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Preparation and reactivity of metal-containing monomers

45.* Determination of stability of monomeric metal chelates of substituted 6-heptene-1,3-diones in solutions

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The stability constants of some bi- and trivalent metal complexes with methyl-, trifluoromethyl-, and phenyl-substituted 6-heptene-1,3-diones have been determined by pH-metric titration at 20 °C and an ionic strength $\mu = 0.1$. It is proposed that vinyl groups of ligands are involved in complexation.

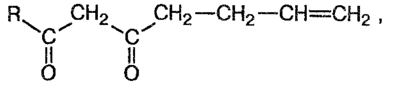
Key words: complexation, pH-metric titration, stability constants, β-diketones, vinyl group, π-complexes.

It is known[1] that metal-containing β-diketonates belong to a well studied class of compounds and possess a broad spectrum of properties that make it possible to utilize them in various areas of science and industry. Polymeric forms of metal diketonate complexes can be obtained, if their ligands contain functional groups that are able to undergo polymeric transformations.[2] The properties of polymeric complexes differ substantially from those of monomeric analogs, which provides additional avenues for searching for new fields of application of coordination compounds.

Important information can be obtained by comparison of quantitative parameters of complexation reactions in these systems. As a rule, polymers manifest weaker donor properties than their low-molecular analogs, although opposite examples are also known. It cannot be excluded that the differences in the stability of the complexes under question can be caused, to a certain extent, by the effect of polymerizable groups that are present in monomeric and absent in polymeric ligands.

In fact, as we have shown previously,[3,4] the stability of metal methacryloylacetonates (MCA), whose ligands contain vinyl groups, is by several orders of magnitude higher than that of the corresponding macrocomplexes. In addition, the increased stability of strontium methacryloylacetonate compared to analogous compounds of magnesium and calcium has been mentioned in Ref. 3 without a discussion of possible reasons. These specific features are likely caused by the presence of a fragment with a multiple bond in the β-diketonate molecule.

In this work, in order to obtain additional information about the possible participation of the vinyl group in complexation and to involve rare-earth elements (REE) in complexation with similar ligands, we have determined the stability of chelates of transition and nontransition metals with monomeric ligands (HL) by pH-metric titration. The following compounds were used as monomeric ligands HL: 7-octene-2,4-dione (HOD), 1-phenyl-6-heptene-1,3-dione (HPHD), and 1,1,1-trifluoro-7-octene-2,4-dione (HTOD)



$$R{-}C({=}O){-}CH_2{-}C({=}O){-}CH_2{-}CH_2{-}CH{=}CH_2\,,$$

where R = Me (HOD), Ph (HPHD), and CF_3 (HTOD).

Experimental

Solutions of metal salts were prepared from the corresponding hydrated perchlorates followed by determination of the concentrations of metal ions by complexonometric titration. The starting solutions for titration (V_0 = 30 mL) contained 0.1—0.2 mmol of metal perchlorate and a fourfold excess of a ligand. The ionic strength $\mu = 0.1$ was created by addition of the calculated amount of $NaClO_4$ (4 mol L^{-1}), and CO_2-free KOH (0.1 mol L^{-1}) was used as a titrating agent. Measurements were carried out on a pH-121 pH-meter with an ESL-43-07 glass electrode and an Ag/AgCl reference electrode at 20 °C. The electrodes were calibrated by aqueous buffer

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solutions with correction for ethanol, according to the known procedure.[5] In order to enhance solubility of the compounds formed over a broad pH range, pH-titration was carried out in aqueous-ethanolic solutions containing 70 % of ethanol. Nevertheless, in several cases, at pH ≈ 8 the solutions became turbid followed by formation of a solid phase, which prevented one from obtaining data for plotting the formation curve in the range of maximum values of the mean number of coordinated ligands. In particular, only two first equilibrium constants were determined for REE chelates.

$$M^{3+} + L^- \Leftrightarrow ML^{2+} \quad K_1 = \frac{[ML^{2+}]}{[M^{3+}][L^-]}$$

$$ML^{2+} + L^- \Leftrightarrow ML_2^+ \quad K_2 = \frac{[ML_2^+]}{[ML^{2+}][L^-]}$$

The mean number of coordinated ligands was not higher than unity on the formation curves of some complexes (7-octene-2,4-diionates of alkaline-earth metals and magnesium as well as all of the strontium and barium complexes). Therefore, only the first constant corresponding to the addition of one HL molecule was determined for these complexes. The constants were calculated by the Bjerrum function modified by Irving and Rossotti.[5] The data were processed on an IBM personal computer, using algorithms analogous to the SCOGS program.[6]

Absorption spectra of solutions of neodymium complexes were recorded on a Perkin-Elmer Lambda-9 spectrophotometer.

Results and Discussion

The series of ligands studied can be compared with derivatives of acetylacetone (AA) with the same substituents adjacent to the dicarbonyl fragment as the compounds under consideration, *viz.*, benzoylacetone (BA) and trifluoroacetylacetone (TFA). The phenyl substituent is more electron-donating, while the trifluoromethyl group is more electron-accepting than the methyl group. Comparison of the values of acid dissociation (pK_a) (Table 1) shows that the effect of these substituents on the acid-base properties does not correlate with their electronic properties, as is the case in the TFA—AA—BA series. For doubly charged metal cations, the stability of complexes with HPHD and HTOD falls in the Irving—Williams sequence and increases in the series: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Zn^{2+} \approx Co^{2+} < Ni^{2+} < Cu^{2+}$. However, calcium and strontium 7-octene-2,4-diionates are more stable than the corresponding magnesium compounds. Although the differences in the $\log K$ values in the group of complexes under discussion are rather low, a "reverse" run of the change in the constants undoubtedly takes place, especially in comparison with metal acetylacetonates. It is noteworthy that the similar dependence has already been observed for methacryloylacetonates of alkaline-earth elements,[3] although it is known that the overwhelming majority of calcium and strontium β-diketonates are less stable than magnesium complexes.

The participation of virtual (unoccupied) d-orbitals of calcium and strontium ions in complexation can be one of the possible explanations of the observed deviation from the usual run of the change in the constants. As a rule,[7] the contribution of the *n*d- and *n*s-orbitals of the central atoms into the delocalized molecular orbitals of oxo compounds of nontransition metals is insignificant, and MO are formed almost only by its valent *n*p-atomic orbitals. Since β-diketones are bidentate ligands, they occupy two adjacent sites in the coordination polyhedron involving two orbitals (usually, s and p) of the central atom. In this case, the stability of the complexes decrease in parallel with an increase in the element number in the periodic system of elements. A tridentate ligand occupies three adjacent vertices of the coordination polyhedron, which requires the participation of d-orbitals in complexation. Therefore, for tridentate ligands, the stability of calcium and strontium complexes with unoccupied low-energy d-orbitals is comparable to that of magnesium complexes.[8] Taking into account the considerations presented above and all data obtained, it can be supposed that 7-octene-2,4-dione is

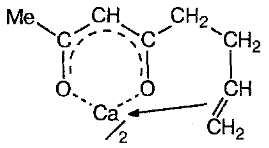
Table 1. Logarithms of stability constants of bivalent metal complexes with substituted 6-heptene-1,3-diones

M^{II}	HOD[a],	HTOD[b]			HPHD[c]		
	$\log K_1$	$\log K_1$	$\log K_2$	$\log\beta$	$\log K_1$ (±0.2)	$\log K_2$ (±0.2)	$\log\beta$
Mg	2.3±0.1	3.35±0.1			4.3	3.7	8.0
Ca	2.5±0.1	3.25±0.2			3.5	2.7	6.2
Sr	2.6±0.1	3.05±0.15			2.8		
Ba	2.4±0.2	2.5±0.1			2.6		
Cu	3.7±0.2	5.5±0.1	4.8±0.1	10.3	9.2	8.0	17.2
Ni	2.6±0.3	4.8±0.2	4.1±0.2	8.9	6.5	5.4	11.9
Co	2.4±0.2	4.6±0.2	4.0±0.2	8.6	6.1	5.2	11.3
Zn	2.6±0.3	4.5±0.2	3.9±0.2	8.4	6.1	5.4	11.5
Mn	2.4±0.3	4.0±0.3	3.3±0.3	7.3	5.0	4.2	9.2

Note. T = 20 °C; μ = 0.1; 75 % EtOH.

[a] $pK_a = 6.25\pm0.03$. [b] $pK_a = 6.30\pm0.05$. [c] $pK_a = 9.89\pm0.04$.

tridentate in this case due to the additional coordination with the vinyl group. The supposed structure of the π-complex formed seems to be the following.



Despite the fact that the majority of ions of 3d transition metals and platinum group elements form π-allylic complexes, the possibility of formation of similar type compounds by Ca^{2+} ions follows from the existence of calcium cyclopentadienide[9] and its diyl adducts[10] and calcium and strontium diene complexes.[11] The participation of d-orbitals of ions of nontransition metals in the formation of π-complexes is also confirmed by the data of quantum-chemical calculations.[12] It is also noteworthy that complex compounds with ligands containing traditional donor groups and coordinated double bonds are described in Ref. 13. Under certain conditions, they can exist in aqueous solutions, which is testified[14] by the potentiometric data on the determination of the stability of mercury(II) π-complexes.

Thus, the equilibrium data for methacryloylacetonates[3] and 7-octene-2,4-diionates of alkaline-earth metals make it possible to consider these ligands as tridentate ones, but additional studies, including X-ray diffraction analysis, are necessary to confirm this hypothesis. As for the possibility of the coordination of the vinyl group in metal complexes with HPHD and HTOD, one cannot judge about it from the data of potentiometric measurements, because this effect cannot apparently be manifested in the presence of such substituents as phenyl and trifluoromethyl groups, whose electronic effects are very strong.

For RE elements, the usual run of the change in the stability constants (Table 2) is observed. It is accompanied by an increase in the stability in the series of cerium subgroup elements followed by a decrease in the stability of the series of yttrium subgroup elements. Of note is that the stability constants of REE complexes with HOD and HTOD differ significantly, although the corresponding pK_a values are almost equal. However, the tendency of the increase in the stability of complex REE compounds on going from HOD to HTOD and then to HPHD is confirmed by the data of spectrophotometry. For example, a considerable increase in the intensity of the band in the range of 16400—17800 cm^{-1} is observed in the f—f spectra of neodymium complexes (Fig. 1). Although its intensity is not related directly to the stability of the complexes and rather reflects the mobility of the π-electron system of the ligand, the values of oscillator strengths ($P \cdot 10^6$) are comparable to those of REE compounds with the corresponding AA derivatives. In addition, the bands shift to the long-wave range, which is caused by the change in the inter-electron interaction (nepheloxetic effect). The value of the latter allows one to judge about a relative distance between a metal ion and donor atoms of a ligand. For example, the correlation, according to which the longer-wave shift in the spectrum corresponds to the shorter metal—ligand distance, was established for the spectral $^4I_{9/2} \rightarrow {}^2P_{1/2}$ (ν_{max} = 23400 cm^{-1}) transition of the Nd^{3+} ion.[15] Since this band is at the boundary between the visible and UV spectral regions, it is difficult to observe it in the case of the majority of the ligands with inherent absorption. As can be seen from Table 3, the similar long-wave shift of the maxima upon complexation is also observed for the absorption bands of Nd^{3+} corresponding to spectral $^4I_{9/2} \rightarrow {}^4G_{7/2}$ (ν = 19000 to 19400 cm^{-1}) and $^4I_{9/2} \rightarrow {}^{2,4}G_{7/2,5/2}$ (ν = 17000 to 18000 cm^{-1}) transitions, which appear in the visible spectral range. The shifts of their maxima relative to the absorption bands of the Nd^{3+} aqua-ion correlate linearly with the stability of

Table 2. Logarithms of stability constants[a] of REE complexes with substituted 6-heptene-1,3-diones

M^{III}	HOD[b]		HTOD[c]		HPHD[d]	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
La	3.54	2.55	5.10	4.59	6.34	5.81
Pr	3.55	2.77	5.36	4.93	6.61	6.20
Nd	3.80	2.84	5.43	4.98	6.77	6.34
Sm	3.65	2.84	5.50	5.00	7.09	6.43
Eu	3.70	2.95	5.65	5.10	7.13	6.41
Gd	3.60	2.91	5.52	5.10	7.04	6.42
Tb	3.55	2.90	5.55	5.15	7.14	6.50
Dy	3.56	2.83	5.60	5.20	7.28	6.67
Ho	3.89	2.90	5.65	5.23	7.36	6.72
Er	3.70	2.97	5.68	5.27	7.33	6.83
Tm	3.65	2.90	5.60	5.20	7.38	6.90
Yb	3.60	2.85	5.55	5.15	7.38	6.90
Lu	3.50	2.78	5.49	5.10	7.31	6.82
Y	3.55	2.80	5.60	5.20	7.21	6.54

Note. T = 20 °C; μ = 0.1; 75 % EtOH.

[a] The values of logarithms of the constants were determined with a confidence interval of ±0.15.

[b] pK_a = 6.25±0.03. [c] pK_a = 6.30±0.05. [d] pK_a = 9.89±0.04.

Table 3. Spectral parameters of bands in absorption spectra of neodymium complexes with ligands containing vinyl groups

Ligand	Spectral transition				
	$^4I_{9/2} \rightarrow {}^{2,4}G_{7/2,5/2}$			$^4I_{9/2} \rightarrow {}^4G_{7/2}$	
	$P \cdot 10^6$	$\nu_{max} \cdot 10^{-3}$	$\Delta\nu$	$\nu_{max} \cdot 10^{-3}$	$\Delta\nu$
		/cm^{-1}			
Aqua-ion	9.76	17.47	0	19.26	0
HOD	22.6	17.33	140	19.20	60
HTOD	24.9	17.29	180	19.16	100
HPHD	71.2	17.26	210	19.09	170
MCA	18.5	17.31	160	19.18	80

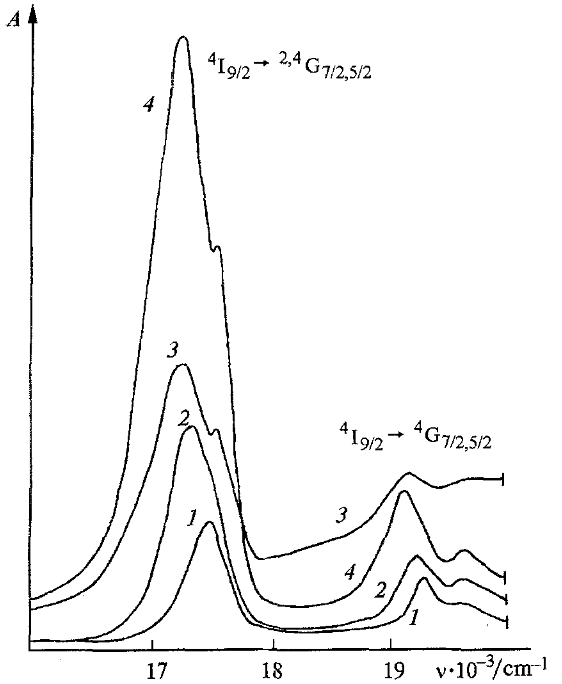


Fig. 1. Absorption spectra of solutions of neodymium perchlorate (*1*) and its complexes with 1-methyl- (*2*), 1-trifluoromethyl- (*3*), and 1-phenyl-substituted 6-heptene-1,3-dione (*4*).

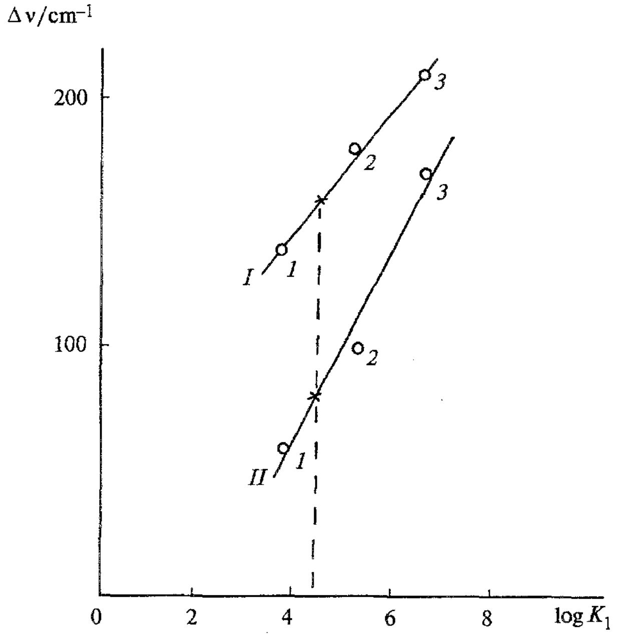


Fig. 2. Dependence of the relative shift of absorption maxima $^4I_{9/2} \rightarrow {}^{2,4}G_{7/2,5/2}$ (*I*) and $^4I_{9/2} \rightarrow {}^4G_{7/2}$ (*II*) in the spectra of neodymium complexes with HOD (*1*), HTOD (*2*), and HPHD (*3*) on their stabilities. The sign × denotes $\Delta\nu$ in the spectrum of neodymium methacryloylacetonate.

the complexes and increases in the ligand series HOD < HTOD < HPHD (Fig. 2). Taking into account this regularity, one can estimate the stability of the neodymium complex with methacryloylacetone. The data on the positions of the absorption maxima in the spectrum of neodymium methacryloylacetonate (see Table 3) were mapped on the plot in Fig. 2, hence the $\log K_1$ value equal to ~4.6 has been found.

The considered specific features of the complexation of metal chelates based on substituted 6-heptene-1,3-diones should also manifest in their polymerization that has recently been analyzed by the example of the radical polymerization of methacryloylacetonates.[16] This analysis is the subject of further studies.

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