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ON THE OXIMINE COMPLEXES OF TRANSITION METALS, PART CXIII
PROTOLYTIC EQUILIBRIA IN THE SOLUTIONS OF SOME COMPLEXES OF THE TYPE [Co(Diox.H)$_2$AB] WITH α-BENZYLDIOXIME AND α-FURYLDIOXIME

Cs. Várhelyi*[1], J. Zsakó*, T. J. Megyes**, K. Majdik** and G. Liptay***

* Transylvanian Museum Association
Dept. of Natural Sciences and Matematics
Cluj, Romania
** Faculty of Chemistry and Ind. Chem.
Babeş–Bolyai University
3400–Cluj, Romania
*** Department of Inorganic Chemistry
Technical University of Budapest
H–1521 Budapest, P.O. Box 92, Hungary

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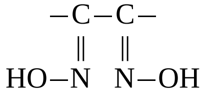
Abstract

11 complexes of the type $[\mathrm{Co(Diox.H)_2\ AB}]^n$ $(\mathrm{Diox.H})_2 - \alpha$ benzyldioxime (Diphenylglyoxime: Dif.H$_2$), α-furyldioxime furox.H$_2$), A, B, – $\mathrm{CN^-}$, $\mathrm{NO_2^-}$, $\mathrm{HSO_3^-}$, $\mathrm{SO_3^{2-}}$, $\mathrm{H_2O}$, amine) were obtained by various substitution reactions, and characterized by middle IR and electronic spectral data. The protolytic equilibria: $[\mathrm{Co(Diox.H)_2\ AB}]^n \leftrightarrows H^+\ [\mathrm{Co(Diox.H)(Diox)AB}]^{n-1} + \leftrightarrows \mathrm{H^+}$ of these complexes in aqueous solutions were studied by potentiometric and spectrophotometric measurements (in Britton-Robinson buffer solutions). The complicated character of these processes (5 equilibria in a wide pH range) was discussed.

Keywords: Co(III) dioxime complexes, protolytic equilibria, aromatic α-dioxime, UV, IR spectra of Co(III) complexes.

1. Introduction

From the stereoisomeric benzyldioximes (syn-, amphi-, anti-) only the anti-(α) isomer shows chelation properties towards transition metal ions. Some physico-chemical properties of this chelating agent and also of the α-furyldioxime (solubility in various solvents, acidity constants, thermal stability) slightly differ from those of the aliphatic and alicyclic α-dioximes. The phenyl- or furyl groups bonded to the  $\begin{array}{c} -\mathrm{C}-\mathrm{C}- \\ \|\quad\ \| \\ \mathrm{HO-N}\quad\mathrm{N-OH} \end{array}$ moiety entail a very slight solubility in water (especially with

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α-benzyldioxime) and reduce the electron density of the N donor atoms. This phenomenon makes the benzyl- and furyl-dioximine chelates less stable as compared to the analogous aliphatic and alicyclic derivatives.

Some mixed cobalt(III) – chelates with α-benzyldioxime (α-diphenylglyoxime: $Dif.H_2$) were obtained and characterized by ABLOV et al. [1] and in our previous papers [2].

The thermal behaviour of some $[Co(Dif.H)_2\,(amine)_2]X$ type complexes was studied by thermoanalytical methods, and some kinetic data were derived for the partial deamination process [3]

The middle IR spectra of some $[Co(Diox.H)_2L_2]^n$ type complexes (L -monodentate ligand) show the formation of strong Co-N covalent bonds and the presence of intramolecular O-H-O bonds, the latter stabilizing the coplanar $Co(Diox.H)_2$ moiety [4,5].

The electronic spectra of some $[Co(Dif.H)_2AB]^n$ type complexes generally show weak bands in the visible (15–20 kK) and 4 bands in the UV region (25–27, 29–31, 37–38 and 47–49 kK).

Of these bands that one at 37.5–38 kK can be assigned to the $Co(Dif.H)_2$ planar group, and it is very little influenced by the nature of the axial (‘trans’) ligands. For the analogous aliphatic and alicyclic oximine derivatives $[Co(Diox.H)_2AB]^n$ ($Diox.H_2$–dimethylglyoxime (DH_2), alicyclic α-dioximes: $Pentox.H_2$, $Niox.H_2$, $Heptox.H_2$, $Octox.H_2$) this band is shifted towards higher frequency values ($\approx$ 40 kK). This is consistent with the above assignment of the mentioned band, since the electron withdrawing effect of the aromatic rings must also influence the spectral properties of this moiety.

In our previous papers [6,7] an attempt was made to derive ligand field parameters from the absorption bands in the visible and in the neighbouring UV regions for bis- dioximine complexes. These calculations performed for dimethylglyoximine and benzyldioximine derivatives showed the aromatic ring to diminish both the covalent character of the metal – ligand bond and the strength of the ligand field.

Frequently the electronic spectra and the colour of aqueous solutions are influenced by the pH. The colour change is generally reversible (after acidification or alkalinization) – with the exception of the complexes $[Co(Diox.H)_2AB]^n$ with $A,B = Cl^-, Br^-, I^-$. This phenomenon indicates the existence of protolytic equilibria in such systems.

Some observations of CHUGAEV [8,9] and ABLOV [10,11] on the preparation of analogous dimethylglyoximine derivatives show the formation of ‘anhydrobases’ involving the deprotonation of the intramolecular O-H-O hydrogen bridges in the presence of NaOH.

$$[Co(DH)_2(amine)_2]^+ + OH^- \leftrightarrows \boxed{\begin{array}{c}\text{hypotetic unstable intermediate}\\ \text{products}\end{array}} -$$

$$-[Co(DH)(D)(amine)_2] + H_2O.$$

By potentiometric studies (titration with NaOH) on some dimethylglyoximine derivatives of this type, ABLOV et al. [10] have determined the equilibrium constants of this reaction, generally in aqueous solutions.

The situation is more complicated in such systems.

One can presume the following protolytic equilibria in a wide pH range: e.g.

$$\underset{\text{I. (pH} < 0)}{[Co(Diox.H_2)_2(Am)_2]^{3+}} \leftrightarrows H^+ \underset{\text{II. (pH} \approx 0.5 - 1 - 2)}{[Co(Diox.H_2)(Diox.H)(Am)_2]^{2+}} \leftrightarrows H^+$$

$$\underset{\text{III. (pH } 3 - 10)}{[Co(Diox.H_2)(Am)_2]^{+}} \leftrightarrows H^+ \underset{\text{IV. (pH } 10.5 - 13)}{[Co(Diox.H)(Diox)(Am)_2]^{0}} \leftrightarrows H^+$$

$$\underset{\text{V. (pH } 13 - 14)}{[Co\ (Diox)_2(Am_2)]^{-}}$$

The complexes I. and V. decompose easily with liberation of free $Diox.H_2$ (in acid solutions) or $Diox^{2-}$ followed by geometrical transpositions (trans – cis) and substitution reactions (formation of $[Co(Diox)(Am)(OH)_n]$, $[Co(Diox)(OH)_4]^{3-}$, etc.) (in strongly basic media).

In the present paper some new α-benzyl – and α-furyl – dioximine Co(III) complexes were obtained and characterized by means of middle IR and electronic spectra (*Table 1*).

The acidity constant, involving the break-up of a hydrogen bridge in alkaline solutions (equilibrium III $\leftrightarrows$ IV) was determined by means of spectrophotometric and potentiometric methods.

2. Results and Discussion

Some middle IR spectral data of the $[Co(Diox.H)_2AB]^n$ type complexes studied (A,B = amine, CN^-, NO_2^-, SO_3^{2-}) are presented in *Table 2*.

The significant shift of the ν O–H frequencies of the free $Dif.H_2$ and $Furox.H_2$ (3250–3100 cm^{-1}) to 2400–2300 cm^{-1} and the appearance of the weak δ OHO band at 1700–1800 cm^{-1} prove the trans octahedral structure of the $[Co(Diox.H)_2AB]^n$ complexes with the $Co(Diox.H)_2$ moiety in the equatorial plane of the octahedral model [4,5].

The ν N–O (oxime) frequencies are shifted towards higher wave numbers as compared to the analogous dimethylglyoxime and alicyclic dioxime derivatives. This is also due to the electron withdrawing effect of the aromatic ring, entailing the strengthening of the N–O bond. The stretching vibrations of the coordinated axial ligands show the formation of strong covalent Co–N (nitro), Co–N (amine) and Co–C (cyan) bonds [12]. The SO_3 ligand, as others of the XY_3 type, has a pyramidal structure giving C_{3v} site symmetry. The studied sulfito complexes are considered as $R–SO_3$ type molecules. The co-ordination of SO_3^{2-} through the sulfur atom leads to a decrease in the negative charge of the oxygen atoms and to an increase

Table 1. Characterization of [Co(Diox.H)$_2$AB]^n type complexes

Formula	Mol. wt. calcd.	Appearance
$H[Co(Dif.H)_2(CN)_2]$	592	yellow needles
$K[Co(Dif.H)_2(NO_2)_2] \cdot 10H_2O$	638	orange needles
$Na_3[Co(Dif.H)_2(SO_3)_2] \cdot 6H_2O$	876	yellow, thin prisms
$Na_3[Co(Furox.H)_2(SO_3)_2] \cdot 4H_2O$		yellow-orange thin prisms
$[Co(Dif.H)_2(HSO_3)H_2O)] \cdot 4H_2O$	710	sparkling yellow irregular plates
$NH_4[Co\ (Dif.H)_2(SO_3)(NH_3)] \cdot 3H_2O$	707	dark yellow prisms
$Py.H[Co(Dif.H)_2(SO_3)(Py)] \cdot 3H_2O$	778	brown prisms
$[Co(Dif.H)_2(Py)_2]Br$	777	irregular brown plates
$[Co(Dif.H)_2(aniline)_2]Br$	805	rhomb. dark brown plates
$[Co(Dif.H)_2(p\text{-toluidine})_2]Br$	833	irreg. thin brown plates
$[Co(Dif.H)_2(\alpha\text{-naphtylamine})_2]Cl$	862	reddish-brown plates

Dif.H$_2$ – benzyldioxime: $C_{14}H_{12}N_2O_2$
Furox.H$_2$ – furyldioxime: $C_{10}H_8N_2O_4$
Analysis: ΔCo% $\pm 0.05 - 0.2$; ΔS% = $\pm 0.1 - 0.25$; ΔN% = $\pm 0.06 - 0.25$
Co% – measured complexometrically after destroying the samples with cc. $H_2SO_4 + KNO_3$; S% as $BaSO_4$; N% by microanal. method

in the bonding order of the S–O bond. Thus, the ν_s(S–O) $= 960 - 970$ cm^{-1} and ν_{as}(S–O) $= 930 - 950$ cm^{-1} frequencies for the free SO_3^{2-} ion are shifted towards higher frequency values [13].

Some electronic spectral data for the [Co(Dif.H)$_2$AB]^n complexes are presented in *Table 3*.

Some absorption bands in the UV region show a pH dependence as illustrated by *Fig. 1*.

As seen from *Fig. 1*, the molar absorbance of the deprotonated molecular species is higher than the absorbance of the protonated one. This allowed us to derive acidity constants (K$_a$) from spectrophotometric data by using the relation:

$$\mathrm{pK}_a = \mathrm{pH} + \lg\frac{E_b - E}{E - E_a}\ , \qquad (1)$$

where E, E_a and E_b stand for the absorbance of the sample in the buffer solution of the given pH, in acidic (a) and alkaline (b) solutions, respectively.

In the determination of E_b some difficulties arise since very often even the most alkaline buffer solutions used cannot ensure a complete deprotonation of the molecules, or the successive two protolytic equilibria may partially overlap each other. This is why E_b values were determined by a trial and error method, by taking

Table 2. Infrared spectral data of some $[Co(Diox.H)_2AB]^n$ complexes

Vibration	I.	II.	III.	IV.	V.
ν O–H (H_2O)	– –	3300-3150 s	3260-3170 s	3350-3180 s	–
ν N–H	–	–	–	–	3130-3060 s
ν O–H (oxime)	2400-2300 m	2360-2300 m	2400-2300 m	2300-2260 m	2350-2280 w
ν C=N (cyan)	2120-2100 s	–	–	–	–
δ O–H–O	1800-1700 w	1760-1720 w	1770-1730 w	1760-1720 w	1800-1700 w
ν C=N (oxime)	1580 v s	1575 v s	1550 v s	1585 v s	1585 v s
δ H_2O	–	1660-1640 m	1660-1640 m	1650-1600 m	–
ν N–O (NO_2)	– –	1440 s 1320 m	–	–	–
ν S–O	–	–	1100 v s 1085 v s	1120-1080 v s	–
ν N–O (oxime)	1300 s 1120-1130 v s	1300 s 1130 v s	1290 v s 1120-1130 v s	1285 v s 1120-1140 v s	1295 v s 1110-1130 v s
ν S–O	–	–	970 v s	980 s	–
γ O–H	930-950 s	930-960- s	990 s	990 s	940 m
δ SO_2	–	–	635-630 m	640-630 m	–
ν Co–N	525 m	520 m	525 m	520 m	525 m

I. – $H[Co(Dif.H)_2(CN)_2]$; II. – $K[Co(Dif.H)_2(NO_2)_2] \cdot 10H_2O$;
III. – $Na_3[Co(Dif.H)_2(SO_3)_2] \cdot 6H_2O$; IV. – $Na_3[Co(Furox.H)_2(SO_3)_2] \cdot 4H_2O$;
V. – $[Co(Dif.H)_2(aniline)_2]Br$

for E_b the value ensuring the minimum standard deviation for pK_a values derived by means of *Eq.* (1) from different experimental E values.

e.g. Formula	λ nm	pH	E_a	E_b	E	pK_a	p$\overline{K}_a$
$[Co(Dif.H)_2(Py)_2]Br$		10.88			0.22	11.69	
		11.20			0.30	11.64	
		212				11.65	
		11.40	0.14	0.74	0.40	11.51	
		11.92			0.50	11.74	
$Na_3[Co(Furox.H)_2(SO_3)_2]$		11.20			0.34	12.05	
		11.70			0.42	12.20	
		210				12.16	
		11.92	0.22	1.20	0.48	12.30	
		12.00			0.74	12.10	

The results are summarized in *Table 4*

An attempt was made to derive acidity constants also by performing potentiometric titrations with NaOH.

K_a values can be calculated by means of the relation

$$K_a = \frac{H(b + H - K_w(H))}{a - (b + H - K_w(H))}, \tag{2}$$

where H stands for the hydrogen ion concentration, measured by means of a glass electrode, K_w for the ionic product of water, $\underline{a}$ and $\underline{b}$ for the analytical concentration of the complex and of the NaOH added, respectively.

The results are presented in *Table 5*.

As seen, the agreement between the spectrophotometric and potentiometric data is quite good.

We mention here that the potentiometric method cannot be used in the case of many complexes, since the solubility of the substances in water is not sufficiently high.

The acidity constants derived are of the same order of magnitude as previously found in the case of analogous dimethylglyoximine complexes [14,15].

Table 3. Electronic spectral data of some $[Co(Dif.H)_2AB]^n$ type complexes

Formula	$\tilde{\nu}_1$	lg ε_1	$\tilde{\nu}_2$	lg ε_2	$\tilde{\nu}_3$	lg ε_3	$\tilde{\nu}_4$	lg ε_4
$[Co(Dif.H)_2(\gamma - \text{picoline})_2]^+$	21.7	2.9	25.3	3.8	29.4	3.8	37.7	4.45
$[Co(Dif.H)_2(\text{m} - \text{toluidine})_2]^+$	22.2	3.25	24.1	3.55	29.8	4.10	37.7	4.30
$[Co(Dif.H)_2(\text{o} - \text{anisidine})_2]^+$	20.4	3.5	25.0	4.10	29.8	4.48	37.7	4.85
$[Co(Dif.H)_2(\beta - \text{naphthylamine})_2]^+$	23.6	3.10	25.0	4.0	29.8	4.32		
					34.5	4.34	37.7	4.63
$[Co(Dif.H)_2(SO_3)(\text{p} - \text{toluidine})]^-$	–	–	–	–	30.5	4.20	38.0	4.45
$[Co(Dif.H)_2(SO_3)(Py)]^-$	–	–	–	–	30.0	3.95	38.5	4.30

$\tilde{\nu}$–kK (1000 cm^{-1})

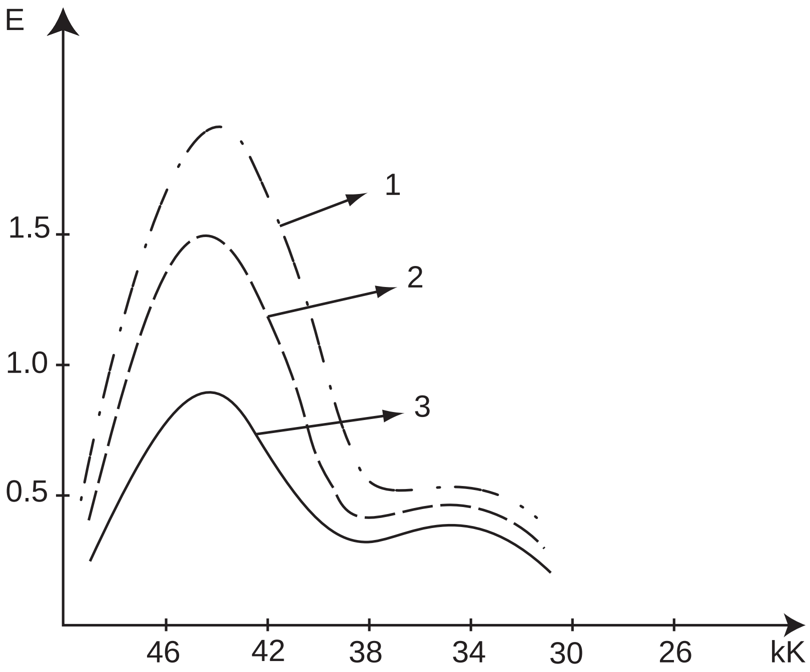

Fig. 1. Electronic spectrum of $K[Co(Dif.H)_2(NO_2)_2]$ 1 – pH = 12.30; 2 – pH =12.00; 3 – pH = 10.38

3. Experimental

Preparation of the ligand and of the complexes. α-benzyldioxime: 25 g of finely powdered benzyl moistened with ethanol are mixed with 20 g of hydroxylamine hydrochloride, 40 g of NaOH and 100 ml of water and kept at room temperature for 4–5 days. The major part of the benzyl dissolves slowly. The dark brown solution is filtered off and the benzyldioxime is precipitated by bubbling CO_2 through the solution. The first part of the separated oxime is the pale pink α-benzyldioxime (after 20–25 min).

The crude product is recrystallized from ethanol. Yield: 25–30%. Observation: By continuation of CO_2 bubbling the dark yellow β- and γ- isomer dioximes are also precipitated in various ratios.

$[Co(Dif.H)_2(H_2O)Cl]$: 0.1 mole of α-benzyldioxime and 0.05 mole of $Co(CH_3COO)_2$ are refluxed in 450–500 ml methanol and oxidized with addition of 20–25 ml 30% H_2O_2 dropwise during 30–40 minutes. The brown solution is filtered off and poured into 500 ml 5% hydrochloric acid. The separated microcrystalline light brown $[Co(Dif.H)_2(H_2O)Cl]$ is filtered off, washed with warm water and dried in air. Yield: 80–90%.

The crude product was used for substitution reactions.

K[Co(Dif.H)$_2$(NO$_2$)$_2$] · 10H$_2$O and H[Co(Dif.H)$_2$(CN)$_2$]:

10 mmoles of [Co(Dif.H)$_2$(H$_2$O)Cl] and 20 mmoles of KNO$_2$ (KCN) in 100 ml 50% ethanol were warmed on a water bath. The aquo-chlorononelectrolyte dissolves slowly. After 30–40 min, the yellow solution was filtered off. The dinitro salt crystallizes from the cold solution after 5–6 hours. The dicyano-acid was separated after acidification with 20% H$_2$SO$_4$. Yields: 60–80%.

Na$_3$[Co(Dif.H)$_2$(SO$_3$)$_2$] · 6H$_2$O can be obtained in an analogous way. From the yellow solution the disulfito salt was precipitated with acetone. Yield: 80–90%.

Na$_3$[Co(Furox.H)$_2$(SO$_3$)$_2$] · 4H$_2$O is formed by oxidation with air of a mixture of 5 mmoles of Co(acetate)$_2$, 10 mmoles of α-furyldioxime and 10 mmoles of Na$_2$SO$_3$ in 100 ml 50% ethanol. For the precipitation of the sulfito complex also in this case acetone can be used. Yield: 75%.

[Co(Dif.H)$_2$(H$_2$O)(HSO$_3$)] · 4H$_2$O was prepared from the aqueous solution of Na$_3$[Co(Dif.H)$_2$(SO$_3$)$_2$] by acidification with 10–20% H$_2$SO$_4$ or HClO$_4$ at room temperature.

(amine.H)[Co(Dif.H)$_2$(SO$_3$)(amine)] was prepared from 5 mmoles of [Co(Dif.H)$_2$-(H$_2$O)(HSO$_3$)] and 12–15 mmoles of amine in 50–60 ml ethanol by allowing to stand the mixture on a water bath for 30–40 minutes. The separated crystalline product was washed with water and dried in air.

[Co(Dif.H)$_2$(amine)$_2$X : 5 mmoles of CoX$_2$ (X = Cl, Br), 10 mmoles of Dif.H$_2$ and 12–15 mmoles of amine in 60–80 ml ethanol were refluxed and oxidized with 5–10 ml 30% H$_2$O$_2$ added dropwise during 30–40 minutes. The crystalline product was filtered off, washed with water and dried in air.

The middle IR spectra were recorded with a Zeiss UR-20 Spectrophotometer

Table 4. Acidity constants of Co(Diox.H)$_2$AB]^n type complexes (mol. species 'III') derived from spectrophotometric data (22 °C)

Complex	pK$_a$
[Co(Dif.H)$_2$(SO$_3$)$_2$]$^{3-}$	12.6
[Co(Dif.H)$_2$(SO$_3$)(H$_2$O)]$^-$	12.1
[Co(Dif.H)$_2$(SO$_3$)(NH$_3$)]$^-$	12.4
[Co(Dif.H)$_2$(SO$_3$)(Py)]$^-$	12.6
[Co(Dif.H)$_2$(CN$_2$)]$^-$	12.2
[Co(Dif.H)$_2$(NO$_2$)$_2$]$^-$	12.4
[Co(Dif.H)$_2$(Py)$_2$]$^+$	11.7
[Co(Dif.H)$_2$(aniline)$_2$]$^+$	11.4
[Co(Dif.H)$_2$(β − naphtylamine)$_2$]$^+$	12.1
[Co(Furox.H)$_2$(SO$_3$)$_2$]$^{3-}$	12.2

Table 5. Acidity constants of some [Co(Dif.H)$_2$AB] type complexes (mol. species 'III') derived from potentiometric titration data

Complex	pK$_a$
$[Co(Dif.H)_2(SO_3)_2]^{3-}$	12.8
$[Co(Dif.H)_2(SO_3)(NH_3)]^{-}$	12.5

(Jena, Germany) in KBr pellets.

The electronic spectra were measured at various pH-values in aqueous solutions with an UV-VIS recording spectrophotometer (Germany) 30 minutes after the preparation of the samples. Concentration of the samples: $5-10\times10^{-5}$ mol/l (5 ml complex (10^{-4} mol/l + 5 ml Britton-Robinson buffer solution $+$ H_2O – 50 ml).

Potentiometric measurements: 50–100 ml aqueous solutions of the complexes (0.5 – 2 $\times$ 10^{-3} mol/l) were titrated with 10^{-2} mol/l NaOH using a glass electrode and a saturated calomel electrode.

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