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Complexation of Cobalt Chloride with O-Bases in Acetone

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Abstract—Complexation of anhydrous cobalt chloride with organic O-bases (dioctyl sulfoxide, triisoamylphosphine oxide, trioctylarsine oxide, diamyl methylphosphonate, tributylphosphine oxide, diamyl sulfoxide) in acetone was studied. The complexation of $CoCl_2$ with triisoamylphosphine oxide was studied by the method of diathermal isopiestic measurements. Conductometric titration in acetone revealed formation of 1 : 1 and 1 : 2 complexes. The enthalpies of donor–acceptor interaction of O-bases with $CoCl_2$ in acetone were determined. These quantities linearly correlate with the donor numbers of the bases.

Complexes of $CoCl_2$ with various O-bases (B) have been studied in numerous works. Yatsimirskii [1] studied in detail the compositions of complexes formed by extraction of $CoCl_2$ with neutral organophosphorus extractants, trialkyl(aryl)phosphine oxides R_3PO. As a rule, $CoCl_2 \cdot 2B$ species are formed, with the tetrahedral surrounding of the Co atom. According to [2], such complexes only slightly dissociate in acetone and tetrahydrofuran: Their molar electrolytic conductivities do not exceed 30 $\Omega^{-1}\,cm^2\,mol^{-1}$. The complexes are very stable. According to [3], the stability constants of the 1 : 1 ($CoCl_2 \cdot B$) and 1 : 2 ($CoCl_2 \cdot 2B$) complexes are of the order of 10^4 and 10^6, respectively. As shown by Fine [4], solutions of $CoCl_2$ in acetone and tetrahydrofuran are weak 1–1 elecrtrolytes. According to [5, 6], organic O-bases interact with $CoCl_2$ in acetone solution without displacement of chloride ion, except the case of trialkyl(aryl)arsine oxides which, when added in superstoichiometric amount to the system $CoCl_2$–acetone ($n = [B]/[CoCl_2] > 2$), displace chloride ion from the inner coordination sphere.

The goal of this work was to study donor–acceptor interaction of cobalt chloride with organic O-bases and obtain the thermodynamic characteristics of its complexing power in nonaqueous media.

As O-bases we chose dioctyl sulfoxide (**I**), triisoamylphosphine oxide (**II**), trioctylarsine oxide (**III**), diamyl methylphosphonate (**IV**), tributylphosphine oxide (**V**), and diamyl sulfoxide (**VI**).

The molecular weight and degree of association were determined by the isopiestic method based on measuring the change in the solution temperature upon condensation transfer of the solvent until the vapor pressures over the solution and pure solvent became equal. Measurements were performed with a Hitachi Molecular Weight Apparatus-115 device calibrated using a solution of dibenzyl in acetone. The results of measuring the total concentration of solute in the system $CoCl_2$–acetone–**II** at a constant molal concentration of $CoCl_2$ and varied concentration of **II** are given in Table 1. The measurement accuracy is estimated at ±3%.

Table 1 shows that the measured concentrations are very close to the initial concentrations (within 1%). It should be noted that, until $n = 2$ is reached, the total concentration of solute is virtually equal to the initial metal concentration (at $n > 1$, measurements were performed at a lower $CoCl_2$ concentration). This fact shows that, at $n \le 2$, the ligand interacts with $CoCl_2$ to form a stable complex. At $n > 2$, the total concentration of solute species grows, approaching the total concentration of free molecules of **II** and of the complex species $CoCl_2 \cdot 2$ (**II**). Hence, the third ligand molecule does not add to $CoCl_2$.

Additional information on the complexation mechanism was derived from the results of conductometric titration of an acetone solution of $CoCl_2$ with solutions of ligands B in acetone. The measurements were performed with a Conductometer–Radiometer–Copenhagen device. Prelimimary measurements of the electrolytic conductivity of $CoCl_2$ in acetone showed that the molar conductivity at a 4×10^{-3} M concentration was 16 $\Omega^{-1}\,cm^2\,mol^{-1}$, i.e., $CoCl_2$ in acetone is a weak 1–1 electrolyte. At the same time, no free chloride ions were detected in solution (using the procedure from [7]). Therefore, the observed electrolytic conductivity should be assigned to autoionization of $CoCl_2$ in acetone.

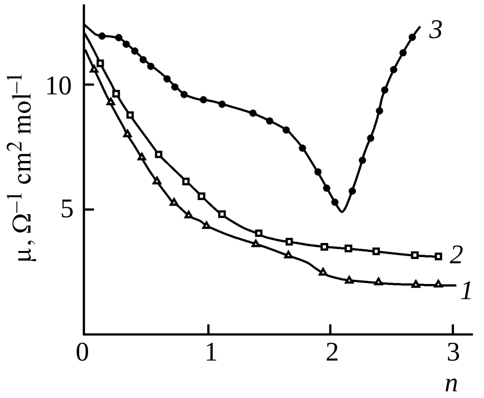

Fig. 1. Electrolytic conductivity μ as a function of the component ratio *n*. Ligand added: (*1*) **I**, (*2*) **II**, and (*3*) **III**.

$$2[\mathrm{CoCl_2}] \rightleftarrows [\mathrm{CoCl}]^+ + [\mathrm{CoCl_3}]^-. \tag{1}$$

Figure 1 shows the results of conductometric titration. As seen from Fig. 1, the conductivity decreases on adding the ligands. The inflection points in the regions of $n = 1$ and 2 suggest formation of 1 : 1 and 1 : 2 complexes. Complexation of $\mathrm{CoCl_2}$ with O-bases added in excess relative to the ratio $n = 2$ was observed with none of the ligands except **III**. Addition of **III** in the ratio $n > 2$ to the $\mathrm{CoCl_2}$ solution results in a sharp growth of the conductivity, attributable to displacement of the chloride ion from the inner coordination sphere. This is confirmed by the results of measuring the concentration of $\mathrm{Cl^-}$ in solution according to [7].

Thus, complexation at $n \leq 2$ can be described by the equilibria

$$\mathrm{CoCl_2\cdot 2S + B \underset{-S}{\rightleftarrows} CoCl_3\cdot S\cdot B \overset{B}{\underset{-S}{\rightleftarrows}} CoCl_2\cdot 2B.} \tag{2}$$

where S is a solvent molecule, and B, an O-base molecule.

With **III**, at $n > 2$, the process goes further:

$$\mathrm{CoCl_2\cdot 2B + B \rightleftarrows [CoCl\cdot 3B]^+ + Cl^-}. \tag{3}$$

To determine the thermodynamic characteristics of complexation of anhydrous $\mathrm{CoCl_2}$ with organic O-bases in acetone, we performed calorimetric titration of the $\mathrm{CoCl_2}$ solution with solutions of the bases in acetone [7]. The results are shown in Fig. 2.

As seen from the integral titration curve, in titration of $\mathrm{CoCl_2}$ with a solution of **VI** (curve *2*) in acetone, either the heats of addition of the first (to form $\mathrm{CoCl_2}\cdot$**VI**) and second [to form $\mathrm{CoCl_2}\cdot$2(**VI**)] molecules of **VI** are equal, or only the 1 : 2 complex is formed.

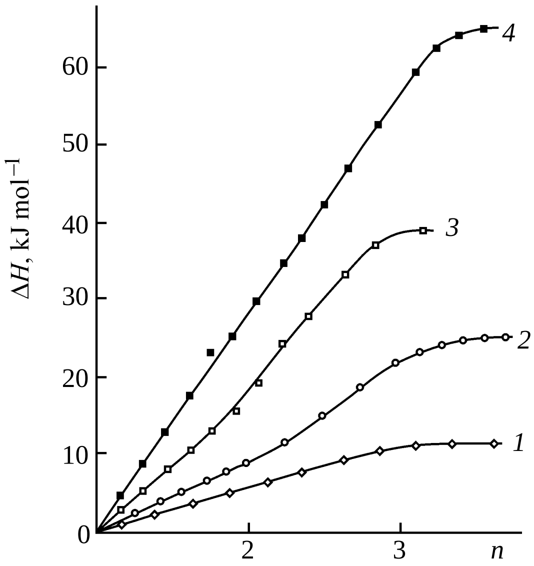

Fig. 2. Curves of calorimetric titration of $\mathrm{CoCl_2}$ in acetone with O-bases: (*1*) **VI**, (*2*) **V**, (*3*) **II** and (*4*) **III**.

In titration of $\mathrm{CoCl_2}$ with solutions of **V** and **II** in acetone, the thermal effects in the range $n = 0$–1 are weaker than in the range $n = 1$–2 (Fig. 2). With **III**, the pattern is similar (Fig. 2, curve *4*).

The observed trend cannot be explained by association–monomerization processes. This is convincingly indicated by the results of isopiestic measurements. The conductometric titration data show that $\mathrm{CoCl_2}$ in

Table 1. Results of determination of the total concentration of solute *C*(total) in the system $\mathrm{CoCl_2}$–**II**–acetone

C(CoClo$_2$), mmol kg^{-1}	*C*(**II**), mmol kg^{-1}	**II**/CoCl$_2$ ratio	*C*(total), mmol kg^{-1}
2.41	–	–	2.35
7.09	–	–	7.01
6.06	–	–	6.00
6.06	1.21	0.20	6.15
6.06	2.42	0.40	6.19
6.06	3.63	0.60	5.98
6.06	4.84	0.80	6.10
6.06	6.05	1.00	6.25
3.03	3.63	1.20	2.95
3.03	4.84	1.60	3.15
3.03	6.06	2.00	3.40
3.14	7.85	2.50	4.90

Table 2. Constants and enthalpies of complexation of $CoCl_2$ with O-bases in acetone

O-base	$-\Delta H$, kcal mol^{-1}	K_1	*DN* [9, 10]
I	1.48	986	30.3
II	4.06	$>10^3$	33.6
III	6.79	$>10^3$	48.4
IV	1.19	320	31.2
V	1.79	$>10^3$	33.8

acetone behaves as a weak 1–1 electrolyte. $CoCl_2$ and its complexes with **V** and **II** do not appreciably dissociate in acetone. Therefore, the influence of dissociation on the thermal effects cannot be significant.

The spectroscopic data show that addition of an O-base to a solution of $CoCl_2$ in acetone in an excess over the 1 : 1 ratio does not alter the configuration of the complex: The number and positions of the *d*–*d*-transition bands in the electronic absorption spectra of the solutions remain unchanged up to $n = 2.2$. Therefore, the increased exothermic effect of complexation of $CoCl_2$ with O-bases at $n > 1$ should be attributed to certain unknown side processes.

All the above facts prevent estimation of the enthalpy of formation of the complexes $CoCl_2 \cdot 2B$ with **V** and **II**. Experimental data allow only estimation of the enthalpy of addition of the first O-base molecule.

The $\Delta H_{1:1}$ values were estimated from the slopes of the initial portions of the integral thermochemical titration curves and were refined by the method of successive approximations using the procedure described in [8]. The results are listed in Table 2. These data show that the enthalpies of formation of the 1 : 1 complexes correlate with the donor numbers [9, 10] of the corresponding bases:

$$\Delta H_{DA}(CoCl_2\text{–}B) = -6.84 + 0.30DN;\ R\ 0.968. \quad (4)$$

EXPERIMENTAL

$CoCl_2$ was recrystallized from aqueous solution and dehydrated by refluxing with thionyl chloride. The water content in $CoCl_2$, determined by Fischer titration, did not exceed 0.97%.

Acetone was purified according to [7]. Compounds **I**, **III**, and **VI** were purified by releated recrystallization from appropriate solvents and dried in a high vacuum over P_2O_5. Compounds **II**, **IV**, and **V** were purified by distillation in a high vacuum; the ester was additionally dried in a high vacuum over P_2O_5.

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