+ + 8H_2O = [Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} + Hac + H_4edta, \quad (6)$$

oxidation of $K[Mo_2(OH)_2(ac)(edta)]\cdot 2H_2O$ by $Fe_2(SO_4)_3$ in 2.5 M HPTS:

$$[Mo_2(OH)_2(ac)(edta)]^- + 6Fe^{3+} + 10H_2O = 2[Mo(OH)_6] + 6Fe^{2+} + 5H^+ + Hac + H_4edta, \quad (7)$$

All products in reactions (4)–(7) were identified by their electronic absorption spectra.

The enthalpy of reaction (2) was calculated using a thermochemical cycle (Figure 1) of reactions (4)–(7). Since oxidation of either the binuclear complex of molybdenum(III) $[Mo_2(OH)_2(ac)(edta)]^-$ or the binuclear complex of molybdenum(V) $[Mo_2O_4(edta)]^{2-}$ by $Fe_2(SO_4)_3$ in 2.5 M HPTS results in $[Mo(OH)_6]$, we can calculate the enthalpy of reaction (2) as follows.

$$\Delta H^0_{298}(2) = \Delta H^0_{298}(4) - \Delta H^0_{298}(5) + \Delta H^0_{298}(7) - \Delta H^0_{298}(6) = -92\pm4 \text{ kJ.}$$

Enthalpy of $[Mo(H_2O)_6]^{3+}$ dimerization. Using the enthalpies of oxidation of mononuclear $[Mo(H_2O)_6]^{3+}$ and binuclear $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ cations by iron(III) sulfate in acidic solutions to the binuclear species $[Mo_2O_4(H_2O)_6]^{2+}$, we can estimate the lower limit of the enthalpy of dimerization of the mononuclear complex of molybdenum(III) (Table 1).

$$2[Mo(H_2O)_6]^{3+} = [Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 2H_2O + 2H^+. \quad (8)$$

The formation of a binuclear complex of molybdenum(III) from two mononuclear fragments is accompanied by a significant exothermic effect (Table 1). Undoubtedly, this is due to the formation of a multiple metal–metal bond[9] in the electronic structure of $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$. Definitely, this value cannot be directly referred to the metal–metal bond energy in the binuclear cluster $[Mo_2(\mu\text{-}OH)_2]^{4+}$ because molecular transformation (8) involves reconstruction of the other bonds, namely, 12 bonds between single molybdenum atoms and terminal H_2O molecules are changed by 8 analogous bonds between cluster nucleus and terminal H_2O molecules and 4 bonds between molybdenum atoms and bridging OH groups. However, we can assume that the energy of the metal–metal bond in the binuclear cluster $[Mo_2(\mu\text{-}OH)_2]^{4+}$ is close to –52±8 kJ.

Thus, we obtained experimental evidence for the energetic stabilization of a binuclear molybdenum(III) complex by the formation of a metal–metal bond. Similar stabilization was predicted by semi-quantitative quantum-chemical calculations.[1]

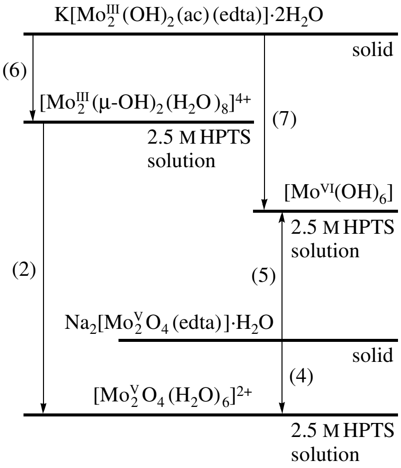

Figure 1 Enthalpy diagram for the dissolution and transformation of molybdenum(III) and molybdenum(V) complexes.

However, it should be taken into account that changes in the geometry of such binuclear complexes (especially affecting valent *d*-orbitals of molybdenum capable of two-centre metal–metal interactions) or in the ligand origin (from weak-field ligands OH or H_2O to strong-field ligands like CO or PR_3) will reduce the energy of stabilization.

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