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Electrochemical reduction of cobalt and nickel complexes with ligands stabilizing metal in low oxidation state

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Electrochemical reduction of cobalt(II) complexes containing π-acceptor ligands (L = bpy, Ph_2Ppy) proceeds through three consecutive reversible steps: one-electron transfer to form a more stable $Co^{I}L$ complex, transfer of two electrons at more negative potentials to form an anionic $[CoL]^-$ complex, and reduction of the ligand to the radical anion. The stability of the cobalt complexes with different ligands decreases in the series $Ph_2Ppy > Ph_3P >$ bpy.

Key words: cobalt, nickel, π-acceptor ligands, 2,2´-bipyridine, diphenyl-2-pyridylphosphine, triphenylphosphine, electrochemical reduction.

Products of cathodic reduction of the $Co(BF_4)_2 \cdot 6H_2O$ cobalt salts are unstable, and ligand stabilization of low-valent cobalt compounds is required to develop related electrocatalytic processes. In this respect, π-acceptor ligands are of interest because they are efficient in electrocatalytic reactions involving the Ni^{II}/Ni^{0} pair[1—3] and in classical catalytic processes involving transition metals. The valent electron shells of nickel(II) and cobalt(II) are different ($3d^84s^0$ and $3d^74s^0$, respectively). This results in different stabilities of compounds of these metals and different stoichiometries of electrochemical reactions. Therefore, it is doubtful to expect that the influence of ligands on the regularities of reduction of the cobalt and nickel complexes would be similar. In this work, we considered the low-valent cobalt compounds capable of π-acceptor interaction with metals in order to choose appropriate ligands for generation of simultaneously stable and sufficiently reactive low-valent cobalt complexes.

The task of this work is to reveal the ability of phosphorus- (Ph_3P) and nitrogen-containing (Py, bpy) ligands and solvents (DMF, MeCN) to coordinate cobalt in different oxidation states and stabilize the complexes that formed, to compare the properties of the mono- and bidentate ligands, and to study the influence of other factors on the reactivity of intermediates of catalytic cycles with respect to substrates (organic halides, white phosphorus, *etc.*). For this purpose, we studied the cobalt and nickel complexes with different π-acceptor ligands, *viz.*, PPh_3, pyridine (Py), 2,2´-bipyridine (bpy), and diphenyl-2-pyridylphosphine (Ph_2Ppy), in aprotic solvents using polarography and cyclic voltammetry (CV).

Experimental

Polarographic studies. Polarograms were detected on a PU-1 polarograph with a cell connected by the three-electrode scheme. A silver $Ag/AgNO_3$ electrode (0.01 *M* solution in MeCN) served as reference. A mercury dropping electrode with a droplet detachment period of 0.5 s and a velocity of 0.7 mg s^{-1} was the working electrode. The curves were detected at a linear potential sweep rate of 10 mV s^{-1} with a two-coordinate recorder. Measurements were carried out in a cell with a constant temperature maintained at 25 °C in argon.

A solution used for the polarographic study of the cobalt(II) complexes contained $5 \cdot 10^{-3}$ mol L^{-1} $Co(BF_4)_2 \cdot 6H_2O$ and 0.5—$2 \cdot 10^{-2}$ mol L^{-1} ligand. The background was 0.1 *M* Et_4NBF_4 in DMF or MeCN.

Cyclic voltammetry. CV curves were recorded using platinum (diameter 1.5 mm), gold (diameter 1.0 mm), and glassy-carbon (diameter 1.5 mm) electrodes. A silver $Ag/AgNO_3$ electrode (0.01 *M* solution in MeCN) served as reference. A platinum wire 1 mm in diameter was used as auxiliary electrode. Measurements were carried out in a cell with a constant temperature maintained at 25 °C in argon. Voltammograms were detected using a PI-50-1 potentiostat with a PR-8 programmer and an electrochemical cell connected by the three-electrode scheme. The CV curves were recorded with a linear potential sweep rate of 50 mV s^{-1} on a two-coordinate recorder.

Tetraalkylammonium tetrafluoroborates were used as background salts. Tetraethylammonium tetrafluoroborate Et_4NBF_4 was synthesized by the reaction of HBF_4 with Et_4NOH, triply recrystallized from aqueous EtOH, and dried *in vacuo* for 72 h at 30 °C. Solvent MeCN was triply distilled over P_2O_5 and $KMnO_4$, using medium fractions for voltammetry. Commercial DMF was distilled *in vacuo*, and dried for 3 days above molecular sieves 4A, which were pre-calcined *in vacuo* at 100 °C, and dried

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for 1 day above anhydrous K_2O prepared by thermal decomposition of K_2CO_3. Then the solvent was decanted and doubly fractionally distilled *in vacuo*.

Results and Discussion

The polarograms of the Co^{II} ions ($Co(BF_4)_2$) solvated by DMF contain one irreversible two-electron peak (number of electrons was estimated by comparison with the current of the first wave of benzophenone reduction). The peaks of ligand reduction lie in the more negative potential region.

The reduction potentials of the π-acceptor ligands in DMF on a mercury dropping electrode *vs.* Et_4NBF_4 (0.1 mol L^{-1}) are presented below.

Compound	PPh_3	Py	bpy
$-E_{1/2}$/V	3.16	2.84	2.47

Reduction of cobalt—Ph_3P complex. The reduction potential of the Co^{II} salt in DMF ($E_{1/2} = -1.68$ V) on the polarograms does not change when a fourfold amount of PPh_3 is added. Only a decrease in the peak height (i_{lim}) from 7.0 to 5.3 μA is observed. This indicates that only an insignificant fraction of cobalt(II) binds with PPh_3 (confirmed by the CV data). It is most likely that mixed or heteroligand complexes containing a Ph_3P molecule in the internal sphere are formed in this system along with the $Co^{II}(DMF)_x$ complex. When $E_{1/2}$ of these mixed complexes are close to $E_{1/2}$ of the $Co^{II}(DMF)_x$ complex prevailing in the solution, minor amounts of such complexes cannot be detected polarographically. In this case, the decrease in i_{lim} can be related to a change in the diffusion coefficient and partial transition from the two-electron $Co^{II}(DMF)_x$ reduction to the one-electron reduction of $Co^{II}(PPh_3)_n$.

The electrochemical behavior of a solution of the Co^{II} salt in DMF in the presence of PPh_3 on the gold and glassy-carbon (GC) electrodes was studied by the CV method. The cathodic peak at the potential $E_p{}^c = -1.69$ V ($i_p{}^c = 21$ μA) and the oxidation peak at $E_p{}^a = -0.48$ V ($i_p{}^a = 26$ μA) are observed in measurements on the Au electrode. Under similar conditions, the cathodic peak with $E_p{}^c = -1.72$ V ($i_p{}^c = 66$ μA) was detected for the GC electrode, and the conjugated oxidation peak was detected at $E_p{}^a = -0.51$ V ($i_p{}^a = 49$ μA). A decrease in the height of the reduction peak of $Co^{II}{}_{solv}$ on the GC and Au electrodes in the presence of PPh_3 (Table 1) is much lower than it could be expected in the case of complete ion binding to form a complex and displacement of the solvent molecules from the coordination sphere by the phosphine ligands. Thus, DMF interacts with the cobalt(II) ions to form sufficiently stable complexes, and the coordinating abilities of DMF and PPh_3 are likely comparable.

Table 1. Parameters of the peaks of electrochemical reduction of Co^{II} and its complexes with PPh_3 in DMF on the Hg, GC, and Au electrodes according to the CV data (supporting salt 0.1 *M* Et_4NBF_4)

$C_{Co^{II}} \cdot 10^3$ /mol L^{-1}	Electrode	$-E_p$/V		n_e	
		Co^{II}	Complex[a]	Co^{II}	Complex[a]
5	Hg	1.70	1.68	2.00	1.20
10	GC	1.72	1.72	2.03	1.60
10	Au	1.69	1.69	2.05	1.50

[a] Co : PPh_3 = 1 : 4.

[b] n_e is the number of electrons estimated by a comparison with the height of the first wave of benzophenone reduction under similar conditions (concentration, solvent, temperature).

The polarogram of a solution of the Co^{II} salt in MeCN in the presence of PPh_3 (1 : 4) exhibits three reduction peaks with $E_{1/2} = -1.20$, -1.47, and -1.99 V (i_{lim} = 3.3, 1.5, and 2.6 μA, respectively) (Fig. 1). The potentials of ligand reduction are not achieved under the experimental conditions.

A similar CV study was carried out on the Au and GC electrodes in MeCN (Fig. 2). The CV curve measured on the Au electrode contains four reduction peaks, and the C_4 peak corresponds to the reduction of the free PPh_3 ligand. Similar results were obtained when the GC electrode was used. The CV curve also exhibits four cathodic peaks; however, the C_1 and C_3 peaks have pronounced anodic components, *i.e.*, they are quasireversible.

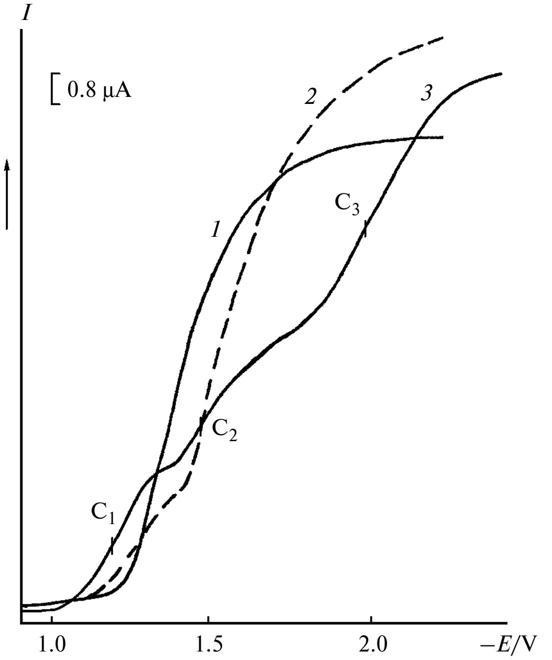

Fig. 1. Polarograms of solutions of Co^{II} ($5 \cdot 10^{-3}$ mol L^{-1}) in MeCN *vs.* Et_4NBF_4 (0.1 mol L^{-1}) in the absence (*1*) and presence of Py ($2 \cdot 10^{-2}$ mol L^{-1}) (*2*) and PPh_3 ($2 \cdot 10^{-2}$ mol L^{-1}) (*3*).

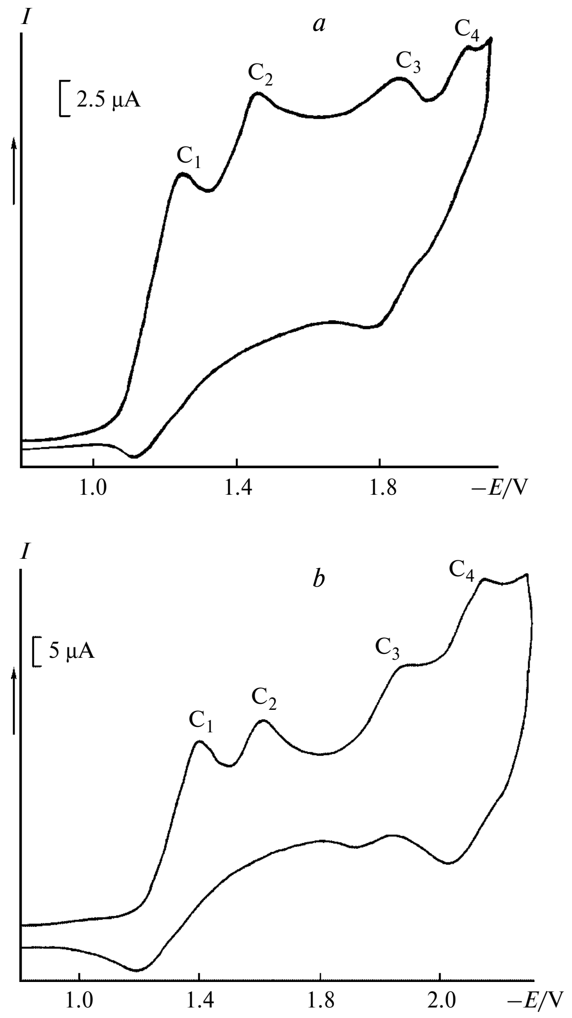

Fig. 2. Cyclic voltammogram of Co^{II} (10^{-2} mol L^{-1}) in the presence of PPh_3 ($4 \cdot 10^{-2}$ mol L^{-1}) in MeCN on the Au electrode (*a*) and GC electrode (*b*).

Some properties of stabilization of the reduced cobalt forms in solution should be mentioned. For example, cobalt(II) reduction becomes partially reversible, and the oxidation peak of metallic cobalt is absent. It can be assumed that the peaks observed in the voltammogram correspond to the reduction of the cobalt complexes with different numbers of the PPh_3 ligands

$$Co^{2+}(PPh_3)_n + e \rightleftharpoons Co^{+}(PPh_3)_n,$$

and $E_p = f(n)$.

Reduction of cobalt—pyridine complex. Pyridine is known to be a weakly coordinating ligand but it can be used in catalytic systems and considered as a potential monodentate ligand for stabilization of low-valent Co intermediates.

We found that the polarographic behavior of the Co^{II}—Py (1 : 4) system in DMF and MeCN is different. In a solution of DMF, the addition of Py slightly decreases i_{lim} (from 7.6 to 6.7 μA) at the unchanged potential $E_{1/2} = -1.68$ V, *i.e.*, noticeable complex formation involving Py is absent.

When MeCN is used as solvent, the addition of Py to a solution of the cobalt salt results in the division of the polarographic peak of Co^{II} into two peaks. The first (smaller) peak appears at $E_{1/2} = -1.23$ V ($i_{lim}^{(1)} = 1.8$ μA), the second peak lies at $E_{1/2} = -1.56$ V ($i_{lim}^{(2)} = 6.8$ μA), and the total current increases by the value equal to $i_{lim}^{(1)}$ (see Fig. 1). It can be assumed that a fraction of the cobalt ions binds to pyridine to form a new complex, which is more easily reduced ($\Delta E_{1/2} = 0.17$ mV). However, the influence of pyridine on the morphology of the curves is not so great that its use for stabilization of cobalt in the low oxidation state could be assumed.

Reduction of cobalt—2,2´-bipyridine complex. *Polarographic study of the cobalt complex with 2,2´-bipyridine.* The character of the polarographic peak of reduction of the bpy-containing Co^{II} complex in DMF depends on the bpy concentration (Table 2). The addition of bpy to a solution of the Co^{II} salt in DMF shifts the peak of Co^{II} towards less negative potentials ($\Delta E_{1/2} = 0.38$ V).

In the presence of bpy, the polarograms manifest a significant decrease in the reduction potential of Co^{II} (to

Table 2. Polarographic characteristics (currents and potentials) of the reduction waves of the cobalt(II) ions in the absence and presence of bpy in DMF and MeCN *vs.* Et_4NBF_4 (0.1 mol L^{-1}); $Co(BF_4)_2 \cdot 6H_2O$ concentration $5 \cdot 10^{-3}$ mol L^{-1}

$C_{bpy} \cdot 10^3$ /mol L^{-1}	$-E_{1/2}^{(1)}$/V		$i_{lim}^{(1)}$/μA		$-E_{1/2}^{(2)}$/V		$i_{lim}^{(2)}$/μA	
	DMF	MeCN	DMF	MeCN	DMF	MeCN	DMF	MeCN
—	1.70	1.40	8.8	10.5	—	—	—	—
5	1.70	1.37	8.4	4.4	—	1.91	—	3.8
10	1.37	1.33	4.5	3.9	1.88	1.91	9.6	8.7
15	1.35	1.29	4.4	3.6	1.84	1.83	11.8	10.8
20	1.32	1.28	4.4	3.6	1.86	1.85	11.8	10.4

Note. $E_{1/2}^{(1)}$ and $E_{1/2}^{(2)}$ are the first and second potentials of the half-wave; $i_{lim}^{(1)}$ and $i_{lim}^{(2)}$ is the limiting current of the first and second waves.

400 mV), although complex formation appears at the molar ratio L : Co > 2. In the absence of bpy, the Co^{II} solvo complex adds two electrons

$$Co^{2+}_{solv} + 2\,e \longrightarrow Co^0\downarrow,$$

whereas the complex with bpy adds one electron at the potentials of the first step, and somewhat more than two electrons are added in the second step

$$[Cobpy_2]^{2+} + e \rightleftharpoons [Cobpy_2]^+,$$

$$[Cobpy_2]^+ + 2\,e \rightleftharpoons [Cobpy_2]^-.$$

It is known that the cobalt(II)—bpy complexes are characterized by reversible reduction waves,[4—6] reversibility being retained for all methods used because the rate constant of electron transfer is sufficiently high. The problem of the "apparent" increase in the number of electrons over the expected value should be considered in more detail. In our case, this increase is observed for the $Co^{II}L_n$ complexes with $n = 3$. The authors of the work[7] considered in detail the difficulties and imperfection of traditional methods for determination of the number of electrons. These methods provide satisfactory results for simple compounds like aromatic hydrocarbons and organic halides but they are poorly appropriate for more complicated systems, for example, labile metal complexes. Under other equivalent conditions, the currents of $[Nibpy]^{2+}$ and $[Nibpy_3]^{2+}$ reduction differ by ~25%, although each reduction process is two-electron.[8,9] The published data[5] confirm the above scheme of reduction of the cobalt complexes for $n = 2$, 3 in which the one-electron step is followed by the two-electron step.

When bpy is added, the color of the solution changes from saturated pink (for Co^{2+}_{solv}) to bright yellow (for $[Cobpy_n]^{2+}$).

An increase in the bpy concentration in a MeCN solution changes the limiting current and $E_{1/2}$ of cobalt(II) (see Table 2). The height of the first peak is slightly lower than the one-electron level (compared to benzophenone), which is related, perhaps, to the differences in diffusion coefficients.

Cyclic voltammetry of cobalt—2,2´-bipyridine complex. The reduction of the $Co^{II}bpy_n$ complex (n = 1—3) on the platinum electrode in a MeCN solution[10] results in the appearance of two groups of cathodic-anodic peaks in the CV curve (Fig. 3). They correspond, most likely, to the formation of the $Co^{I}bpy_n$ complexes at potentials of the first peak $E_p^{(1)}$. At potentials of the second peak, the number of transferred electrons is $n_e = 1$ at $n = 1$ and $n_e = 2$ at $n = 2$, 3 ($E_p^{(2)}$). The currents of all peaks are diffusionally controlled, which is confirmed by linear plots of the peak currents *vs.* square root of the potential sweep rate. These results agree with the polarographic data (see Table 2).

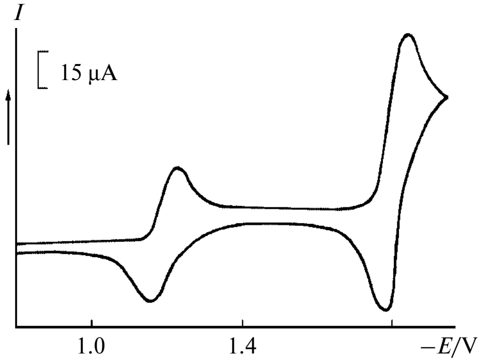

Fig. 3. Cyclic voltammogram of $Co^{II}bpy_3$ (10^{-2} mol L^{-1}) in MeCN on the Pt electrode *vs.* Et_4NBF_4 (0.1 mol L^{-1}).

Thus, the $i_p^{(2)}$ values depend on the number of ligands bound to the metal. It can be assumed that the unstable 13-electron Co^0bpy_n ($n = 1$) or 18-electron $[Cobpy_n]^{\bullet -}$ ($n = 2$, 3) complex is formed at $E_p^{(2)}$.

The ESR study of the products of electrochemical reduction of the $Cobpy_3(BF_4)_2$ complexes in the accessible potential region revealed no paramagnetic cobalt species, *i.e.*, unlike similar nickel complexes, which are characterized by the formation of paramagnetic $[Ni^0L]^{\bullet -}$ in the region of the second peak,[11] $Cobpy_m^-$ is likely an anionic complex.

The presence of the pairs of redox peaks indicates a relative stability of the reduced form of the complex. Therefore, the Co—bpy system can be used in electrocatalytic reactions, for example, for dehalogenation of organic substrates.

Comparison of electrochemical reduction of cobalt and nickel complexes containing π-acceptor ligands

Reduction of coordinatively saturated complexes. The cobalt complexes with bpy, PPh_3, and diphenyl(2-pyridyl)phosphine (Ph_2Ppy) were chosen for the study. The latter ligand can form monodentate or chelate coordination through the N and P atoms, depending on the oxidation state of the metallic center. However, the N atom is a stronger σ-donor and a weaker π-acceptor than the P atom, and Ph_2Ppy is usually bound through the P atom in a monodentate complex, while N-monodentate complexes are unknown. The nature of binding also depends on the metal oxidation state. For example, the Re^I and Tc^I complexes are characterized by coordination through the P atom, and chelate complexes with bidentate binding are formed in the case of Re^{IV}, Re^V, and Tc^V.[12,13]

Cobalt is characterized by both monodentate complexes with Ph_2Ppy and homobinuclear bridged complexes with simultaneous coordination to phosphorus and nitrogen.[13]

Table 3. Parameters of the peaks of electrochemical saturation (with respect to ligand) of the Co^{II} and Ni^{II} complexes in MeCN on the Au electrode according to the CV data

Compound	$-E_p^c$/V	$-E_p^a$/V	n_e	i_a/i_c
$Ni^{II}bpy_3$	1.53	1.47	2.0	0.88
	2.26	2.17	1.0	0.70
$Ni^{II}(Ph_2Ppy)_6$	0.71	0.41	1.0	0.53
	1.10	0.97	1.0	0.70
$Ni^{II}(PPh_3)_6$	1.03	0.89	2.0	0.32
$Co^{II}bpy_3$	1.22	1.16	1.0	0.90
	1.86	1.79	2.5	0.65
$Co^{II}(Ph_2Ppy)_6$	0.80	0.66	0.5	0.55
	1.38	1.28	0.5	0.67
$Co^{II}(PPh_3)_6$	1.23	—	1.0	—
	1.83	1.76	0.3	0.67
	2.04	—	0.2	—

The characteristics of the cathodic peaks of the ligand-saturated complexes are presented in Table 3. The data for similar nickel complexes are considered for comparison.[14—16] It follows from the data on the reversibility and morphology of the curves that the chosen ligands are always capable of stabilizing the reduced forms of both metals because the reverse potential scan (CV method) results in the corresponding peaks of anodic oxidation of these forms. The bpy ligand is most efficient in this respect because it allows one to attain the maximum i_a/i_c value (see Table 3, Figs. 4—6).

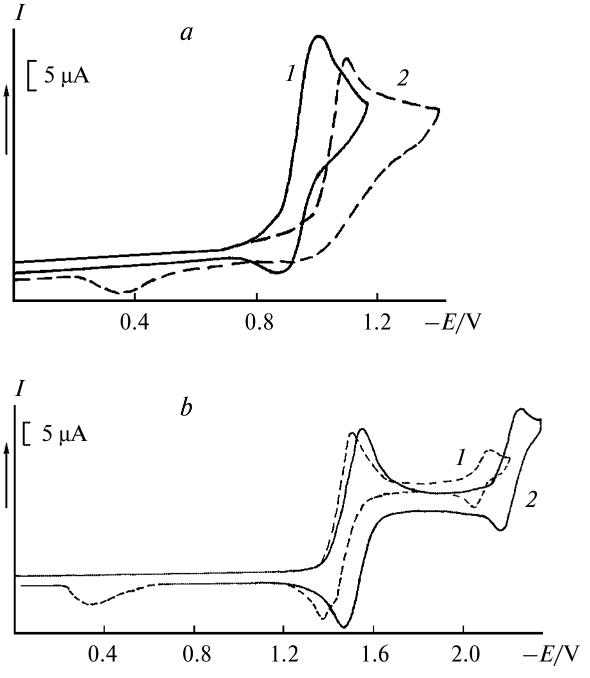

Fig. 4. Cyclic voltammogram of Ni^{II} (10^{-2} mol L^{-1}) in MeCN on the Au electrode in the presence of PPh_3 (*a*) and bpy (*b*) at the ligand content 10^{-2} (*1*) and $6 \cdot 10^{-2}$ mol L^{-1} (*2*).

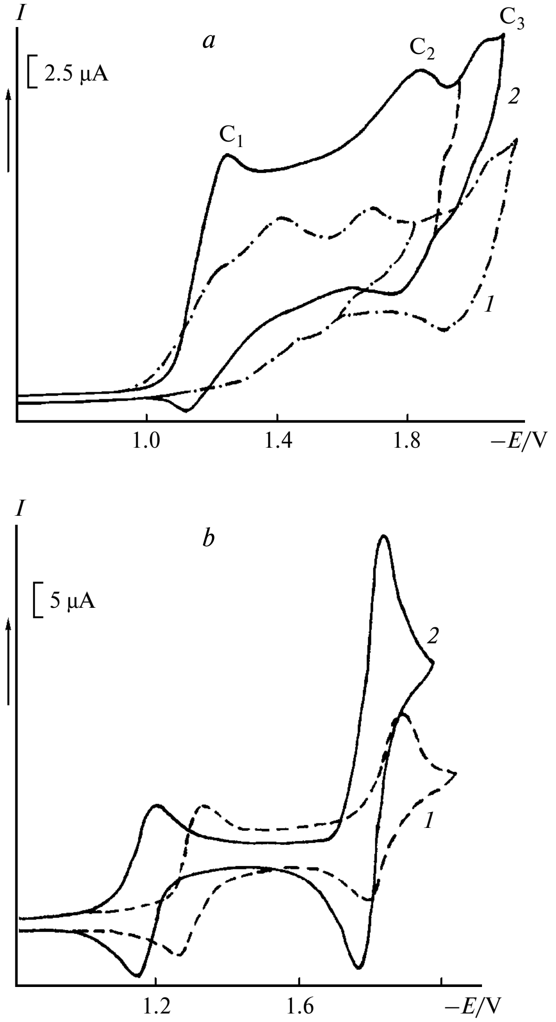

Fig. 5. Cyclic voltammograms of Co^{II} (10^{-2} mol L^{-1}) in MeCN on the Au electrode in the presence of PPh_3 (*a*) and bpy (*b*) at the ligand content 10^{-2} (*1*) and $6 \cdot 10^{-2}$ mol L^{-1} (*2*).

When free ligands are absent, the reduction potentials of these Co^{II} complexes and Co^{II} solvo ions in MeCN differ remarkably (see Table 2). The redox process becomes reversible at the ratio M : L = 1 : 1.

The shift of the E_p^{red} potential toward more positive values upon the addition of the ligand indicates that the reduced metal forms a stronger complex than the oxidized metal does. The value of this shift suggests the complex-forming properties of the ligands. For example, the greatest shift is observed in the case of the Ph_2Ppy ligand (ΔE_p = 0.6 and 0.7 V for Co^{II} and Ni^{II}, respectively) for the first reduction wave (Fig. 7).

When low concentrations of the ligand are added to a solution of MeCN (Co : L = 1 : 1), Ph_2Ppy is likely coordinated with Co^{II} to the P atom (most popular type of coordination[12—17]) because E_p of the complex coincides with E_p of Ph_3P (1.08 V), and the N atom is not involved in coordination. For this coordination of the

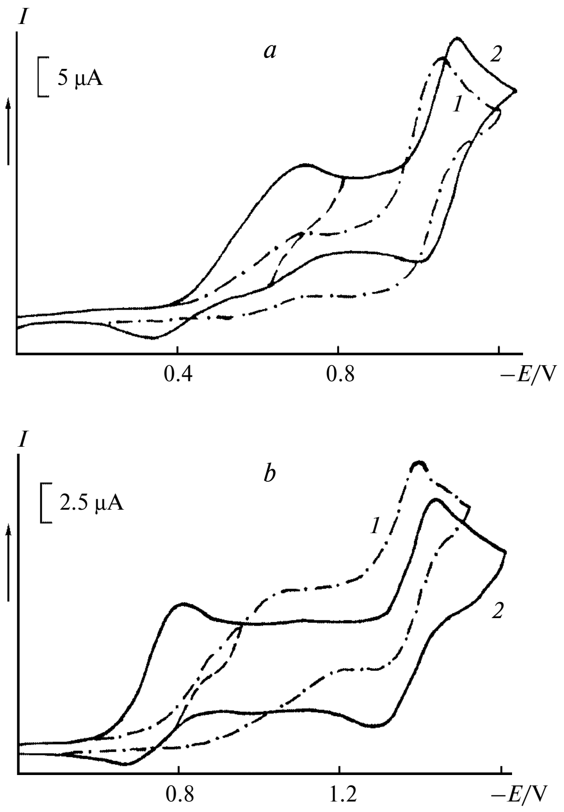

Fig. 6. Cyclic voltammograms of solutions of Ni^{II} (*a*) and Co^{II} (*b*) (10^{-2} mol L^{-1}) in MeCN on the Au electrode in the presence of 10^{-2} (*1*) and $6 \cdot 10^{-2}$ mol L^{-1} (*2*) Ph_2Ppy.

Ph_2Ppy ligand, the complex should manifest the properties close to those of $MPPh_3$.

However, at high concentrations of Ph_2Ppy (Co : L = 1 : 6), new, more stable complexes (E_p = –0.8 V), probably, with bidentate Co^{II} coordination involving both heteroatoms P and N are formed.

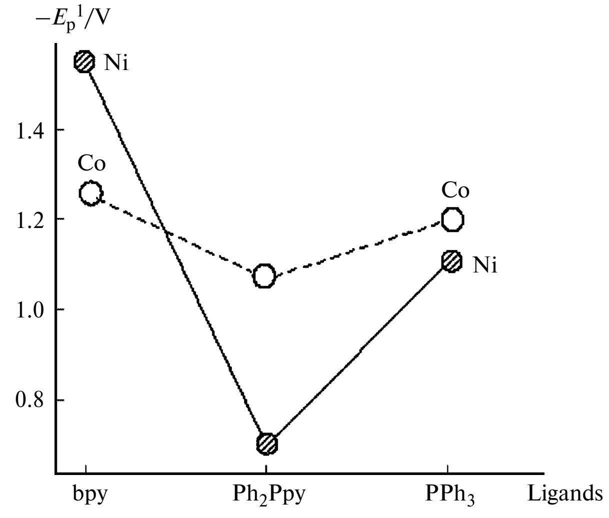

Fig. 7. Change in the potentials of the first steps of reduction of the Ni and Co complexes with the π-acceptor complexes with the ligand nature.

The stability of the complexes decreases in the series $Ph_2Ppy > PPh_3 >$ bpy. The anomalous behavior of Ph_2Ppy indicates a possible P,N-coordination of the ligand with metal, which considerably shifts the electron density from the metal to ligand and facilitates reduction. It is known that coordination to the P atom is characteristic of P,N-containing ligands in mononuclear complexes.[18,19] However, in the case under question, coordination with the heteroatom of only one type (P or N) exerts a much smaller effect on E_p^{red} of M^{II}.

The reduction of the metal solvo ions occurs as the two-electron process $M^{2+} + 2e \rightarrow M^0$ (polarography). A comparison of the Ni^{II} and Co^{II} complexes shows that the Ni^{II} complexes with bpy and PPh_3 are reduced *via* two-electron mechanism in one step at the potential of the first peak[14] (see Table 3, Fig. 4), while similar cobalt(II) complexes are reduced through one-electron transfer (see Fig. 5).

The reduction of $Ni^{II}L_n$ (L = PPh_3, n = 6, m = 4; L = bpy, n = 3, m = 2) can be presented as three reversible steps[1]

$$Ni^{II}L_n + 2e \rightleftharpoons Ni^0L_m + (n-m)\,L,$$

$$Ni^0L_m + e \rightleftharpoons [Ni^0L_m]^{\cdot -},$$

$$L + e \rightleftharpoons L^{\cdot -}.$$

The Ni^0 complex with the electron configuration $3d^{10}$ is formed in the first step. The cobalt(II) complexes with the bpy and PPh_3 ligands are reduced to Co^I with the stable 16-electron configuration $3d^84s^0$

$$Co^{II}L_n + e \rightleftharpoons Co^IL_m + (n-m)\,L.$$

Unlike the 18-electron Ni^0bpy_2 complex (i_a/i_c = 0.9), a similar 17-electron Co^0bpy_2 complex is unstable (i_a/i_c = 0.35).[10] In the presence of two and more bpy ligands, Co^I reduction is accompanied by the transfer of two electrons to the more stable complex with the even number of electrons, *viz.*, $[Cobpy_2]^-$ (i_a/i_c = 0.70). Here the formal oxidation state of cobalt is –1; however, it seems most probable that the charge is delocalized on the π-acceptor ligands. In the case of electron delocalization on the ligand bound to the metal, $bpy^{\cdot -}$ would be detected by ESR but no ESR signal was observed.[10] The formation of a product of three-electron $Co^{II}bpy_3$ reduction has also been assumed previously.[5]

For example, for n = 3

$$Co^{II}bpy_3 + e \rightleftharpoons Co^Ibpy_3 \rightleftharpoons Co^Ibpy_2 + bpy,$$

$$Co^Ibpy_2 + 2e \rightleftharpoons [Cobpy_2]^{\cdot -},$$

$$bpy + e \rightleftharpoons bpy^{\cdot -}.$$

The reduction of the metal complexes containing the Ph_2Ppy ligand is more complicated. The peak corresponding to the Ni^{II}/Ni^0 and Co^{II}/Co^I transitions is divided into two peaks approximately equal in height, and their total sum is equal to the height of one peak with the PPh_3 ligand (see Fig. 6).

The division observed for the first peak is likely related to the formation of complexes of two types. The peak at more positive potentials should correspond to a more stable complex with P,N-coordination of the ligand, and the second peak can be attributed to a less stable complex with coordination to the P atom. This assumption is based on a comparison of reduction potentials of complexes with different ligands. For example, the complex with bpy (coordination only to the N atom) is reduced at relatively negative potentials in one step (for example, Ni^{II}/Ni^0). The complex with PPh_3 coordinated to the P atom is reduced at less negative potentials but also in one step. The Ph_2Ppy-containing complex with two coordinating atoms is characterized by two peaks, and E_p of the first peak is strongly shifted toward positive potentials. Since the reduction potential can serve, to a certain extent, as a characteristic of the lowest unoccupied molecular orbital (LUMO) for reversible systems, the LUMO energy of the complex with two heteroatoms in the ligand decreases strongly. This suggests that both heteroatoms are involved in bonding with metal, cleaving the energy levels. This is indirectly confirmed by the fact that cathodic peaks are absent from the region of reduction potentials of the complexes with coordination to the N atom (that is, no bonding with nitrogen only) and the second peak lies in the region of reduction potentials of the complexes with coordination to the P atom. Therefore, the new most positive peak can be assigned to a complex with simultaneous binding to two heteroatoms.

The following conclusions are based on the results of voltammetric studies of the cobalt(II) complexes with π-acceptor ligands. Only in MeCN the formation of the cobalt—ligand complexes results in the appearance of new characteristic peaks. Dimethylformamide manifests a higher coordinating ability toward cobalt ions and is inappropriate for studying complex formation processes. Among the ligands studied (PPh_3, Py, Ph_2Ppy, and bpy), 2,2´-bipyridine forms a stable reversible redox pair

$$Co^{II}bpy_n + e \rightleftharpoons Co^{I}bpy_m + (n - m)\ bpy.$$

In this case, the most distinct, easily interpreted pattern of reduction is observed and, hence, a more complete information on the mechanism of the process can be obtained.

The reduction potentials of the Co^{II} complexes with different ligands and Co^{II} solvo ions (see Tables 1 and 2 and Ref. 10) differ noticeably, and E_p of the complex depends on the ligand concentration, whose increase shifts E_p toward the anodic direction. The influence of the ligand on the reduction potential due to the different stabilities of complexes of the oxidized and reduced metal species can be considered only when two conditions are fulfilled: reversibility of the redox process and mobility of the complex formation equilibrium. In the systems under study, these conditions are fulfilled already at the ratio M : L = 1 : 1 because the redox process becomes reversible. The shift of the E_p values toward positive potentials upon ligand addition indicates that the reduced metal forms a more stable complex than the oxidized metal does. Under standard conditions, based on the shift of the reduction potential of cobalt with ligand from the reduction potential of free cobalt ions ΔE_p (or $\Delta E_{1/2}$), the ligands can be arranged in stability of the complexes in the following series: $Ph_2Ppy > Ph_3P > bpy > Py$ ($\Delta E_p = 0.61$, 0.19, 0.18, and 0.17 V, respectively).

All ligands are characterized by the shift of the peak of cobalt reduction toward less negative potentials. The shift of the peak potential with an increase in the organic ligand concentration in the anodic direction indicates that the reduced Co^I metal forms a more stable complex than the oxidized Co^{II} metal does.

Reduction of coordinatively unsaturated complexes. The influence of the metal : ligand ratio on the voltammetric behavior of the catalysts was studied to estimate the catalytic properties of the chosen cobalt complexes in electrochemical dehalogenation reactions.

It is known that less coordinatively saturated complexes are often more reactive than their more saturated analogs.[20,21] The characteristics of the complexes under study are presented in Table 4 and Figs. 4—6.

It is seen that the coordinatively unsaturated cobalt and nickel complexes form less reversible Co^{II}/Co^{I},L and Ni^{II}/Ni^0,L redox pairs than saturated complexes do, and the heights of the subsequent reduction peaks depend on the M : L ratio. The potentials of the first peaks of the more saturated complexes are shifted toward positive potentials, which confirms the results of this work. The

Table 4. Parameters of the peaks of electrochemical reduction of the coordinatively unsaturated Ni^{II} and Co^{II} complexes containing the π-acceptor ligands in MeCN on the Au electrode according to the CV data

Complex	$-E_p^{(1)}$/V	$n_e^{(1)}$	$-E_p^{(2)}$/V	$n_e^{(2)}$
$Ni(BF_4)_2bpy$*	1.51	1.9	2.15	0.7
$Ni(BF_4)_2Ph_2PPy$	0.71	0.5	1.01	1.2
$Ni(BF_4)_2PPh_3$*	1.10	1.8	—	—
$Co(BF_4)_2bpy$	1.33	1.0	1.90	0.9
$Co(BF_4)_2Ph_2PPy$	1.05	0.5	1.40	0.5
$Co(BF_4)_2PPh_3$**	1.21	0.7	1.41	0.1

* E_p^a (M^0) = −0.38 V (ads.).

** $E_p^{(3)} = -1.68$ V, $n_e^{(3)} = 0.14$; $E_p^{(4)} = -2.05$ V, $n_e^{(4)} = 0.2$.

Ph_2Ppy and PPh_3 ligands, most likely, attach the cobalt ions insufficiently strongly at M(L) : M(Co^{II}) = 1 because the voltammogram contains the reduction peaks of free ions. However, the number of peaks and currents of the peaks are close, on the whole, to those characteristic of the ligand-saturated complexes. Therefore, we may conclude that the nickel complexes with bpy and PPh_3 are reduced with simultaneous transfer of two electrons at the potentials of the first peaks, the cobalt complexes with bpy and PPh_3 are reduced with one-electron transfer at the potentials of the first peaks, while similar peaks of the complexes with Ph_2Ppy are divided into two peaks with the total current in the peak corresponding to ~2e/Ni and 1e/Co.

Thus, the study of the electrochemical reduction of the cobalt(II) complexes containing ligands with the π-acceptor properties and stabilizing the low oxidation states of the metal (bpy, Ph_2Ppy, Ph_3P) suggests the easiness of reduction of the complexes, elucidates the redox properties of different forms of the complexes in solution, and assumes the coordinating properties of the ligands and stability of the complexes.

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