Electrochemical properties of 2,2´:6´,2″-terpyridine complexes of platinum(II) with arenethiolate ligands. Alkylation of reduced forms of the complexes

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Three mixed-ligand terpyridine-thiolate Pt^{II} complexes containing 2,2´:6´,2″-terpyridine (tpy) and *para*-substituted thiophenolate ions, [(tpy)Pt(SC$_6$H$_4$-4-X)]BF$_4$ (X = NMe$_2$, H, NO$_2$) were synthesized. The complexes were isolated as chlorides or tetrafluoroborates and characterized by electrochemistry, visible electronic spectroscopy and ^{1}H NMR spectroscopy, and elemental analysis. Remarkable influence of the electron-donating/withdrawing properties of the substituent in the thiolate ligand on the physicochemical properties of the complexes, in particular, on the electrochemical reduction potentials, was found. The reduced forms of the complexes undergo electrochemically initiated alkylation with alkyl halides, resulting in the formation of Pt alkyl compounds.

Key words: platinum(II), 2,2´:6´,2″-terpyridine, arenethiolates, terpyridine thiolate complexes, electrochemistry, electrochemical alkylation.

In the last two decades, transition metal complexers with polypyridines, in particular, platinum(II) complexes with bipyridine (bpy) and 2,2´:6´,2″-terpyridine (tpy), have attracted considerable attention of researchers, mainly for two reasons. First, they can react with biomolecules.[1—6] Indeed, the [(tpy)PtCl]$^+$ cation is known as an intercalator for DNA molecules,[1—4] which penetrates through a double helix and reacts with complementary bases as with ligands without substantial change in the helix geometry. Second, such complexes have adjustable photophysical properties and are capable of luminescence; therefore, they can be used in various molecular devices.[7] The above-mentioned chloro platinum complex is oligomerized in aqueous solutions[1,8] and in the solid state;[1,8—11] evidence for the existence of both metal—metal and π—π ligand—ligand interactions between the monomers in the oligomer was obtained.[11] Stacking of [(tpy)PtCl]$^+$ molecules (having a square planar configuration of the Pt center) in the solid state gives rise to a low-energy absorption band in the electronic absorption spectrum, which is due to charge transfer from the metal—metal fragment to the tpy ligand (MMLCT band).[11]

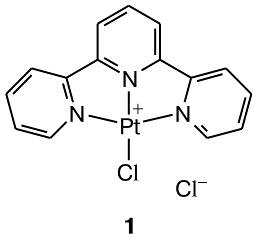
Electrochemical study of terpyridine systems was carried out using Pt,[12,13] Zn,[12,13] Fe,[14] Ru,[13] Os,[15,16] and Eu[17] complexes. For platinum complexes [(4´-X-tpy)PtCl]$^+$ substituted in position 4´ by π-acceptor (X = CN, SO$_2$Me) or π-donor (X = SMe, NMe$_2$) groups, the substituent was found to exert a strong influence on the first-wave reduction potential of the complex (in the region of 700 mV),[12] which indicates that the primary electron changes are mainly localized on the tpy ligand. Spectroelectrochemical measurements[13] showed that both the [(tpy)PtCl]$^+$ complex and its reduced forms exist as equilibria between the monomeric and dimeric species in solutions (DMF, 0.1 *M* Bu$_4$NPF$_6$) and the oxidized and reduced forms of the molecule interact with each other to the greatest extent. Analysis of the temperature dependence of the ESR spectra showed that the first step of electrochemical reduction involves the acceptor orbital of the ligand with some contribution of Pt^{II} 5d$_{y,z}$ and 6p$_z$ orbitals (4—6 and 3—4%, respectively). The second step involves, apparently, the acceptor 5d$_{x^2,y^2}$ orbitals of the metal. On the basis of these results, in the subsequent discussion of the behavior of our complexes, we will assume that the first electron is accepted by the ligand and the second, by the metal.

The purpose of this work is to study the electrochemical properties of a number of Pt^{II} terpyridine complexes containing arenethiolate ligands from which charge transfer to the tpy ligand can take place through the Pt atom. Particular attention is devoted to the possibility of redox alkylation (oxidative addition) on treatment of the reduced forms of the initial complexes with alkylating re-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1089—1095, May, 2003.

1066-5285/03/5205-1150 $25.00

agents. Such electrochemically induced reactions have not yet been studied for Pt terpyridine complexes.



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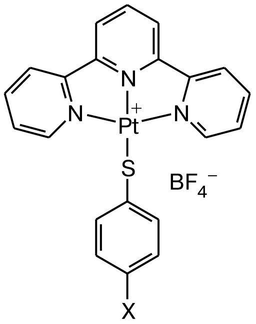


2—4

X = H (**2**), NMe_2 (**3**), NO_2 (**4**)

Experimental

Dimethylformamide (reagent grade) was stirred with anhydrous K_2CO_3 (20 g L^{-1}) for 4 days at ~20 °C, decanted from the solid phase, and then purified by successive refluxing and vacuum distillation (b.p. 42 °C, 10 Torr) over CaH_2 (10 g L^{-1}) and anhydrous $CuSO_4$ (10 g L^{-1}). The purified solvent was stored over 4 Å molecular sieves.

2,2′:6′,2″-Terpyridine (Aldrich), potassium *tert*-butoxide (Aldrich), benzenethiol, and 4-nitrobenzenethiol (Aldrich) were used as received. The $[(tpy)PtCl]Cl \cdot 2H_2O$ complex was prepared by refluxing K_2PtCl_4 and 2,2′:6′,2″-terpyridine in distilled water for 100 h.[18]

Electrochemical measurements were carried out using a PI-50-1.1 potentiostat. Glassy carbon (d = 1.8 mm) or platinum (d = 2.8 mm) discs pressed in Teflon served as working electrodes; a 0.05 *M* solution of Bu_4NBF_4 served as the supporting electrolyte, and an Ag/AgCl/KCl(sat.) electrode was the reference electrode. All the measurements were carried out under argon.

^1H NMR spectra were recorded on a Varian VXR-400 instrument in DMSO-d_6 and UV-Vis spectra were run on a Shimadzu UV-2401 PC spectrometer.

***N*,*N*′,*N*″-(2,2′:6′,2″-Terpyridino)(arenethiolato)platinum(II) chlorides, $[(tpy)Pt(SC_6H_4\text{-}4\text{-}X)]Cl$ (general procedure).** Terpyridine thiolate complexes of Pt^{II} were prepared from the chloride complex according to the procedure described previously.[19] A solution of *para*-substituted benzenethiol (10% excess) in EtOH containing an equivalent amount of Bu^tOK was added dropwise with vigorous stirring under argon over a period of 1 h to a suspension of $[(tpy)PtCl]Cl \cdot 2H_2O$ (265 mg, 0.495 mmol) in 96% EtOH. The addition of the thiolate was accompanied by dissolution of the initial compound and the change in the solution color from orange to red-vinous (X = NO_2), lilac (X = H), or crimson (X = NMe_2). After the addition of the whole solution of the ligand, stirring was continued for 5—6 h until the starting chloride complex was entirely consumed. Completion of the reaction required slight heating of the reaction mixture (X = NO_2, H). In the case of X = NMe_2, heating resulted in decomposition. On completion of stirring, the solution was filtered, and a double volume of Et_2O was slowly added to the filtrate. The resulting mixture was cooled to +4 °C over a period of 1 h. The precipitate was filtered off, washed with small portions of an EtOH—Et_2O mixture (1 : 1, v/v), and dried in a vacuum dessicator over P_2O_5 at ~20 °C.

***N*,*N*′,*N*″-(2,2′:6′,2″-terpyridino)(benzenethiolato)platinum(II) tetrafluoroborate, $[(tpy)Pt(SPh)]BF_4$ (2).** The [(tpy)Pt(SPh)]Cl complex was dissolved in 96% EtOH and a dilute aqueous solution of HBF_4 was added until the medium was weakly acidic against the universal indicator. The resulting lilac-colored precipitate was filtered off, washed several times with distilled water and EtOH, and dried in a vacuum dessicator over P_2O_5. Found (%): C, 40.41; H, 2.56; N, 6.59. $C_{21}H_{16}BF_4N_3PtS$. Calculated (%): C, 40.38; H, 2.58; N, 6.73. ^1H NMR, δ: 9.08 (d, 2 H, J = 5.6 Hz); 8.70 (m, 5 H); 8.47 (td, 2 H, J = 8.0 Hz, J = 1.2 Hz); 7.87 (t, 2 H, J = 6.0 Hz); 7.65 (dd, 2 H, J = 8.4 Hz, J = 1.2 Hz); 7.06 (t, 2 H, J = 7.2 Hz); 6.96 (t, 1 H, J = 7.2 Hz). UV-Vis (DMF), λ_{max}/nm (log ε): 549 (1500).

***N*,*N*′,*N*″-(2,2′:6′,2″-Terpyridino)(4-dimethylaminobenzenethiolato)platinum(II) tetrafluoroborate, $[(tpy)Pt(SC_6H_4\text{-}4\text{-}NMe_2)]BF_4$ (3).** The crimson-colored crystals were prepared from $[(tpy)Pt(SC_6H_4\text{-}4\text{-}NMe_2)]Cl$ by a procedure similar to the synthesis of complex **2**. Found (%): C, 40.28; H, 3.04; N, 8.47. $C_{23}H_{21}BF_4N_4PtS$. Calculated (%): C, 41.39; H, 3.18; N, 8.40. ^1H NMR, δ: 8.90 (dd, 2 H, J = 5.6 Hz, J = 1.2 Hz); 8.60 (t, 2 H, J = 8.4 Hz); 8.43 (td, 2 H, J = 5.6 Hz, J = 1.2 Hz); 8.63 (m, 5 H); 7.40 (d, 2 H, J = 8.4 Hz); 6.51 (d, 2 H, J = 7.2 Hz); 2.78 (s, 6 H). UV-Vis (DMF), λ_{max}/nm (log ε): 603 (1500).

***N*,*N*′,*N*″-(2,2′:6′,2″-Terpyridino)(4-nitrobenzenethiolato)platinum(II), $[(tpy)Pt(SC_6H_4\text{-}4\text{-}NO_2)]BF_4$ (4).** Red-orange crystals were prepared from $[(tpy)Pt(C_6H_4\text{-}4\text{-}NO_2)]Cl$ by a procedure similar to that described previously for complex **2**. Found (%): C, 37.52; H, 2.09; N, 8.28. $C_{21}H_{15}BF_4N_4O_2PtS$. Calculated (%): C, 37.70; H, 2.24; N, 8.37. ^1H NMR, δ: 9.03 (d, 2 H, J = 5.2 Hz); 8.70 (m, 5 H); 8.50 (td, 2 H, J = 7.9 Hz; J = 1.41 Hz); 7.88 (m, 6 H). UV-Vis (DMF), λ_{max}/nm (log ε): 503 (1900).

Results and Discussion

We studied platinum(II) complexes with terpyridine **1—4** by cyclic voltammetry (CV) on a glassy carbon electrode in DMF (the number of transferred electrons was determined using a rotating disc electrode, by comparing the height of the corresponding wave with the height of the wave for the single-electron oxidation of ferrocene of the same concentration). The results are summarized in Table 1.

Compounds **1** and **2** exhibit one oxidation peak each, while **4** has two and **3** has four oxidation peaks. All the peaks are irreversible. In line with the results obtained earlier,[12] we believe that oxidation processes do not affect the (tpy)Pt core, being localized on either the outer-sphere chloride ion (in the case of complex **1**) or the arenethiolate ligand (in the case of complexes **2—4**).

$$[(tpy)Pt{-}SAr]^+ - e \longrightarrow (tpy)Pt^{2+} + 0.5\ ArSSAr$$

Compound **3** contains the *para*-dimethylaminothiolate ligand rich in electrons (lone electron pairs of the S and

Table 1. Oxidation (E_p^{Ox}) and reduction (E_p^{Red}) potentials of complexes **1—4** in DMF (0.1 *M* solution of Bu_4NBF_4, Pt electrode, Ag/AgCl/KCl (sat.), 20 °C)

Complex	Oxidation[a] E_p^{Ox}/V	Reduction					
		$-E_p^{Red,1}$ /V	$E_{p,a}^1 - E_{p,c}^1$ [b] /mV	$i_{p,a}^1/i_{p,c}^1$ [c]	$-E_p^{Red,2}$ /V	$E_{p,a}^2 - E_{p,c}^2$ [b] /mV	$-E_p^{Red,3}$ [d] /V
1 [e]	1.14	0.60	100	0.60	1.14	90	2.04 [a]
2	1.17	0.76	90	1.00	1.31	70	2.04 [a]
3	0.87, 1.23, 1.41, 1.68	0.75	90	0.81	1.26	60	2.26 [a]
4	1.46, 1.55	0.73	120	1.00	1.22	110	1.39

[a] All peaks are irreversible.

[b] The difference between the potentials of the reverse ($E_{p,a}$) and forward ($E_{p,c}$) peaks.

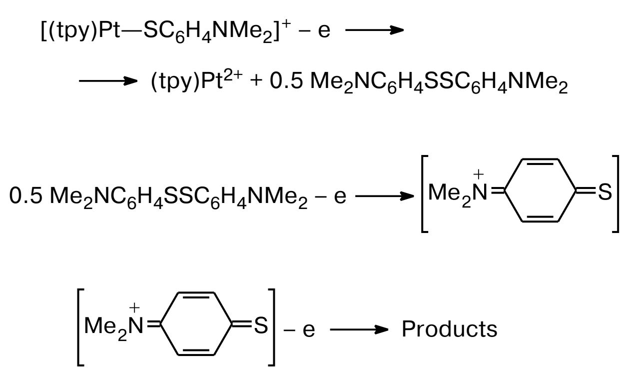
[c] Ratio of the heights of reverse and forward peaks.

[d] On a glassy carbon electrode.

[e] On a Pt electrode. The following reduction potentials of the $[(tpy)PtCl]PF_6$ complex were determined:[12] $E_p^{Red,1} = -0.74$, $E_p^{Red,2} = -1.30$ and $E_p^{Red,3} = -2.2$ V. The former two steps are quasi-reversible ($E_{p,a} - E_{p,c}$ = 80—90 mV); the third step becomes chemically reversible only at temperatures below −20 °C.

N atoms) and, therefore, its oxidation gives rise to four peaks, three of which can be attributed to the hypothetical reactions shown in Scheme 1.

Scheme 1



This mechanism of electrooxidation is based on the following experimental findings. First, the free tpy ligand is not oxidized in DMF over the accessible range of potentials; second, dimethylaniline is oxidized at a potential of ~0.72 V;[20] third, bis(*N*,*N*′-dimethylaminophenyl) disulfide which we synthesized by the reaction of *N*,*N*-dimethylaniline with S_2Cl_2 is oxidized at E_p = 1.22 V, which is very close to the second-peak potential (1.23 V) present in the voltammograms for oxidation of complex **3** (see Table 1). This electrooxidation mechanism is, apparently, applicable in general terms to compound **4**.

The electrooxidation of compounds **2—4** is subject to an appreciable influence of substituents in the *para*-position relative to the S atom on the first oxidation potential. *para*-Dimethylamino derivative **3** is oxidized at a 300 mV lower potential (*i.e.*, more easily) and *para*-nitro derivative **4** is oxidized at a 290 mV higher potential (*i.e.*, more difficultly) than unsubstituted compound **2**. These results show that electrooxidation involves particularly the arenethiolate ligand.

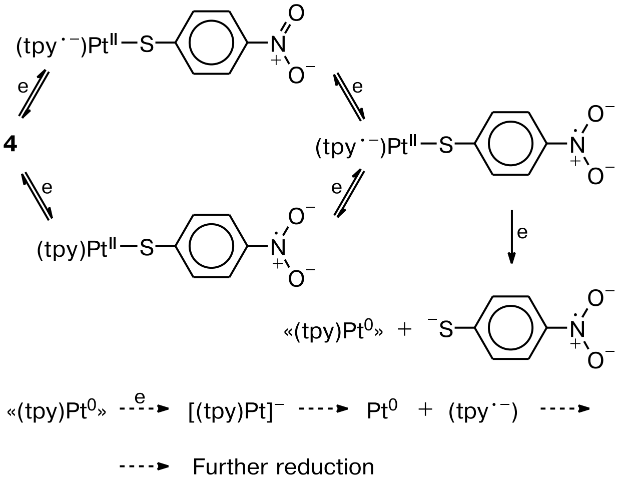
As has been noted previously,[12] the effect of substituents in position 4′ of the terpyridine ligand in chloride complex **1** was studied, and these substituents were shown to influence only slightly the oxidation potential. Thus, the tpy ligand remains almost intact during oxidation. However, the reduction potentials of 4′-substituted chloride complexes depend appreciably on the nature of the substituent,[12] whereas the reduction potentials of the complexes we studied are slightly sensitive to the nature of the *para*-substituents in the arenethiolate ligand (see Table 1). These data suggest that the first step of reduction involves the tpy ligand.

All of these compounds exhibit three reduction peaks in the cathodic region of potentials, the first two peaks being reversible or quasi-reversible ($E_{p,a} - E_{p,c}$ = 60—120 mV). The third peak, which markedly exceeds the former two peaks in height, is irreversible at 20 °C. The potential of the first peak for compounds **2—4** depends only slightly on the substituent in the arenethiolate ligand. This indicates that the primary electron changes occurring upon the elctroreduction are not related to this ligand.

The potentials for the first step of reduction of complexes **1—4** are much less negative than the reduction potentials of free tpy. This effect of coordination to the metal indicates that electroreduction actually involves mainly the vacant orbitals of the tpy ligand; this is in line with the conclusion drawn previously.[12] The second step of reduction corresponds, apparently, to the transfer of the second electron to give a negatively charged species, which retains the structure of the initially positively charged complex. This conclusion is based on the fact that the polarization curves recorded during the reverse scan always exhibit an anodic peak. However, the ratio of the heights of the reverse and forward peaks for the second step is equal to 0.66—0.45 (see Table 1), *i.e.*, partial destruction still does occur.

Compound **4**, which contains two potential reduction centers, namely, the tpy ligand and the NO_2 group, deserves particular attention. The first step of reduction may involve either the ligand or the NO_2 group (Scheme 2).

Scheme 2



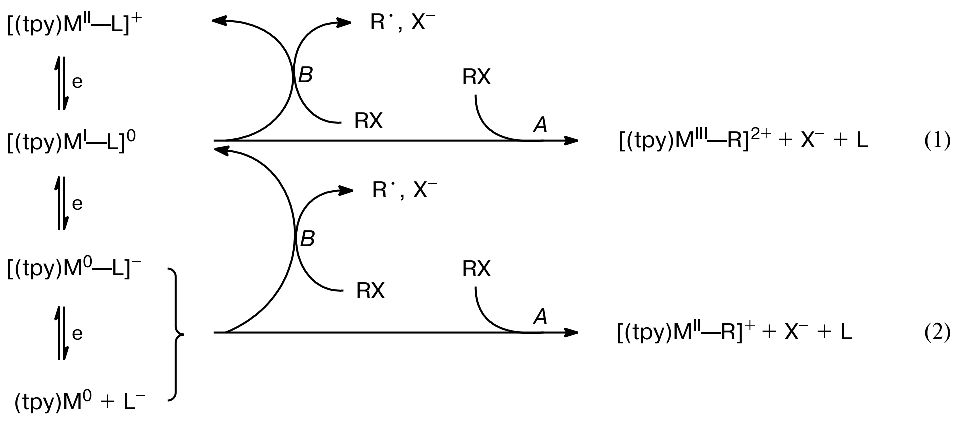
After transfer of the second electron, the same product is formed in both cases. This product is shown in Scheme 2 as a Pt^{II} complex with the $(tpy)^{\bullet -}$ radical anion and with the *para*-nitrobenzenethiolate radical anion, although the real electronic structure of this species may be different, for example, $(tpy^{\bullet -})Pt^{I}—SC_6H_4NO_2$-4.

The third irreversible multielectron wave for compounds **1—3** seems to correspond to further reduction of "$(tpy)Pt^0$" (the other possible electronic structure is $(tpy^{\bullet -})Pt^{I}$) to give the negatively charged $[(tpy)Pt]^-$ complex with extrusion of platinum metal and further reduction of the terpyridine radical anion (see Scheme 2).

In this connection, note that evidence for the existence of paramagnetic 19-electron $(bpy)Ni^-$ and $(phen)Ni^-$ complexes (phen is 1,10-phenanthroline) rather stable on the CV time scale have been obtained recently.[21] These complexes are electrochemically produced from $(bpy)Ni^0$ and $(phen)Ni^0$ at high cathodic potentials (−2.46 and −2.30 V for the bpy and phen complexes, respectively; free ligands are reduced at even higher potentials, −2.68 and −2.60 V), and they are efficient homogeneous reducing agents. Owing to the clearly pronounced π-acceptor properties of polypyridine ligands, the electron density in these complexes should be largely shifted to the ligand; hence, the electronic structure can be represented more reasonably as $(L^{\bullet -})Ni^0$, which is confirmed by ESR spectra.

The reduced forms of transition metal complexes containing, for example, Ni^0, Pd^0, or Co^I, are simultaneously potent nucleophiles and potent reducing agents. These species, which are usually rather unstable during storage, are readily generated *in situ* by electroreduction of appropriate metal complexes in stable valence states. When acting as a nucleophile, the reduced complex easily replaces the nucleofugal groups in organic substrates giving rise to compounds with a carbon—metal bond. When acting as a reducing agent, this complex converts organic substrates into reactive radical anions and/or radicals. Scheme 3 shows two possible reaction routes for the initial four-coordinate complex formed by a divalent late transition metal with the neutral tridentate tpy ligand and

Scheme 3



M is metal, L is ligand

the anionic monodentate L^- ligand. Pathway *A* corresponds to the nucleophilic properties and pathway *B* represents the reducing properties.

The electrochemical activation of metal complex catalysts of diverse organic reactions has been vigorously studied in the last decade.[22,23]

Pathway *A* is most important for organic and organometallic syntheses, because the carbon—metal bond in the resulting organometallic complex is relatively weak and the organic group can be transferred (as a cation, anion, or radical) to other organic or inorganic molecules or ions.

In this work, the possibility of alkylation of the electrochemically generated low-valence platinum complexes was studied using Bu^nI, Bu^nBr, and $(dmgH)_2Co—Me$ (methylcobaloxime) as alkylating agents. There exists a diagnostic electrochemical test, which allows one to find out whether the reaction between the reduced forms of complexes and the alkylating agents follows pathway *A* or pathway *B* (see Scheme 3). If the process follows pathway *B*, the difference between the morphologies of the CV curves recorded in the absence and in the presence of an alkylating agent would be an increase in the reduction current of the starting complex (so-called catalytic current) and a decrease or total disappearance of the signs of reversibility of the reduction of the starting complex (a decrease or disappearance of the anodic peak when scanning the potential in the opposite direction). If the reaction follows pathway *A*, a new peak corresponding to reduction of the *alkylation product* is expected to appear. This new peak usually appears at more cathodic potentials relative to the potentials of generation of low-valence complexes reactive toward the alkylation. Some exceptions are known.[24] If reactions along pathways *A* and *B* are slow on the time scale of a given electrochemical method, no changes will occur in recording the first polarization pattern on a clean electrode surface in the presence of an alkylating agent; these changes would be visible only after relatively long-term electrolysis at potentials where species susceptible to alkylation are generated.

When recording CV curves for compounds **1—4** in the presence of Bu^nBr or Bu^nI, an additional peak appears already during the first scan for all compounds (Fig. 1, *a*, *b*, peak *C*), the corresponding potential being −1.31 (complex **1**), −1.46 (complex **2**), −1.49 (complex **3**), and −1.45 V (complex **4**). Simultaneously, the reversibility of the second reduction peak of complexes **1—4** almost disappears, and a peak (or two peaks) for the oxidation of the corresponding halide ion appears during the reverse anodic scan in the anodic region (0.96 V for the use of Bu^nBr and 0.30 and 0.70 V for the use of Bu^nI). The reversibility of the first reduction peak decreases insignificantly in all cases.

In the range of Bu^nI concentrations from $5 \cdot 10^{-3}$ to $1 \cdot 10^{-1}$ mol L^{-1}, only one additional reduction peak for the product is observed in the polarization patterns. This means that under these conditions, alkylation starts only together with the formation of the formally zerovalent platinum complex $(tpy)Pt^0$ (see Scheme 3). The alkylation of the singly reduced species, $[(tpy)Pt^ISAr]$, proceeds slowly, if at all.

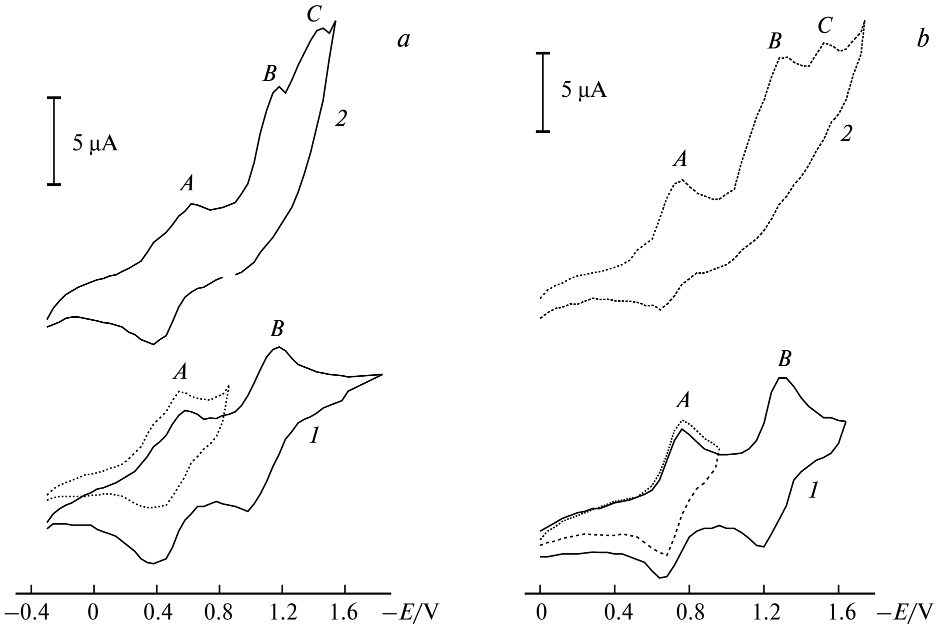


Fig. 1. Cyclic voltammograms of $1 \cdot 10^{-3}$ *M* solutions of $[(tpy)Pt^+Cl]Cl^-$ (**1**) (*a*) and $[(tpy)Pt^+SC_6H_4\text{-}4\text{-}NMe_2]BF_4^-$ (**3**) (*b*) in DMF (0.05 mol L^{-1} of Bu_4NBF_4) in the absence of Bu^nI (*1*) and in the presence of Bu^nI (0.01 mol L^{-1}) (*2*).

The polarization patterns shown in Fig. 1, *a*, *b* can be interpreted in the following way. The addition of an alkylating agent entails a fast reaction with the doubly reduced form of the complex, which can formally be described as (tpy)Pt^0, resulting in the formation of $[(tpy)Pt^{II}Alk]^+X^-$. During further potential scan to the cathodic region, this product is reduced to give the alkyl anion Alk^- and (tpy)Pt^0, the latter being rapidly alkylated. In the presence of an alkylating agent, the concentration of (tpy)Pt^0 in the near-electrode area diminishes; therefore, during the reverse potential scan to the anodic region, the peak of (tpy)Pt^0 oxidation substantially decreases. In the case of rather high concentration of the alkylating agent, this peak totally disappears. Further scan to the anodic region implies transition to a potential region where (tpy)Pt^0 no longer exists, but the singly reduced (tpy)Pt^ISAr still exists. The latter species is slowly alkylated; therefore, the anodic peak corresponding to its oxidation is changed only slightly.

However, when the concentration of the alkylating agent is $>1 \cdot 10^{-1}$ mol L^{-1}, the alkylation of the singly reduced form becomes sufficiently fast to show itself in the voltammograms. Thus, a second extra peak with a potential of −0.95 (compound **1**), −1.12 (compound **2**), −1.13 (compound **3**), or −1.18 V (compound **4**), appears just after the first reduction peak of the initial complex. Thus, at high concentrations, one can observe the alkylation of formally monovalent platinum giving rise to an alkyl derivative of the formally trivalent platinum (see Scheme 3, reaction (1)).

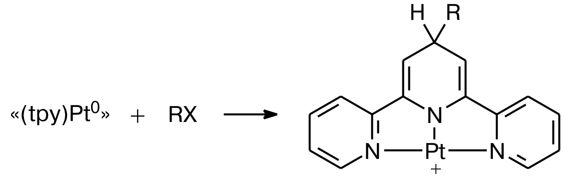
A convenient alkylating agent is the dimethylglyoximate complex of methylcobalt, which can act as a carrier for methyl cations (in the case of formation of $(dmgH)_2Co^-$), methyl radicals (in the case of formation of $(dmgH)_2Co^{II}$), or methyl carbanions (in the case of formation of $(dmgH)_2Co^{III}$). The voltammogram of an equimolar mixture ($1 \cdot 10^{-3}$ mol L^{-1}) of (tpy)$PtCl_2$ and $(dmgH)_2Co$—Me recorded from 0 to −1.4 V does not show any changes with respect to the voltammograms of neat specimens; however, switching to anodic polarization after $E_p = -1.4$ V (*i.e.*, after the second reduction peak of complex **1**) brings about two new peaks: an anodic peak ($E_p^{Ox} = -0.96$ V) and a cathodic peak ($E_p^{Red} = -1.04$ V). According to our data, these peaks correspond to a reversible transition for demethylated methylcobaloxime.

$$(dmgH)_2Co^{II} \underset{-e}{\overset{+e}{\rightleftharpoons}} [(dmgH)_2Co^{I}]^-$$

The reversible pair at −0.96/−1.04 V appears only in the case where the sweep was reversed after the two-electron reduction potential of complex **1**. However, no peaks indicating alkylation of this complex (−0.95 and −1.31 V) appear. Apparently, in this case, mediator reduction of $(dmgH)_2Co$—Me with the product of two-electron reduction of complex **1** takes place (see Scheme 3, pathway *A*, reaction (2)).

The two-electron reduction of complexes **2—4** may give "(tpy)Pt^{0}" and ArS^- in the near-electrode layer. In principle, both of these species can be alkylated. In our opinion, the substantial changes in the CV curves (see Fig. 1, *a*, *b*) are related to alkylation of the doubly reduced complex because similar changes are observed not only for compounds **2—4** but also for compound **1**, which does not contain a thiolate ligand. The alkylation of the doubly reduced complex involves the metal atom. In the case of ligand alkylation, the alkylated product would, probably, have the structure shown in Scheme 4.

Scheme 4



In this case, during the reverse potential scan, the CV curves would exhibit the reversible $(tpy)Pt^+$—SAr/(tpy)Pt—SAr pair (see Fig. 1, *a*, *b*, peaks *A*).

Thus, the electrochemical data show that the electronic structure of the studied complexes is determined by the charge transfer between the donor thiolate ligands and the acceptor tpy ligand with participation of the Pt atom. The electrochemical reduction does not deteriorate substantially the molecular structures of complexes but may activate them towards alkylation at the metal atom.

This work was supported by the Russian Foundation for Basic Research (Project No. 00-03-32888).

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Received May 24, 2002;
in revised form December 24, 2002