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ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS. XCI. POLAROGRAPHIC STUDIES ON VARIOUS TYPES OF DIOXIMINE COMPLEXES OF COBALT(III)

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Abstract

The polarographic behaviour of some dioximine chelates of cobalt(III) (α-dioxime: Diox.H_2, DH_2-dimethylglyoxime, Nyox.H_2=nyoxime, Heptox.H_2=heptoxime):$[Co(DH)_2(amine)_2]^+$, $[Co(Nyox.H)_2(amine)_2]^+$, $[Co(Diox.H)_2XY]^-$(X, Y=Cl, Br, I, NO_2, N_3, CN), $[Co(DH)_2(SO_3)(amine)]^-$, (alkyl-$Co(DH)_2$ (amine) were studied at various pH-values (cathodic reductions and in some cases also anodic oxidations).

The Co(II)-nyoxime system and the formation of $[Co(Diox.H)_2en]^-$ by the substitution reactions of 1,2- and 1,6-$[Co(en)_2Cl_2]^+$ and $[Co(en)_2Cl(H_2O)]^{2+}$ with α-dioximes were studied in this way.

Keywords: polarography, cobalt(III) dioximine complex.

Introduction

In our previous paper [1] the reduction on the dropping mercury electrode of some cobalt(III) complexes with ethylenediamine was studied and the character of the two reduction waves (Co(III)+e=Co(II) and Co(II) ligand +2e=Co(0)) were discussed on the basis of literature data [2–4].

It was mentioned that on the polarograms of the $Co(C_2O_4)_3^{3-}$ and $Co(EDTA)(H_2O)^-$ only a single step appears (Co(III)→Co(II))[5], and some cyano-complex acids of Co(III) are reduced in a single two-electron irreversible wave (Co(III)→Co(I)) [6–7].

In the present paper various types of Co-dioximine complexes: bases, acids, organyl- cobalt- oximes and some substitution reactions of cobalt(III)-amines with oximes were studied by polarography.

Results and Discussion

α-dioximes are reduced at the dropping mercury electrode in a multielectronic process, depending on the pH of the supporting electrolyte. The polarograms of nyoxime (1,2-cyclohexane dione dioxime) at various pH-values are presented in *Fig. 1*.

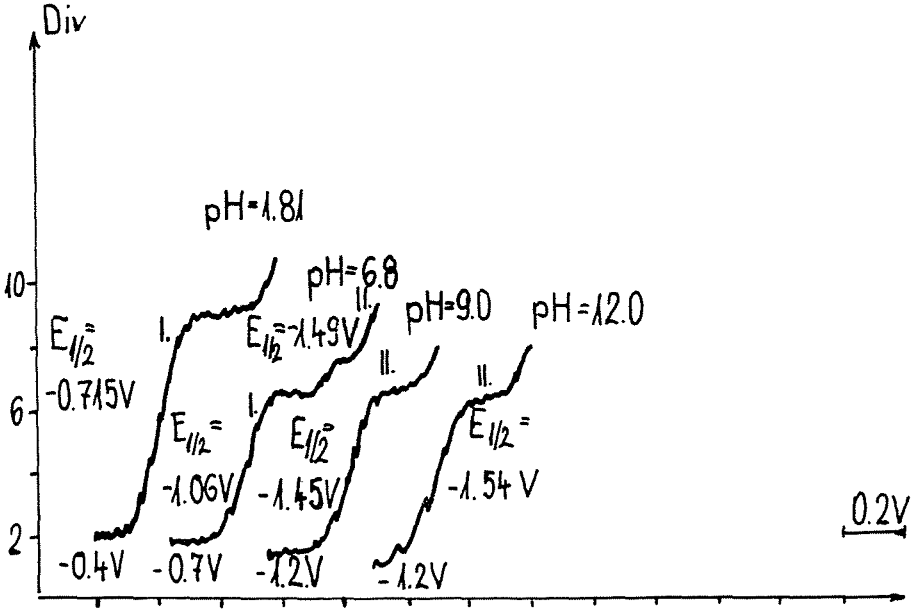
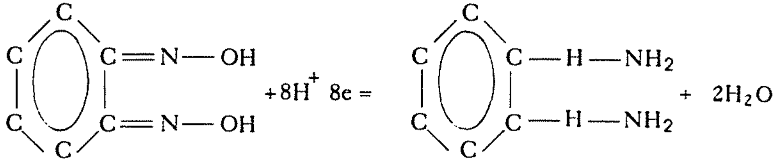


Fig. 1. Polarograms of nyoxime at various pH-values $[Nyox.H_2]=4 \times 10^{-4}$ mol/l; Britton–Robinson buffer solution; Supporting electrolyte: $[NaClO_4]=0.1$ mol/l. Sensitivity: 8×10^{-8} A/Div

The well formed curves are in agreement with an eight-electron reduction process according to the equation



In acidic medium a partial desoximation process takes place with the formation of a new wave (α-keto-oxime).

This phenomenon can be used for the determination of the kinetic parameters of the mentioned process [8–10].

1. The Co(II)-nyoxime System

If a cobalt(II) salt ($CoCl_2$, $CoSO_4$) is added to the solution of nyoxime in a molar ratio Co:oxime=1:2, in a borax buffer, the $[Co(Nyox.H)_2(H_2O)_2]$ chelate is formed (brown solution). This is also reduced polarographically at a half-wave potential of –1.10 V (vs. SCE), a more positive value as compared with that of the free nyoxime in analogous experimental conditions (–1.45 V vs. SCE). The height of the wave shows that besides the $Co(II)+2e=Co(0)$ process, the partial or total reduction of the co-ordinated oxime ligands takes place, too.

In a previous paper [1] we have mentioned that the hexamminecobalt(III) complexes ($[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5(H_2O)]^{3+}$, $[Co(en)_3]^{3+}$), are inert to substitution reactions with α-dioximes. The first one-electron polarographic wave of these complexes [Co(III)→Co(II)] is not modified in the presence of the mentioned chelating agents. However, the second one is changed substantially, its height being greater than that of the wave corresponding to a two-electron electrode process [Co(II)→Co(0)], due to the simultaneous reduction of the co-ordinated oximes. An analogous phenomenon can also be observed in the polarographic behaviour of the above mentioned $CoCl_2$-nyoxime system (In both cases $E_{1/2}$=–1.10 V vs. SCE).

2. $[Co(en)_2Cl_2]^+$($[Co(en)_2Cl(H_2O)]^{2+}$)-nyoxime systems

The polarograms of cis- and trans-$[Co(en)_2Cl_2]$.Cl, and cis-$[Co(en)_2Cl\ (H_2O)]Cl_2$ in borax buffer solutions were taken 10 minutes after the preparation of the solutions in the absence or presence of nyoxime (molar ratio 1:2), respectively. Using samples without nyoxime the half-wave potentials of the first wave [Co(III)→Co(II)] vary between –0.10 and –0.35 V (vs. SCE). In the presence of nyoxime in all cases the same $E_{1/2}$ value –0.75 and –0.75 V (vs. SCE) is obtained irrespective of the nature of the starting chloro-complex.

This reduction step appears as an extended irreversible wave with a much greater height than that corresponding to a one-electron reduction step.

In *Fig. 2* the polarograms of the trans-$[Co(en)_2Cl_2]$.Cl and $[Co(en)_2Cl(H_2O)]Cl_2$ in the absence and presence of nyoxime are presented.

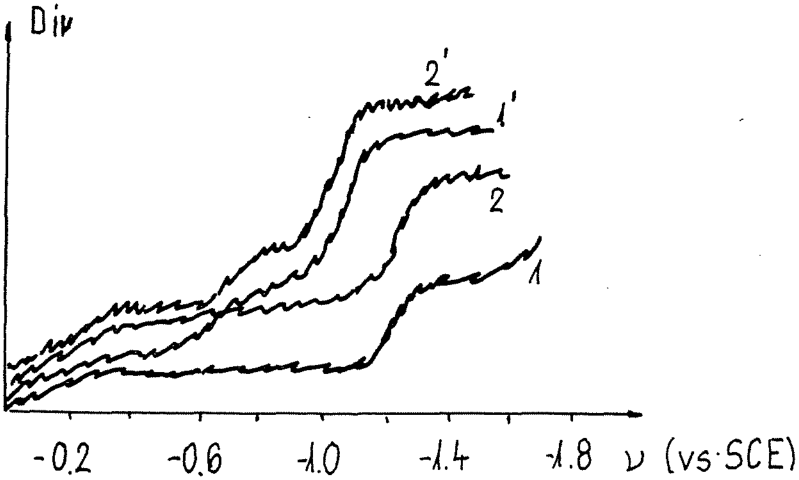


Fig. 2. 1, 1′-polarograms of trans-$[Co(en)_2Cl_2]^+$in the absence and in the presence of nyoxime, respectively
2, 2′-polarograms of cis-$[Co(en)_2Cl(H_2O)]Cl_2$ in the absence and in the presence of nyoxime, respectively
[Complex]=2×10^{-3} mol/l; supporting electrolyte K_2SO_4+ borax; maximum suppressor: gelatine 0.04 %

This means that unlike the hexammines, the dichloro- and aquo-chloro-Co(III) complexes undergo a substitution reaction with oximes and the product of this process is the same chelate, irrespective of the nature and geometric configuration of the starting material.

This phenomenon was confirmed by our earlier spectrophotometric studies on the kinetics and mechanism of this reaction [11]. In all cases a yellow solution ($[Co(Nyox.H)_2en)]^{2+}$) was formed from the green trans-$[Co(en)_2Cl_2]Cl$, the violet cis-$[Co(en)_2\ Cl_2]Cl$ and the reddish violet $[Co(en)_2\ Cl(H_2O)]Cl_2$.

The second wave [Co(II)→Co(0)+ nyoxime] has an $E_{1/2}$ value of −1.10 V (vs. SCE) like the $CoCl_2$-nyoxime system showing an identical reduction mechanism on the dropping mercury electrode.

3. $[Co(Diox.H)_2(amine)_2]$.Cl

The polarograms of a series of chelates of this type with dimethylglyoxime, nyoxime and heptoxime and with 'amine'-aromatic and heterocyclic

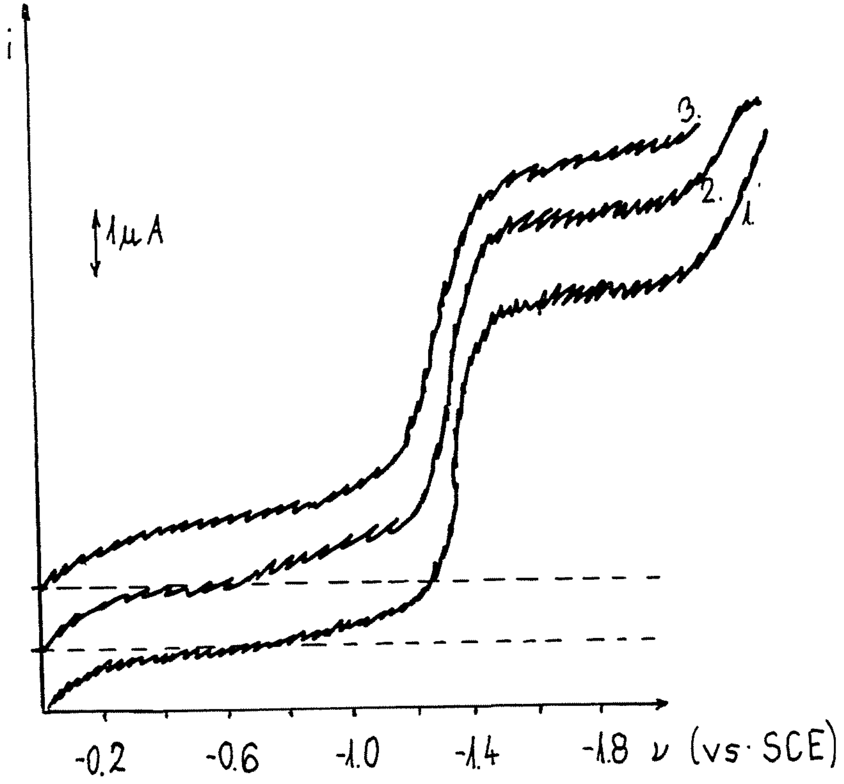


Fig. 3. Polarogram of
1 — $[Co(DH)_2(p\text{-toluidine})_2]Cl$
2 — $[Co(Nyox.H)_2(aniline)_2]Cl$
3 — $[Co(Heptox.H)_2(aniline)_2]Cl$
Supporting electrolyte: K_2SO_4+ borax ... 0.1 mol/l
Maximum suppressor: gelatine 0.04 %

amines, were taken in 0.1 M K_2SO_4-borax buffer solutions (pH=9.0) Some typical polarograms are presented in *Fig. 3*.

The half-wave potential of the first wave cannot be determined exactly being situated between –0.15 and –0.70 V (vs. SCE). This reduction step is very badly formed, irrespective of the nature of components in the inner co-ordination sphere of the mentioned complexes. The second wave [Co(II-Co(0)+ oxime] shows a well defined reduction step with $E_{1/2}$=–1.13 – –1.14 V (vs. SCE), as in the case of the $CoCl_2$-nyoxime, $[Co(en)_2Cl_2].Cl$

+ nyoxime systems. This phenomenon is an argument for an identical mechanism of the reduction of cobalt-dioximine complexes under the above mentioned experimental conditions.

The experimental data are presented in *Table 1*.

Table 1

Polarographic data for some $[Co(Diox.H)_2(amine)_2]Cl$ type complexes

Compound	E^{I}	$E^{II}_{1/2}$
$[Co(DH)_2(aniline)_2]Cl$	-0.15..0.70	-1.13 V
$[Co(DH)_2(o\text{-}phenetidine)_2]Cl$	-0.20..0.70	-1.13 V
$[Co(DH)_2(p\text{-}phenetidine)_2]Cl$	-0.15..0.75	-1.15 V
$[Co(DH)_2(o\text{-}toluidine)_2]Cl$	-0.08..0.70	-1.13 V
$[Co(DH)_2(p\text{-}toluidine)_2]Cl$	-0.10..0.65	-1.14 V
$[Co(Nyox.H)_2(aniline)_2]Cl$	-0.20..0.70	-1.15 V
$[Co(Nyox.H)_2(p\text{-}toluidine)_2]Cl$	-0.10..0.65	-1.16 V
$[Co(Heptox.H)_2(aniline)_2]Cl$	-0.10..0.75	-1.14 V

In comparison with the polarographic behaviour of the free oxime, one can observe that the oxime groups co-ordinated to the cobalt atom are reduced more easily (at more positive potential values) as compared with the free oxime at identical pH-values. The increased heights of the second waves are in agreement with this presumption.

4. $[Co(DH)_2(SO_3)(amine)]^-$ Complexes

The polarograms of some sulphito-amine-bis-dimethyl-glyoximato-Co(III) complexes, obtained by substitution reactions from $NH_4[Co(DH)_2(SO_3)(H_2O)]$ and the corresponding aromatic and heterocyclic amines [12,13] were recorded in supporting electrolytes at pH=7.0 (Britton–Robinson buffer solutions).

The first wave [Co(III)→Co(II)] appears as a flat step at –0.15..–0.40 V (vs. SCE), followed by a well formed wave, with $E_{1/2}$=–0.75–0.80 V (vs. SCE). The latter wave is probably due to the partial reduction of the chelating agent in the presence of the SO_3-group.

As compared with the polarograms of the $[Co(DH)_2(amine)_2]X$ type complexes, the wave with an $E_{1/2}$ value of –1.10..–1.15 V (vs. SCE) corresponds to the simultaneous reduction of the co-ordinated dioximes and of the Co(II) to Co(0).

The $[Co(DH)_2(amine)_2]^+$ and $[Co(DH)_2(SO_3)(amine)]^-$ complexes are very inert to substitution reactions in neutral medium. Their

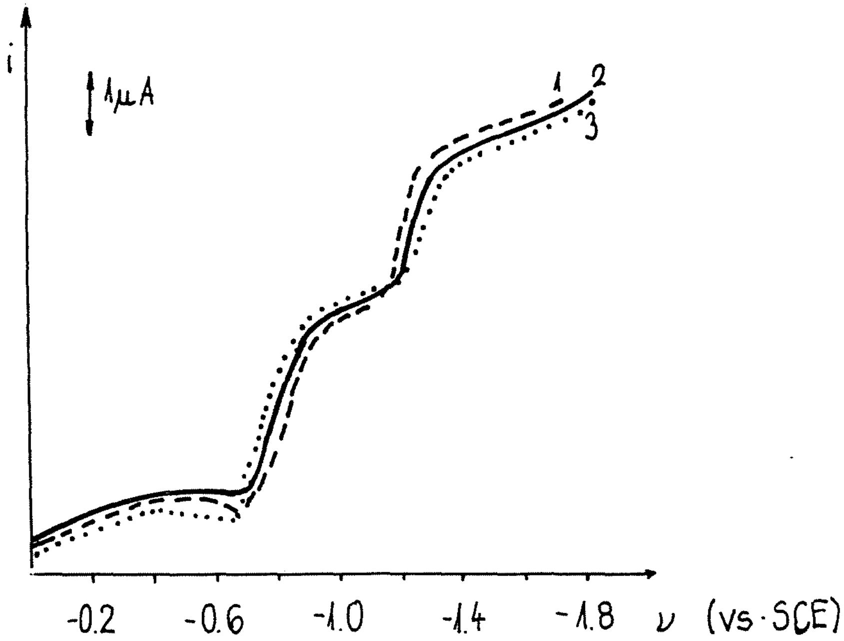


Fig. 4. Polarogram of
1 — $[Co(DH)_2(SO_3)(p\text{-toluidine})]^-$
2 — $[Co(DH)_2(SO_3)(p\text{-anisidine})]^-$
3 — $[Co(DH)_2(SO_3)(pyridine)]^-$
Supporting electrolyte: Britton–Robinson buffer, pH=7.00,
Maximum suppressor: gelatine 0.04 %

10^{-3} mol/l solutions at pH=7.0 show no change in the polarographic behaviour even 48 hours after dissolution.

In acidic media (pH≤1.8) an important change has been observed. At –0.40 V (vs. SCE), there appears a well defined wave corresponding to the reduction of the evolved SO_2 liberated on the acidification of the solution. In this case the polarograms of all $[Co(DH)_2(SO_3)(amine)]^-$ type complexes are similar and the Co(III)→Co(II) step is superimposed on the SO_2-wave. The height of the SO_2-mixed wave increases on addition of Na_2SO_3.

The polarograms of Na_2SO_3 solution at three different pH-values are represented in *Fig. 6*.

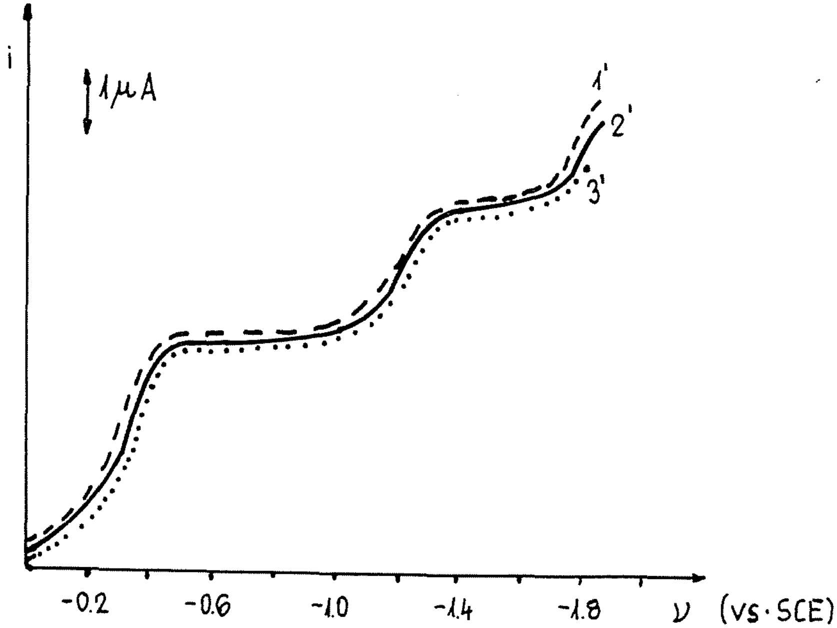


Fig. 5. Polarogram of
1′ — $[Co(DH)_2(SO_3)(p\text{-toluidine})]^-$
2′ — $[Co(DH)_2(SO_3)(p\text{-anisidine})]^-$
3′ — $[Co(DH)_2(SO_3)(pyridine)]^-$
Supporting electrolyte: Britton–Robinson buffer, pH=1.81
Maximum suppressor: gelatine 0.04 %

As seen from *Fig. 6*, the height of the SO_2-wave decreases with increasing pH. In acidic medium, at pH=1.80, the sulphito-wave is well formed.

One can expext the sulphito-ligand to be exchanged by water:

$$[Co(DH)_2(SO_3)(amine)]^- + 2H^+ = [Co(DH)_2(H_2O)(amine)]^+ + SO_2.$$

The hydration occurs rapidly and the mixing time of the sulphito-complex solution with the acidic supporting electrolyte is enough for a quantitative reaction. It is possible that the protonation of the sulphito-ligand by acidification ($-HSO_3$ formation) facilitates the breakage of the Co–SO_3 bond [14].

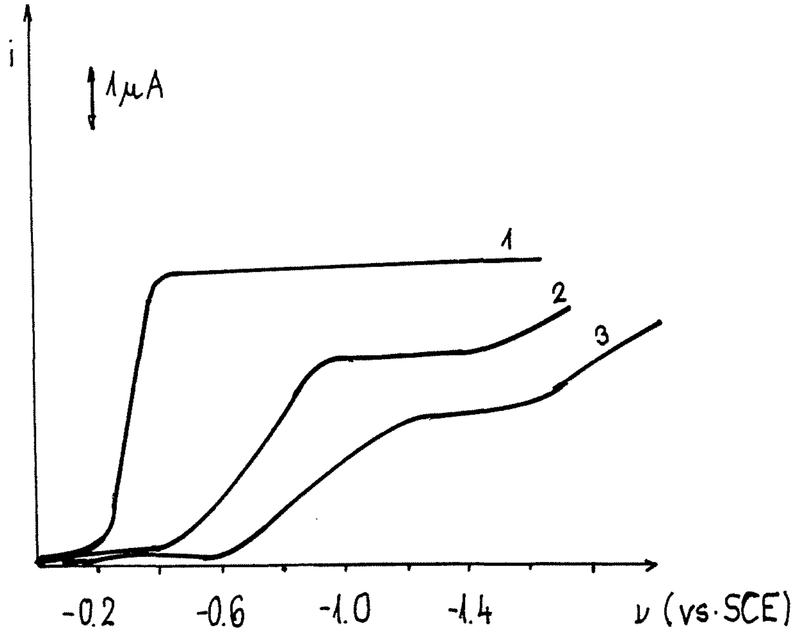


Fig. 6. Polarograms of Na_2SO_3
$[Na_2SO_3]=2 \times 10^{-3}$ mol/l, Britton–Robinson buffer,
Maximum suppressor: gelatine 0.04 %
1—pH=1.81, 2—pH=2.4, 3—pH=3.0

5. $[Co(DH)_2XY]^-$ and $[Co(Niox.H)_2XY]^-$ Complexes

From the monobasic complex acids of this type some derivatives with X,Y=Cl, Br, I, N_3, NO_2 were studied by polarography.

Cathodic Reductions

Some typical polarograms taken at various pH-values (pH=3.29, 5.02, 7.96) are presented in *Figs.* 7 and 8.

The cathodic waves generally consist of two steps in acidic media. The first wave with $E_{1/2}$=–0.70..–0.80 V (vs. SCE) corresponds to the simultaneous reduction of Co(III) to Co(II) and to the partial reduction

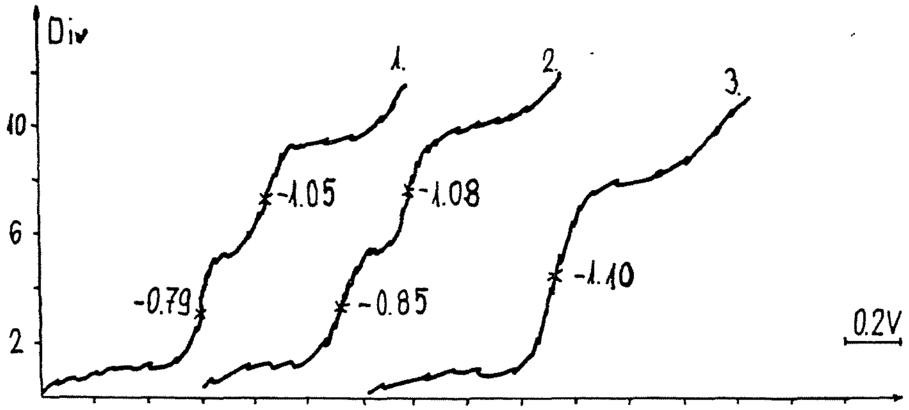


Fig. 7. Polarograms of $H[Co(DH)_2(N_3)_2]$ in Britton–Robinson buffer solutions; Maximum suppressor: gelatine 0.05 %
1—pH=3.29, 2—pH=5.02, 3—pH=7.96

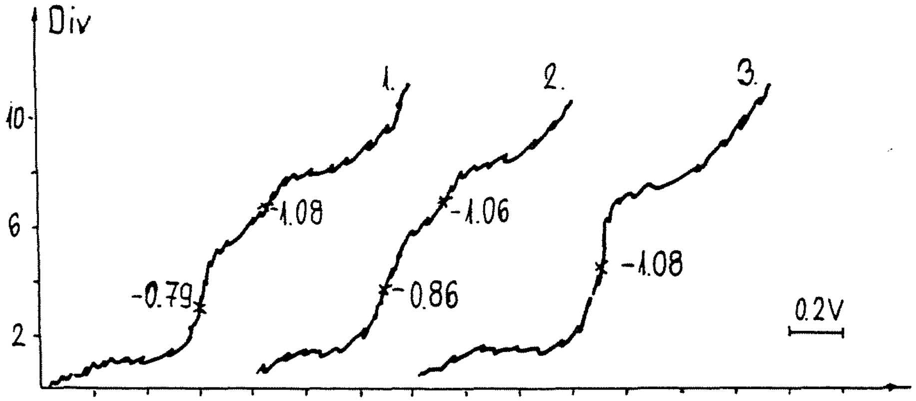


Fig. 8. Polarograms of $H[Co(Heptox.H)_2(N_3)_2]$ in Britton–Robinson buffer solutions; Maximum suppressor: gelatine 0.05 %
1—pH=3.29, 2—pH=5.02, 3—pH=7.96

of the dioximes facilitated by the presence of N_3^- or NO_2^- groups. The height of this wave is much greater than that corresponding to a one-electron electrode process. In slightly alkaline media (e. g. pH=7.96) the first wave is very allonged, between –0.4..–0.8 V (vs. SCE), with a small height. Probably the reduction of the co-ordinated dioximes does not take place under these conditions.

In the case of the nitro-derivative, the situation is more complicated due to the simultaneous reduction of Co(III), the NO_2-group and the co-ordinated chelating agent. This phenomenon is reflected by the increased height of the mentioned first wave.

The second wave at –1.08..–1.10 V (vs. SCE), similarly to the $[Co(Diox.H)_2(amine)_2]^+$, $[Co(Diox.H)_2(SO_3)(amine)]^-$ and $CoCl_2$-Diox.H_2 systems, indicates the simultaneous reduction of Co(II)→Co(0) and the dioximine ligands.

Anodic Oxidations

DRUDING et al. [15] observed that the co-ordinated azide can be determined in the presence of free azide ion by anodic oxidation on the dropping mercury electrode, based on the observation that the co-ordinated azido-groups are oxidized more easily ($E_{1/2}$=+0.11..+0.17 V (vs. SCE) than the free ones ($E_{1/2}$=+0.200..+0.270 V (vs. SCE) [16, 17]. (e. g. $[Co(NH_3)_5(N_3)]^{2+}$, $[Co(en)_2(N_3)_2]^+$, etc.).

We studied the anodic oxidation of the mixed azido-derivatives: $Na[Co(DH)_2(N_3)_2]$, $Na[Co(Nyox.H)_2(N_3)_2]$, $Na[Co(Heptox.H)_2(N_3)_2]$ and $Na[Co(DH)_2X(N_3)]$ (X=Cl,Br,I), respectively.

The polarographic measurements were carried out in 0.1 mol/l $NaClO_4$ supporting electrolyte without maximum suppressor.

The anodic oxidation of the diazido-derivatives begins in the negative range of polarization at –0.100 V (vs. SCE).

The anodic wave with $E_{1/2}$=+0.055 (0.060, 0.062 V) (vs. SCE) is well formed. The height of the anodic wave increases linearly with the concentration of the diazido-complexes in the concentration range of 10^{-4} – 10^{-3} mol/l.

The polarograms of the $5 \cdot 10^{-4}$ mol/l solutions of $[Co(Diox.H)_2(N_3)_2]^-$ complexes (Diox.H=DH, Nyox.H, Heptox.H) are presented in *Fig. 9 a, b* and *c*.

Curves a′, b′ and c′ in the figure represent the polarograms of the mentioned complexes in the presence of equal quantity of free NaN_3 ($5 \cdot 10^{-4}$ mol/l). In the latter cases a second, well defined wave appears ($E_{1/2}$=+0.270 V vs. SCE). The height of this second wave is approximately

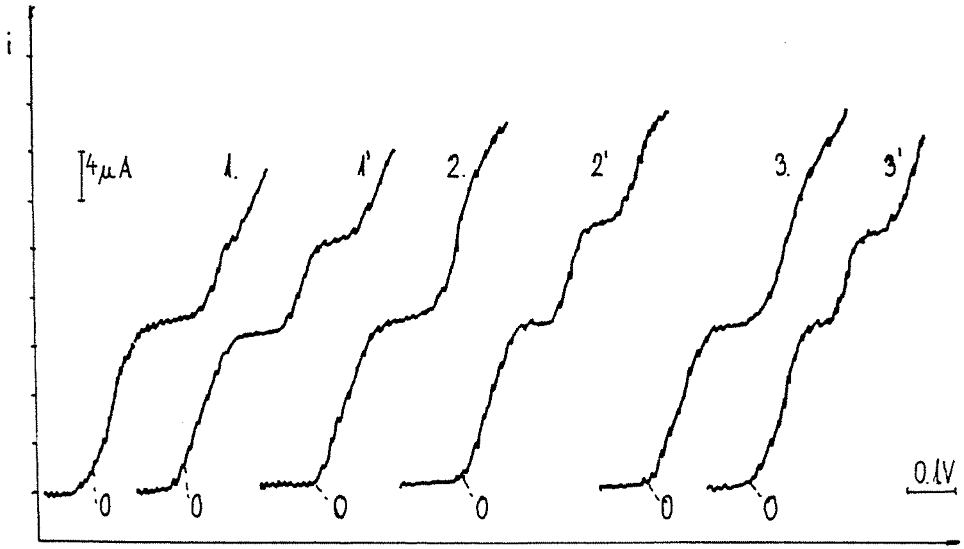


Fig. 9. Polarogram of
1 — $Na[Co(DH)_2(N_3)_2]$
1′ — $Na[Co(DH)_2(N_3)_2]+NaN_3$
2 — $Na[Co(Nyox.H)_2(N_3)_2]$
2′ — $Na[Co(Nyox.H)_2(N_3)_2]+NaN_3$
3 — $Na[Co(Heptox.H)_2(N_3)_2]$
3′ — $Na[Co(Heptox.H)_2(N_3)_2]+NaN_3$
[Complex]: $5 \cdot 10^{-4}$ mol/l; $[NaN_3]$: $5 \cdot 10^{-4}$ mol/l
Supporting electrolyte: $[NaClO_4]$ 0.1 mol/l

half that of the first one. This means that the first wave corresponds to the oxidation of the co-ordinated azide and the second to that of the free one. The presence of two dioximine ligands bonded in the equatorial plane of the $[Co(Diox.H)_2(N_3)_2]^-$ octahedral complexes facilitates the oxidation of the trans-situated N_3-ligands, as compared with free N_3^-.

The azido-groups do not undergo aquation reactions on standing in aqueous solutions. The polarograms remain unchanged even after 5–6 h.

The co-ordinated azido-group remains unaltered also in the case of $[Co(DH)_2(N_3)X]^-$ (X=Cl, Br, I), but the co-ordinated halogens undergo an aquation process with a measurable reaction rate.

The polarograms of a $5 \cdot 10^{-4}$ mol/l solution of $[Co(DH)_2(N_3)Cl]^-$ were run immediately after dissolution of the sample or after standing for 0.5, 1 and 2 hours, respectively. Under these conditions two distinct waves appear with $E_{1/2}=+0.65$ V and +0.280 V (vs. SCE), respectively. The height of the first wave is half that of the $[Co(Diox.H)_2(N_3)_2]^-$ derivatives. This wave appears due to the oxidation of the co-ordinated azido-group. The height of the second wave increases with time and equals the first one after two hours, in the case of $[Co(DH)_2(N_3)Br]^-$ after 3–3 1/2 hours and for $[Co(DH)_2(N_3)I]^-$ only after 5–5 1/2 hours. The rate of the halogen exchange is smaller in the latter cases. This means that the second wave appears during the equation of the $[Co(DH)_2(N_3)X]^-$ leading to the liberation of halogen ions.

The anodic oxidation of the free halogen ions is responsible for the appearance of this wave. The co-ordinated bonded halogens cannot be oxidized in this way.

It is worth mentioning that the anodic oxidation of mercury under these experimental conditions, in the absence of complexing anions for this metal begins at +0.400 V (vs. SCE).

The oxidation of the co-ordinated N_3-ligands in the mentioned mixed cobalt(III)-chelates occurs without a change in the oxidation state of the central cobalt(III) ion.

The polarograms of $[Co(DH)_2(N_3)Cl]^-$ after dissolution and after 0.5 and 2 hours of standing, respectively, are presented in *Fig. 10*.

6. Cobalt-dioximine Complexes with Co–C σ-bonding

The polarographic behaviour of the cobalt complexes with Co–C σ-bonding differs significantly from that of the classical cobalt(III) complexes and chelates.

For example the cyano-complexes $[Co(CN)_5(H_2O)]^{2-}$ and $[Co(CN)_5X]^{3-}$ are reduced in a two-electron process to Co(I) in a single irreversible wave [18–20], [6,7].

We have taken the polarograms of some cyano-dioximine chelates ($H[Co(Diox.H)_2(CN)_2]$; Diox.H_2-dimethylglyoxime, nyoxime and heptoxime) and of the organyl-cobalt.dioximines: $[CH_3\text{-}Co(DH)_2(\text{pyridine})]$ and $[n\text{-}C_3H_7\text{-}Co(DH)_2(\text{triphenylphosphine})]$ in aqueous solution at pH=5.02 and 9.62, respectively.

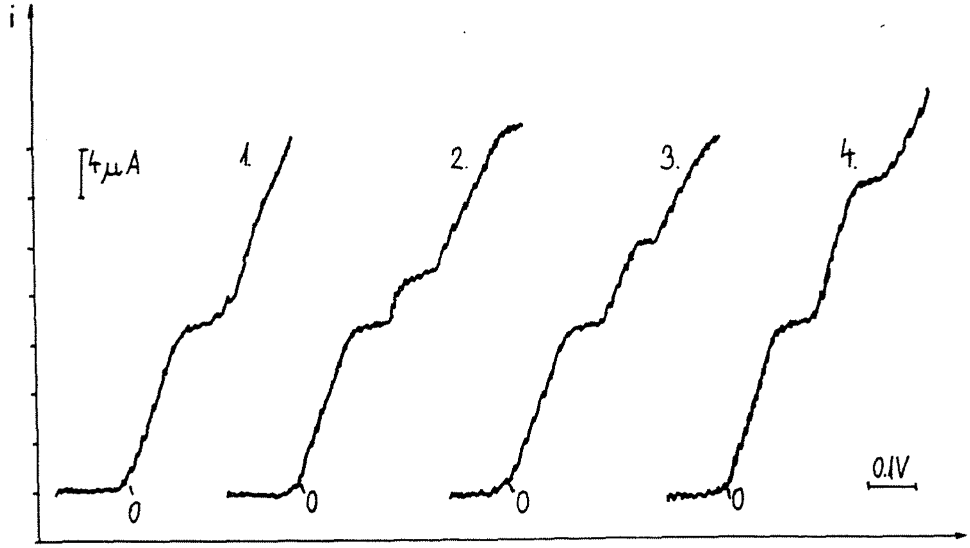


Fig. 10. Polarogram of Na[Co(DH)$_2$(N$_3$)Cl]: $5 \cdot 10^{-4}$ mol/l
1 — after dissolution
2 — after 0.5 h standing
3 — after 1.0 h standing
4 — after 2.0 h standing
Supporting electrolyte: [NaClO$_4$] : 0.1 mol/l

The polarograms in *Fig. 11* show a single two-electron step: Co(III)→ Co(I) with an $E_{1/2}$ value of −1.10 V (vs. SCE). Generally, the Co(I) derivative formed is a polarographically inactive species.

The two-electron reduction step on the dropping mercury electrode (M(III)+2e=M(I)) appears also on the polarograms of the hydrated rhodium(III) salts ($Rh(H_2O)_6^{3+}$) and of various classical rhodium(III) complexes and chelates with NH$_3$, en, dioxime, etc. ligands.

$$\mathrm{Rh(III)+2e = Rh(I)} \tag{1}$$

$$\mathrm{Rh(I)+e = Rh(0)} \tag{2}$$

In the case of the dioximine chelates of the type $[Rh(Diox.H)_2X_2]^-$ the electrode process is more complicated due to the multielectronic reduction

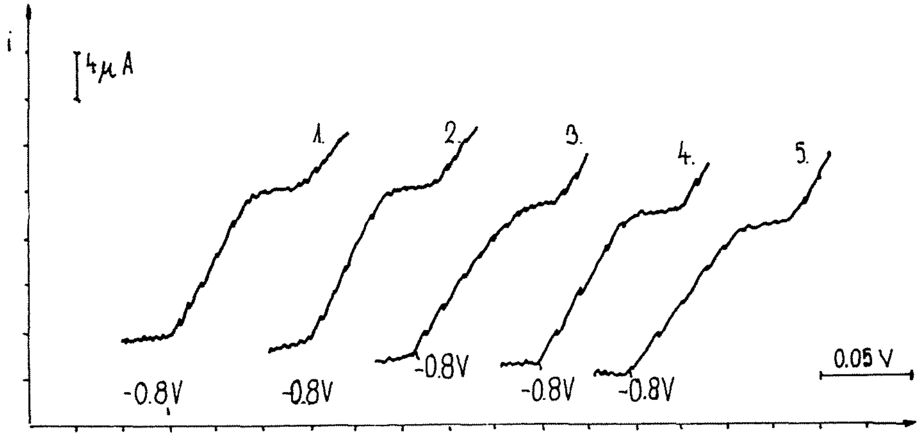


Fig. 11. Polarogram of
1 — $H[Co[DH)_2(CN)_2]$
2 — $H[Co(Nyox.H)_2(CN)_2]$
3 — $H[Co(Heptox.H)_2(CN)_2]$
4 — $[CH_3\text{-}Co(DH)_2\text{-}Py]$
5 — $[i\text{-}C_3H_7\text{-}Co(DH)_2\text{-}Ph_3P]$
$[\text{Complex}]=3 \cdot 10^{-4}$ mol/l
Supporting electrolyte: Britton–Robinson buffer solutions: pH=5.02
Maximum suppressor: gelatine 0.05 %

of the chelating agent simultaneously with the Rh(III)→Rh(I) step. In some cases a third wave also appears at more negative potential values [19–22].

ADDISON et al. [23], and VLCEK [24–25], comparing the polarographic behaviour of some mono- and binuclear complexes of Co(III), Rh(III) and Ir(III), have found that with identical co-ordination sphere composition, the cobalt(III) derivatives can be reduced most easily due to their greatest electron affinity.

Experimental

$[Co(Diox.H)_2(amine)_2]Cl$, $Na[Co(Diox.H)_2(N_3)_2]$ were obtained by the oxidation of the mixture of the components $CoCl_2$, -Dioxime, amine (NaN_3) in dilute alcohol by air bubbling. (molar ratio= Co:Diox.H_2:L=1:2:3).

The compounds $Na[Co(DH)_2(N_3)X]$ (X=Cl, Br, I) are formed from $H[Co(DH)_2X_2]$ by a substitution reaction with NaN_3 (molar ratio= 1:1) in dilute alcohol [26, 27].

$H[Co(Diox.H)_2(CN)_2]$ were obtained from $[Co(Diox.H)_2Cl(H_2O)]$ by a substitution reaction with KCN (molar ratio=1:2.2) and precipitated with an excess of 20 % HCl.

$NH_4[Co(DH)_2(SO_3)(amine)].3H_2O$ was obtained from $NH_4Co(DH)_2(SO_3)(H_2O)$ and the corresponding amine (molar ratio=1:1.2) in aqueous solution on a water bath and precipitated with an excess of acetone.

$[CH_3\text{-}Co(DH)_2\text{-}(pyridine)]$ and $[i\text{-}C_3H_7\text{-}Co(DH)_2\text{-}Ph_3P]$. These organyl-cobalt(III)-oximines are formed from the solution in methanol of the components, $CoCl_2$, dimethylglyoxime, axial base (Py, Ph_3P) (molar ratio=1:2:2) under CH_4 or H_2 atmosphere. The mixture is cooled to –10 °C and treated with a 50 % excess of NaOH and $NaBH_4$. After reduction the mixture is treated with the alkylation reagent $(CH_3)_2SO_4$ and $i\text{-}C_3H_7.I$ and evaporated on a water bath in air atmosphere.

Polarographic measurements

The polarograms were taken by a Radelkis Type OH-120 polarograph with a Tast-Rapid-OH 9991 adapter to ensure a forced dropping of mercury. A conventional polarographic cell was used with a saturated calomel electrode, connected to the cell by means of an agar bridge (1 mol/l KNO_3). The polarization range of the mercury dropping electrode lies between –1.60 V and +0.50 V vs. SCE. The oxygen was eliminated from the solutions with purified methane.

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