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ON THE OXIMINE COMPLEXES OF TRANSITION METALS. PART CXIV.

NEW MIXED SULFITO – COBALT(III) – COMPLEXES WITH ALICYCLIC α-DIOXIMES[1]

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Abstract

20 new sulfito-complexes of the type: Cation $\cdot$[Co(Diox.H)$_2$(SO$_3$)(amine)] $\cdot$ n H$_2$O and Cation $\cdot$[Co(Diox.H)$_2$(SO$_3$)$_2$] $\cdot$ H$_2$O (Cation: Na$^+$, NH$_4^+$ amine.H$^+$, CoL$_6^{3+}$, CrL$_6^{3+}$; $L = $ H$_2$O, NH$_3$, en, urea; Diox.H$_2$ = dimethylglyoxime or alicyclic α-dioxime with C$_5 \ldots$ C$_8$) were obtained and characterized by middle and far FTIR, – electronic – and mass spectra.

The protolytic equilibria of [Co(Diox.H)$_2$(SO$_3$)$_2$]$^{3-}$ and [Co(Diox.H)$_2$(SO$_3$)(amine)]$^-$ were studied by spectrophotometric and potentiometric measurements.

Keywords: transition metal complexes, FTIR spectroscopy, mass spectrometry, spectrophotometry, thermal analysis.

1. Introduction

Sulfite ion (SO_3^{2-}) with a pyramidal structure may be coordinated to a metal ion as a unidentate, bidentate or bridging ligand.

For unidentate coordination the following two structures can be expected

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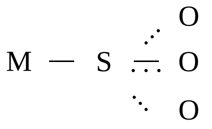
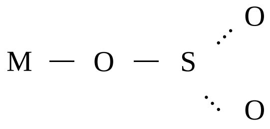
[1] Sponsored by the Soros Foundation



C_{3v}



C_s

If coordination occurs through sulfur, the C_{3v} symmetry of free SO_3^{2-} will be preserved. In the case of coordination through oxygen, the local symmetry will be lowered to C_s.

Generally, this structural problem may be solved by means of IR spectroscopic data. Coordination through sulfur will shift the ν_{S-O} bands to higher frequencies, whereas coordination through oxygen will shift them to lower frequencies compared to those of the free ion. The ν_{S-O} stretching bands at 1200–850 cm^{-1} are useful in distinguishing these structures [1,2].

The number of reported sulfito-complexes with $M-O-SO_2$ bonding is small: $Tl_2[Cu(SO_3)_2]$ [3], $Na_8[Os(SO_3)_6]$ [4], $[UO_2(SO_3)_2]^{2-}$ [5], $[Cr(SO_3)_2]^-$ [6], etc. In the sulfito-complexes of most transition metals the coordination occurs through the sulfur atom, e.g. $[Ir(NH_3)_4(SO_3)_2]^-$ [7], $[Rh(NH_3)_2(SO_3)_4]^{5-}$ [8], various Co(III)-derivatives with NH_3, en, heterocyclic diamines, etc. [9,10].

The structures of complexes containing bidentate sulfito-groups are rather difficult to deduce from their IR spectra. Bidentate sufito-groups may be chelating (e.g. $[Co(en)_2(SO_3)]X$ [11] or bridging through either oxygen or sulfur or both, all resulting in C_s local symmetry.

The IR spectra of $K_2[Pt(SO_3)_2] \cdot 2H_2O$ and $K_3[Rh(SO_3)_3] \cdot 2H_2O$ show the bidentate coordination of the sulfito-group [12]. A $Co-O-SO_2-Co$ bridge appears in the binuclear $[Co_2(SO_3)(OH)_2(NH_3)_6] \cdot S_2O_6$ complex [13].

2. Results and Discussion

The nucleophilic properties of the SO_3^{2-}-group are the most significant behind those of CN^- and for this reason this anion replaces a considerable number of ligands (halides: Cl^-, Br^-, I^-), pseudohalides (NCX^-, X = O,S,Se), neutral molecules: H_2O, NH_3, amines, phosphines) in various substitution reactions.

In previous papers [14–18] some $[Co(Diox.H)_2(SO_3)_2]^{3-}$, $[Co(Diox.H)_2(SO_3)(amine)]^-$ complexes (Diox.H_2 = dimethylglyoxime, monomethylglyoxime, benzyldioxime) were characterized.

As a continuation of our studies concerning the coordination chemistry of the oximes, we report in the present paper on the synthesis and some physico-chemical properties (FTIR, electronic, mass spectra and thermal behaviour) of some new

$[Co(Diox.H)_2(SO_3)_2]^{3-}$ and $[Co(Diox.H)_2(SO_3)\ (amine)]^{-}$ type complexes with alicyclic dioximes (with $C_5 \ldots C_8$ rings) and dimethylglyoxime.

The classical air oxidation applied to the $Co^{2+} - \alpha$ dioxime – Na_2SO_3 mixture yields $[Co(Diox.H)_2(SO_3)_2]^{3-}$:

$$2\,Co^{2+} + 4\,Diox.H_2 + 1/2\,O_2 + 4\,SO_3^{2-} = 2\,[Co(Diox.H)_2(SO_3)_2]^{3-} + H_2O + 2\,H^{+}. \qquad (1)$$

The disulfito-complex acids were isolated as alkaline and cobalt(III)amine salts by double decomposition reactions.

Table 1. New disulfito–complexes of the type: Cation · $[Co(Diox.H)_2(SO_3)_2]$ · n H_2O

Formula	Mol. wt. calc.	Yield (%)	Appearance	*Analysis* (%)	Calcd.	Found
$Na_3[Co(Pentox.H)_2(SO_3)_2]\cdot$	637	60	yellow rhomb.	Co	9.3	9.7
$\cdot 5\,H_2O$			plates	S	10.1	9.9
$Na_3[Co(Niox.H)_2(SO_3)_2]\cdot$	731	55	small yellow	Co	8.0	8.2
$\cdot 9\,H_2O$			needles	S	8.7	8.7
				H_2O	22.1	21.8
$Na_3[Co(Heptox.H)_2(SO_3)_2]\cdot$	670	75	yellow thin	Co	8.8	8.6
$\cdot 4\,H_2O$			plates	S	9.6	10.0
$Na_3[Co(Octox.H)_2(SO_3)_2]\cdot$	752	60	yellow	Co	7.8	7.9
$\cdot 7\,H_2O$			hexagonal	S	8.5	8.2
$[Co(NH_3)_6][Co(Pentox.H)_2(SO_3)_2]\cdot$	778	70	yellow	Co	15.1	15.0
$\cdot 8\,H_2O$			crops	S	8.2	8.0
$[Co(NH_3)_5(H_2O)][Co(Pentox.H)_2]\cdot$	724	50	dark yellow	Co	16.2	15.8
$(SO_3)_2 \cdot 5\,H_2O$			silky plates	S	8.8	8.9
$[Co(en)_3][Co(Pentox.H)_2(SO_3)_2]\cdot$	802	75	yellow	Co	14.6	14.3
$\cdot 5\,H_2O$			crops	S	8.0	8.2
$[Co(NH_3)_6][Co(Heptox.H)_2(SO_3)_2]\cdot$	870	80	sparkling yel-	Co	13.5	13.3
$\cdot 10\,H_2O$			low plates	N	16.1	16.6
$[Co(en)_3][Co(Heptox.H)_2(SO_3)_2]\cdot$	858	80	yellow	Co	13.7	13.4
$\cdot 5\,H_2O$			crops	N	16.3	15.9
$[Co(NH_3)_5(H_2O)][Co(Heptox.H)_2(SO_3)_2]\cdot$	871	70	orange short	Co	13.5	13.2
$\cdot 10\,H_2O$			needles	S	7.3	7.2
$[Cr(en)_3][Co(Heptox.H)_2(SO_3)_2]\cdot$	851	75	irregular yel-	N	16.4	16.22
$\cdot 5\,H_2O$			low crystals			
$[Cr(urea)_6][Co(Heptox.H)_2(SO_3)_2]\cdot$	1108	50	dark brown	S	5.8	5.9
$\cdot 9\,H_2O$			microcrystals	H_2O	14.6	14.44
$[Co(NH_3)_6][Co(Octox.H)_2(SO_3)_2]\cdot$	844	60	yellow	Co	14.0	14.11
$\cdot 7\,H_2O$			disks	S	7.6	7.22

Sulfito-amine derivatives of the type $[Co(Diox.H)_2(SO_3)(amine)]^{-}$ were obtained by anation reaction of $[Co(Diox.H)_2(SO_3)(H_2O)]^{-}$ with aromatic primary amines ($pK_b = 9 - 12$) and pyridine bases ($pK_b \sim 6 - 8$). The starting material for this purpose, $[Co(Diox.H)_2(SO_3)(H_2O)]^-$, is obtained according to the reaction:

$$[Co(Diox.H)_2(H_2O)X] + (NH_4)_2SO_3 = NH_4[Co(Diox.H)_2(SO_3)(H_2O)]$$

$$+NH_4X \qquad (X = Cl, Br, I, NCS, NCSe). \qquad (2)$$

By using Na_2SO_3 or K_2SO_3 for this ligand exchange process only $[Co(Diox.H)_2(SO_3)_2]^{3-}$ is obtained as the final product.

Some amine.H[Co(Diox.H)$_2$(SO$_3$)(amine)] binary complex salts are characterized in *Table 2*.

Table 2. New amine.H[Co(Diox.H)$_2$(SO$_3$)amine] $\cdot$ nH_2O type binary sulfito-complex salts

Formula	Mol. wt. calc.	Yield (%)	Appearance	*Analysis* (%)	Calcd.	Found
$NH_4[Co(DH)_2(SO_3)(NH_3)]\cdot$	476	50	yellow	Co	12.3	12.1
$\cdot 4\,H_2O$			prisms	S	6.7	7.1
$NH_4[Co(DH)_2(SO_3)$(p-xylidine)]$\cdot$	580.3	55	dark yellow	Co	10.1	10.4
$\cdot 4\,H_2O$			needles	S	5.5	5.3
				H_2O	12.4	12.0
$NH_4[Co(DH)_2(SO_3)$(m-anisidine)]$\cdot$	582.2	40	sparkling yel-	Co	10.1	9.8
$\cdot 4\,H_2O$			low prisms	S	5.5	5.8
				H_2O	12.4	12.6
o-toluidine.H[Co(Niox.H)$_2$(SO$_3$)$\cdot$	726	60	dark yellow	Co	8.1	7.8
(o-toluidine)] $\cdot$ 5 H_2O			long plates	N	11.6	11.5
				H_2O	12.4	12.0
p-xylidine.H[Co(Niox.H)$_2$(SO$_3$)$\cdot$	753	70	yellow square	Co	7.8	7.6
(p-xylidine)] $\cdot$ 5 H_2O			plates	S	4.2	4.4
				H_2O	11.9	11.4
p-phenetidine.H[Co(Niox.H)$_2$(SO$_3$)$\cdot$	785	75	yellow	Co	7.7	8.1
(p-phenetidine)] $\cdot$ 5 H_2O			needles	S	4.1	4.5
				H_2O	11.4	12.0
p-anisidine.H[Co(Niox.H)$_2$(SO$_3$)$\cdot$	740	55	yellow	Co	8.0	7.8
(p-anisidine)] $\cdot$ 4 H_2O			prisms	S	4.3	4.7
				H_2O	9.7	9.3

The *FTIR – spectra* of some sulfito–cobalt(III) complexes show the presence of strong intramolecular O..H..O hydrogen bridges stabilizing the coplanar $Co(Diox.H)_2$ ring system, i.e. the ‘trans’ geometric configuration of the $[Co(Diox.H)_2(SO_3)_2]^{3-}$ and $[Co(Diox.H)_2(SO_3)L]^-$ complexes.

The frequencies of the $\nu_s(S - O)$, and especially those of the $\nu_{as}(S - O)$ stretching vibrations are increased as compared to the values of the corresponding vibrations for the free SO_3^{2-}-ion ($\nu_s(S-O)$: 960–970 cm^{-1} and $\nu_{as}(S-O)$ 930–950 cm^{-1}).

For the Co(III) – and Rh(III) – sulfito – amine mixed complexes they are situated at about $\nu_s(S-O)$: 960–1010 and $\nu_{as}(S-O)$: 1020–1075 cm^{-1}. The bending vibrations $\delta_s(SO_3)$ appear approximately in the same interval ($\delta_s(SO_3)$: 610–680 cm^{-1}) as for the free SO_3^{2-} (610–655 cm^{-1}). The asymmetric bending vibrations $\delta_{as}(SO_3)$ are shifted a little towards higher wave number values (500–560 cm^{-1}) as compared to $\delta_{as}(SO_3)$: 445–510 cm^{-1} for the free SO_3^{2-} ion.

In the case of the studied sulfito–dioxime derivatives the exact assignment of ν_{as}(S–O) and $\delta_{as}(SO_3)$ is rather difficult due to the overlapping by the stretching vibrations of $\nu(N-O)$ and $\nu(Co-N)$ in the 950–1100 and 480–530 cm^{-1} regions.

The FTIR spectral data given in *Table 3* prove that all the Co-sulfite bondings are realized through the sulfur atom.

The ν(C–H) (2950–2970, 2860–80 cm^{-1}) and $\delta(CH_2)$ (1450, 1360 cm^{-1}) vibrations of the alicyclic rings are not influenced by coordination.

The characteristic vibrations of the SO_3^{2-} group in the far IR region (500–25 cm^{-1}) have not been mentioned in the literature. At low frequencies various deformation vibrations appear:

$$\delta N_{ox}-Co-N_{ox}\,, \quad \delta N_{ox}-Co-N_{am}\,,$$

$$\delta O_3S-Co-SO_3\,, \delta N_{ox}-Co-SO_3\,, \quad \delta N_{am}-Co-SO_3\,,$$

sometimes overlapped by skeletal vibrations of the chelating agents and especially by those of the hydroaromatic and chelate ring system. Generally, these problems have not been studied before.

Some data can be obtained for the mixed sulfito-derivatives by comparison of the far FTIR spectra of the $[Co(Diox.H)_2(SO_3)_2]^{3-}$ derivatives with those of the $[Co(Diox.H)_2X_2]^-$ and $[Co(Diox.H)_2L_2]^+$ complexes (X = Cl, Br, I,; L = H_2O, NH_3).

The $\nu Co-N$ (oxime) band appears at 510–515 cm^{-1}, the $\nu Co-S(SO_3)$ at 464–466 cm^{-1}. The $\delta_s(SO_3)$ and $\delta_{as}(SO_3)$ vibrations can be observed at 614–625 cm^{-1} and 540–560 cm^{-1} and are only very little influenced by coordination.

With respect to the deformation vibrations

$$\delta N_{ox}-Co-N_{ox}\,, \quad \delta N_{ox}-Co-S(SO_3)$$

$$\delta(SO_3)S-Co-S(SO_3)\,, \quad \delta L-Co-S(SO_3)$$

it was found that in the spectra of all the mentioned types of complexes only one medium strong band appeared at 196–198 cm^{-1} due probably to the $\delta N_{ox}-Co-N_{ox}$ or skeletal $Co(Diox.H)_2$ vibrations.

In the spectra of the disulfito- and monosulfito-complexes, derivatives of the above mentioned types one can observe several weak and medium strong bands (325–330, 240–245, 140–150, 135, 102–103, 95 cm^{-1}) corresponding to other skeletal and deformation vibrations [19].

Table 3. FTIR data of some sulfito–Co(III)-dioximino complexes

Charac-teristic frequency	I.	II.	III.	IV.	V.
ν O–H (H_2O)	3425 s	3430-3380 s	3425-3380 s	3385-3300 s	3500-3320 s
ν C–H	2943 s 2869 s	2943 s 2854 s	2945 s 2869 s	2925 m 2853 m	2960 s 2870 s
ν N–H	–	–	–	3211 m 3156 s	3220 m 3100 m
ν O–H (oxime)	2350-2200 m	2300-2200 m	2300-2160 m	2400-2120 m	2400-2300 m
δ O..H..O	1750 w	1770-1720 w	1780-1750 w	1780-1720 w	1800-1720 w
δ H_2O	1646 s	1642 s	1640s	1633 s	1660 s
ν C=N	1567 s	1567 s	1570 s	1573 v.s.	1580 s
δ CH_2	1455 m 1423 m 1335 m	1448 s 1357 m 1338 s	1440 s 1360 m 1340 m	1455 w 1425 w 1305 s	1450 s 1380 s
ν N–O (oxime)	1228 v.s.	1234 v.s.	1236 v.s.	1238 v.s.	1240 s
ν N–O (oxime)	1150 w	1147 w	1130 w	1102 v.s.	1120-
ν S–O	1083 v.s.	1111 v.s. 1083 s	1080 v.s.	1090 w	1080 s
ν S–O	954 v.s.	953 v.s.	955 v.s.	974 v.s.	970-950 s
δ $(NH)_2$ (amine)	–	–	–	830-820 w	830 m
δ_s SO_2	624 s	633 v.s.	630 s	624 v.s.	640 s
δ_{as} SO_2	553 m	535 m	540 w	560 w	560-540 w
ν Co–N (oxime)	518 m	511 s	512 s	515 s	512 s
ν Co–N (am)	–	–	–	490 m	490 m
ν Co–S (SO_3)	450 m	452 m	450 m	441 m	460 m
$\delta N_{ox} - Co - N_{ox}$	200 m	198 m		198m	198 m
other freq.	330 m 245 m 135 m	240 m 325 m 102 m			245 m 330 m 135, 102 m

I. $Na_3[Co(Niox.H)_2(SO_3)_2] \cdot Aq$; II. $Na_3[Co(Heptox.H)_2(SO_3)_2] \cdot Aq$;

III. $Na_3[Co(Octox.H)_2(SO_3)_2] \cdot Aq$; IV. $NH_4[Co(DH)_2(SO_3)(NH_3)] \cdot 4H_2O$;

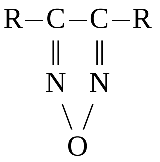
V. p-xylidine.$H[Co(Niox.H)_2(SO_3)$(p-xyl.)$] \cdot 5H_2O$

Table 4. Mass spectral data of some $(Cation)_3[Co(Diox.H)_2(SO_3)_2]$ and $(Cation)[Co(Diox.H)_2(SO_3)(amine)]$ type complexes

Formula	M/Z
$Na_3[Co(DH)_2(SO_3)_2]$	116(10%), 99(9%), 83(5%), 64(100%), 58(6%) 57(8%), 41.5(25%), 28(5%)
$Na_3[Co(Niox.H)_2(SO_3)_2]$	149(18%), 129(3%), 123(4%), 111(5%), 107(6%) 105(8%), 99(3%), 97(6%), 96(4%), 85(2%) 82(3%), 73(7%), 64(100%), 57(12%), 55(13%)
$Na_3[Co(Heptox.H)_2(SO_3)_2]$	157(15%), 138(5%), 122(3%), 108(5%), .. 64(100%), 28(6%)
$NH_4[Co(DH)_2(SO_3)(NH_3)]$	116(25%), 99(15%), 84(4%), 64(100%), 58(15%) 41.5(28%), 28(50%)
$NH_4[Co(DH)_2(SO_3)$(p-xylidine)]	121(100%), 116(10%), 106(48%), 99(4%), 91(8%) 77(13%), 64(25%), 42(22%), 41.5(24%), 28(55%)
o-toluidine.H[Co(Niox.H)$_2$ (SO$_3$)(o-toluidine)]	142(10%), 124(8%), 107(100%), 110(15%) 97(3%), 64(70%), 41.5(20%), 28(12%)
p-xylidine.H[Co(Niox.H)$_2$(SO$_3$)(p-xylidine)]	142(10%), 124(7%), 121(100%), 97(5%) 64(50%), 41.5(15%), 28(10%)
p-phenetidine.H[Co(Niox.H)$_2$(SO$_3$)(p-phenetidine)]	137(100%), 142(10%), 124(6%), 98(6%) 64(60%), 41.5(10%), 28(12%)

137 – phenetidine, 121 – xylidine, 116 – dimethylglyoxime, 124, 99 – furazans, 41–42 – acetonitrile, 64 – SO_2 – 28 – N_2

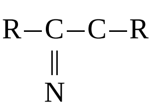
The *mass spectral data* of some $NH_4[Co(Diox.H)_2(SO_3)(amine)]$ and $Na_3[Co(Diox.H)_2(SO_3)_2]$ complexes are listed in *Table 4*. The thermal decomposition of these compounds is a very complicated process including a number of simultaneous and successive processes.
In the mass spectra free α-dioximes, 3,4-furazans



$$\begin{array}{c} R-C-C-R \\ \| \quad \| \\ N \quad N \\ \backslash\ / \\ O \end{array}$$

,

free radicals e.g.



$$\begin{array}{c} R-C-C-R \\ \| \\ N \end{array}$$

amines, nitriles (e.g. acetonitrile), hydrocarbon fragments, SO_2, N_2 appear in non-stoichiometric ratios.

Our previous derivatographic studies [20,21] show the thermal decompositin of the Cation.$[Co(DH)_2(SO_3)(amine)] \cdot n\ H_2O$ salts to begin with a dehydration process in one or two stages (1–2 endothermic peaks on the DTA curves between 60–100 °C). The decomposition of the anhydrous salt takes place in a more complicated way as compared to the $[Co(DH)_2(amine)_2]X$ derivatives, where generally the first stage is a partial deamination in stoichiometric ratio:

$$[\mathrm{Co(DH)_2(amine)_2}]X = [\mathrm{Co(DH)_2(amine)}X] + \mathrm{amine} \tag{3}$$

suitable also for kinetic studies.

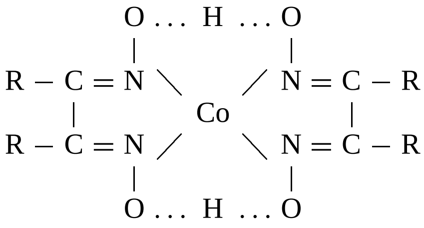
The mixed Cation.$[Co(Diox.H)_2(SO_3)$ (amine)] complexes lose also the amine ligand, but in non-stoichiometric ratios, and also other elimination and destruction reactions take place simultaneously some endo- and exothermic peaks on the DTA curves (between 180 and 400 °C).

The present mass spectral studies provide some data on the nature of the fragments eliminated during these complicated simultaneous and successive processes. The mass spectral data show that also redox phenomena occur (Co(III)→Co(II)) and oxidations with the participation of the O from the $\rangle\mathrm{C} = \mathrm{NOH}$ groups.

The *electronic spectra* of the $[Co(Diox.H)_2AB]^n$ type complexes in neutral solutions exhibit 4–6 bands, 1..2 bands in the visible (15–20 kK), and 2..4 bands in the UV region (25..47 kK).

The bands in the visible region with small molar absorption coefficients (lg : 1.5–2) may be considered to correspond to crystal field transitions, i.e. to Laporte forbidden d–d transitions.

Of the UV bands (lg : 3–5), the one appearing at about 40 kK in the spectra of all $Co(Diox.H)_2AB$ type complexes can be assigned to the common moiety of all derivatives in the mentioned class:



The A,B axial ligands influence only slightly the position of this band.

The electronic spectra of $[Co.(Diox.H)_2AB]$ type complexes are influenced by the pH of the solution.

This phenomenon shows the existence of protolytic equilibria in a wide pH range (0 . . . 14).

E.g. in the case of $[Co(Diox.H)_2L_2]^+$ type complexes ($L = NH_3$, amine, phosphine) the following complex species appear:

$$[Co(Diox.H_2)_2L_2]^{3+} \quad (I.), \quad [Co(Diox.H_2)(Diox.H)L_2]^{2+} \quad (II.),$$

$$[Co(Diox.H_2)L_2]^{+} \quad (III.), \quad [Co(Diox.H)(Diox)L_2]^{0} \quad (IV.),$$

$$[Co(Diox)_2L_2] \quad (V.)$$

($Diox.H^-$, $Diox^{2-}$ –mono– and double deprotonated dioxime molecule).

The species (I.) and (V.) appear only in strong acidic and alkaline media, respectively, and decompose easily. For kinetic and equilibrium studies only the proton transfer between species II., III. and IV. can be taken into account.

If A and/or B is SO_3^{2-} the equilibria become more complicated, especially in acidic media ($pH < 7$), due to the protonation of this group, e.g.

$$Co(Diox.H)_2(SO_3)_2^{3-} + \overset{H^+}{\rightleftarrows} Co(Diox.H)_2(SO_3)(HSO_3)^{2-}. \tag{4}$$

It is worth mentioning that similarly to the protonation of the SO_3^{2-} group, some other ligands, e.g. NO_2^-, N_3^-, appear also in protonated forms (HNO_2, HN_3) as ligands. This phenomenon was evidenced by our earlier kinetic studies on the quation of some

$$[Co(Diox.H)_2(NO_2)_2]^- \text{ and } [Co(Diox.H)_2(NO_2)L]$$

type complexes [20, 21]. The protonation of the azido group was observed only in strongly acid media.

The bisulfito group (HSO_3^-), analogously with the protonated nitro group, can be more easily replaced by solvent molecules (e.g. H_2O), as compared to the non-protonated one.

For this reason, the formation of $[Co(Diox.H)_2(SO_3)(HSO_3)]^{2-}$ is followed, probably, by the aquation process:

$$[Co(Diox.H)_2(SO_3)(HSO_3)]^{2-} + H_2O = [Co(Diox.H)_2(SO_3)(H_2O)]^- + HSO_3^-. \tag{5}$$

In more acidic solutions the appearance of other protonated species: e.g.

$$[Co(Diox.H)(Diox.H_2)(H_2O)(SO_3)]^0,$$

$$[Co(Diox.H)(Diox.H_2)(H_2O)(HSO_3)]^+,$$

probably also $[Co(Diox.H_2)(H_2O)(HSO_3)]^{2+}$ can be expected. In alkaline media only the deprotonation of the coordinated α-dioximes takes place and the metal-bonded SO_3 groups remain unaltered.

Our polarographic measurements on the $[Co(DH)_2(SO_3)(H_2O)]^+$ and some $[Co(DH)_2(SO_3)(amine)]^+$ derivatives in acidic media have shown the elimination of SO_2 from these complexes [22].

3. Derivation of Acidity Constants from Spectrophotometric Data

Let us denote the protonated complex species as HA and the deprotonated one as A^-. By neglecting the activity coefficients, the acidity constant may be written as

$$K_a = \frac{[H^+][A^-]}{[HA]}. \tag{6}$$

Logarithmization of *Eq.* (6) yields

$$\lg K_a = \lg [H^+] + \lg \frac{[A^-]}{[HA]},$$

i.e.

$$\mathrm{pK}_a = \mathrm{pH} + \lg \frac{[HA]}{[A^-]}. \tag{7}$$

By using a monochromatic light of a wavelength at which the molar absorptivities of the two molecular species are different, the concentration ratio may be expressed by means of the extinction (absorbance) and *Eq.* (7) becomes:

$$\mathrm{pK}_a = \mathrm{pH} + \lg \frac{E_b - E}{E - E_a}, \tag{8}$$

where E, E_a and E_b stand for the extinction (absorbance) of a solution of a certain analytical concentration of the complex at the pH given in *Eq.* (8), in acidic medium (where the only molecular species is HA), in alkaline medium, (where A^- is the only species), respectively.

As an example, in *Fig. 1* the UV absorption spectrum of $\mathrm{Na_3[Co(DH)_2(SO_3)_2]}$ is given at three different pH values. Obviously, the wavelength $\lambda = 332.5$ nm (≈ 30000 $\mathrm{cm^{-1}}$) is very suitable for deriving pK_a values, since at this λ the species A^- has an absorption band and the species HA has not. Therefore the extinction (absorbance) $E = 0.25$ measured at pH $= 3.78$ can be taken for E_a, the $E = 1.11$ value obtained at pH $= 9.62$ for E_b and by measuring E at intermediate pH values, *Eq.* (8) allows us to calculate pK_a from each experimental value. By performing measurements at 6 intermediate pH values

$$\mathrm{pK} = 5.62 \pm 0.14$$

was obtained.

We mention that in some cases the determination of E_a and E_b presents some difficulties due to the partial overlap of successive protolytic equilibria. Thus with increasing pH a systematic variation of the pK_a values appear. In such cases E_a and/or E_b values have been obtained by means of an iterative calculation procedure, viz. the standard deviation of the individual pK_a values from their arithmetical mean has been minimized.

Additivity constants derived by means of the above procedure are presented in *Table 5*. Since the protonation or deprotonation of the coordinated oxime molecules

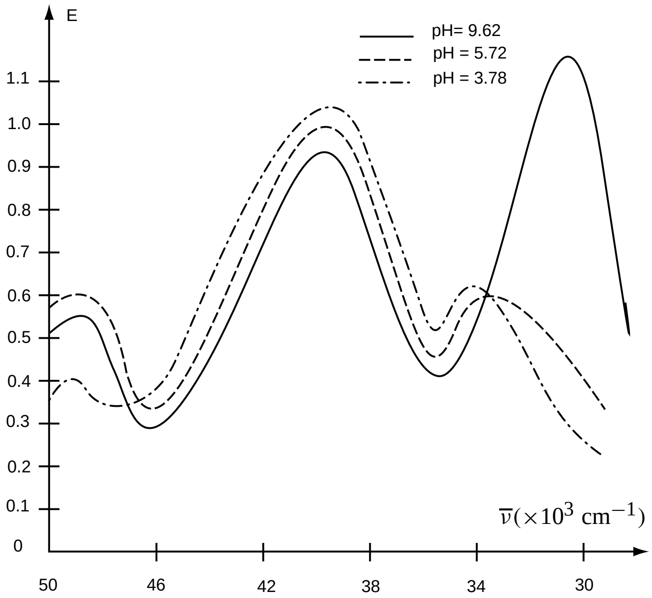


Fig. 1.

Table 5. pK_a values derived from spectrophotometric data

Complex ion	pK_a
$[\mathrm{Co(DH)_2(SO_3)_2}]^{3-}$	5.62
$[\mathrm{Co(Pentox.H)_2(SO_3)_2}]^{3-}$	5.13
$[\mathrm{Co(Niox.H)_2(SO_3)_2}]^{3-}$	5.54
$[\mathrm{Co(Heptox.H)_2(SO_3)_2}]^{3-}$	4.92
$[\mathrm{Co(Octox.H)_2(SO_3)_2}]^{3-}$	5.03
$[\mathrm{Co(DH)_2(H_2O)_2}]^{+}$	6.76

implies the break up of the hydrogen bridge, these phenomena occur at much lower or much higher pH values and pK_a values are of 2..3 and 9..12, respectively [24–31]. Therefore one may presume that the coordinated $\mathrm{SO_3}$ is easily protonated and pK_a values given in *Table 5* correspond to the reaction

$$\mathrm{RSO_3H = RSO_3^- + H^+}$$

with R : $\mathrm{Co(Diox.H)_2SO_3^-}$.

In the case of the aquo derivative pK_a represents the acidity constant of the coordinated water molecule. This value is in good agreement with earlier data found with analogous complexes [24–29].

3.1. Derivation of Acidity Constants from Potentiometric Titration Data

By performing a potentiometric titration of various complexes with HCl or NaOH solution, pH values were measured by using a glass electrode.

From the titration curves acidity constants were derived by using the following formulae:

Titration with HCl:

$$K_a = \frac{H(a - X - H)}{X - H}.$$

Titration with NaOH:

$$K_a = \frac{H(X + H - Kw/H)}{a - (X + H_w - K_w/H)},$$

where H stands for the hydrogen ion concentration, a for the analytical concentration of the complex, K_w for the ionic product of water and $X = \frac{v_t}{v_{ep}} \cdot a$, v_t and v_{ep} representing the actual volume of the titrant added and the volume belonging to the equivalence point, respectively.

The mean values of pK_a obtained from 8 to 10 experimental points of each titration curve are presented in *Table 6.*

In the last column is indicated the protolytic equilibrium to which the pK_a value might be assigned taking into account our earlier results [24–31]. Results presented in *Table 6* are in good agreement with our earlier observations as well as with the pK_a values derived from spectrophotometric data. For the acidity constant of the coordinated water molecules practically the same value is obtained by means of both methods. In the case of the coordinated SO_3H group pK_a is a little lower as compared to the similar values derived from spectral data. Nevertheless, one may consider the pK_a values derived from spectroscopic and potentiometric data to be in agreement which each other, allowing an insight into the complicated protolytic equilibria occurring in the solutions of the bis–dioximino complexes of Co(III).

Table 6. pK_a values derived from potentiometric titration data

Complex	Titrating agent	pK_a	Assignment	
$H[Co(DH)_2(CN)_2]$	NaOH	2.31	$R(DH_2)$	$R(DH)^-$
$Na_3[Co(Pentox.H)_2(SO_3)_2]$	HCl	2.74	$R(Pentox.H_2)$	$R(Pentox.H)^-$
$Na_3[Co(DH)_2(SO_3)_2]$	HCl	4.76	$R(SO_3H)$	$R(SO_3)^-$
$[Co(DH)_2(H_2O)_2]NO_3$	NaOH	6.74	$R(H_2O)$	$R(OH)^-$
$NH_4[Co(DH)_2(SO_3)(H_2O)]$	NaOH	9.51	$R(DH)$	$R(D)^-$
$Na_3[Co(Pentox.H)_2(SO_3)_2]$	NaOH	10.16	$R(Pentox.H)^-$	$R(Pentox)^{2-}$
R : $Co(Diox.H)_2\ (SO_3)^-$				

4. Experimental

Preparation of $Na_3[Co(Diox.H)_2(SO_3)_2] \cdot n\ H_2O$

20 mmoles of Co(II)-acetate and 40 mmoles of α–dioxime in 150 ml dil. alcoholic solution (1:2) were oxidized by air bubbling for 3–5 hours, then 40 mmoles of $Na_2SO_3 \cdot 7H_2O$ were added and after 1 h the disulfito–salts were precipitated from the filtered dark yellow solutions with 120–150 ml acetone. The formed yellow crystalline products are readily soluble in water.

We observed the aqueous solutions of the sodium salts to give sparingly soluble crystalline precipitates with hexamine type complexes of Co(III), Rh(III) and Cr(III) (e.g. luteo and rozeo salts). The monoacido pentamine and diacido tetramine derivatives are unable to enter into double decomposition reactions of this type.

Synthesis: 2 mmoles of hexamine salt in 100 ml water were treated with 2 mmoles of $Na_3[Co(Diox.H)_2(SO_3)_2]$ in 100 ml aqueous solution. The crystalline precipitates were filtered off after 5–10 min standing, washed with water and dried on air (48–72 h).

Preparation of Cation.$[Co(Diox.H)_2(SO_3)(amine)]$ *salts*

20 mmoles of $[Co(Diox.H)_2(H_2O)Br]$ obtained by the classical air oxidation of $CoBr_2$ + dioxime mixture in 150 ml dil. alcohol, were treated with 20 mmoles of freshly prepared $(NH_4)_2(SO_3)$ in 30–50 ml water. After allowing to stand for 3–4 h the brown solutions were treated with a mixture of 30 mmoles of amine and 30 mmoles of amine.HCl. The crystalline products formed were filtered off after 24–48 h, washed with ice-cold water and dried on air.

Analyses: Cobalt was determined complexometrically, sulfur as $BaSO_4$, nitrogen gas-volumetrically.

The *electronic spectra* were recorded in dil. alcoholic and aqueous solutions. (Concentration of the complexes: $10^{-4} - 10^{-5}$ mol/l in UV).

Equilibrium measurements: 5 ml solution of the complex + 5 ml Britton–Robinson buffer solution + H_2O diluted to 50 ml, after 30 min standing.

The *mass spectra* we recorded with KRATOS-MS-902-AEJ spectrometer without solvent. Ionization energy 70 eV, temperature of the ion source: 250°C.

The *FTIR spectra* were recorded in the 4000–500 cm^{-1} range with a Perkin–Elmer – 2000 apparatus in the KBr pellets, and in the 500–50 cm^{-1} range with a Bio–Rad–Winn spectrophotometer in polyethylene pellets.

Symbols

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;
DH_2 – dimethylglyoxime.

References

[1] Baldwin, M. E. (1960): *J. Chem. Soc.* p. 4369.
[2] Nyberg, B.–Larsson, B. (1973): *Acta Chem. Scand.*, **27**, p. 63.
[3] Nakamoto, K. (1980): Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, Chichester.
[4] Rosenheim, E.–Sasserath, E. A. (1899): *Z. anorg. allg. Chem.*, **21**, p. 122.
[5] Zacharova, F. A–Orlova, M. M. (1967): *Zhur. neorg. Khim.*, **12**, p. 3211.
[6] Schelokov, R. N.–Belomestyki, V. J. (1969): *Doklady Akad. Nauk SSSR*, **186**, p. 623.
[7] Baranovskii, J. B.–Babaeva, A. V. (1968): *Zhur. neorg. Khim.*, **13**, p. 1377.
[8] Pikareva, L. M.–Baranovskii, J. B. (1972): *Zhur. neorg. Khim.*, **17**, p. 3374.
[9] Baggio, S.–Becka, L. N. (1969): *Acta Cryst. Sect. B.*, **25**, p. 949.
[10] Murray, R. S.–Stranks, D. R.–Jandell, J. K. (1969): *J. Chem. Soc (D)*, 604.
[11] Chem, H. H.–Gower, R. W.–Tewari, P. H. (1966): *Inorg. Chem.*, **5**, p. 1913.
[12] Newman, G.–Powell, D. B. (1960): *J. Chem. Soc.*, p. 4369.
[13] Siebert, H.–Wittke, G.: *Z. anorg. allg. Chem.* (1974): **406**, p. 282.
[14] Syrzova, G. P.–Ablov A. V.–Korletyanu, L. N.: *Zhur. neorg. Khim.*, **11**, p. 1124, p. 2302 (1966); **13**, p. 2161, p. 2715 (1968), **15**, p. 470, (1970).
[15] Ablov, A. V. – Syrzova, G. P. (1960): *Zhur. neorg. Khim.*, **5**, p. 122.
[16] Várhelyi, Cs.–Somay, M.–Ádámosy, G. (1979): *Rev. Roum. Chim.*, **24**, p. 423.
[17] Várhelyi, Cs.–Somay, M.–Koch, A.– Grünwald, E. (1978): *Monatsh. Chem.*, **109**, p. 1311.
[18] Várhelyi, Cs.–Benkő, A.–Somay, M. – Koch, A. (1978): *Acta Chim. Acad. Sci. Hung.*, **97**, p. 167.
[19] Ferraro, J. R. (1971): Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New-York.
[20] Rose, M. E. – Johnstone, R. A. W. (1982): Mass Spectrometry for Chemists and Biochemists, Cambridge Univ. Press, Cambridge.
[21] Zsakó, J.–Várhelyi, Cs. – Liptay, G. – Borbély - Kuszmann, A. (1986): *J. Thermal Anal.*, **31**, p. 285.
[22] Várhelyi, Cs.–Zsakó, J.–Liptay, G. – Somay, M. (1985): *Rev. Roum. Chim.*, **30**, p. 695.
[23] Mánok, F. – Várhelyi, Cs. – Somay, M. (1979): *Stud. Univ. Babeş-Bolyai, Chem.*, **24**, No. 1, p. 19.
[24] Zsakó, J.– Várhelyi, Cs.–Finta, Z.–Kiss–Jakab, J. (1975): *Z. Naturforsch.*, **30b**, p. 393.
[25] Zsakó, J.–Várhelyi, Cs. – Finta, Z.: *J. Inorg. Nuclear Chem.*, **34**, p. 2887 (1972), **35**, p. 2839, (1973).
[26] Finta, Z.–Várhelyi, Cs.–Zsakó, J. (1973): *Rev. Roum. Chim.*, **18**, p. 417.
[27] Ripan, R. – Finta, Z.–Várhelyi, Cs. (1974): *Rev. Roum. Chim.*, **19**, p. 37.
[28] Finta, Z.–Várhelyi, Cs.–Dakó, E. (1976): *J. Inorg. Nuclear Chem.*, **38**, p. 2261.
[29] Finta, Z.–Várhelyi, Cs.–Zsakó, J. (1988): *Rev. Roum. Chim.*, **33**, p. 263.
[30] Ganescu, I.–Várhelyi, Cs.–Zsakó, J.–Chirigiu, L. (1993): *Polish J. Chem.*, **67**, p. 15.
[31] Zsakó, J.–Várhelyi, Cs.– Makkay, F.–Kovács–Ludescher, K. (1994): *Stud. Univ. Babeş-Bolyai, Chem.*, **39**, p. 85.