# ELECTROCHEMICAL BEHAVIOR OF METAL COMPLEXES OF DERIVATIVES OF DIBENZO[c,j]DIPYRAZOLO[3,4-f:3',4'-m][1,2,5,8,9,12]-HEXAAZACYCLOTETRADECYNES ON A PYROGRAPHITE ELECTRODE

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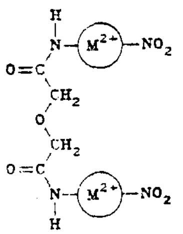
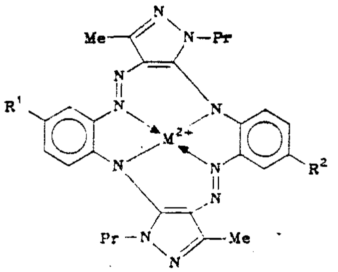
The electrochemical behavior in the adsorbed state (on a pyrographite electrode) of metal complexes of a number of derivatives of dibenzo[c,j]dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecynates was studied by cyclic voltammetry. The determining role of the nature of the side groups of the complex on the character of its electrochemical behavior on the electrode surface was noted. The reversible redox transitions observed on the potentiodynamic curves were ascribed to reduction and oxidation of the aza groups of the complexes. The irreversible redox processes were ascribed to reduction of the side groups of the complex, which is accompanied by attachment to the electrode surface, and to their oxidative destruction.

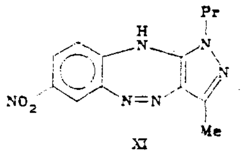
Metal complexes of highly conjugated nitrogen macroheterocyclic compounds are of interest in connection with their manifestation of catalytic activity in redox reactions in both homogeneous and heterogeneous catalysis. A rather large volume of data on the use of electrodes surface-modified by such complexes for the electrocatalysis of a number of important redox reactions has been accumulated in the literature [1]. In the synthesis of new classes of macroheterocyclic compounds important information can be obtained by drawing upon a number of electrochemical methods, particularly the cyclic potentiodynamic method, which makes it possible to investigate the electrochemical behavior of complexes on the electrode surface and the electrocatalytic activity of such systems.



X



I-IX



XI

I, IV, VI—VIII $M^{2+}=Ni$; II $M^{2+}=Pd$; III $M^{2+}=Co$; V, IX $M^{2+}=Cu$; I $R^1, R^2=H$; II—VI $R^1=NO_2$; II—V $R^2=NO_2$; VII $R^1=NH_2$; VI, VII $R^2=NH_2$; VIII $R^1=R^2=NHAc$; IX mixture $R^1, R^2=NH_2$, $R^1=NH_2$, $R^2=NO_2$; X — binuclear $Cu^{2+}$ complex

In the present research, we investigated the electrochemical behavior in the adsorbed state (on the electrode) of complexes (I-VIII) of a number of derivatives of dibenzo[c,j]-dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecynates, binuclear copper complex X, and triazepine XI.

It was shown that complexes II-V applied to the surface of a pyrographite electrode exist primarily in an electrochemically inactive state; the potentiodynamic curves over the

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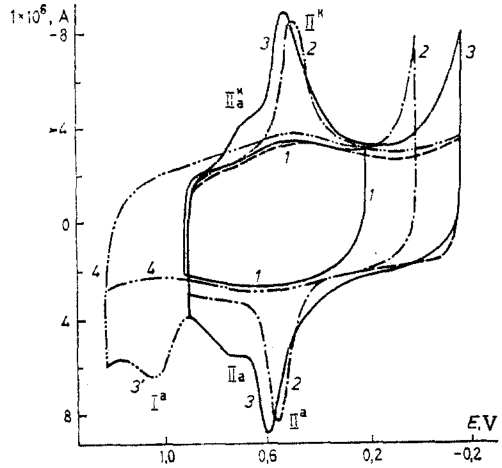

Fig. 1

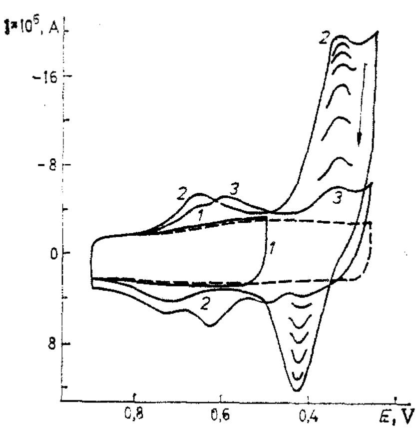

Fig. 2

Fig. 1. Potentiodynamic curves of a pyrographite electrode modified by complex V ($5 \cdot 10^{-9}$ mole) at various potential amplitudes (the dotted curve pertains to the unmodified electrode): 1-4) successive change in the potential range of the electrode modified by the complex (phosphate buffer solution, pH 7.5, v = 0.1 V/sec).

Fig. 2. Potentiodynamic curves of a pyrographite electrode modified with triazepine derivative XI (the designations are the same as in Fig. 1).

range of potentials 0.8-0.3 V virtually coincide with the background curves (Fig. 1, dotted line and curve 1). However, when the sweep amplitude is increased to the cathode side, the existence of a cathode process leading to the appearance of reversible maxima II ($E^*_{c2}$ = 0.52 V and $E^*_{a2}$ = 0.55 V for complex V) can be detected. The cathode process at potentials below 0.2 V is displayed on the first part of the curve in the form of maxima I and III, the potentials of which are presented in Table 1. With a further increase in the sweep amplitude to the cathode side up to −0.2 V (up to the start of maximum III) maxima II are shifted somewhat to the anode side, and yet another maximum appears at potentials of 0.65/0.70 V. It is interesting that the electrochemical behavior of triazepine derivative XI (which contains the same functional groups but does not contain a metal ion) is qualitatively similar to that of metal complexes II-V (Fig. 3). This constitutes evidence that the metal ion does not participate directly in the redox processes; however, the metal ion does have a substantial effect on the redox processes of the complexes to which maxima I correspond, in that it disrupts their reversibility (Figs. 2 and 3) and causes a shift in the potentials of cathode maxima I to the cathode side. With respect to their stabilizing effect on the oxidized form, the metal ions can be arranged in the order $Ni^{2+} > Cu^{2+} > Co^{2+} \approx Pd^{2+}$ (Table 1), which is similar to the order of the change in magnitude of the negative charge of the porphyrin ring [2]. Anode polarization of the electrodes modified by complexes II-V up to potentials more positive than 1.0 V entails irreversible oxidation, which is evidently accompanied by desorption of the complex. This is indicated by the fact that the corresponding anode maximum (Fig. 1, curves 3' and 4) can be detected only on the first part of the curve. Let us note that maintaining the electrode modified by the complex, which exists in an electrochemically inactive state (it does not undergo strong cathode polarization), at anode potentials of 1.2 V does not cause its destruction (desorption).

Complexes VI and IX, which have one nitro group and one amino group, behave similarly; however, their oxidation does not lead to desorption (Fig. 3). Complex VII, which contains two side amino groups, behaves differently. It is adsorbed on the surface immediately in an electrochemically active state, as evidenced by the appearance of maxima on the potentiodynamic curve at 0.60/0.76 V even at a sweep amplitude of 0.9-0.4 V. Considerably more profound (than for complexes I-V) cathode polarization up to potentials of −0.2 V is required for conversion of complex VIII, which contains partially acylated side amino groups, to an electrochemically active state. In general, binuclear complex X behaves like complexes II-VI and VIII. The only difference consists in the fact that in the case of complex X anode

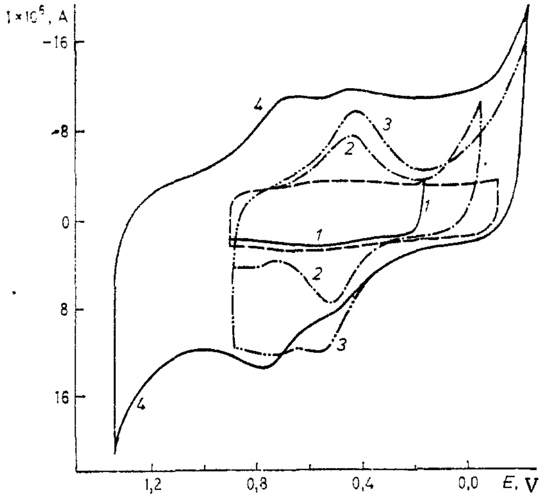

Fig. 3. Potentiodynamic curves of a pyrographite electrode modified by complex VII (the designations are the same as in Fig. 1).

maximum I at 1.23 V appears not only on the single potentiodynamic curve but also on the cyclic potentiodynamic curve.

It follows from the data obtained that the nature of the side groups has the determining effect on the electrochemical behavior of the complexes. One might assume that initially, when it is applied to the electrode surface, the complex that has two side amino groups is adsorbed flatly on the electrode surface due to the fact that in this case the conjugated macrocyclic system has strongly expressed regions of negative charge under and above the plane of the complex molecule because of the strong π-donor character of the amino groups ($\sigma\text{-}NH_2^i = 0.13$; $\sigma\text{-}NH_2^r = -0.79$) [3]; the amino groups, which are close to the electrode surface, can react with the surface oxygen-containing groups, thereby forming amide bonds. A complex that does not have side amino groups or has only one amino group, because of the absence of a region of negative charge under the macrocyclic ring ($\sigma\text{-}NO_2^i = 0.63$; $\sigma\text{-}NO_2^r = 0.15$) [3], is oriented primarily at such a large angle to the electrode surface that direct exchange of electrons between the molecule and the electrode surface is hindered and cannot occur with either the central metal atom or with the conjugated π-electron system of the macrocyclic ligand. Partial π-electron character of the amide bond theoretically should lead to electron pairing between the amide groups and the aromatic system and, as a consequence, with the entire conjugated π-electron system, thereby causing charge transfer through the amide bridge. However, a comparison of the properties of complexes that contain various combinations of side nitrogen-containing groups (complexes VI, IX and V, VII) provides evidence that this mechanism of electron transfer, as in [4], is not realized.

The conversion of complexes that contain side nitro groups to an electrochemically active state can be explained by assuming that a shift of the electrode potential to the cathode side may cause reorientation of a molecule bearing a partially positive charge; in this case the angle between the plane of the molecule and the electrode surface decreases, and the possibility of exchange of electrons between the complex molecule and the electrode surface arises. If this orientation cannot be fixed by covalent bonds, a shift of the electrode potential to the anode side again leads to reorientation of the molecule and its conversion to an electrochemically inactive state. This is observed in the case of complex I, which does not have side groups. Maximum II on the potentiodynamic curve is noted for this complex only for the first pulses after prior cathode polarization up to −0.3 V. When the sweep amplitude is decreased, the maximum slowly disappears and can be obtained again after repolarization at a negative potential. This phenomenon can be observed repeatedly. If reorientation of the molecule is accompanied by reduction of the side nitro groups with the formation of amino groups, which are capable of chemical reaction with the surface groups of pyrographite, the planar orientation is retained over a rather broad range of potentials; the complex acquires the possibility of exchanging electrons with the electrode in this case (complexes II-VI). Maximum I for complexes II-VI can then be explained by reductive attachment of the nitro groups to the electrode surface. This attachment should be realized simultaneously through both amino groups in this case. This is indicated by the difference in the behavior of the diamino complex of nickel (VII) and the dinitro and nitro amino complexes of nickel (IV, VI). The considerably more pronounced cathode polarization that is required for conversion of the complex to an electrochemically active state when $R^1$, $R^2$ = NHAc (complex VIII, Table 1) can be explained within the framework of this assumption by the

TABLE 1. Potentials of the Maxima on the Potentiodynamic Curves of a Pyrographite Electrode Modified by Complexes I-XI

| Complex | Sweep interval, V | $E^*_{c1}$ | $E^*_{c2}$ | $E^*_{c3}$ ($E^*_{a1}$) | $E^*_{a2}$ |
|---|---|---|---|---|---|
| I | 0,90—0,00 | — | — | — | — |
| | 0,90—0,30 | | 0,61 | | 0,73, 0,86 |
| | 0,90—0,40 | | 0,61 | | 0,73, 0,90 |
| II | 0,90—0,25 | — | — | — | — |
| | 0,90—0,10 | 0,10 | 0,56 | | 0,60 |
| | 0,90—0,15 | 0,10 | 0,53 | −0,10 | 0,60 |
| III | 0,90—0,05 | — | — | — | — |
| | 0,90—0,05 | 0,10 | 0,50 | | 0,60 |
| | 0,90—0,20 | 0,10 | 0,73, 0,48 | −0,24 | 0,77, 0,60 |
| IV | 0,90—0.25 | — | — | — | — |
| | 0,90—0,15 | | 0,52 | | 0,55 |
| | 0,90—0,20 | 0,04 | 0,65, 0,52 | −0,13 | 0,70, 0,60 |
| V | 0,90—0,25 | | — | — | — |
| | 0,90—0,00 | 0,00 | 0,48 | | 0,54 |
| | 0,90—0,20 | 0,00 | 0,63, 0,45 | −0,35 | 0,65 |
| VI | 0,90—0,10 | — | — | — | — |
| | 0,90—0,05 | | 0,47 | | 0,53 |
| | 0,90—0.20 | | 0,45 | | 0,54 |
| | 1,35—0,10 | | 0,67, 0,45 | | 0,77, 0,55 |
| VII | 0,90—0,40 | | 0,60 | | 0,76 |
| VIIa | 0,90—0,40 | — | — | — | — |
| | 0,90—0,30 | | 0,57, 0,48 | | 0,69, 0,55 |
| | 1,40—0,10 | — | — | — | — |
| VIIb | 0,90—0,20 | | 0,32 | | 0,37 |
| | 1,40—0,10 | — | 0,68, 0,32 | | 0,76, 0,37 |
| VIII | 0,90—0,10 | — | — | | — |
| | 0,90—0,20 | | 0,57 | | 0,80 |
| | 0,90—0.30 | | 0,57 | | 0,80, 0,65 |
| | 1,40—0,20 | | 1,15, 0,57 | | 1,15, 0,95, 0,80, 0,65 |
| IX | 0,90—0.10 | — | — | — | — |
| | 1,10—0,20 | −0,25 | 0,60 | −0,40 | 0,75 |
| X | 0,90—0,10 | — | — | — | — |
| | 0,90—0,05 | | 0,48 | | 0,56 |
| | 1,40—0,05 | 1,15 | 0,48 | (1,23) | 0,56 |
| XI | 0,90—0,40 | — | — | — | — |
| | 0,90—0.25 | 0.33 | 0,65 | (0,42) | 0,73 |
| | 0,90—0,10 | 0,33 | 0,65, 0,60 | 0,17<br>(0,42) | 0,73 |

fact that either splitting out or rotation of the acetyl group, which exerts steric hindrance to a planar orientation of the complex, is required.

The redox process in the region of maxima II evidently corresponds to reversible reduction of the aza groups of the complex. The shift of the potentials of the maxima to the anode side and the appearance of additional maxima IIa with retention, for a number of complexes, of the amount of electricity corresponding to a redox process in the region of maximum II (Fig. 1) constitute evidence that the aza groups exist in an energically nonequivalent state with respect to electron transfer from the electrode surface and vice versa. The presence on the surface of aggregated particles, the formation of which is highly likely in the method used to apply the complex, may serve as an alternative explanation for the appearance of maximum IIa and the shift, in a number of cases, of maximum II. One also cannot exclude the possibility that maxima II and IIa (or one of them) are related to redox transformations of the central metal atom, as observed, for example, in the case of many porphyrin complexes [1]. However, the close locations of the potentials of maxima II on the potentiodynamic curves obtained on electrodes modified by complexes of different metals and by the triazepine make this assumption unlikely.

The conclusions presented above are confirmed by the data presented by Sharp [4], who demonstrated in the case of two isomers the existence of a reversible redox process in the modification of the carbon surface by 1-amino-9,10-anthraquinone, which is capable of orienting itself parallel to the electrode surface, and the absence of pronounced redox processes in modification of the surface by 2-amino-9,10-anthraquinone, which is not capable of this orientation.

In the case of complex VII we compared the electrochemical behavior as a function of the method of modification of the electrode surface. We used intermediate treatment of the electrode with thionyl chloride with subsequent application of complex VII at room temperature (complex VIIa) and at 390 K (complex VIIb). We showed that the temperature at which modification is carried out is of great significance. Complex VIIa, in contrast to complex VII, initially exists in an electrochemically inactive state. Polarization of this electrode at the cathode potentials makes it possible to convert the complex to an electrochemically active state: two cathode and two anode maxima (0.57/0.69 and 0.48/0.55 V), which vanish in the case of anode polarization at 1.2 V, are observed on the potentiodynamic curve. This character of the electrochemical behavior, which coincides qualitatively with the behavior of complexes II-V, constitutes evidence that chemical attachment of the complex under the given conditions occurred only via one of the side amino groups. The shift of the potentials of maxima II for complex VIIa, as compared with complex VII, to the cathode side indicates that under these modification conditions the amino group may react not only with a surface acid chloride group but also partially with the >C—Cl group. This gives rise to redistribution of the electron density in such a way (by increasing the effective charge density of the conjugated system) that the oxidized form of the complex is stabilized. Anode polarization leads to cleavage of the bond and causes desorption of the complex, as in the case of complexes II-V.

Complex VIIb, attachment of which was realized at 390 K, behaves differently. On the very first part of the curve one can detect reversible maxima at potentials of 0.32/0.37 V. It might be assumed that in this case the reaction of the side amino groups proceeds preferably with the surface >C—Cl and >C—OH groups and is realized for both side groups, which gives rise to a stronger (as compared with VIIa) shift of maxima II to the cathode side. In contrast to VIIa, anode polarization of the electrode does not lead to disappearance of these maxima even in the case of prolonged maintenance at a potential of 1.4 V. A reversible maximum at 0.68/0.76 V, which is close to maximum II of complex VII (Table 1), additionally appears in this case; this may be associated with migration of the bridge bond to a surface carboxylate group.

Thus, the electrochemical properties of the complexes of the investigated series depend substantially on the presence of side groups and their nature, as well as on the method used to apply complexes containing $R^1$, $R^2 = NH_2$ to the electrode surface. These factors determine the possibility and conditions for conversion of the complex to an electrochemically active state as a result of fixing the necessary orientation of the complex on the surface. Chemical and electrochemical methods for modification of the electrode surface lead to the formation of rather stable electrochemically active coatings over the range of potentials determined by the nature of the bonds of the side substituents of the investigated complexes with surface groups of pyrographite and the nature of the central metal ion.

## EXPERIMENTAL

Complex I was synthesized by the method in [5], macrocyclic compounds II-IX were obtained by the method in [6], and triazepine derivative XI was synthesized by the method in [7].

The pyrographite electrode (a new one for each experiment) in the form of a 5 × 10 mm plate obtained by spallation was purified by refluxing in alkali for 15 min with subsequent repeated refluxing in twice-distilled water. It was then activated by cathode-anode polarization over the range −0.2 to 1.4 V. A solution of the complex in acetone ($5 \cdot 10^{-9}$ mole) was applied to the electrode surface, and the electrode was dried at room temperature. Chemical modification of the surface was carried out as follows. The pyrographite electrodes, which were previously purified by refluxing in alkali, were acylated in $SOCl_2$ at the boiling point for 2 h. After drying in a vacuum desiccator over $H_2SO_4$ for 12 h, the electrodes were transferred to a solution of the diamino complex of Ni (complex VII) in dimethylformamide (DMFA), in which the Cl atoms of the surface groups of the modified pyrographite electrode were replaced by amino groups of the complex. Modification by the complex was carried out for 4 h at 300 K (complex VIIa) and 390 K (complex VIIb), after which the electrodes were washed thoroughly with benzene and chloroform and refluxed in methanol for 5 h.

The measurements were made in a phosphate—alkali buffer solution ($\mu = 0.15$, pH 7.5). The buffer solution was prepared from twice-distilled water, very pure-grade NaOH, and recrystallized $KH_2PO_4$.

The electrochemical measurements were made by imposition of potentiodynamic triangular pulses [8] with the aid of a potentiodynamic device developed in the A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, in a three-electrode glass cell with separated electrode spaces at a potential imposition rate of 0.1 V/sec. All of the potentials were reduced relative to the potential of a hydrogen electrode in the same solution.

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# SYNTHESIS AND STRUCTURE OF 1-BENZOYL-2,5-DIMETHYL- AND 1,2,5-TRIMETHYL-4-ARYLPIPERIDEINS

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Isomeric 1-benzoyl-2,5-dimethyl-$\Delta^3$-piperidein and 1-benzoyl-2,5-dimethyl-$\Delta^4$-piperidein were prepared from disubstituted γ-piperidols and were hydroxylated with osmium tetroxide. The isomeric 1,2,5-trimethyl-4-(p-nitrophenyl)-$\Delta^3$- and -$\Delta^4$-piperideins were obtained from trisubstituted γ-piperidols.

Some piperideins are known to exhibit physiological activity; a related compound, the alkaloid phecolin, for example, is used in medicine. In our laboratory, piperideins, prepared by the dehydration of disubstituted and trisubstituted γ-piperidols, are intermediates in the synthesis of pyridine bases [1, 2]. However, very little is known about the structure (position of the double bond) of these piperideins.

We have synthesized a number of piperideins in order to determine their structure and to study their biological action. A mixture of isomeric substituted γ-piperidols, obtained by benzoylation of a mixture of the isomers of 2,5-dimethylpiperidin-4-ol, was used for the synthesis. At this stage in the synthesis of 1-benzoyl-2,5-dimethylpiperidin-4-ol (I), we obtained information on the spacial structure of one of its isomers, isolated as a crystalline material with mp 131-133°C. Its configuration and conformation were determined by $^1$H and $^{13}$C NMR, and also by x-ray structural analysis.

The $^1$H NMR spectrum showed a quadruplet with coupling constant 3.5 Hz ($H_{3a,4} \approx J_{3e,4} \approx J_{4,5}$) for the proton at the 4-position. This, together with the absence of large (>3 Hz) coupling constants for the 6a and 6e protons allows the substituents at $C_{(4)}$ and $C_{(5)}$ to be assigned axial positions. The coupling constants for the $C_{(2)}$ proton ($J_{3a,2}$ = 6.4 Hz and $J_{3e,2}$ = 2.7 Hz) are considerably lower than typical values, such as those for 2,6-diphenyl- and dimethyl-derivatives of piperidol-4 with equatorially disposed substituents [3]. This agrees with the report [4] that in 1-benzoyl-2-methyl- and 1-benzoyl-cis-2,6-dimethylpiperidines, the methyl groups occupy axial positions due to spatial overlap of the 2e-methyl and phenyl groups on rotation around the N—C amide bond. Thus, all three substituents have the axial orientation and compound I has the configuration 4r-OH, 2c-$CH_3$, 5t-$CH_3$.

The $^{13}$C NMR spectra of compound I confirm this conclusion. The difference between experimentally obtained $\delta_e$ and the theoretically expected $\delta_t$ values for the piperidine ring carbon atoms are as follows:

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