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THERMOCHEMICAL PROPERTIES OF THE CHELATE COMPLEXES OF SOME 3*d*-ELECTRON ELEMENTS WITH 2,2,6,6-TETRAMETHYLHEPTANE-3,5-DIONE. PART I. COMPLEXES OF Mn(II), Fe(II) AND Co(II)

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ABSTRACT

The standard molar enthalpies of formation of Mn(II), Fe(II) and Co(II) complexes with 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane, HDPM) were determined calorimetrically. The values of $\Delta H_f^0(\text{M(DPM)}_2(\text{s})\ 298.15\ \text{K})$ (kJ mol^{-1}) were found to be as follows: Mn(DPM)_2, $-(1325.7 \pm 7.6)$; Fe(DPM)_2, $-(1252.0 \pm 7.6)$; Co(DPM)_2, $-(1227.1 \pm 7.6)$. The enthalpies for hypothetical processes of complex formation in the gaseous state were calculated. Mean bond-dissociation energies $\langle D \rangle$(M–O) and mean coordinate bond-dissociation energies $\langle D_{\text{CB}} \rangle$(M–O) were determined.

INTRODUCTION

The thermochemical characteristics of the first group transition metal acetylacetonates were given in a preceding paper [1]. Now we have extended the study to dipivaloylmethanates, which are a very convenient subject for investigation, because of their monomeric structure in the solid state [2]. Our goal was to find out how far the enlargement of the aliphatic chain in the chelate ring would influence the metal–ligand bond energy value in the isolated complex molecule in the gaseous state.

EXPERIMENTAL

The solution calorimeter

The isoperibol calorimeter is described in a previous paper [1]. The accuracy of the system was checked by measurements of the heat of dissolution of KCl (Suprapur, Merck) in water. The value of 17.54 ± 0.03 kJ mol^{-1} obtained for the process $\text{KCl}_{(\text{s})} + 200\ \text{H}_2\text{O}_{(\text{l})} = \text{KCl} \cdot 200\ \text{H}_2\text{O}_{(\text{l})}$ at 298.15 K was consistent with the literature data [3].

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Materials

Dipivaloylmethane (EGA Chemie K.G.) was purified by repeated distillation under reduced pressure using the fraction of boiling point temperature 367–368 K, under a pressure of 47 kPa.

$MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ of analytical purity were used.

$HCl \cdot 11.618\ H_2O$ was prepared by dilution of concentrated acid; its concentration was checked by titration.

Dioxan was purified according to the method described elsewhere [4].

Chelates

Mn(II) dipivaloylmethanate was obtained under an argon atmosphere according to the method outlined by Gerlach and Holm [5]. The carefully deoxidized aqueous solution of Mn(II) acetate, buffered by sodium acetate was followed by methanolic solution of dipivaloylmethane. The pale yellow precipitate was removed, washed with methanol–water solution and dried in vacuo over P_2O_5 in an oxygen-free atmosphere. The results of the elemental analysis were: Mn, 13.09; C, 62.42; H, 9.02; calc: Mn, 13.03; C, 62.69; H, 9.09 mass%.

Iron(II) dipivaloylmethanate was obtained by the method described by Fackler et al. [6]. To the acidic, aqueous Fe(II) sulphate solution the stoichiometric amount of dipivaloylmethane in methanol was added in an oxygen-free atmosphere. After the addition of an aqueous solution of NaOH, a yellow precipitate was obtained. The complex was filtered off, washed with *n*-hexane to remove traces of $Fe(DPM)_3$, and dried in vacuo at room temperature. The results of the elemental analysis were: Fe, 13.50; C, 62.22; H, 9.12; calc: Fe, 13.22; C, 62.56; H, 9.07 mass%.

Cobalt(II) dipivaloylmethanate was obtained under argon atmosphere according to Cotton and Soderberg's method [7]. After mixing of Co(II) nitrate with a small excess of dipivaloylmethane, concentrated ammonia was added dropwise. The complex was dried in a desiccator over P_2O_5 and purified by sublimation in vacuo. A purple product was obtained. The results of the elemental analysis were: Co, 13.82; C, 62.40; H, 8.87; calc: Co, 13.85; C, 62.10; H, 9.00 mass%.

Measurement procedure

The HCl solution calorimetry method was used to determine the standard molar enthalpies of formation of the complexes examined. The principles of this method were described in detail by Ko [8]. The reactions of decomposition (7) were a basis for calculations. The enthalpies, $\Delta H(7)$, were determined from the thermodynamic cycle shown in the scheme in Table 1.

TABLE 1

Reaction scheme for calculation of enthalpies of reaction (7) $\Delta H(7)=\Delta H(1)+2\Delta H(2)-\Delta H(3)-2\Delta H(4)-(23.236-n)\Delta H(5)+\Delta H(6)$

No.	Reaction scheme	
1	$M(DPM)_{2(s)}$ + solvent	= solution 1
2	2 $HCl \cdot 11.618\ H_2O_{(l)}$ + solution 1	= solution 2
3	$MCl_2 \cdot n\ H_2O_{(s)}$ + solvent	= solution 3
4	2 $HDPM_{(l)}$ + solution 3	= solution 4
5	$(23.236-n)\ H_2O_{(l)}$ + solution 4	= solution 5
6	solution 2	= solution 5
7	$M(DPM)_{2(s)}+2\ HCl \cdot 11.618\ H_2O_{(l)}$	$= MCl_2 \cdot n\ H_2O_{(s)}+2\ HDPM_{(l)}+(23.236-n)\ H_2O_{(l)}$

Preservation of the stoichiometry of reaction (7) leads to the thermodynamic equilibrium of solutions (2) and (5), i.e., $\Delta H(6)=0$ A solution containing 75% (v/v) dioxane and 25% (v/v) 4.36 M HCl was used as a solvent.

RESULTS AND DISCUSSION

The detailed results of the calorimetric measurements are presented in Table 2.

It was found experimentally that the enthalpies of reactions (2), (4) and (5) do not depend upon the composition of solutions 1, 3 and 4, respectively.

The standard molar enthalpies of formation were determined from the calculated $\Delta H(7)$ value and the following literature data for ΔH_f^0 (kJ mol^{-1}): $MnCl_2 \cdot 4\ H_2O_{(s)}$, -1702.9 [9]; $FeCl_2 \cdot 4\ H_2O_{(s)}$, -1551.0 [9]; $CoCl_2 \cdot 6\ H_2O_{(s)}$, -2129.2 [9]; $HDPM_{(l)}$, -587.7 ± 3.8 [10]; $HCl \cdot 11.618\ H_2O_{(l)}$, -3482.79 [11]; $H_2O_{(l)}$, -285.83 ± 0.04 [11]. The results are presented in Table 3.

The enthalpy of sublimation measured by the Knudsen effusion technique is known only for Ni(II) dipivaloylmethanate and is 145.2 ± 10 kJ mol^{-1} [12]. There is an experimentally confirmed rule that the heats of sublimation of β-diketonates depend mainly on their molecular structure. Isostructural complexes, e.g., Sc(III), V(III) and Fe(III) acetylacetonates, have very close heats of sublimation (within a couple per cent) [13]. On this basis, and on consideration of the fact that the dipivaloylmethanates are isostructural tetrahedrons [2], we have assumed for them the same heat of sublimation value as for $Ni(DPM)_2$, i.e., 145 ± 20 kJ mol^{-1}. Calculated enthalpies of formation of the complexes in the gaseous phase are presented in Table 3.

As a real measure of the metal–ligand bond energy we have assumed the enthalpies of formation of the isolated complex molecule (from radicals or

TABLE 2

Calorimetric results at 298.15 K and mean molar enthalpy changes, each with the standard deviation of the mean ($\Delta\theta$ = corrected temperature change, γ = the heat capacity of the calorimeter)

Metal	n (mmol)	$\Delta\theta \times 10^3$ (K)	γ ($J\ K^{-1}$)	Q (J)	ΔH ($kJ\ mol^{-1}$)
Reaction (1): $M(DPM)_{2(s)}$ + solvent = solution 1					
Mn(II)	0.052385	5.30	438.9	2.326	−44.41
	0.056395	5.60	443.7	2.485	−44.07
	0.056561	5.40	454.1	2.452	−43.35
	0.057486	5.80	437.9	2.540	−44.18
	0.073548	7.30	441.4	3.222	−43.80
			$\langle \Delta H(1) \rangle = -(43.96 \pm 0.18)$		
Fe(II)	0.049952	3.00	454.7	1.364	27.30
	0.058475	3.50	453.1	1.586	27.12
	0.059588	3.50	454.3	1.590	26.68
	0.071022	4.30	448.6	1.929	27.16
	0.072964	4.30	460.2	1.979	27.12
			$\langle \Delta H(1) \rangle = (27.08 \pm 0.08)$		
Co(II)	0.055614	4.30	441.9	1.900	34.16
	0.080005	6.10	443.8	2.707	33.84
	0.088102	6.80	442.9	3.012	34.19
	0.097413	7.40	444.4	3.289	33.76
	0.12433	9.40	448.5	4.216	33.91
			$\langle \Delta H(1) \rangle = (33.97 \pm 0.08)$		
Reaction (2): $HCl \cdot 11.618\ H_2O_{(l)}$ + solution 1 = solution 2					
	0.085247	3.80	450.3	1.711	−20.07
	0.10323	4.65	447.2	2.079	−20.14
	0.12256	5.55	444.8	2.469	−20.14
	0.12487	5.60	449.0	2.514	−20.14
	0.18691	8.45	446.1	3.770	−20.17
			$\langle \Delta H(2) \rangle = -(20.13 \pm 0.02)$		
Reaction (3): $MCl_2 \cdot n\ H_2O_{(s)}$ + solvent = solution 3					
Mn(II)	0.052212	0.30	483.3	0.145	−2.77
	0.056595	0.35	462.9	0.162	−2.87
	0.056613	0.35	437.1	0.153	−2.70
	0.057285	0.35	465.7	0.163	−2.85
	0.073314	0.45	462.2	0.208	−2.83
			$\langle \Delta H(3) \rangle = -(2.80 \pm 0.03)$		
Fe(II)	0.049725	1.05	466.7	0.490	−9.84
	0.058512	1.30	460.0	0.598	−10.22
	0.059780	1.30	456.9	0.594	−9.94
	0.071122	1.55	464.5	0.720	−10.12
	0.072817	1.55	461.3	0.715	−9.82
			$\langle \Delta H(3) \rangle = -(9.99 \pm 0.08)$		

TABLE 2 (continued)

Metal	n (mmol)	$\Delta\theta \times 10^3$ (K)	γ ($\mathrm{J\,K^{-1}}$)	Q (J)	ΔH ($\mathrm{kJ\,mol^{-1}}$)
Co(II)	0.055728	3.30	447.6	1.477	26.50
	0.079433	4.75	448.4	2.130	26.81
	0.088114	5.30	450.0	2.385	27.07
	0.097321	5.70	447.8	2.552	26.22
	0.12542	7.40	448.9	3.322	26.49
			$\langle \Delta H(3) \rangle = (26.62 \pm 0.12)$		
Reaction (4): $HDPM_{(l)}$ *+ solution 3 = solution 4*					
	0.080444	1.95	444.1	0.866	10.77
	0.14593	3.55	447.9	1.590	10.90
	0.15428	3.65	441.3	1.611	10.44
	0.16675	4.00	442.4	1.770	10.61
	0.18532	4.45	447.5	1.991	10.75
			$\langle \Delta H(4) \rangle = (10.69 \pm 0.08)$		
Reaction (5): $H_2O_{(l)}$ *+ solution 4 = solution 5*					
	0.52518	1.05	442.3	0.464	−0.88
	0.63427	1.30	440.9	0.573	−0.90
	0.92431	1.90	449.2	0.853	−0.92
	1.37146	2.80	448.3	1.255	−0.92
	1.52872	3.25	444.1	1.443	−0.94
			$\langle \Delta H(5) \rangle = -(0.91 \pm 0.01)$		

ions) in the gaseous phase, where the intermolecular interactions and solvation effects are eliminated

$$\mathrm{M_{(g)} + 2\,DPM^{\cdot}_{(g)} = M(DPM)_{2(g)}} \qquad (8)$$

$$\mathrm{M^{+2}_{(g)} + 2\,DPM^{-}_{(g)} = M(DPM)_{2(g)}} \qquad (9)$$

The enthalpy of formation of liquid dipivaloylmethane, determined by the bomb calorimetry method, is −587.7 ± 3.8 kJ $\mathrm{mol^{-1}}$ [10]. NMR studies of keto-enol equilibrium revealed that the liquid phase of dipivaloylmethane contained (at 298.15 K) 98% of the enol form [14]. The enthalpy of

TABLE 3

Enthalpies of reaction (7) and standard molar enthalpies of formation of the complexes in solid and gaseous phases

Complex	$-\Delta H(7)$ ($\mathrm{kJ\,mol^{-1}}$)	$-\Delta H^0_{f(s)}$ ($\mathrm{kJ\,mol^{-1}}$)	$-\Delta H^0_{f(g)}$ ($\mathrm{kJ\,mol^{-1}}$)
$\mathrm{Mn(DPM)_2}$	85.30 ± 0.32	1325.7 ± 7.6	1180.7 ± 21.4
$\mathrm{Fe(DPM)_2}$	7.07 ± 0.28	1252.0 ± 7.6	1107.0 ± 21.4
$\mathrm{Co(DPM)_2}$	38.61 ± 0.28	1227.1 ± 7.6	1082.1 ± 21.4

enolisation of dipivaloylmethane, determined from variable temperature proton magnetic resonance measurements, is -17.53 kJ mol^{-1} [15]. From the above data, $\Delta H_f^0(\mathrm{HDPM, enol_{(l)}})$ was calculated as -588.0 ± 3.8 kJ mol^{-1}. The calorimetrically determined enthalpy of vaporization of the enol form of dipivaloylmethane is 59.54 ± 0.12 kJ mol^{-1} [16], and, hence, $\Delta H_f^0(\mathrm{HDPM, enol_{(g)}}) = -528.5 \pm 3.8$ kJ mol^{-1}.

On the assumption that substituents in the aromatic ring of the enol form of β-diketone have no influence on the dissociation energy of the O–H bond, we have taken $D(\mathrm{DPM^{\cdot}{-}H})\mathrm{enol} = D(\mathrm{ACAC^{\cdot}{-}H})\mathrm{enol} = 418 \pm 20$ kJ mol^{-1}. It could, however, be noted that some authors believe that the O–H bond dissociation energy in the enol form of acetylacetone (ACAC) should be close to the D(O–H) value in phenol, and is about 365 kJ mol^{-1} [17]. In recent reports [18] it was stated, that $D(\mathrm{ACAC^{\cdot}{-}H})$enol is rather comparable with the D(O–H) value in alcohols, i.e., 418 ± 20 kJ mol^{-1}. This value and $\Delta H_f^0(\mathrm{H^{\cdot}_{(g)}}) = 218.00 \pm 0.01$ kJ mol^{-1} [19] were used for calculation of the enthalpy of formation of the radical

$$\Delta H_f^0(\mathrm{DPM^{\cdot}_{(g)}}) = -(328.5 \pm 20.4)\ \mathrm{kJ\ mol^{-1}}$$

Taking advantage of the fact that the electron affinity of dipivaloylmethane is the same as that of acetylacetone, i.e., 33 kJ mol^{-1} [20], the enthalpy of formation of the dipivaloylmethane ion was calculated as

$$\Delta H_f^0(\mathrm{DPM^{-}_{(g)}}) = -361.5 \pm 20.4\ \mathrm{kJ\ mol^{-1}}$$

The enthalpies of reactions (8) and (9) were calculated using the literature values [21] for $\Delta H_f^0(\mathrm{M_{(g)}})$ (kJ mol^{-1}) and $\Delta H_f^0(\mathrm{M^{+2}_{(g)}})$ (kJ mol^{-1}): Mn, 283.3; Mn^{2+}, 2522.0 ± 0.1; Fe, 416.3 ± 1.7; Fe^{2+}, 2751.6 ± 2.3; Co, 424.7 ± 2.1; Co^{2+}, 2841.7 ± 3.4. The results are presented in Table 4.

The equivalence of the metal–oxygen bond of dipivaloylmethanates in the solid phase [2] should also be preserved in the gaseous phase, which is why mean bond dissociation energies, $\langle D \rangle$(M–O), and mean coordinate bond dissociation energies, $\langle D_{\mathrm{CB}} \rangle$(M–O), were calculated as $-\Delta H(8)/4$ and $-\Delta H(9)/4$, respectively (Table 4). Comparison of these values with those found for acetylacetonates [1] and the precision of our calculations allowed

TABLE 4

The enthalpy changes, $\Delta H(8)$, of the radical and, $\Delta H(9)$, of the ionic complex-formation processes in the gaseous phase with metal-oxygen bond energies ($\langle D \rangle$(M–O) = mean bond dissociation energy, $\langle D_{\mathrm{CB}} \rangle$(M–O) = mean coordinate bond dissociation energy)

Complex	$-\Delta H(8)$ (kJ mol^{-1})	$-\Delta H(9)$ (kJ mol^{-1})	$\langle D \rangle$(M–O) (kJ mol^{-1})	$\langle D_{\mathrm{CB}} \rangle$(M–O) (kJ mol^{-1})
Mn(DPM)$_2$	806 ± 46	2980 ± 46	201 ± 11	745 ± 11
Fe(DPM)$_2$	866 ± 46	3136 ± 46	217 ± 11	784 ± 11
Co(DPM)$_2$	850 ± 46	3201 ± 46	212 ± 11	800 ± 11

the statement that the enlargement of the aliphatic chain of a ligand has no influence on the metal–ligand bond energies.

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