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State of Molybdenum Clusters in Solutions: II.[1] Thermodynamics of Formation of Dimolybdenum(II) Tetrakis(trifluoroacetate) Complexes with Hexamethylphosphotriamide in 1,2-Dichloroethane

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Abstract—Formation of $Mo_2(CF_3COO)_4$ and HMPTA 1 : 1 and 1 : 2 adducts in 1,2-dichlorethane was found by IR spectroscopy. The enthalpies and equilibrium constants of reactions (298.15 K) of the consecutive formation of $Mo_2(CF_3COO)_4\cdot$HMPTA and $Mo_2(CF_3COO)_4\cdot$2HMPTA adducts, the enthalpies of the $[Mo_2(CF_3COO)_4]_{cr}$ dissolution in 1,2-dichlorethane and HMPTA, and the enthalpy of the $[Mo_2(CF_3COO)_4\cdot$2HMPTA] crystallization were determined by calorimetric titration with continuous titrant input.

Keywords: molybdenum, clusters, donor–acceptor bond, metal–metal bond, bond energy, enthalpy, thermochemical cycle

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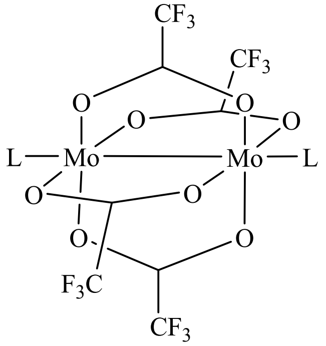
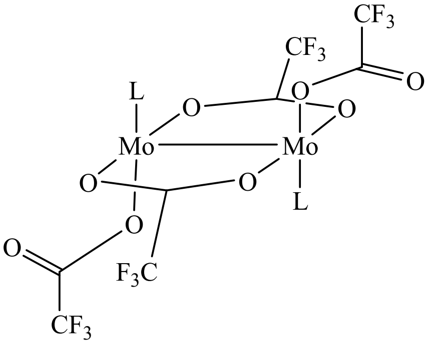
The structure of the adduct $Mo_2(CF_3COO)_4\cdot$2HMPTA in 1,2-dichloroethate was determined from the number of asymmetric vibration bands of carboxy groups ν(OCO) in the IR spectra in the region of 1500– 1800 cm^{-1}. It was shown in [2–6] on the basis of the X-ray structural analysis and IR spectroscopy that the mode of a donor ligand coordination to molybdenum tetracabroxylates can be defined from the number and position of the cabroxylate group absorption bands.



A



B

When donor molecules are in the axial position to the Mo–Mo fragment (**A**) a single signal of the asymmetric carboxy group vibration is observed in the IR spectra of solutions, as the chelate bonds of carboxy ligands are identical. The molecules of HMPTA are coordinated in the $Mo_2(CF_3COO)_4\cdot$2HMPTA adduct precisely in such a way (see the table). In the spectrum of the $Mo_2(CF_3COO)_4$ solution in HMPTA two signals of asymmetric vibrations at 1618 and 1693 cm^{-1} are observed. Hence carboxy ligands in the solvate are

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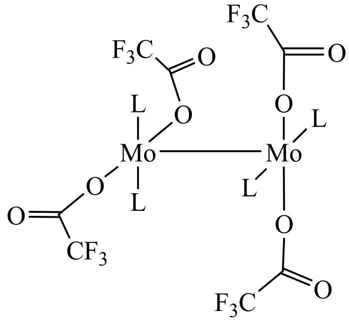
[1] For communication I, see [1].

The IR-spectroscopy data for $Mo_2(CF_3COO)_4$ solutions in HMPTA and 1,2-dichloroethane

Solution of a complex	ν(OCO), cm^{-1}	Arrangement of donors
$Mo_2(CF_3COO)_4$ in 1,2-dichloroethate	1593	Axial
$Mo_2(CF_3COO)_4$·2HMPTA in 1,2-dichloroethate	1612	Axial
$Mo_2(CF_3COO)$·*n*HMPTA in HMPTA	1618, 1693	Equatorial

terminal and all four HMPTA molecules are coordinated in the equatorial position.



The enthalpies of $[Mo_2(CF_3COO)_4]$ dissolution in 1,2-dichloroethane, the enthalpies and equilibrium constants of reactions of consecutive formation of adducts were determined by the method of titration with continuous titrant input. Thermodynamic characteristics of $[Mo_2(CF_3COO)_4]$ dissolution in 1,2-dichloroethane (DCE) and of formation of this complex adducts with HMPTA were calculated from the equations of reactions (1) and (2):

$$[Mo_2(CF_3COO)_4]_{DCE} + (HMPTA)_{DCE} = [Mo_2(CF_3COO)_4{\cdot}HMPTA]_{DCE},\ \Delta_1H^0,\ K_1, \qquad (1)$$

$$[Mo_2(CF_3COO)_4{\cdot}HMPTA]_{DCE} + (HMPTA)_{DCE} = [Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{DCE},\ \Delta_2H^0,\ K_2. \qquad (2)$$

Several titration thermograms of various weighted samples of the complex were obtained. In the case of high-weight samples of the initial complex the thermal effect of the $[Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{cr}$ crystallization was detected in the titration curve. One of such titration curves is presented in the figure.

The values of Δ_1H^0, Δ_2H^0, K_1, and K_2 for reactions (1) and (2) were calculated on the basis of the data of calorimetric titration with continuous titrant input. The calculated values of Gibbs free energy (kJ/mol) and entropy (J mol^{-1} K^{-1}) of the two-step reaction of the $Mo_2(CF_3COO)_4$·2HMPTA adduct formation in DCE are presented below:

Δ_1H^0	Δ_2H^0	K_1	K_2	Δ_1G^0	Δ_2G^0	Δ_1S^0	Δ_2S^0
–38.0±0.2	–30.9±0.6	1.4×10^6	3.7×10^5	–29.3±1.1	–20.3±1.2	–16±4	–14±4

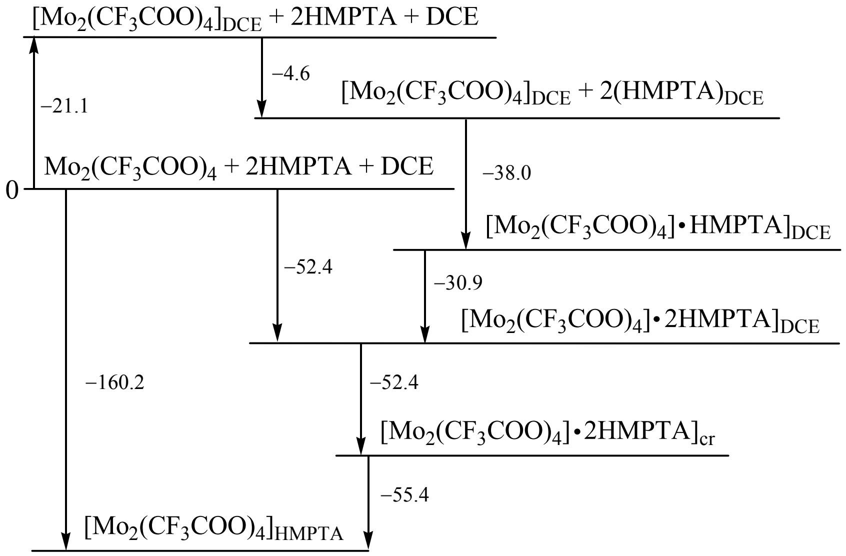
The enthalpy of $Mo_2(CF_3COO)_4$·2HMPTA crystallization in standard conditions was determined. The total effect of the formation of the 1 : 1 and 1 : 2 adducts in a solution and of the 1 : 2 adduct crystallization was calculated from the following relation: $Q_{tot} = S/k$, where S (mV s) is the area limited by the titration curve and the baseline, and k is a calorimeter constant. The total effect of the formation of the 1 : 1 and 1 : 2 adducts was calculated from the following relation: $Q_{add} = (\Delta H_1 + \Delta H_2)\nu$, where ν is the number of $Mo_2(CF_3COO)_4$ moles in the solution. The effect of crystallization was determined from the relation $Q_{cr} = Q_{tot} - Q_{add}$. We calculated the amount of the precipitate ν_{add} (mol) from the titration curve and then the enthalpy of crystallization.

$$\Delta_{cr}H^0 = Q_{cr}/\nu_{add} = -52.4\pm1.3 \text{ kJ/mol}.$$

The enthalpies $\Delta_{dis}H^0$ of the $[Mo_2(CF_3COO)_4]_{cr}$ dissolution in 1,2-dichloroethate and HMPTA are presented below.

Compound	1,2-Dichloroethane	Number of experiments	HMPTA	Number of experiments
$[Mo_2(CF_3COO)_4]_{cr}$	21.0±0.3	5	–160.2±1.4	5
HMPTA	–4.6±0.1	5	–	–

Scheme 1.



The cumulative result is presented in the form of a thermochemical cycle (Scheme 1).

Enthalpies of reactions (3)–(7) were calculated from the thermochemical cycle.

$$[Mo_2(CF_3COO)_4]_{cr} + 2HMPTA + DCE = [Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{DCE}, \qquad (3)$$
$$\Delta_3H^0 = -52.4\pm1.5 \text{ kJ/mol},$$

$$(Mo_2(CF_3COO)_4)_{DCE} + 2(HMPTA)_{DCE} + DCE = [Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{DCE}, \qquad (4)$$
$$\Delta_4H^0 = -68.9\pm0.8 \text{ kJ/mol},$$

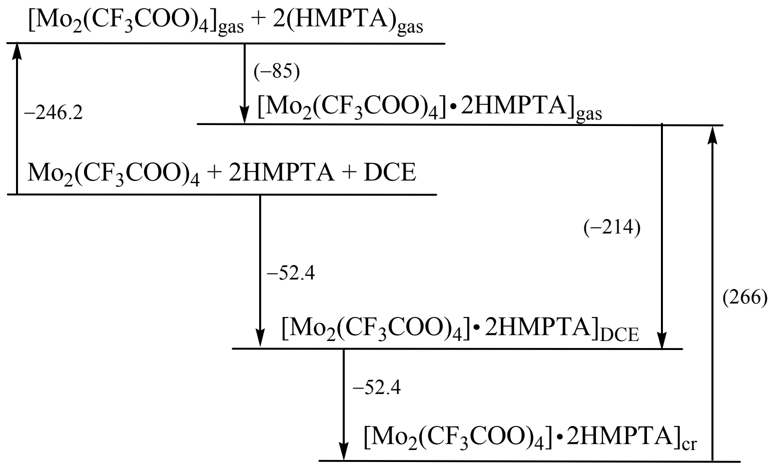
$$[Mo_2(CF_3COO)_4]_{cr} + 2HMPTA = [Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{cr}, \qquad (5)$$
$$\Delta_5H^0 = -04.8\pm2.6 \text{ kJ/mol},$$

$$[Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{cr} + (n + x - 2)HMPTA = [Mo_2(CF_3COO)_4{\cdot}xHMPTA]_{nHMPTA}, \qquad (6)$$
$$\Delta_6H^0 = -55.4\pm0.8 \text{ kJ/mol},$$

$$[Mo_2(CF_3COO)_4]_{cr} + (n + x)HMPTA = [Mo_2(CF_3COO)_4{\cdot}xHMPTA]_{nHMPTA}. \qquad (7)$$

A special structural feature of the $[Mo_2(CF_3COO)_4{\cdot}xHMPTA]n$HMPTA solvate consists in the fact that donor molecules occupy the site of the broken chelate bond of the cabroxy group in the cluster fragment. The ratio of the enthalpies of formation of the adducts $[Mo_2(CF_3COO)_4{\cdot}xHMPTA]_{HMPTA}$ (–160.2 kJ/mol) and $[Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{DCE}$ (–52.4 kJ/mol) is close to three. If we assume that the formation enthalpy of the solvates (reaction 4 and 9) is proportional to the number of attached donor molecules, then x should be equal to six. However, in this case breaking the chelate bond of carboxy groups requires no energy consumption. It is obvious that reaction (6) occurs with an entropy decrease, and the dissociation energy of chelating bonds is completely compensated by the formation of the bond with the donor (HMPTA). Taking into account steric difficulties connected with a high volume of HMPTA molecules and a decrease in the energy of the metal-donor bond caused by the increase in the number of HMPTA molecules in the coordination sphere of the molybdenum cluster, we may state that the number of HMPTA molecules in the solvate should not exceed four. All HMPTA molecules occupy equatorial positions in the $[Mo_2(CF_3COO)_4{\cdot}4HMPTA]$ solvate and the carboxyl ligands are terminal. This conclusion is supported by the IR

Scheme 2.



spectroscopy data. Only two bands of asymmetric vibrations of carboxy group are detected in the IR spectrum (see the table) that points to the complete breaking of all chelate bonds between molybdenum and the carboxy groups in the complex.

To construct a cycle connecting formation of adducts in gas and solution [7], it is necessary to know the enthalpy of the adduct $Mo_2(CF_3COO)_4{\cdot}2HMPTA$ solvation in DCE. Its experimental value cannot be calculated from the ratio $\Delta_{solv}H_{add}/DCE = \Delta_{subl}H_{add} - \Delta_{dis}H_{add}/DCE$ (where $\Delta_{dis}H_{add}/DCE$ is the enthalpy of the adduct dissolution in 1,2-dichloroethane) because of the adduct thermal decomposition. As the dipole–dipole interaction at the level of locally arising dipole moments in voluminous molecules is levelled the more strongly the greater is the volume of solvated molecules, and molecules of the adduct $Mo_2(CF_3COO)_4{\cdot}2HMPTA$ are tens of times more voluminous than solvent molecules, it is presumable that the solvation enthalpy of such compounds will be defined mainly by dispersive interaction forces [8, 9]. The solvation enthalpy of organic compounds $\Delta_{solv}H_{X/S}$ linearly depends on the molar refraction of a solvated compound $X(MR_X)$ and can be calculated from the ratio: $\Delta_{solv}H_{X/S} = a_S + b_S MR_X$, where a_S and b_S are constant for the solvent S [10]. The solvation enthalpy of the complex $Mo_2(CF_3COO)_4$ in 1,2-dichloroethane (102±3 kJ/mol) was determined from relation (8).

$$\Delta_{solv}H[Mo_2(CF_3COO)_4]/(1,2\text{-DCE}) = \Delta_{subl}H[Mo_2(CF_3COO)_4] - \Delta_{dis}H[Mo_2(CF_3COO)_4/(DCE). \quad (8)$$

Molar refraction of the complex was estimated using the empirical relation: $\Delta_{solv}H_X/_{DCE} = 4.98 + 1.17MR_X$ [10], $MR\{[Mo_2(CF_3COO)_4]\} = 8$ cm^3. The value of the adduct $[Mo_2(CF_3COO)_4]{\cdot}2HMPTA$ molar refraction calculated by the additive scheme was 178 cm^3. The enthalpy of the adduct solvation in 1,2-dichloroethane, which is necessary for drawing the cycle, was calculated with the use of the same equation and appeared to be –214±8 kJ/mol. To draw up the thermochemical cycle (Scheme 2), we used the enthalpy of HMPTA vaporization ($\Delta_{vap}H^0 = 61.1 \pm 0.5$ kJ/mol [11]), the enthalpy of $[Mo_2(CF_3COO)_4]_{cr}$ sublimation ($\Delta_{subl}H^0 = 123 \pm 3$ kJ/mol [12]), and the data from the thermochemical cycle shown in Scheme 1.

Equations (9) and (10) can be deduced from the thermochemical cycle.

$$[Mo_2(CF_3COO)_4]_{gas} + 2(HMPTA)_{gas} = [Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{gas}, \quad \Delta_9H^0 = -85 \pm 6 \text{ kJ/mol}, \quad (9)$$

$$[Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{cr} = [Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{gas}, \quad \Delta_8H^0 = -266 \pm 10 \text{ kJ/mol}. \quad (10)$$

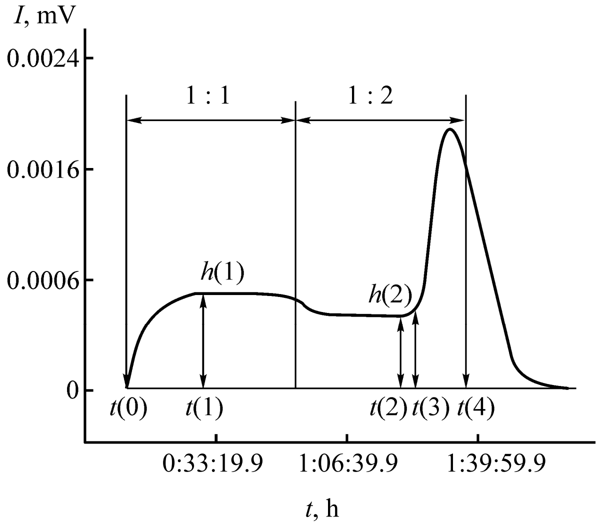
The enthalpy of the complex $Mo_2(CF_3COO)_4{\cdot}2HMPTA$ formation in the gas phase $\Delta_9H^0 = -85 \pm 6$ kJ/mol exceeds the formation enthalpy $\Delta_3H^0 = -68.9 \pm 0.8$ kJ/mol in 1,2-dichloroethane. The difference in the Δ_9H^0 and Δ_3H^0 values of ≈ 16 kJ is equal to the difference between the sum of solvation enthalpies of components and the complex in 1,2-dichloroethane. From the viewpoint of the continual model of solution structure this difference is caused by the effect of the reactive field [9] created by polar HMPTA molecules ($\mu = 3.96$ D) in 1,2-dichloroethane ($\varepsilon = 10.1$). It follows from the value $\Delta_9H^0 = -85 \pm 6$ that breaking of the donor-acceptor bond in the $[Mo_2(CF_3COO)_4{\cdot}2HMPTA]_{gas}$ complex requires 43±3 kJ/mol. According to the Gutmann scale, HMPTA is the strongest donor (*DN* = 38.2 [12]) and a rather low value of the *DA* bond dissociation energy in the $[Mo_2(CF_3COO)_4\cdot 2HMPTA]_{gas}$ adduct allows us to assign $Mo_2(CF_3COO)_4$ to moderate-force acceptors. The estimated value of the $[Mo_2(CF_3COO)_4\cdot 2HMPTA]_{cr}$ sublimation enthalpy is 266±10 kJ/mol.

EXPERIMENTAL

“Analytically pure” grade crystallohydrate $Mo_2(CF_3COO)_4\cdot 2H_2O_{(cr)}$ was synthesized from MoO_3 by the technique [13] and dried in a vacuum. A sample of the crystalline hydrate was purified and dehydrated by sublimation in a vacuum of 10^{-3} mmHg at 120°C.

The IR spectra were taken on a Perkin-Elmer BX II spectrophotometer in the range 1400–1800 cm^{-1}. Calorimetric measurements were carried out on a differential heat-conducting calorimeter at 298.15 K without contact of the solution under investigation with atmospheric air [14]. The volume of calorimetric vessels was 80.0 cm^3. A thin-walled spherical glass ampule with a weighted sample of crystalline $Mo_2(CF_3COO)_4$ was sealed in a vacuum and placed in a bottletight working calorimetric vessel with a preset amount of a solvent (50.0 mL). The same volume of the solvent was placed in a reference cell. When the calorimeter reached the thermal equilibrium mode, the ampoule was crushed and the thermal effect of the complex dissolution in a solvent was measured. After the dissolution termination the titration by an HMPTA solution in 1,2-dichloroethane was carried out. The solution was fed with a constant rate of 4.577± 0.045 mL/h. No less than 3-5 experiments were fulfilled for each reaction. To determine the crystallization enthalpy of the complex $Mo_2(CF_3COO)_4\cdot 2HMPTA$ and to neutralize the influence of HMPTA excess on the adduct solubility, the titration time was chosen so that the total amount of the entered titrant HMPTA in a solution corresponded to the ratio $HMPTA:Mo_2(CF_3COO)_4 = 2:1$.

We calculated ΔH_1^0, ΔH_2^0, K_1, and K_2 values for reactions (1) and (2) from the curves of calorimetric titration with continuous titrant input, using a computer program [15]. To calculate ΔH_1^0, ΔH_2^0, K_1, and K_2, we chose a region of the titration curve $t(1)$–$t(2)$ (see the figure), which corresponded to the thermal equilibrium in the calorimetric system and entered the indications $h = f(t)$ taken from the titration curve and the following parameters: the initial titrant concentration (b_0, M), the concentration of the unbound titrant (b, M), the initial concentration of titrated substance in a beaker (a_0, M), the volume of solution in a calorimetric beaker (V_0, L), the rate of the titrant solution input (vb, mol/s), the titration time (t, s), the calorimeter constant (k, mV/mW), the equilibrium constant K_1 of reaction (1), the equilibrium constant K_2 of reaction (2), the enthalpy of dissolution reaction (1) (ΔH_1, kJ/mol), the enthalpy of dissolution reaction (2) (ΔH_2, kJ/mol), and the titration curve $h = f(t)$ (mV), $p = b_0vb/V_0$ (mol L^{-1} s^{-1}).



Calorimetric curve of titration of 50.0 mL of $Mo_2(CF_3COO)_4$ (c = 0.005360 M) solution by HMPTA solution (c = 0.08592 M) in 1,2-dichloroethane. $t(0)$ is the titration beginning, $t(1)$–$t(2)$ is the region of thermal equilibrium [used in the program for calculating ΔH_1^0, ΔH_2^0, K_1, and K_2 of formation reactions of (1 : 1 and 1 : 2) adducts], $t(3)$ is the time of the beginning of the adduct $[Mo_2(CF_3COO)_4\cdot 2HMPTA]_{cr}$ crystallization, and $t(4)$ is the time of the termination of the titrant solution input.

Values of ΔH_1 and ΔH_2 were calculated from relation (11).

$$b(t)/k = dQ/dt = V\Delta H_1[(dn_1 + dn_2)/dt] + V\Delta H_2(dn_2/dt). \quad (11)$$

In the first stage of the calculation we specified numerical values of K_1, and K_2 and calculated the concentration (b) of the unbound injected ligand from relation (12), taking into account the fact that the volume V of titrant solution depends on time.

$$\begin{gathered}(V/V_0)K_1K_2b^3 + K_1[K_2(2a_0 - pt) + 1]b^2 \\ + [K_1(a_0 - pt) + 1]b - pt = 0, \qquad (12) \\ V = V_0 + v_0t.\end{gathered}$$

From these values we determined quantities n_1 and n_2 of successively formed adducts (1 : 1 and 1 : 2) and then calculated derivatives $(dn_1 + dn_2)/dt$ and dn_2/dt.

In the second stage we calculated the values of heat capacity dQ/dt in the chosen region of the titration curve, specifying numerical values of ΔH_1 and ΔH_2 [Eq. (11)]. The treatment of thermograms by means of the nonlinear regress program based on the least squares method allowed us to find the values of ΔH_1, ΔH_2, K_1, and K_2.

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