PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 44, NO. 2, PP. 111–122 (2000)

ON THE OXIMINE COMPLEXES OF TRANSITION METALS.
PART CXVIII.
STUDY ON THE PROTOLYTIC EQUILIBRIA IN THE SOLUTIONS OF MIXED CHELATES OF THE TYPE $[Co(Diox.H)_2AB]^n$ WITH ALICYCLIC α-DIOXIMES[1]

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Received: Febr. 11, 2002

Abstract

16 new chelate compounds of the type $[Co(Diox.H)_2AB]^n$ ($Diox.H_2$-alicyclic α-dioxime with $C_5..C_8$ in the hydroaromatic ring, A, B monodentate ligands: NCO^-, NO_2^-, $S_2O_3^{2-}$, NH_3, pyridine, aromatic amine) were obtained by air oxidation of the components and by various substitution reactions, respectively. The complexes were characterized by FTIR spectra. The complicated protolytic equilibria with the participation of the intramolecular O – H..O hydrogen bridges of the $Co(Diox.H)_2$ moieties were studied by spectrophotometric and potentiometric measurements.

Keywords: cobalt(III) mixed complexes, complexes with oximes, FTIR spectroscopy, protolytic equilibria, UV-spectrophotometry.

1. Introduction

Earlier potentiometric studies have shown that the aquo-amine complexes of Co(III) and Cr(III) : $Co(NH_3)_5(H_2O)^{3+}$, $Co(NH_3)_4(H_2O)_2^{3+}$, $Cr(NH_3)_5(H_2O)^{3+}$, $[Co(NH_3)_2(H_2O)_4]^{3+}$, $[Cr(en)_2(H_2O)_2]^{3+}$, etc. exhibit acidic character, which increases parallel with the number of the coordinated water molecules.

The protolytic equilibria of this type, e.g.

$$[Co(NH_3)_5(H_2O)]^{3+} \rightleftarrows [Co(NH_3)_5(OH)]^{2+} + H^+ \qquad (1)$$

were studied by the above mentioned method [1].

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[1] Sponsored by the Soros Foundation

Proton release processes can be observed also in the solutions of ammoniacal complexes of Pt(IV) and Co(III). e.g.

$$[Pt(NH_3)_5Cl]^{3+} + OH^- \rightleftarrows [Pt(NH_3)_4(NH_2)Cl]^{2+} + H_2O \qquad (2)$$

$$[Co(NH_3)_6]^{3+} \rightleftarrows [Co(NH_3)_5(NH_2)]^{2+} + H^+ \qquad (3)$$

The formed amido-complexes were identified in preparative and spectrophotometric ways [2]–[5]. Analogous study was reported also for the trans-$[Co(en)_2(H_2O)_2]^{3+}$ complex [6].

Some metal chelate compounds coordinated with amine derivatives are thought to dissociate the proton reversibly depending on the pH of the solutions. This phenomenon has been observed with Fe(III) complexes of Schiff bases derived from 1,2-diketone-monoximes and amines [7, 8], and in the case of analogous derivatives with methyl-2-pyridyl-ketoximes and pyridine-2-aldoximes, especially for Fe(II),(III), Ni(II), Pd(II) and Pt(II) [9]. The proton dissociation constants (pK_s), corresponding to the above reaction have been also determined [10].

Generally, an oxime group may be expected to increase its tendency to dissociate the proton when coordinated to a transition metal ion, e.g. in the case of the iron (II) and palladium (II) complexes with pyridine-2-aldoxime the pK_a is 5.36 and 4.0, respectively. The free pyridine-2-aldoxime gives $pK_a = 10.22$ to its oxime group.

The α-dioximes form $[Co(Diox.H)_2AB]^n$ type derivatives ($Diox.H_2$ = aliphatic-, aromatic-, and heterocyclic α-dioximes), A and B various monodentate anions and neutral molecules.

The FTIR spectra of these mixed chelates show the octahedral structure to be stabilized with two intramolecular O – H..O hydrogen bondings in the equatorial plane [11].

The first $[Co(DH)_2AB]^n$ type complexes (DH_2 – dimethylglyoxime) were obtained by CHUGAEV [12]. The formation of 'anhydrobases' was observed from the solution of $[Co(DH)_2(amine)_2]^+$ type complexes with NaOH [12]–[15]. e.g.

$$[Co(DH)_2(pyridine)_2]^+ + OH^- \rightleftarrows [Co(DH)(D)(pyridine)_2] + H_2O \qquad (4)$$

('D' – double deprotonated dimethylglyoxime molecule).

This reaction is accompanied by the change of some electronic spectral characteristics and the pH-values of the solutions [16].

Unlike the amino-oxime – and hydroxy-oxime derivatives of the transition metals [7]–[10], in the case of $[Co(Diox.H)_2AB]^n$ complexes the oxime group does not show such a spectacular change of its pK_a values, since in the planar $Co(Diox.H)_2$ moieties both oximic protons are involved in the formation of strong intramolecular hydrogen bridges. Therefore the deprotonation becomes even more difficult than in the case of free oximes.

BIRK et al. [17] presume that the deprotonation in alkaline media is a general process for all dimethylglyoximine complexes of the type $[Co(DH)_2AB]^n$. The reaction is reversible and the starting derivatives are reformed by acidulation of the solutions

$$[Co(DH)(D)AB]^{n-1} + H^+ \rightleftarrows [Co(DH)_2AB]^n. \qquad (5)$$

By total reversible processes the alkaline solutions regain their original spectral characteristics after acidulation. (e.g. $[Co(DH)_2(pyridine)_2]^+$, $[Co(DH)_2(CN)_2]^-$).

ABLOV et al. [16] observed in some cases modifications in the spectral data after acidulation of the mentioned alkaline solutions, due probably to an irreversible aquation process

$$[Co(DH)(D)(amine)_2]^\circ + H_2O = [Co(DH)(D)(amine)(H_2O)]^\circ + amine. \qquad (6)$$

In the case of some reversible changes the equilibrium constants of reaction (4) were also determined.

The proton dissociation of this type was observed also in the case of the analogous $[Co(Dif.H)_2(amine)_2]^+$ derivatives. ($Dif.H_2$ – α-benzyldioxime).

In the present paper the protolytic equilibria in the aqueous solutions of some similar compounds with alicyclic α-dioximes (with $C_5 \ldots C_8$ carbon atoms in the hydroaromatic rings) were studied.

2. Results and Discussion

16 new $[Co(Diox.H)_2AB]^n$ type complexes ($Diox.H_2$– 1,2- cyclopentane-, cyclohexane-, cycloheptane- and cyclooctane dione dioxime; A and B – aromatic amines, NH_3, pyridine, H_2O, NCO^-, NO_2^-, $S_2O_3^{2-}$) were obtained by air oxidation of the components and by various substitution reactions, respectively.

The complexes are characterized in *Table 1*.

The significant FTIR spectral data of some derivatives of this type are presented in *Table 2*.

The shifts of the ν_{O-H}, $\nu_{C=N}$, ν_{N-O} frequencies of the free dioximes and of the KNO_2 towards lower frequency values by coordination prove the strong covalent character of the $Co–N_{ox}$ and $Co–NO_2$ bondings.

We observed that by treating the $[Co(Diox.H)_2AB]^n$ solutions ($c = 10^{-4} - -10^{-5}$ mol/l) with NaOH solutions a colour modification occurs and in more concentrated ones ($c = 2..5.10^{-3}$ mol/l) also crystalline precipitates can be separated. This means that the mentioned protolytic equilibria appear also in the aqueous solutions of the mentioned complexes with alicyclic dioximes.

The pH dependence of the spectral characteristics of these alicyclic dioximine derivatives shows the complexity of this phenomenon. One can presume the following equilibria:

Table 1. New complexes of the type: Co(Diox.H)$_2$AB^n ($A \neq B$ or $A = B$)

Formula	Mol. wt. calc.	Yield (%)	Appearance	Analysis (%)		
					Calcd.	Found
[Co(Pentox.H)$_2$(p – anisidine)$_2$]·ClO$_4$	659	80	brown needles	Co	8.9	8.8
				N	12.7	13.11
[Co(Niox.H)$_2$(o – anisidine)$_2$]·Cl	623	75	brown fibrous prisms	Co	9.4	9.5
				Cl	5.7	5.5
[Co(Niox.H)$_2$(o – phenetidine)$_2$]·Br	691	80	brown prisms	Co	8.5	8.9
				Br	11.5	11.9
[Co(Niox.H)$_2$(aniline)$_2$]·Br	607	60	brown needles	Co	9.7	9.9
				Br	13.2	12.9
[Co(Niox.H)$_2$(p – Br – aniline)$_2$]·Br·1/2 H$_2$O	774	85	brown stars	Co	7.7	7.6
[Co(Niox.H)$_2$(p – toluidine)$_2$]·Br	635.4	70	brown quadrat. plates	Co	9.2	9.0
				Br	12.6	12.5
[Co(Niox.H)$_2$(m – xylidine)$_2$]·Cl	619	50	brown irregular crystals	Co	9.5	9.8
				Cl	5.7	5.4
[Co(Niox.H)$_2$(m – amino – phenol)$_2$]·Br·4H$_2$O	711.5	60	brown hexagonal plates	Co	8.3	8.0
				Br	11.2	10.9
K[Co(Niox.H)$_2$(NCO)$_2$	464	40	brown irregular cryst.	Co	12.7	12.5
NH$_4$[Co(Niox.H)$_2$(S$_2$O$_3$)(pyridine)]·	550.4	40	short brown prisms	Co	10.7	11.2
				S	11.6	11.9
[Co(Niox.H)$_2$(H$_2$O)(NO$_2$)]	405	90	orange crops	Co	14.6	14.5
[Co(Heptox.H)$_2$(aniline)$_2$]·Br	635.4	80	brown prisms	Co	9.3	9.1
				Br	12.6	12.9
[Co(Heptox.H)$_2$(NH$_3$)$_2$]·BF$_4$	490.1	55	short, orange prisms	Co	12.0	12.1
[Co(Heptox.H)$_2$(β – naphthyl–amine)$_2$]·I	782	85	dark brown irregular crystals	Co	7.5	7.4
				I	16.2	15.9
Na[Co(Octox.H)$_2$(NO$_2$)$_2$]	512	60	orange needles	Co	11.5	11.4
[Co(Octox.H)$_2$(aniline)$_2$]·Br	663	75	brown prisms	Co	8.9	8.8
				Br	12.0	12.3

Symbol: Pentox.H$_2$ – 1,2-Cyclopentane dione dioxime; Niox.H$_2$ – 1,2-Cyclohexane dione dioxime; Heptox.H$_2$ – 1,2-Cycloheptane dione dioxime; Octox.H$_2$ – 1,2-Cyclooctane dione dioxime

Table 2. Infrared spectral data of some Co(Diox.H)$_2$AB]^n type complexes

Vibration	I.	II.	III.	IV.
ν N–H	3270 s 3080 m	3265 s 3225 s 3070 m	–	–
ν O–H	–	–	–	3320 – 3120 s
ν C–H	2950 s 2870 m	2940 vs 2870 m	2970 – 2950 s 2880 s	2950 – 2930 s 2860 m
ν O–H (oxime)	2360 – 2340 m	2350 m	2370 – 2350 m	2360 – 2330 m
δ O–H..O	1740 – 1710 w	1780 – 1750 w	1770 – 1700 m	1750 – 1710 w
δ H_2O	–	–	–	1625 m
ν C=N	1575 s	1565 vs	1562 s	1570 – 1550 s
ν CH_2	1460 s 1345 s	1465 s 1340 vs	1480 s 1360 m	1460 s 1380 m
ν as N–O (NO_2)	–	–	1450 s	1445 s
ν s N–O (NO_2)	–	–	1328 m	1327 m
ν N–O (oxime)	1238 vs 1075 vs	1245 vs 1080 s	1238 vs 1072 vs	1240 s 1080 s
γ O–H	972 s	960 m	980 m	975 m
γ C–H	755 s	760 vs	760 s	755 s
γ NH_2	827 m	825 m	–	–
δ s NO_2	–	–	840 m	825 m
δ w NO_2	–	–	610 m	617 m
ν C–N (oxime)	513 s	512 s	515 s	511 s
ν Co–N (amine)	480 m	485 m	–	–
ν Co–N (NO_2)	–	–	420 s	425 m

I. [Co(Niox.H)$_2$ (m-xylidine)$_2$]Cl; II. [Co(Heptox.H)$_2$ (aniline)$_2$]Br;
III. Na[Co(Octox.H)$_2$ (NO_2)$_2$]; IV. [Co(Niox.H)$_2$ (H_2O)(NO_2)]

$$[\mathrm{Co(Diox.H_2)_2(Am)_2}]^{3+} \underset{H^+}{\overset{k_1}{\rightleftarrows}} [\mathrm{Co(Diox.H_2)(Diox.H)(Am)_2}]^{2+} \underset{H^+}{\overset{k_2}{\rightleftarrows}}$$

I. $(\mathrm{pH} < 0)$ II. $(\mathrm{pH} \approx 0.5 - 1..2)$

$$[\mathrm{Co(Diox.H)_2(Am)_2}]^{+} \underset{H^+}{\overset{k_3}{\rightleftarrows}} [\mathrm{Co(Diox.H)(Diox)(Am)_2}]^{\circ} \underset{H^+}{\overset{k_4}{\rightleftarrows}}$$

III. $(\mathrm{pH}\ 3 - 9)$ IV. $(\mathrm{pH}\ 9.5 - 12.5)$

$$[\mathrm{Co(Diox)_2(Am)_2}]^{-}$$

V. $(\mathrm{pH}\ 13 - 14)$ (Am = amine)

The complexes I. and V. decompose easily with liberation of free $\mathrm{Diox.H_2}$ (in strong acidic media) and with complicated substitution reactions (in strong alkaline solutions), respectively.

The formation of double deprotonated Diox^{2-} at pH: 13–14 is followed by geometrical trans-cis transpositions and substitution reactions (formation of mixed hydroxo-complexes: $\mathrm{Co(Diox)_2(Am(OH)]^{\circ}}$, $[\mathrm{Co(Diox)(OH)_4}]^{3-}$). It is worth to mention that the $[\mathrm{Co(Diox)_3}]^{3-}$ asymmetric structure, without O..H–O intramolecular hydrogen bondings, can be synthesized only in strong alkaline media.

In the case of $[\mathrm{Co(Diox.H)_2AB}]^{n}$ type complexes, besides the protolytic equilibria of the $\mathrm{Co(Diox.H)_2}$ moiety, also other protonation or deprotonation processes may occur, e.g. in the case of $\mathrm{NO_2^-}$, $\mathrm{SO_3^{2-}}$, $\mathrm{H_2O}$, $\mathrm{NH_3}$, primary amines, etc. [18]–[20].

The electronic spectra of the $[\mathrm{Co(Diox.H)_2AB}]^{n}$ complexes with alicyclic α-dioximes exhibit, generally, 1–2 weak absorption bands in the visible – and 3–4 bands in the UV part.

The absorption bands in the visible region and partially the first UV band also, are due to Laporte forbidden crystal field transitions, the last one generally overlapped by charge transfer bands. A strong absorption band at about 39–40 kK appears in the spectrum of all complexes of this type and it was assigned already by ABLOV et al. [21] to the $\mathrm{Co(Diox.H)_2}$ moiety. The other bands are metal → ligand and ligand → metal charge transfer bands and own bands of the coordinated ligands. Their assignment is rather complicated.

Some of the absorption bands exhibit a pH dependence allowing us to derive acidity constant by recording the absorption spectra at different pH values.

By defining the acidity constant as

$$\mathrm{K}_a = \frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{AH}]}$$

logarithmic yields

$$\lg \mathrm{K}_a = \lg\,[\mathrm{H}^+] = \lg \frac{[\mathrm{A}^-]}{[\mathrm{AH}]}, \quad \text{i.e.}$$

$$\mathrm{pK}_a = \mathrm{pH} + \lg \frac{[\mathrm{AH}]}{[\mathrm{A}^-]} = \mathrm{pH} + \lg \frac{\mathrm{E} - \mathrm{E}_b}{\mathrm{E}_a - \mathrm{E}}, \tag{7}$$

where $[\mathrm{H}^+]$, $[\mathrm{A}^-]$, $[\mathrm{AH}]$ stand for the concentration of the hydronium ions, of the deprotonated and protonated complex species, respectively, E, E_a and E_b for the extinction absorbance of the sample at the working pH, in acidic and in basic media, respectively, in which only a single complex species is present. Obviously, in all 3 solutions, the analytical concentration of the complex must be the same.

By recording the electronic spectra in various buffer solutions, pK_a values were derived by means of *Eq.* (7).

Mean values of the acidity constants are presented in *Table 3*.

Table 3. Acidity constants of some$[\mathrm{Co(Diox.H)_2AB}]^n$ type complexes

	pK_a (22 °C)	
	spectrophotometrically	potentiometrically
$[\mathrm{Co(Pentox.H)_2(p\text{-}anisidine)_2}]^+$	10.44	–
$[\mathrm{Co(Niox.H)_2(o\text{-}anisidine)_2}]^+$	10.70	10.46
$[\mathrm{Co(Niox.H)_2(o\text{-}phenetidine)_2}]^+$	11.72	10.60
$[\mathrm{Co(Niox.H)_2(aniline)_2}]^+$	11.77	–
$[\mathrm{Co(Niox.H)_2(p\text{-}Br\text{-}aniline)_2}]^+$	10.11	–
$[\mathrm{Co(Niox.H)_2(p\text{-}toluidine)_2}]^+$	11.68	–
$[\mathrm{Co(Niox.H)_2(m\text{-}xylidine)_2}]^+$	11.14	–
$[\mathrm{Co(Niox.H)_2(m\text{-}amino\text{-}phenol)_2}]^+$	10.53	–
$[\mathrm{Co(Niox.H)_2(NCO)_2}]^-$	11.20	10.80
$[\mathrm{Co(Niox.H)_2(NCO)_2}]^-$	2.55	–
$[\mathrm{Co(Niox.H)_2(S_2O_3)(pyridine)}]^-$	2.82	–
$[\mathrm{Co(Niox.H)_2(NO_2)(H_2O)}]^\circ$	7.31	–
$[\mathrm{Co(Heptox.H)_2(aniline)_2}]^+$	11.01	–
$[\mathrm{Co(Heptox.H)_2(NH_3)_2}]^+$	10.47	9.80
$[\mathrm{Co(Heptox.H)_2(\beta\text{-}naphthylamine)_2}]^+$	11.90	–
$[\mathrm{Co(Octox.H)_2(NO_2)_2}]^-$	11.22	–
$[\mathrm{Co(Octox.H)_2(aniline)_2}]^+$	11.93	–

The electronic spectra of some complexes of the type $[\mathrm{Co(Diox.H)_2AB}]^n$ in Britton–Robinson buffer solutions are shown in *Figs. 1* and *2*.

Table 3 contains also several pK_a values determined by performing a potentiometric titration of the complex with 0.1 mol/l NaOH solution. A glass electrode was used as sensor.

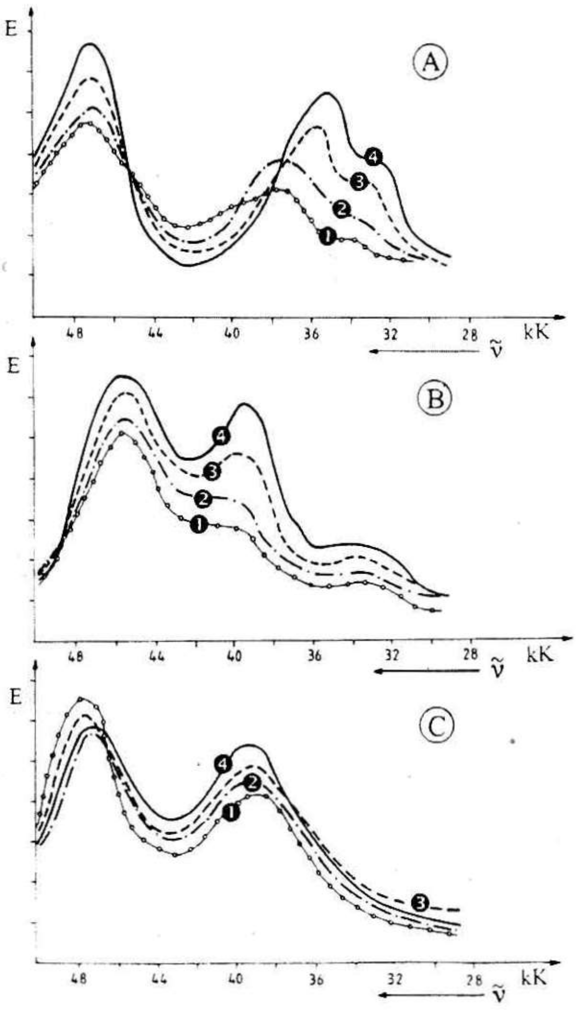

Fig. 1. Electronic spectra of some $[Co(Diox.H)_2AB]^n$ type complexes in 5% ethanol solutions at various pH-values
'A': $K[Co(Niox.H)_2(NCO)_2]$; 1. pH = 1.81; 2. pH = 4.10; 3. pH = 9.91; 4. pH = 11.92.
'B': $Na[Co(Niox.H)_2(S_2O_3)(pyridine)]$; 1. pH = 1.81; 2. pH = 6.59; 3. pH = 9.91; 4. pH = 11.92.
'C': $Na[Co(Octox.H)_2(NO_2)_2]$; 1. pH = 8.36; 2. pH = 9.91; 3. pH = 11.20; 4. pH = 11.92.

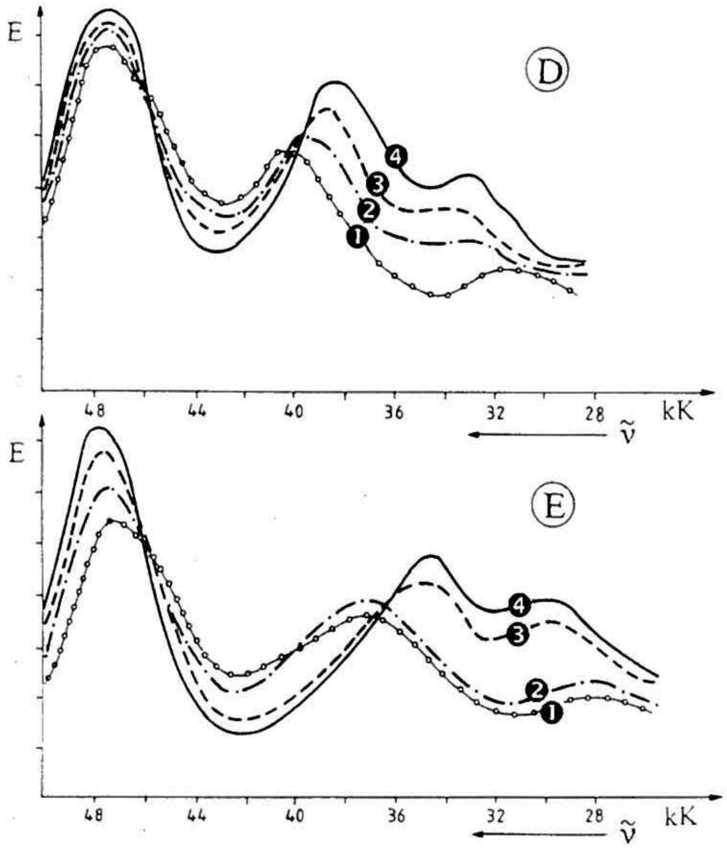

Fig. 2. Electronic spectra of some $Co(Diox.H)_2(amine)_2^+$ type complexes in 5% ethanol solutions at various pH-values
'D': $[Co(Niox.H)_2(o\text{-}anisidine)_2Br$; 1. pH = 3.78; 2. pH = 8.36; 3. pH = 10.88; 4. pH = 11.92.
'E': $[Co(Heptox.H)_2(NH_3)_2]BF_4$; 1. pH = 9.91; 2. pH = 10.38; 3. pH = 11.20; 4. pH = 11.70.

Calculations were made by means of the formula:

$$K_a = \frac{H(c_b + H - K_w/H)}{c - (c_b + H - K_w/H)}, \tag{8}$$

where H, c and c_b stand for the concentration of hydronium ions, analytical concentration of the complex and of NaOH, respectively, K_w being the ionic product of water.

As seen, potentiometric pK_a values are lower than the spectrophotometric ones, but the agreement with each other may be considered to be acceptable.

The major part of pK_a values are between 10 and 12, which means that they correspond to the break of the hydrogen bridge, due to the deprotonation reaction $Diox.H^- = Diox^{2-} + H^+$.

In two cases, with $[Co(Niox.H)_2(NCO)_2]^-$ and $[Co(Niox.H)_2(S_2O_3)(pyridine)]^-$ the pK_a value is between 2 and 3, which implies also the break up of a hydrogen bridge, but in this case due to the protonation process; $Diox.H^- + H^+ = Diox.H_2$.

It is worth mentioning that although the measurements were performed in the first case with $[Co(Niox.H)_2(NCO)_2]^-$, actually the pK_a value caracterizes the aquo complex: $[Co(Niox.H)_2(H_2O)_2]^+$, since the parent compound is not stable in acidic media, it decomposes according to the equation:

$$[Co(Niox.H)_2(NCO)_2]^- + 4\,H^+ + 4\,H_2O = [Co(Niox.H)_2(H_2O)_2]^+ + \\ +2\,NH_4^+ + 2\,CO_2. \tag{9}$$

The pK_a value obtained for $[Co(Niox.H)_2(NO_2)(H_2O)]$ gives actually the acidity constant of the coordinated water molecule in good agreement with our earlier results concerning analogous complexes, for which also pK_a values between 6 and 7 have been found [22].

As for the conjugate bases of III, i.e. $[Co(Diox)(Diox.H)AB]^{n-1}$ type complexes the remaining hydrogen bridge was not observed to dissociate the proton up to $pH = 13$ in our experimental conditions.

This seems to be mainly due to the stronger hydrogen bonding in the $[Co(Diox)(Diox.H)AB]^{n-1}$ as compared to $[Co(Diox.H)_2AB]^n$, since the increase in the negative charges of a complex ion of this type might only slightly increase the pK_a value.

3. Experimental

Alicyclic α-dioximes

0.5 moles of alicyclic monoketone (with $C_5..C_8$) and 1.2 moles of SeO_2 in 250 ml ethanol were refluxed on a water bath during 5–6 hours. The formed red selenium was filtered off, the solvent distilled off at atmospheric pressure and the dark yellow oil (α-diketone) at 10–12 mm Hg. Yields: 30–60% b.p. 80–120 °C (in function of the number of CH_2-groups in the hydroaromatic ring). The separated α-diketones were transformed into the corresponding α-dioximes by refluxing with an excess of hydroxylamine hydrochloride and pyridine (molar ratio: 1:2).

The crude solid products were recrystallized from hot water. Yields: 50–80%. [23].

[Co(Diox.H)$_2$(amine)$_2$]X

A mixture of 20 mmoles of Co(acetate)$_2$, 40 mmoles of α-dioxime and 60 mmoles of amine in 150 ml ethanol (50%) were oxidized by air bubbling for 3–5 hours. The brown solutions were filtered off and used for double decomposition reactions with aqueous solutions of 5–20% NaX (X = Cl, Br, I, ClO_4, BF_4).

K[Co(Diox.H)$_2$(NCO)$_2$]

Analogous method using KNCO instead of amine for the synthesis. The cyanato-complex crystallizes from the solution after 24–48 hours of standing.

Na[Co(Diox.H)$_2$(NO$_2$)$_2$] and [Co(Diox.H)$_2$(H$_2$O)(NO$_2$)]

10 mmoles of $Na_3[Co(NO_2)_6]$ and 20 mmoles of α-dioxime in 80-100 ml water were warmed on a water bath for 30–40 minutes. The chelating agent was dissolved slowly. After filtration, from the half part of the dark orange solution the dinitro-salt was crystallized on standing at room temperature (Yields: 50–60%). The other part of the solution was treated with 10 ml H_2SO_4 20% and warmed on the water bath. The aquo-nitro nonelectrolyte crystallizes after 30 min. The solid product was filtered off, washed with ice cold water and dried on air. (Yield: 70–90%).

(NH$_4$)[Co(Niox.H)$_2$(S$_2$O$_3$)(pyridine)]

10 mmoles [Co(Niox.H)$_2$Cl(H$_2$O)]° and 10 mmoles $(NH_4)_2S_2O_3$ in 100 aqueous solution were warmed on a water bath. The [Co(Niox.H)$_2$(S$_2$O$_3$)(H$_2$O)] dark brown solution was treated with 5 ml pyridine. The mixed thiosulphate-complex crystallized after a standing of 4–5 hours. Yield 25–30%.

The *electronic spectral measurements* at various pH-values were carried out with an UV-VIS recording spectrophotometer Jena (Germany) 30 minutes after the preparation of the samples. Composition of the samples: 5 ml Co(III)-complex: $10^{-4} - 10^{-5}$ mol/l, 5 ml Britton-Robinson buffer solution and water to 50 ml volume.

The *FTIR spectra* were recorded in KBr (4000–500 cm^{-1}) with Perkin–Elmer–2000 apparatus and in polyethylene pellets (600–100 cm^{-1}) with a Bio-Rad-Win spectrophotometer.

Analysis

Cobalt was determined complexometrically in the presence of murexide indicator after digesting the samples with conc. sulfuric acid.

Chloride, bromide and iodide were determined volumetrically using 0.01 mol/l $AgNO_3$ for this purpose.

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