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Synthesis and Thermodynamic Characteristics of Molybdenum Carboxylates $Mo_2((CH_3)_3CCOO)_4$, $Mo_2(CF_3COO)_4$, and $MoO_2((CH_3)_3CCOO)_2$

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Abstract—Dimolybdenum tetratrimethylacetate (tetrapivalate) and tetratrifluoroacetate are synthesized, and their evaporation is studied by the Knudsen effusion method with mass spectral analysis of the gas phase. The standard enthalpies of formation of crystalline and gaseous $Mo_2(CF_3COO)_4$ are estimated for the first time by the study of dissociative ionization. The solid-phase reactions of silver pivalate $(CH_3)_3CCOOAg$ with molybdenum are studied by thermography (TG), differential scanning calorimetry (DSC), and mass spectrometry. The reaction in a temperature range of 410–480 K affords molybdenum oxopivalate MoO_2Piv_2. The obtained experimental data make it possible to estimate the standard enthalpy of formation of this compound: $\Delta_f H^\circ_{298}(MoO_2Piv_2, cr) = -1476$ kJ/mol.

Keywords: TG, DSC, mass spectrometry, molybdenum carboxylates, standard enthalpy of formation, evaporation

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INTRODUCTION

Molybdenum compounds form the largest group of compounds with quaternary bonds between metal atoms. Molybdenum acetate was the first structure with the quaternary bond published in 1965 [1]. The further numerous crystallographic studies showed that the structure of molybdenum acetate (D_{4h}) [2] is typical of other molybdenum carboxylates [3–7]. The structural characteristics of the molybdenum(IV) complexes based on monocarboxylic acids are studied rather well. As for the thermodynamic characteristics of these complexes, they are few and only known to be sufficiently volatile and congruently transit to the gas phase in the molecular form [8, 9]. The standard enthalpies of sublimation of dimolybdenum tetrapropionate, tetraacetate, tetraformate, and tetratrifluorocetate were determined in rather detailed studies [10, 11] by the static method using the Bourdon zero pressure gauge in a temperature range of 240–320°C. The standard enthalpy of formation of crystalline dimolybdenum tetraacetate was determined only in one work ($\Delta_f H^\circ_{298} = -1970.7 \pm 8.4$ kJ/mol) by the calorimetric dissolution method, and the estimate $\Delta_f H^\circ_{298} = -1826$ kJ/mol was given for gaseous dimolybdenum tetraacetate [8]. A high volatility and knowledge of the main thermodynamic characteristics of the molybdenum(IV) carboxylate compounds can become the determining factors for using the compounds in the CVD procedure when producing heat-resistance metallic or carbide coatings. Interestingly, many dimolybdenum tetracarboxylates with complicated organic ligands are highly resistant to air oxygen [12], which significantly simplifies their storage and use in various industrial procedures. Therefore, we started the works on the synthesis of the molybdenum carboxylate compounds and study of their structural and thermodynamic characteristics.

This work is devoted to the synthesis of molybdenum pivalate (trimethylacetate) $Mo_2(Piv)_4$ (Piv = $(CH_3)_3CCOO)_4$), trifluoroacetate $Mo_2(CF_3COO)_4$, and oxopivalate $MoO_2(Piv)_2$ and determination of their thermodynamic characteristics.

EXPERIMENTAL

Anhydrous molybdenum pivalate and trifluoroacetate were synthesized using the well-known procedure based on the transcarboxylation of dimolybdenum tetraacetate [4, 13–15] with an excess of the corresponding acid. The syntheses and isolation of the products were conducted in an anhydrous medium using the standard Schlenk technique. Hexane (reagent grade, Khimmed) was dried with metallic sodium and stored over sodium mirror. Dimolybdenum tetraacetate (98%, Aldrich), trimethylacetic acid (reagent grade, Khimmed), and trifluoroacetic acid (reagent grade, Khimmed) were used as received.

IR spectra were recorded in a range of 400–4000 cm^{-1} on a Perkin Elmer Spectrum 65 spectrophotometer equipped with a Quest ATR Accessory (Specac) by the attenuated total internal reflectance (ATR) method. Elemental analysis was carried out on a EuroEA-3000 automated C,H,N analyzer (EuroVektor).

Synthesis of $Mo_2(Piv)_4$. Weighed samples of dimolybdenum tetraacetate (2.0 g, 4.67 mmol) and trimethylacetic acid (10.0 g, 98 mmol) were placed in a glass ampule, which was degassed in a dynamic vacuum for 20 min. Then the sealed ampule was heated at 130°C in an oily bath until the reactants were completely dissolved (1 h) and the reaction mixture turned yellow. The reaction mixture was cooled (10°C/h) to 40°C, and the formation of yellow needle-like crystals was observed. The crystals were decanted and washed with anhydrous hexane. The yield was 2.6 g (93%).

For $C_{20}H_{36}O_8Mo_2$		
Anal. calcd., %	C, 40.28	H, 6.08
Found, %	C, 40.21	H. 6.03

IR (ATR; ν, cm^{-1}): 2962 m, 2927 m, 2902 m, 2870 w, 1709 w, 1479 vs, 1412 vs, 1365 s, 1214 vs, 1027 w, 936 w, 895 m, 797 m, 775 m, 611 vs, 441 vs.

Synthesis of $Mo_2(CF_3COO)_4$. A weighed sample of molybdenum acetate (0.426 g, 1.0 mmol) was placed in a glass ampule, trifluoroacetic acid (20 mL) was added, and the reaction mixture was degassed in a dynamic vacuum. Then the sealed ampule was heated at 130°C in an oily bath to the complete dissolution of the reactants (1 h), and the reaction mixture turned yellow. The reaction mixture was cooled to room temperature, and the formation of yellow needle-like crystals was observed. The crystals were decanted and washed with anhydrous hexane. The yield was 0.445 g (66%).

For $C_8F_{12}O_8Mo_2$	
Anal. calcd., %	C, 14.92
Found, %	C, 14.86

IR (ATR; ν, cm^{-1}): 3664 w, 2984 w, 2899 w, 1589 m, 1450 w, 1406 w, 1246 m, 1149 vs, 857 m, 779 m, 726 s, 688 w, 503 m.

The thermal behavior of the Mo–AgPiv system was studied by thermography (TG) and differential scanning calorimetry (DSC) on a 204 F1 Phoenix instrument (NETZSCH) in a temperature range of 30–250°C at a constant heating rate of 2, 5, or 10 K/min. Aluminum crucibles with punctured caps were used. The studies were carried out under an atmospheric pressure in a dynamic nitrogen atmosphere (flow rate 40 mL/min) with a protection inert gas flow of 70 mL/min. The instrument was preliminarily calibrated to temperature and sensitivity in the temperature range from –100 to 500°C by the parameters of phase transitions of high-purity standards of Hg, In, Sn, Zn, Bi, Pb, and CsCl. A change in the weight of the samples was detected on a TG 209 F1 Libra thermal balance (NETZSCH) in a temperature range of 30–300°C. The measurements were carried out in alundum crucibles at a constant heating rate of 10 K/min in a nitrogen atmosphere (flow rate 30 mL/min) with a protection inert gas flow of 10 mL/min. Samples of the Mo–AgPiv system were prepared by the thorough trituration of powdered silver pivalate and molybdenum in an agate mortar with periodical stirring for 2–3 h until homogeneous mixtures formed.

The thermodynamic characteristics of dimolybdenum tetracarboxylates were studied by the Knudsen effusion method with mass spectral analysis of the gas phase. Standard molybdenum effusion chambers with the ratio of the evaporation to effusion surface areas $S_{evap}/S_{eff} = \sim 600$ were used, and the temperature was measured with a Pt–Pt/Rh thermocouple and was maintained constant with an accuracy of ±1 K.

RESULTS AND DISCUSSION

The mass spectra of the gas phase above dimolybdenum tetrapivalate and tetratrifluoroacetate are given in Tables 1 and 2 where the isotopic compositions were taken into account.

The studies of the energy of the ionization processes showed that the gas phase above dimolybdenum carboxylates consisted of $Mo_2(CF_3COO)_4$ and $Mo_2(Piv)_4$ molecules only. For instance, only molecular ions $Mo_2L_4^+$, where L is carboxylate, are observed in the mass spectrum of the saturated vapor at the ionizing electron energy lower than 15 eV.

Experiments on the complete isothermal sublimation of the known weighed samples were carried out to determine the character of the evaporation of the complexes and to calculate the absolute partial pressure. The results of an experiment on studying dimolybdenum tetrapivalate are shown in Fig. 1. The facts that all ion currents (proportional to the partial pressure of $Mo_2(Piv)_4$ molecules) are constant and no nonvolatile residue is observed in the effusion chamber after the sublimation completion indicate in favor of the congruent character of evaporation of this compound

$$\begin{aligned} &Mo_2\left((CH_3)_3COO\right)_4(s) \\ &= Mo_2\left((CH_3)_3COO\right)_4(g). \end{aligned} \qquad (1)$$

The congruent character of evaporation of the complex and the monomolecular composition of the saturated vapor made it possible to calculate the partial pressure of dimolybdenum tetrapivalate by the Hertz–Knudsen equation

$$q_{\mathrm{Mo_2L_4}} = S_{\mathrm{eff}}(M_{\mathrm{Mo_2L_4}}/2\pi RT)^{1/2} p_{\mathrm{Mo_2L_4}} t, \qquad (2)$$

where S_{eff} is the effective effusion surface area, $M_{\mathrm{Mo_2L_4}}$ is the molecular weight of the gas phase component, $p_{\mathrm{Mo_2L_4}}$ is the partial pressure of the gas phase component, and t is the sublimation time of the weighed sample $q_{\mathrm{Mo_2L_4}}$.

The found value turned out to be $p = 0.30$ Pa at $T = 410$ K. The partial pressure of dimolybdenum tetratrifluoroacetate was determined similarly: $p = 0.43$ Pa at $T = 397$ K.

The study of the temperature dependences of intensities of the main ion currents in the mass spectra of dimolybdenum tetrapivalate (Table 3) in a temperature range of 369–437 K and dimolybdenum tetratrifluoroacetate (Table 4) in a temperature range of 358–408 K made it possible to calculate the enthalpies of sublimation of these molecular species by the Clausius–Clapeiron least-squares method: $\Delta_s H_T^\circ$ ($\mathrm{Mo_2Piv_4}$) = 133.8 ± 2.5 kJ/mol and $\Delta_s H_T^\circ$ ($\mathrm{Mo_2(CF_3COO)}$) = 130.0 ± 5.2 kJ/mol. The calculated characteristics allowed us to present the temperature dependences of the partial pressures (Pa) of $\mathrm{Mo_2(Piv)_4}$ and $\mathrm{Mo_2(CF_3COO)_4}$ molecules as the following equations (in the equations, the pressure was assigned to a standard pressure of 101 325 Pa)

$$\log p = -(6990 \pm 130)/T + 16.52 \pm 0.10, \quad 369 < T < 437 \text{ K},$$

$$\log p = -(6900 \pm 270)/T + 16.73 \pm 0.13, \quad 358 < T < 408 \text{ K}.$$

As can be seen from Table 1, the dissociative ionization of dimolybdenum tetratrifluoroacetate is accompanied by the formation of a significant amount of $\mathrm{Mo^+}$ ions. A similar ionization mechanism makes it possible to estimate the standard enthalpy of formation of this complex, because one of its fragmentation processes can be presented by the equation

$$\mathrm{Mo_2(CF_3COO)_4} + \bar{e} \rightarrow \mathrm{Mo^+} + \mathrm{Mo} + 4\mathrm{CF_3COO^\bullet} + 2\bar{e}.$$

The study of this ionization process of dimolybdenum tetratrifluoroacetate molecules made it possible to determine the energy of molybdenum ion formation by the vanishing ion current method using the ionization energy of mercury as the standard: EP($\mathrm{Mo^+}$) = 11.2 ± 0.3 eV. Using this value, the enthalpies of formation of the molybdenum atom and ion [16], and the enthalpy of formation of radical $\mathrm{CF_3COO^\bullet}$ ($\Delta_f H_T^\circ = -797.0$ kJ/mol [17]), the upper limit of the standard enthalpy of formation of the molybdenum complex in the gas phase was estimated: $\Delta_f H_T^\circ \le -2273 \pm 50$ kJ/mol.

Table 1. Mass spectrum of the main ions of the saturated vapor of $\mathrm{Mo_2(CF_3COO)_4}$ ($T = 380$ K, $U_{\mathrm{ioniz}} = 65$ V)

Ion*	Relative intensity, %
$\mathrm{Mo_2L_4^+}$	31
$\mathrm{[Mo_2L_4\text{-}F]^+}$	19
$\mathrm{Mo_2L_3F^+}$	59
$\mathrm{Mo_2L_3^+}$	15
$\mathrm{Mo_2L_2F_2^+}$	100
$\mathrm{MoL_2F^+}$	13
$\mathrm{[Mo_2L_2\text{-}F]^+}$	10
$\mathrm{Mo_2LCF_3^+}$	51
$\mathrm{Mo_2L^+}$	21
$\mathrm{Mo_2^+}$	34
$\mathrm{Mo^+}$	30
$\mathrm{CF_3^+}$	14

* L = $\mathrm{CF_3COO}$.

Table 2. Mass spectrum of the main ions of the saturated vapor of $\mathrm{Mo_2(Piv)_4}$ ($T = 410$ K, $U_{\mathrm{ioniz}} = 70$ V)

Ion*	Relative intensity, %
$\mathrm{Mo_2L_4^+}$	100
$\mathrm{[Mo_2L_4\text{-}CH_3]^+}$	15
$\mathrm{Mo_2L_3^+}$	25
$\mathrm{[Mo_2L_3\text{-}CH_3]^+}$	5
$\mathrm{[Mo_2L_3\text{-}3CH_3]^+}$	10
$\mathrm{Mo_2OL_2^+}$	7
$\mathrm{Mo_2L_2^+}$	7
$\mathrm{Mo_2O_2L^+}$	8
$\mathrm{Mo_2OL^+}$	9
$\mathrm{Mo_2L^+}$	15

* L = Piv.

As mentioned above, there are almost no published data on the standard enthalpies of formation of the

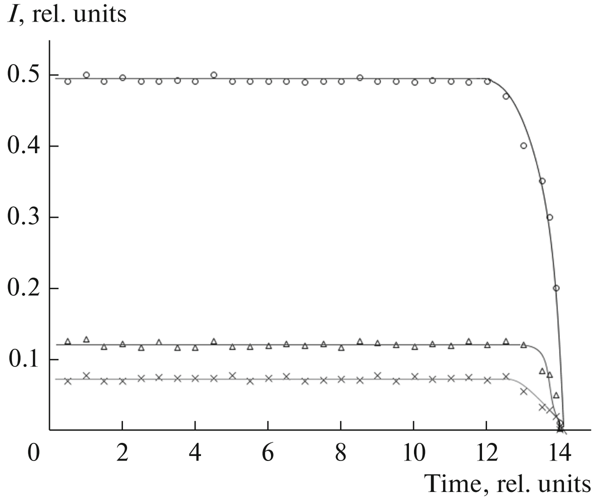

Fig. 1. Isotherm of the complete sublimation of a weighed sample of dimolybdenum tetrapivalate (T = 410 K): (○) $Mo_2L_4^+$, (Δ) $Mo_2L_3^+$, and (×) Mo_2L^+.

molybdenum(IV) carboxylate compounds with the Mo—Mo quaternary bond. A similar situation is associated, most likely, with experimental problems that arise when synthesizing the complexes and determining their thermodynamic characteristics by various calorimetric procedures. In this work, we attempted to determine the standard enthalpy of formation of the molybdenum complex $Mo_2(Piv)_4$ by the earlier proposed method [18] based on the study of the heterophase reaction between crystalline silver carboxylate and metal. The essence of the approach is the DSC determination of the thermal effect of the reaction between fine-grained molybdenum and AgPiv, which represent a thoroughly homogenized mixture with a significant metal excess. The formed reaction products are easily detected by an additional mass spectral analysis.

The mass spectrum of the gas phase of the Mo—AgPiv system at an ionizing electron energy of 70 eV in a temperature range of 400—520 K exhibited molybdenum-containing ions and high-intensity ions with the mass numbers $m/z = 57$ and $m/z = 28$ (Table 5), which were poorly sensitive to the mobile screen of the mass spectrometer. The studies of the energy of the ionization processes and profile of the molecular beam flowing from the Knudsen chamber showed that the gas phase above the studied system consisted of MoO_2Piv_2, CO, and 2,2,3,3-tetramethylbutane molecules. Thus, the reaction of molybdenum with silver pivalate can be presented as the equation

$$\begin{aligned}\mathrm{Mo(s)} + 4\mathrm{AgPiv(s)} &= \mathrm{MoO_2Piv_2(s,\ g)} + 2\mathrm{CO(g)} \\ &+ \mathrm{(CH_3)_3C{-}C(CH_3)_3(g)} + 4\mathrm{Ag(s)}.\end{aligned} \tag{3}$$

The enthalpy of reaction (3) was estimated from the TG and DSC experimental data. Some experimental conditions were varied when determining the heat of reaction (3) in the DSC studies and evaluating the influence of different factors on the heat of reaction (3) (Table 6): (a) a change in the reagent ratio (AgPiv : Mo), (b) the variation of the heating rate (2, 5, and 10 K/min), (c) a change in the contact surface area of the particles (pressing on a hydraulic press), (d) a change in the sample weight, and (e) prolong purging with an inert gas on the isothermal segment at t = 45°C before measurements. This experimental set up made it possible to find optimum synthesis conditions for molybdenum oxopivalate. For example, a large weight of the molybdenum sample allows one to decrease the mass loss of silver pivalate to undesirable side reactions during experiments. Pellet pressing increases contact between the particles and favors a faster occurrence of the heterogeneous reaction. The ratio between AgPiv and Mo with a molybdenum excess by 8 and more times (by weight) weakly affects the side processes.

Table 3. Standard enthalpies of sublimation of $Mo_2(Piv)_4$ molecules (T = 369—437 K)

$\Delta_s H_T^\circ$, kJ/mol			
for ion $Mo_2Piv_4^+$	for ion $Mo_2Piv_3^+$	for ion $Mo_2O_2Piv^+$	for ion $Mo_2OPiv_2^+$
133.6 ± 0.9	131.5 ± 2.3	132.3 ± 4.2	131.4 ± 2.3
131.8 ± 1.6	137.3 ± 2.5	133.1 ± 2.8	132.8 ± 3.0
135.4 ± 1.1	136.0 ± 5.7	135.1 ± 3.2	134.4 ± 2.4
132.4 ± 1.3	132.9 ± 1.5	134.5 ± 2.0	133.9 ± 1.1
135.1 ± 1.2			
133.7 ± 2.0	134.4 ± 2.7	133.8 ± 3.3	133.1 ± 1.7
Recommended value	133.8 ± 2.5		

Table 4. Standard enthalpies of sublimation of $Mo_2(CF_3COO)_4$ molecules (T = 358–408 K)

$\Delta_s H_T^\circ$, kJ/mol			
for ion* $Mo_2LCF_3^+$	for ion* $Mo_2L_2F_2^+$	for ion* $Mo_2L_3^+$	for ion* $Mo_2L_4^+$
129.8 ± 3.0	132.5 ± 5.0	139.6 ± 6.1	124.9 ± 6.2
129.4 ± 1.6	129.0 ± 1.0	133.6 ± 2.0	128.6 ± 1.2
134.0 ± 5.3	133.3 ± 5.7	129.1 ± 5.7	135.3 ± 8.4
128.0 ± 1.6	125.7 ± 1.4	125.3 ± 2.5	122.8 ± 1.1
129.9 ± 2.6	130.1 ± 3.5	131.9 ± 6.1	127.9 ± 5.5
Recommended value	130.0 ± 5.2		

* L = CF_3COO.

Almost in all cases, it is highly probable that the measured thermal effect (Fig. 2) is the sum of heats of two reactions (4) and (5)

$$4Ag(Piv) + 2Mo = Mo_2(Piv)_4 + 4Ag, \quad (4)$$

$$Mo_2(Piv)_4 + 4Ag(Piv) = 2MoO_2(Piv)_2 + 4CO + 4((CH_3)_3C)_2 + 4Ag \quad (5)$$

or heats of three reactions (4), (6), and (7).

$$4Ag(Piv) = 4Ag + 4CO_2 + 4((CH_3)_3C)_2, \quad (6)$$

$$Mo_2(Piv)_4 + 4CO_2 = 2MoO_2(Piv)_2 + 4CO, \quad (7)$$

which predetermine overall equation (3). It should be mentioned that reaction (6) is the heatless decomposition of silver pivalate [18]. Since $MoO_2(Piv)_2$ is the final product, the heat released upon all processes is proportional to the reacted mass (initial weight) of silver pivalate (Fig. 3), which is easily calculated by Eq. (3) from the mass loss (CO, $(CH_3)_3CC(CH_3)_3$) of the reaction mixture (Table 6). Such a relatively approximate estimate gives the heat of reaction (3) equal to 56 ± 20 kJ/mol. This value and the known published data [19–21] made it possible to estimate the standard enthalpy of formation of solid molybdenum oxopivalate: $\Delta_f H_T^\circ = -1476$ kJ/mol. It should be emphasized once more that the determined value is a rather approximate estimate of the enthalpy. This is due to the fact that, when considering the reaction of molybdenum with silver pivalate, the formation of other products was completely excluded, for example, molybdenum oxides of different oxidation states. It was ignored that the synthesized solid oxopivalate can be amorphous. Temperature changes in the heat capacities and heat losses for the removal of gaseous products of reaction (3) were ignored in the DSC analysis of the thermal effects. However, in spite of the estimation values of the thermodynamic characteristics of molybdenum carboxylates, these compounds can be recommended as precursors in the CVD procedure for the preparation of metallic, carbide, and oxide coatings and films, and molybdenum pivalate can be the most promising precursor for the use in this procedure. Molybdenum pivalate is a highly volatile compound and is inert toward air oxygen due to a complicated structure of the ligand [12].

One of the assumed purposes of this work was the determination of the standard enthalpies of formation of molybdenum(IV) carboxylates using a known procedure [18]. However, the interaction of fine-grained molybdenum and silver pivalate unexpectedly gave molybdenum oxopivalate MoO_2Piv_2. This interesting result can be explained using the studies on the cleavage of the Mo–Mo quaternary bond [22, 23], according to which the π-acceptor ligands coordinate to the axial position of the molybdenum complex and form intermediate substance {L···M–M···L}. As mentioned in the same studies [22, 23], this coordination leads to

Table 5. Mass spectrum of the gas phase above the Mo–AgPiv system (T = 425 K, U_{ioniz} = 70 eV)

Ion	m/z	Relative intensity, %	Molecule
$MoOPiv^+$	212	5	MoO_2Piv_2
$(MoOPiv + 57)^+$	272	23	
MoO_2Piv^+	233	100	
$(MoO_2Piv + 57)^+$	290	8	
$(Mo_2O_2Piv\text{-}50)^+$	376	5	$Mo_2O_4Piv_4$
$(Mo_2O_4Piv_3 + 13)^+$	566	4	
$(Mo_2O_4Piv_3)^+$	553	<1	
$*((CH_3)_3C)^+$	57	>1000	C_8H_{18}
$*(CO)^+$	28	>1000	CO

* For clarification, see text.

Table 6. DSC results for the Mo–AgPiv system

Mixture	Pressing	Overall weight of system, mg	Composition of system, wt % AgPiv	Mass loss in reaction (3), mg	Weight of AgPiv entered into reaction (3), mg	Measured heat quantity *Q*, mJ	*Q*, J/g of AgPiv	$-\Delta H$, kJ/mol
1	Yes	56.00	10.6	1.33	5.91	1741	294.4	61.5
1	Yes	18.2	10.6	0.5	1.92	477	248.1	51.9
1	No	13.35	10.6	0.48	1.41	344	244.4	51.1
2	No	20.36	5.1	0.33	1.04	169	163.2	34.1
2	No	18.15	5.1	0.25	0.92	132	143.1	29.9
2	No	15.67	5.1	0.21	0.80	147	184.1	38.5
3	Yes	71.43	6.3	0.61	3.00	1298	432.7	90.4
3	Yes	79.69	6.3	0.65	3.20	1397	437.0	91.3
Average								56 ± 20

an appreciable weakening of the π component of the M–M bond and an enhancement of the M–L bond. As a result, the molecule becomes more sensitive to the further nucleophilic attack with the M–M bond cleavage and formation of two monomeric molecules. An analogous pattern should be observed in our case. The dimolybdenum tetrapivalate complex formed at the initial stage of the radical synthesis

$$2\mathrm{Mo(s)} + 4\mathrm{Piv}^{\bullet} \rightarrow \mathrm{Mo_2(Piv)_4}$$

is surrounded by a significant excess of free radicals of pivalic acid [18] (π-acceptor ligands), which results in the formation of an intermediate compound that decomposes to form monomeric molecules $\mathrm{MoO_2Piv_2}$ because of Mo–Mo bond weakening

$$\left\{\mathrm{Mo_2(Piv)_4\cdots 2(Piv)^{\bullet}}\right\}$$
$$\rightarrow 2\mathrm{MoO_2Piv_2} + 2\mathrm{CO} + \left(\left(\mathrm{CH_3}\right)_3\mathrm{C}\right)_2.$$

Although the possibility that these reactions would proceed via the considered mechanism [22, 23] seems disputable in this study, the use of such solid-phase heterogeneous reactions can help to synthesize easily monomeric volatile molybdenum carboxylate compounds when preparing oxide, carbide, and metallic films and coatings directly during the CVD method.

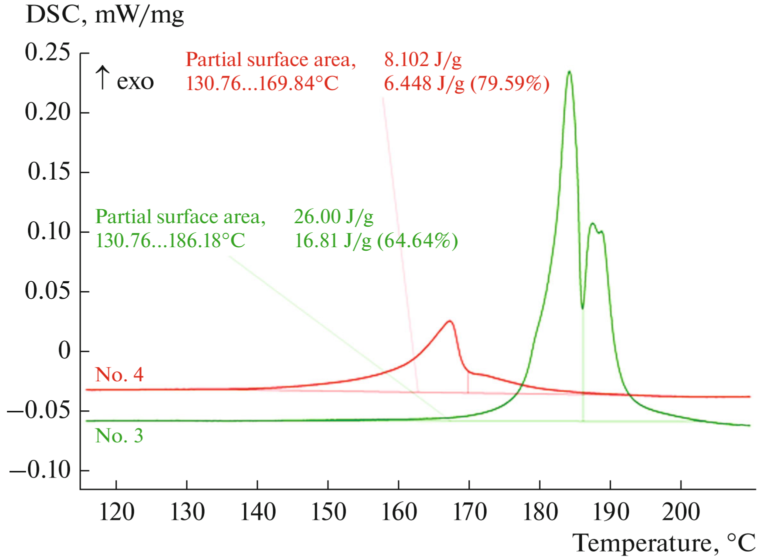

Fig. 2. DSC curves for the first and second mixtures (sample no. 3 is shown by green, and sample no. 4 is red-colored) for the powder at a heating rate of 5 K/min.

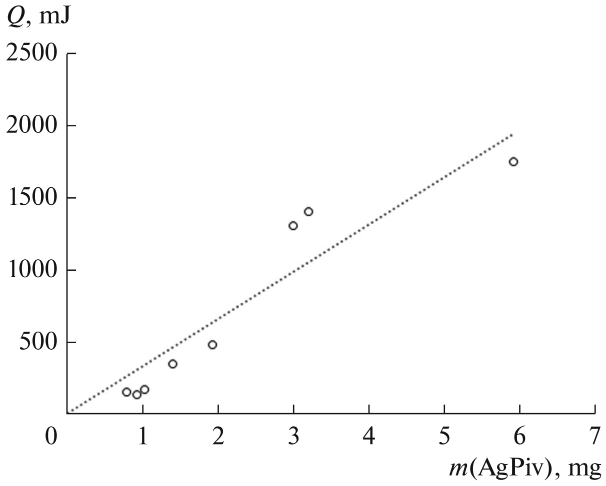

Fig. 3. Dependence of the heat of reaction (3) on the initial weight of silver pivalate.

To conclude, the structure of the synthesized complex $Mo_2((CH_3)_3CCOO)_4$ is described in the literature by three polymorphic modifications: triclinic [5], monoclinic, and orthorhombic [7]. In these works, molybdenum(IV) carboxylate was synthesized by the same method [24]: the reaction of $Mo(CO)_6$ with pivalic acid in boiling *o*-dichlorobenzene. The only difference was that the synthesized sample was resublimed in vacuo in a sealed ampule at 100°C [5], whereas in [7] some crystals with a good surface were selected using a polarization microscope and their structures were studied by XRD. It cannot be excluded that a mixture of polymorphic modifications of the complexes in which phase transitions occurred upon sublimation with triclinic crystal system formation was initially formed in [5]. Taking onto account low sublimation temperatures in [5], one can accept that the enthalpies of phase transitions between different polymorphic modifications range from 0.2 to 0.5 kJ/mol. Thus, the enthalpy of sublimation of $Mo_2((CH_3)_3CCOO)_4$ determined in our work can correspond to the sublimation of any of polymorphic modifications if taking into account its confidence interval.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Lawton, D. and Mason, R., *J. Am. Chem. Soc.*, 1965, vol. 87, p. 921. https://doi.org/10.1021/ja01082a046
2. Cotton, F.A., Mester, Z.C., and Webb, T.R., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1974, vol. 30, p. 2768. https://doi.org/10.1107/S0567740874008053
3. Hochberg, E., Walks, P., and Abbott, E.H., *Inorg. Chem.*, 1974, vol. 13, p. 1824. https://doi.org/10.1021/ic50138a008
4. Cotton, F.A., Norman, J.G., Jr., Stults, B.R., et al., *J. Coord. Chem.*, 1976, vol. 5, p. 217. https://doi.org/10.1080/00958977608073014
5. Cotton, F.A., Extine, M., and Gage, L.D., *Inorg. Chem.*, 1978, vol. 17, p. 172. https://doi.org/10.1021/ic50179a033
6. Garner, C.D., Hillier, I.H., Walton, I.B., et al., *J. Chem. Soc. Dalton*, 1979, p. 1279. https://doi.org/10.1039/DT9790001279
7. Don, S.M. and Hai-Wei Huang, *Inorg. Chem.*, 1990, vol. 29, p. 3674. https://doi.org/10.1021/ic00344a011
8. Cavell, K.J., Garner, C.D., Pilcher, G., et al., *Dalton Trans.*, 1979, p. 1714. https://doi.org/10.1039/DT9790001714
9. *Multiple Bonds between Metal Atoms*, Cotton, F.A. and Walton, R.A., Eds., New York: Springer, 2005.
10. Slyusareva, I.V., Kondrat’ev, Yu.V., Kozin, A.O., et al., *Vestn. SPbGU. Fiz. Khim.*, 2007, no. 3, p. 138.
11. Slyusareva, I.V., Kondrat’ev, Yu.V., Kozin, A.O., et al., *Vestn. SPbGU. Fiz. Khim.*, 2008, no. 3, p. 64.
12. Hochberg, E., Walks, P., and Abbott, E.H., *Inorg. Chem.*, 1974, vol. 13, no. 8, p. 1824. https://doi.org/10.1021/ic50138a008
13. Holste, G., *Z. Anorg. Allg. Chem.*, 1975, vol. 414, p. 81.
14. Cotton, F.A. and Norman, J.G., *J. Coord. Chem.*, 1971, vol. 1, p. 161. https://doi.org/10.1080/00958977208070758
15. Mureinik, R.J., *J. Inorg. Nucl. Chem.*, 1976, vol. 38, p. 1275.
16. *Termicheskie konstanty veshchestv: spravochnik v 10 tomakh* (Thermal Characteristics of Substances: 10-volume Reference Book), Glushko, V.P., Ed., Moscow: VINITI, 1974, vol. 7, part 1.
17. Yu-Ran Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC Press LLC, 2003.
18. Morozova, E.A., Dobrokhotova, Zh.V., and Alikhanyan, A.S., *J. Therm. Anal. Calorim.*, 2017, vol. 130,

no. 3, p. 2211.
https://doi.org/10.1007/s10973-017-6583-y

19. *Termicheskie konstanty veshchestv: spravochnik v 10 tomakh* (Thermal Characteristics of Substances: 10-volume Reference Book), Glushko, V.P., Ed., Moscow: VINITI, 1974, vol. 4, part 1.
20. NIST Chemistry WebBook. https://webbook.nist.gov/chemistry/.
21. Lukyanova, V.A., Papina, T.S., Didenko, K.V., et al., *J. Therm. Anal. Calorim.*, 2008, vol. 92, no. 3, p. 743. https://doi.org/10.1007/s10973-008-9019-x
22. Voss, K.E., Hudman, J.D., and Kleinberg, J., *Inorg. Chim. Acta*, 1979, vol. 20, p. 97.
23. Cotton, F.A., Darensbourg, D.J., and Kolthammer, B.W.S., *J. Organomet. Chem.*, 1981, vol. 217, p. C14. https://doi.org/10.1016/S0022-328X(00)86032-5
24. McCarley, R.E., Templeton, J.L., Colburn, T.J., et al., *Adv. Chem. Ser.*, 1976, no. 150, p. 318.

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