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LETTERS TO THE EDITOR

Oxidation State of Cobalt in the Coordination Compounds with *N*-(Thio)phosphorylated Acylamidophosphinates in Solutions

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Acylamidophosphates and their thio analogs of the general formula $RC(X)NHP(Y)R'_2$ form fairly stable chelates with a series of double-charged metal ions, in particular, with Co(II) ions [1, 2]. The presence of coordination-active (thio)carbonyl and (thio)phosphoryl groups and of a relatively acidic proton in the molecules of *N*-(thio)phosphorylated (thio)ureas and (thio)amides predetermines the possibility of chelating coordination of these ligands through the sulfur and oxygen donor centers with the formation of a stable six-membered chelate ring [3, 4]. The oxidation state of the central ion, in particular, of the cobalt ion, in such complexes previously seemed doubtless and hence was not evaluated.

In this study we performed the electroreduction of complexes of cobalt with $C_6H_5NHC(S)NHP(S)\cdot(OC_3H_7\text{-}i)_2$ (L^I), $C_6H_5NHC(S)NHP(O)(OC_3H_7\text{-}i)_2$ (L^{II}), $C_6H_5C(S)NHP(O)(OC_3H_7\text{-}i)_2$ (L^{III}), and $C_6H_5C(O)NHP(O)[N(CH_3)_2]_2$ (L^{IV}). According to the published data, cobalt reacts with *N*-(thio)acylamidophosphates to give complexes of the composition CoL_2 with cobalt oxidation state +2 [1, 2, 5], which can be preparatively isolated. In this study we found that, depending on the donor atoms of the ligand and substituents at the C(X)NHP(Y) fragment, the central Co(II) ion in solutions in the course of the complex formation can be oxidized to Co(III).

To determine the oxidation state of cobalt in the complexes with L^I, L^{II}, L^{III}, and L^{IV} in solution, we used cyclic voltammetry in isopropanol, with 0.1 N $LiClO_4$ as supporting electrolyte. The data obtained show that, in the presence of L^1, cobalt forms a single complex species with oxidation state of the central atom +2. This is confirmed by the presence of a two-electron irreversible peak at –1.17 V in the cyclic voltammogram. This peak corresponds to the reduction of Co(II) in the complex to Co(0), accompanied by the release of the ligand. An increase in the concentration of L^I leads to an increase in the current of the second cathodic peak at –1.8 V, which confirms the scheme of the electrode process involving the release of the free ligand species.

The replacement of the thiophosphoryl (P=S) group at the thiocarbonyl fragment by the phosphoryl (P=O) group changes the electroreduction pattern. The voltammogram of CoL_2^{II} contains two cathodic peaks and one anodic peak. The pair of one-electron cathodic-anodic peaks at –0.83 and –0.62 V, respectively, can be assigned to the reversible reduction of coordination-bound Co(III) to Co(II) in the complexes with sulfur-containing organic compounds [6]. At the same time, the presence of one two-electron peak at –1.15 V in the cathodic wave is indicative of the reduction of Co(II) to Co(0). Thus, in the presence of L^{II} cobalt forms a mixture of the complex species CoL_3^{II} and CoL_2^{II} with cobalt oxidation states +3 and +2, respectively. These complexes could not be preparatively isolated. Replacement of the thiophosphoryl group by the phosphoryl group slightly facilitates the reduction of the chelates and shifts the potentials to the anodic region.

Further replacement of the phenylamino substituent (C_6H_5NH) at the thiocarbonyl group by the phenyl substituent (C_6H_5) leads to formation of three stable complex species CoL_2^{III}, $CoL_2^{III}\cdot 2HL^{III}$, and $CoL_3^{III}\cdot 2HL^{III}$ [1], which could be preparatively isolated. The two-electron irreversible peak at the potentials of –1.0 and –1.1 V in the voltammograms of the solutions of Co_2^{III} and $CoL_2^{III}\cdot 2HL^{III}$, respectively, corresponds to the electroreduction of Co(II) to Co(0) in the solutons

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of these complexes. In the case of CoL_3^{III}, the voltammograms of the solutions contain two catodic (E_p –0.80 and –1.05 V) and one anodic (E_p –0.60 V) peaks corresponding to the consecutive reduction of Co(III) to Co(II) and then to Co(0) in solution.

In going from phosphorylated thioamides to triamides [replacement of the thiocarbonyl (C=S) group by the carbonyl (C=O) group] changes the electroreduction pattern. The cyclic voltammogram of reduction of the complex CoL_3^{IV} contains a pair of strong three-electron cathodic-anodic peaks at –0.44 and –0.20 V, suggesting the presence in solution of a single complex species with cobalt oxidation state +3.

Thus, replacement of the thiophosphoryl group in compounds under study by the phosphoryl group allows us to detect (in the case of L^{II}) and, in some cases, to isolate preparatively (in the case of L^{III}) not only the traditional Co(II) complex species, but also the coordination compounds of Co(III). In going from the thio derivatives of *N*-acylamidophosphates to the compounds of the same class containing exclusively the oxygen donor atoms leads to stabilization in solution of the complex species with cobalt oxidation state +3 only (L^{IV}). In this case, it is difficult to isolate Co(II) complexes from the solution.

Our results are consistent with the theoretical concepts, in particular, with the Pearson concept according to which the "hard" Co(III) ion coordinates mainly with the "hard" oxygen atoms of the phosphoryl and carbonyl groups of the ligand HL with the formation of stable chelates. The observed formation of Co(III) complexes with L^{II}, L^{III}, and L^{IV} is associated not only with the oxidation of the Co(II) complex with the dissolved atmospheric oxygen (CoL_2 + HL + [O] $\rightarrow$ CoL_3), but also with the effect of the donor atoms and substituents in the coordinated ligands.

The electrochemical studies were performed with an SBA-1BM voltammetric system (Bulgaria) with the three-electrode cell thermostated at 25 ± 0.05°C. The stationary mercury film electrode with the silver support and the salt bridge was used as the working electrode. The reference electrode was the silver chloride electrode. The platinum wire was an auxiliary electrode. Oxygen was removed from the solution with an argon flow. Cyclic voltammograms were recorded with 0.1 M $LiClO_4$ in 96% isopropanol as supporting electrolyte. The linear potential sweep rate was 200–500 mV s^{-1}. The potentials were measured in the range from –0.125 to –2.0 V at the concentration of cobalt complexes of 5×10^{-4} M.

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