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ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS. Part LXXXVIII

NEW MIXED NITRO-COMPLEXES OF COBALT(III) WITH 1,2-CYCLOHEXANE DIONE DIOXIME

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Abstract

New mixed nitro-complexes of cobalt(III) have been obtained by substitution reactions from $Na_3[Co(NO_2)_6]$ and by various anation reactions from $[Co(Niox.H)_2(H_2O)(NO_2)]$ with halides (Cl^-, Br^-), pseudohalides (CN^-,NCX^-; X=O,S,Se) and with aromatic and heterocyclic amines, respectively.

A series of binary salts of the type Cation $[Co(Niox.H)_2(NO_2)Y]$ (Y=halide or pseudohalide) and nonelectrolytes $[Co(Niox.H)_2(NO_2)(amine)]$ have been isolated and characterized.(Niox.H_2 - nyoxime - 1,2-cyclohexane dione dioxime). Some structural problems are discussed on the basis of UV and IR spectra.

Keywords: dioxime complexes, preparation, IR, UV spectra.

Introduction

The nitro-group having an ambidentate character, can be co-ordinated to some transition metal ions through the oxygen atom (nitrito-complexes: M-ONO) or through the nitrogen atom (nitro-complexes: M-NO_2). Nitrito complexes are characteristic of chromium(III), $[(Cr(NH_3)_5(ONO)]^{2+}$, $[Cr(en)_2(ONO)_2]^+$), uranium and neptunium [1]. Nitro-complexes were described in a considerable number for Rh(III) ($[Rh(NO_2)_6]^{3-}$, $[Rh(NH_3)_5 (NO_2)]^{2+}$, etc.), platinum ($[Pt(NO_2)_4]^{2-}$, $[Pt(NO_2)_2(NH_3)_2]$, [2,3]). Cobalt(III)-complexes with the above mentioned group were described as nitro-pentamines $[Co(NH_3)_5NO_2]^{2+}$, $Co(en)_2(NH_3)(NO_2)]^{2+}]$ [4, 5], dinitro-tetramines $[Co(en)_2(NO_2)_2]^+$, $[Co(dip)_2(NO_2)_2]^+$ [6,7], trinitro- and tetranitro-derivatives (e.g. $[Co(NH_3)_3(NO_2)_3]$, $NH_4[Co(NH_3)_2(NO_2)_4]$, etc. [8,9], mixed nitro-complexes with various aliphatic and heterocyclic polyamines [10,11], etc.

The kinetics of some substitution reactions of these nitro-complexes (aquation kinetics) has also been studied [12-14].

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Results and Discussion

CHUGAEV [15] has mentioned the hexanitro-cobaltiat to react with dimethylglyoxime forming the dinitro-complex: $[Co(DH)_2(NO_2)_2]^-$. Some halogeno-nitro-complexes of the type: $[Co(DH)_2X(NO_2)]^-$ (X=Cl,Br,I) have been described by ABLOV et al.[16,17].

We have observed the alicyclic α-dioximes (1,2-cyclopentane, -cyclohexane-, -cycloheptane dione dioximes to react easily in aqueous medium with $Na_3[Co(NO_2)_6]$ [18,19]. E.g. with 1,2-cyclohexane dione dioxime (nyoxime: $C_6H_{10}N_2O_2$) four nitro groups can be substituted as follows:

$$Na_3[Co(NO_2)_6]+2Niox.H_2 = Na[Co(Niox.H)_2(NO_2)_2]+2NaNO_2+2HNO_2.$$

The free monobasic acid: $H[Co(Niox.H)_2(NO_2)_2]$ can be separated from the solution of the sodium salt by treatment with cold dilute H_2SO_4.

By warming the acidic solution on a water bath an aqua-nitro-nonelectrolyte is precipitated following the aquation reaction:

$$[Co(Niox.H)_2(NO_2)_2]^- + H^+ + H_2O = [Co(Niox.H)_2(H_2O)(NO_2)] + HNO_2.$$

This substance can be used as starting material for a series of substitution reactions (See *Fig. 1*).

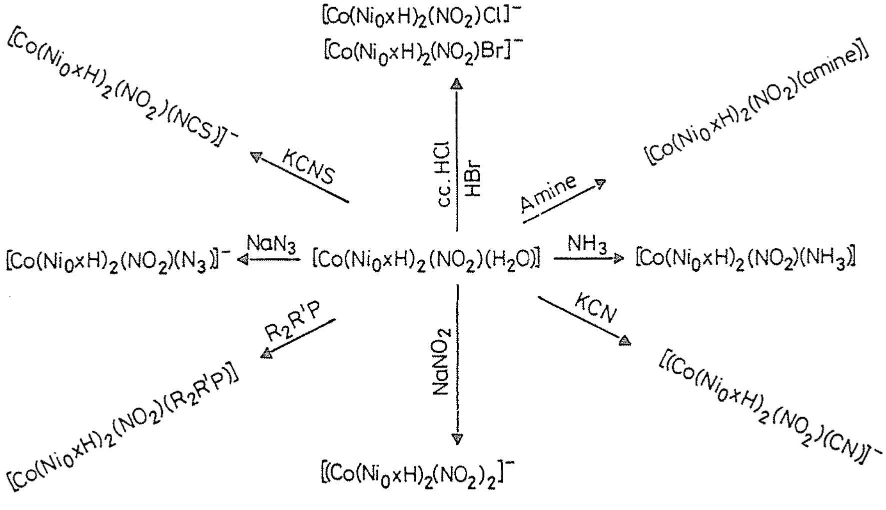

Fig. 1. Substitution reactions of $[Co(Niox.H)_2(NO_2)(H_2O)]$

The anation process with halides (Cl^-, Br^-) and pseudohalides (CN^-, NCX^- ; X=O,S,Se; N_3^-) leads to the formation of other monobasic nitro-acids (or their alkaline salts):

$$[Co(Niox.H)_2(H_2O)(NO_2)]+NaX = Na[Co(Niox.H)_2(NO_2X]+H_2O.$$

The aqueous alcoholic solutions of the alkaline salts: $Na[Co(Niox.H)_2(NO_2)X]$ gives characteristic slightly soluble, crystalline salts with the hydrochlorides of some heterocyclic N-bases, alkaloids and especially with diacido-tetramine type complex cations of Co(III), Cr(III) and Rh(III).

The hexamines and monoacido-pentamines $[M(NH_3)_6]^{3+}$, $[M(NH_3)_5X]^{2+}$ are not suitable for this purpose. Their salts are more easily soluble. Because of the special formation conditions these slightly soluble salts (from *Tables (1-3)*) are not suitable for analytical purposes (determination of Co, Cr, Rh). It is worth mentioning that the sulfito- and thiosulfato groups with much greater trans effect than the nitro-ligand, replace both the water molecule and the NO_2-ligand:

Table 1

New derivatives of the $H[Co(Niox.H)_2Cl(NO_2)]$ and $H[Co(Niox.H)_2Br(NO_2)]$ acids

No	Formula	Mol.wt. calcd.	Appearance	Analysis(%)		
					Calcd.	Found
1.	$[Co(DH)_2(pyridine)_2].A$	870	sparkling brown	Co	13.54	13.45
			rhombic plates	N	17.71	17.34
2.	$[Co(DH)_2(aniline)_2].A.H_2O$	916	brown prisms	Co	12.86	12.48
				N	16.82	16.50
3.	$[Co(pyridine)_4Cl_2].A$	869	green-yellow	Co	13.56	13.25
			irregular short prisms	N	14.51	14.70
4.	$[Co(DH)_2(pyridine)_2].B$	914.5	brown	Co	12.89	12.64
			dendrites	N	16.85	17.14
5.	$[Co(DH)_2(aniline)_2].B.H_2O$	960.5	yellow-brown	Co	12.27	12.20
			needles	H_2O	1.82	1.90
				N	16.04	16.30
6.	$[Co(pyridine)_4Cl_2].B$	913.5	yellow-green	Co	12.90	12.79
			thin prisms	N	13.90	13.77

A - $[Co(Niox.H)_2Cl(NO_2)]^-$; B - $[Co(Niox.H)_2Br(NO_2)]^-$
(Co was determined complexometrically after destroying the complexes with cc. H_2SO_4; N - determination gas volumetrically)

$$[Co(Niox.H)_2(H_2O)(NO_2)]+2SO_3{}^{2-}=[Co(Niox.H)_2(SO_3)_2]^{3-}+NO_2^-+H_2O$$

$$[Co(Niox.H)_2(H_2O)(NO_2)]+2S_2O_3^{2-}=$$
$$=[Co(Niox.H)_2(S_2O_3)_2]^{3-}+NO_2{}^-+H_2O.$$

A series of new derivatives of the mentioned types are characterized in *Tables 1-3.*

Table 2

New derivatives of the $H[Co(Niox.H)_2(CN)(NO_2)]$ acid

No.	Formula	Mol.wt. calcd.	Appearance		Analysis(%) Calcd.	Found
1.	$Ag[Co(Niox.H)_2(CN)(NO_2)]$ $.H_2O$	539.2	yellow micro-crystals	Co	10.39	11.0
				H_2O	3.33	3.50
				N	15.56	15.90
2.	$K[Co(Niox.H)_2(CN)(NO_2)]$ $.3H_2O$	507.4	dark orange prisms	Co	11.61	11.50
3.	$[Co(DH)_2(pyridine)_2]C.H_2O$	878.6	yellow needles	Co	13.41	13.40
				H_2O	2.10	2.20
4.	trans-$[Cr(en)_2(NCS)_2].C$	701.4	yellow stars	Co+Cr	15.89	15.75
				S	9.13	9.40

C - $[Co(Niox.H)_2(CN)(NO_2)]^-$; DH_2 -dimethylglyoxime;
S determined as $BaSO_4$

Table 3

New derivatives of the $H[Co(Niox.H)_2(NCO)(NO_2)]$ and $H[Co(Niox.H)_2(NCSe)(NO_2)]$ acids

No.	Formula	Mol.wt. calcd.	Appearance		Analysis Calcd.	Found
1.	trans-$[Co(en)_2Cl_2].D.H_2O$	715.1	short yellow prisms	Co	16.49	16.60
2.	trans-$[Co(en)_2Cl_2].E$	742.1	long yellow prisms	Co	16.49	16.60
				N	18.88	18.65
3.	$[Co(pyridine)_4Cl_2].D$	875.6	yellow-green needles	Co	13.46	13.40
4.	$[Co(pyridine)_4Cl_2].E$	938.6	yellow needles	Co	12.56	12.35
				N	14.92	14.57
5.	$[Co(DH)_2(pyridine)_2].D$	876.6	sparkling gold yellow dendrites	Co	13.45	13.60
6.	$[Co(DH)_2(pyridine)_2].D$	939.6	brown stars	Co	12.54	12.67
				N	17.88	27.60
7.	$[Co(DH)_2(aniline)_2].D$	904.6	sparkling yellow dendrites	Co	13.03	11.89
8.	$[Co(DH)_2(aniline)_2].E$	967.7	brown crystalline crops	Co	12.18	11.89
				N	17.37	17.14
9.	$[Co(DH)_2(p\text{-phenetidine})_2].D$	992.7	sparkling yellow dendrites	Co	11.87	11.56
10	$[Co(DH)_2(p\text{-phenetidine})_2].E$	1055.8	brown stars	Co	11.16	10.87
				N	15.93	16.10

D - $[Co(Niox.H)_2(NCO))(NO_2)]^-$; E - $[Co(Niox.H)_2(NCSe)(NO_2)]^-$

The anation reactions with aromatic amines (pK_b :9-13), N-heterocyclic amines and tertiary alkyl-aryl-phosphines lead to the formation of [Co(Niox.H)$_2$(NO$_2$)(am)] type non-electrolytes.

Some new complexes of this type are characterized in *Table 4*.

Table 4

Some new non-electrolytes of the type [Co(Niox.H)$_2$(NO$_2$)(amine)]

No.	Amine	Mol.wt	Appearance		Analysis (%)	
		calcd.			calcd.	found
1.	NH_3	404.3	brown prisms	Co	14.57	14.41
				N	20.78	21.10
2.	thiourea	463.4	sparkling brown spears	Co	12.72	12.47
3.	pyridine	466.3	hexagonal plates	Co	12.63	12.50
				N	18.02	18.23
4.	*β*-picoline	480.4	short yellow dendrites	Co	12.26	12.10
5.	*γ*-picoline	480.4	sparkling brown rhombic plates	Co	12.26	12.04
				N	17.50	17.35
6.	benzylamine	494.4	yellow-brown needles	Co	11.92	12.10
7.	*o* -toluidine	494.4	yellow-brown prisms	Co	11.92	12.03
8.	*p*-toluidine .2H_2O	530.6	greatbrown prisms	Co	11.10	10.88
				H_2O	6.70	7.10
9.	*m*-xylidine	508.4	regular rhombic plates	Co	11.59	11.42
				N	16.53	16.40
10.	*o*-ethylaniline	508.4	short brown prisms	Co	11.59	11.45
				N	16.53	16.40
11.	*o*-anisidine	510.4	short brown prisms	Co	11.59	11.37
12.	*p*-anisidine .2H_2O	546.5	oval brown plates	Co	10.78	10.66
				H_2O	6.50	6.90
13.	*p*-phenetidine	524.4	sparkling thin plates	Co	11.23	11.19
				N	16.02	16.20
14.	*p*-Cl-aniline .2H_2O	550.8	sparkling brown hexagonal plates	Co	10.70	10.68
				H_2O	6.50	6.90
				N	15.25	15.42
15.	*p*-Br-aniline	595.3	sparkling irregular prisms	Co	9.90	9.77
				H_2O	6.00	6.50
16.	*p*-I-aniline	606.3	long yellow prisms	Co	9.72	9.68
				N	13.86	13.60
17.	phenetylamine	508.4	irregular crops	Co	11.59	11.68
				N	16.52	16.43

The Cation.[Co(Niox.H)$_2$(NO$_2$)X] binary salts and the nitro-amine-non-electrolytes are stable up to 120-150 °C depending on the nature of the

Table 5
Wave numbers (in kK) and molar extinction coefficients of the absorption bands in the electronic spectra of some $[Co(Niox.H)_2(NO_2)X]$ type non-electrolytes

X	A	B	C	D	E
pyridine	29.5i	33.5i	39.7	44.8	48.8
	2400	3430	13370	13030	16880
β-picoline	28.5i	34.0i	39.2	45.0i	48.4
	2160	4320	13930	14400	18700
NH_3	28.0i	33.5i	39.5	-	48.3
	1570	3300	12200		13600
o-ethyl aniline	29.2i	33.1i	38.9	-	48.5
	3840	4650	10500		16200
m-xylidine	28.1	33.2i	39.8	-	47.6
	4560	6160	14100		19800
o-anisidine	27.8	33.4i	39.3	45.5i	48.1
	3180	3700	10100	11400	15200
p-anisidine	26.8	32.5	39.5	45.2	48.6
	4980	3390	12300	13200	14200
p-phenetidine	27.5	33.0i	39.2	-	48.7
	5300	4800	12500		20300
p-Cl-aniline	29.5i	33.2i	39.5	-	48.5
	5100	5800	13000		18200
p-Br-aniline	29.5	33.5	39.6	-	48.5
	4800	4400	10700		14700
thiourea	30.0i	36.0i	40.8	-	49.0
	5200	8100	11000		16200

cation and of the amine component, respectively, and decompose over this temperature range generally instantaneously or with explosion with the formation of gaseous products: N_2, NO, CO, CO_2, H_2O in non-stoichiometric ratios. On the thermal curves of some derivatives stoichiometric final products are not observed. On the differential thermal analysis curves sharp, intense exothermic peaks (120-150 °C) show the oxidative character of the decomposition processes.

At 20± 0.1 °C the electric conductivity measurements of some Cation. $[Co(Niox.H)_2X(NO_2)]$ derivatives (X = Cl, Br, CN) yield molar conductivity values of 90-110 $ohm^{-1}cm^2mol^{-1}$ at a dilution of V=1000 l/mol and V=2000 l/mol. These values are characteristic of binary complex salts of the AB type. Analogous conductivity studies on some

[Co(Niox.H)$_2$(NO$_2$)(amine)] type complexes give 2-6 ohm^{-1}cm^{2}mol^{-1} values for the derivatives with NH$_3$, aniline, *m*-, *p*-toluidine and anisidine showing the non-electrolytic character of these compounds. The non-electrolytes are generally soluble in CCl$_4$, CHCl$_3$, benzene, etc.

Electronic spectra of 11 non-electrolytic type complexes have been recorded. All spectra contain 4 or 5 absorption bands similar to other bis-dioximine type complexes. Wave numbers and molar extinction coefficients of these bands are given in *Table 5*. The most characteristic bands of dioximine-cobalt complexes are the charge transfer (C_T) bands B and C, situated at about 34-38 and 41-42 kK, respectively, in the case of dimethylglioximato-Co(III)-derivatives [20].

Band B has been assigned to a Co ⟶ dioxime CT[21], band D to a dioxime ⟶ Co CT. In bands C and E the main contribution may be expected from the part of Co ⟶ axial ligand CT transitions. The position of band A corresponds to *d-d* type ligand field transition, but the absorbance is too high. Presumably, the *d-d* transition is overlapped by a CT transition.

From the wave number values presented in *Table 5* no conclusions can be drawn concerning the influence of the axial ligand X.

Table 6
Mean wave numbers (in kK)of the absorption bands
in the electronic spectra of some bis-dioximine complexes

Type	A	B	C	D	E	Ref.
[Co(DH)$_2$(Am)$_2$]	27.6	32.6	39.9		49.0	22
[Co(DH)$_2$(SO$_3$)X]	-	33.7	41.2		-	23
[Co(Niox.H)$_2$(NO$_2$)X]	28.5	33.5	39.5		48.5	this paper
[Co(Niox.H)$_2$(SO$_3$)X]	-	33.1	40.7		49.6	24
[Co(Diph.H)$_2$(Am)$_2$]	26.8	31.5	38.6		49.3	25

The above spectral data can be compared with our earlier results, [22-25], obtained for some dimethylglyoxime (DH$_2$), Niox.H$_2$ and Diphenylglyoxime (Diph.H$_2$) containing complexes. For this purpose the arithmetic mean has been calculated from the wave numbers of different absorption bands. The results are presented in *Table 6*. The mean values for band B are in good agreement with the assumption that this band is due to a Co⟶ dioxime CT transition since it has, practically the same value, excepting the Diph.H$_2$ derivatives having a large delocalized π-bond system. Data concerning band C are also consistent with the assumption that this band implies a Co ⟶ axial ligand CT transition, since for the SO$_3$ derivatives clearly enhanced values are obtained. Nevertheless, the low value observed with Diph.H_2 derivatives suggests a contribution also from the part of the dioxime ligands.

Infrared spectra. In the case of mononitro-complexes where a C_{2v} local symmetry may be assumed, the normal vibrations of the nitro group linked to a metal ion can be treated as with Z X Y_2 type planar molecules [26]. Six normal vibrations appear, their representation being

$$T_{\mathrm{vibr}} = 3A_1 + 2B_2 + B_1,$$

viz. $\nu_{\mathrm{s(M\text{-}N)}}$ (A_1), $\nu_{\mathrm{s(NO_2)}}$ (A_1), $\delta_{\mathrm{s(NO_2)}}$ (A_1), $\nu_{\mathrm{as(NO_2)}}$ (B_2), $\delta_{\mathrm{r(NO_2)}}$ (B_2) and $\delta_{\mathrm{w(NO_2)}}$ (B_1). All these are active in IR, but for $\delta_{\mathrm{r(NO_2)}}$ the wave number $\bar{\nu}$ ¡ 400 cm^{-1}.Therefore, in the IR spectra of the complexes studied and recorded by us 5 vibration bands can be observed. By comparing the spectra with those of analogous complexes containing other ligands in lieu of NO_2, these bands have been identified and their wave numbers are given in *Table 7.*

Table 7
Wave numbers (in cm^{-1}) of the vibration bands
in the IR spectra of $[Co(Niox.H)_2X(NO_2)]^{n-}$ type complexes

No.	n	X	$\nu_{\mathrm{M\text{-}N}}$ A_1	$\delta_{\mathrm{w(NO_2)}}$ B_1	$\delta_{\mathrm{s(NO_2)}}$ A_1	$\nu_{\mathrm{s(NO_2)}}$ A_1	$\nu_{\mathrm{as(NO_2)}}$ B_2
1	0	*p*-Cl-aniline	445	600	825	1330	1420
2	0	*p*-phenetidine	425	600	830	1324	1430
3	0	H_2O	425	617	825	1327	1443
4	0	NH_3	410	-	830	1332	1449
5	0	pyridine	440	650	825	1328	1435
6	1	Cl	435	600	828	1327	1448
7	1	Br	435	616	826	1320	1440
8	1	NO_2	435	616	825	1328	1450
9	1	CN	405	630	830	1330	1450

In the case of harmonic vibrations the calculation of the force constants can be performed by forming the secular equation

$$[\mathbf{G}_T\mathbf{F} - \lambda] = 0 \tag{1}$$

where $\mathbf{G}_T$ and $\mathbf{F}$ stand for the kinetic energy and the force constant matrix, respectively, using as basis the internal co-ordinates. λ is a diagonal matrix, its elements being $\lambda_i = 4\pi^2c^2\tilde{\nu}_i{}^2$, where $\tilde{\nu}_i$ stands for the wave number of the vibration band. By expressing $\tilde{\nu}_i$ in cm^{-1}, λ_i may be calculated as

$$\lambda_i = \left[\frac{\tilde{\nu}_i}{130.283}\right]^2 \tag{2}$$

and the solution of Eq.(1) gives the force constants in N/m.

The model of the complex molecule is given in *Fig .2.*

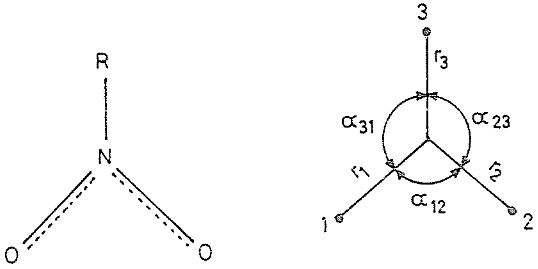

Fig. 2. Molecular model of the complexes studied

The variations of the intermolecular distances r_1, r_2, r_3, and as well as of the bond angles $\alpha_{12}, \alpha_{23}, \alpha_{31}$ will be taken as internal co-ordinates. In order to describe the out-of-plane deformation of the molecule, one more internal co-ordinate must be defined, viz. the solid angle τ between r_1, r_2 and r_3.

The elements of the matrix $\mathbb{G}$ can be calculated by using the formulae given by DECIUS [26,27].

By neglecting the repulsion terms between the O atoms and R, the matrix $\mathbb{F}$ will contain the following elements: force constant f_{11} of the attraction between N and O atoms, force constant f_{12} of the repulsion between both O atoms, force constant f_{33} of the attraction between R and the N atom, and force constants $f_{\alpha_{12}}$, $f_{\alpha_{23}}$, and f_τ, characterising the modification of the angles $\alpha_{12}, \alpha_{23} = \alpha_{31}$ and τ.

By introducing the symmetry co-ordinates a partial diagonalization of matrices $\mathbb{G}$ and $\mathbb{F}$ can be performed and the secular equation(1) can be decomposed into 3 equations [28].

The matrix elements of $\mathbb{G}$ have been calculated using the atomic masses and the following approximate values: $r_1 = r_2 = 1.22 \times 10^{-10}$m, $\alpha_{12} = 120°$. In the Central Force Field (CFF) approximation $f_{\alpha_{12}}=f_{\alpha_{23}}=f_\tau=0$ and one obtains [28] for the vibrations of A_1 symmetry:

$$\begin{bmatrix} 0.0982X - \lambda_i & -0.0505Y & 0 \\ 0.0505X & RY - \lambda_i & 0 \\ -7.17 \times 10^8 \times X & 10.1 \times 10^8 Y & -\lambda_i \end{bmatrix} = 0. \qquad (3)$$

For the vibrations of B_2 symmetry, one has:

$$\begin{bmatrix} 0.169Z - \lambda_i & 0 \\ (e-h)Z & 0 \end{bmatrix} = 0; \quad \text{i.e.} \quad \lambda_i = 0.169Z, \qquad (4)$$

where $X = f_{11} + f_{12}$, $Y = f_{33}$, $Z = f_{11} - f_{12}$:

$$R = \frac{1}{M_R} + 0.0714.$$

e and h stand for some elements of the matrix **G** and $\mathbf{M}_R$ is the molar mass of the moiety R.

Since in the CFF approximation the force constants of bond angle deformations are neglected, only the wave numbers of the stretching vibrations can be used. Thus, by calculating λ_i from the wave numbers of the A_1 symmetry vibration bands $\nu_{M\text{-}N}$ and $\nu_{s(NO2)}$ one obtains two linear equations from *Eq.*(3) allowing the calculation of X and Y. Using the wave number of the B_2 symmetry $\nu_{as(NO_2)}$ vibration, one obtains Z from *Eq.*(4).

Table 8
Force constants in N/m calculated from the wave numbers of the stretching vibrations

No.	f_{11}	f_{12}	f_{13}
1	842.2	139.3	265.1
2	847.2	134.4	238.4
3	857.1	130.7	236.6
4	866.1	134.2	218.5
5	849.4	131.6	257.2
6	856.5	125.6	249.3
7	846.6	123.7	251.2
8	858.5	125.6	249.7
9	866.0	133.1	212.4
1-5	852.4	134.0	243.2
6-9	856.9	127.0	240.7
1-3	848.8	134.8	246.7
4-9	857.2	129.0	239.7

Consequently, the calculation of f_{11}, f_{12} and f_{33} possible from our experimental data presented in *Table 7.*

By comparing *Tables 7* and *8* one observes that f_{33} increases with increasing wave number of the $\nu_{s(NO_2)}$ vibration. The strength of the Co-N bond [26] [26] must increase in the same direction the . With increasing f_{12} the wave number of $\nu_{s(NO_2)}$ increases, but that of $\nu_{as(NO_2)}$ decreases, i.e. with increasing O-O repulsion the former will be less, the latter will be more easily excited.

The force constant of the N-O bond, f_{11}, varies in parallel with the sum of the wave numbers of the $\nu_{s(NO_2)}$) and $\nu_{as(NO_2)}$ bands, since both wave numbers increase with increasing bond strength.

In order to compare the non-electrolytes ($n=0$) with the anionic complexes ($n=1$), the arithmetic mean of the force constants has been calculated and given in *Table 8.* Obviously, f_{11} is larger in the case of the anionic complexes (6-9), as compared to the non-electrolytic ones (1-5). With the force constants f_{12} and f_{33} the reverse is observed. Since in the anionic complexes a possibility of Co-X π-bond formation arises, one might assume the above effect to be due to this π -bond formation. Therefore it seems to be reasonable to transfer the pyridine derivative from the first to the second class. It is interesting that for the NH_3 derivative force constant values have been obtained which are nearer to the values characteristic of the anionic complexes. By assuming a hyperconjugation the Co-N π-bond formation might be possible also in the case of the NH_3 derivatives, the arithmetic means calculated for the complexes not having the possibility of Co-X π-bond formation (1-3) and for the complexes in which π-bond might be formed between Co and X (4-9), are presented in *Table 8.* Obviously, the differences between the force constants increase, as compared to the previous classification.

The π-bond formation implies a shift of the Co π-electrons towards the X ligand and therefore weakens the π-bond between the Co and N atom of the nitro moiety, which explains the diminution of f_{33}. In the same time, due to he shift of the π-electrons the electronic charge of the O atoms becomes less and, consequently, f_{33} also diminishes. The π-bond formation between the Co atom and the NO_2 ligand occurs with the participation of the antibonding π-orbital of the O-N-O moiety, i.e. this bond diminishes the N-O bond strength. Thus the Co-X π-bond formation weakens the Co-NO_2 π-bond and increases the N-O bond strength, which leads to the increase of f_{11}, observed in *Table 8* [29].

Experimental

$[Co(Niox.H)_2(H_2O)(NO_2)]$:40.8 g (100 m-moles) of $Na_3[Co(NO_2)_6]$ were dissolved in 250 ml water and a solution of 28.4 g nyoxime (200 m-moles) in 300 ml ethanol were added. The mixture was heated on a water bath until its volume was reduced to about 250-300 ml. It was filtered and to the reddish-brown solution 40 ml 30 % H_2SO_4 solution were added. The reddish-brown $H[Co(Niox.H)_2(NO_2)_2]$ precipitate transformed gradually into a dark brown crystalline mass after further heating for about 3/4-1 hour on the bath. The product was filtered, washed with water and dried in air. Hexagonal plates. Yield: 80-85 p.c.

Analysis: Found Co 14.40, N 17.35
Calcd. for $Co(C_6H_9N_2O_2)_2(H_2O)(NO_2)$ (Mol.wt. cacd. 405.3)

Co 14.54, N 17.28

$H[Co(Niox.H)_2(NO_2)Cl].3.5H_2O$ and $H[Co(Niox.H)_2(NO_2)Br].2H_2O$ 40 mmoles of $[Co(Niox.H)_2(NO_2)(H_2O)]$ were treated on a water bath with 25 ml 25% HCl, or 25ml 30% HBr, respectively. After 40-60 min standing the crystalline mass was filtered off. The crude products were dissolved in alcohol and poured into 80-100 ml 25 % HCl, or 30 % HBr, respectively. The crystalline products formed were filtered off and washed acid free with ether.

$H[Co(Niox.H)_2Cl(NO_2)].3.5\ H_2O$ (red-brown plates).

Analysis: Co calc. 11.69, found 12.30,
H_2O calc. 11.40.,found 10.90,
N calc. 14.39, found 14.28.

$H[Co(Niox.H)_2Br(NO_2)].3.5\ H_2O$ (dark brown hexagonal plates)

Analysis: Co calc. 11.69, found 11.70,
H_2O calc. 11.40, found 7.30,
N calc. 13.90, found 13.66.

$K[Co(Niox.H)_2X(NO_2)]$-solutions (X= CN, NCO, NCS, NCSe) 20 mmoles of $Co(Niox.H)_2(NO_2)(H_2O)$ in 200 ml aqueous suspension were treated on a water bath with a slight excess of KCN, KCNO, KCNS, KCNSe; molar ratio 1:1.1). The aqua-nitro-non-electrolyte dissolves gradually and an orange to red-brown solution is formed depending on the nature of KX. After filtration and dilution the mother liquors were used for double decomposition reactions. The cyano-nitro-acid was isolated with an excess of 40% H_2SO_4.

$H[Co(Niox.H)_2(CN)(NO_2)].H_2O$(thin yellow prisms)

Analysis
Co calc. 13.09, found 12.98,
N calc. 15.55, found. 15.76.

Cation.$[Co(Niox.H)_2X(NO_2)]$-salts

2-3 moles of $K[Co(Niox.H)_2X(NO_2)]$ in 30-40 ml aqueous solution were treated with an excess (10 mmoles) of diacido tetramine type cobalt(III) and chromium(III)-complex salts (chlorides or acetates) in 50-100 ml water, or aqueous alcohol (1:1).The crystalline binary salts were filtered off after standing for 30-60 minutes, washed with water and dried in air.

The $[Co(DH)_2(amine)_2]$ acetate precipitating agents were prepared by air oxidation of the components in dilute alcohol.

$[Co(Niox.H)_2(NO_2)(amine)]$

I.method. 2 mmoles of $[Co(Niox.H)_2(H_2O)(NO_2)$ in 60-80 ml aqueous suspension were treated at water bath temperature with 3 mmoles of corresponding amine in 10-15 ml alcohol and 2g ammonium acetate buffer. The $[Co(Niox.H)_2(H_2O)(NO_2)]$ dissolves gradually and the nitro-amine-non-electrolyte precipitates as a crystalline mass. The product is filtered off, washed with water and dried in air.

II.method. 2 mmoles of $H[Co(Niox.H)_2Cl(NO_2)]$ in 50 ml water were treated with 2g ammonium acetate and 3 mmoles of amine in 10-15ml alcohol. The nitro-amine-non-electrolyte crystallizes after standing 30-40 minutes on a water bath.

The electronic spectra were recorded with a Specord (GDR) spectrophotometer in methanol.

The infrared spectra were recorded with an UR 20 Carl Zeiss Jena spectrophotometer in potassium bromide pellets.

The electric conductance measurements were carried out with a Radelkis (Hungary) conductometer.

The thermal measurements were made with a MOM Derivatograph (Budapest).

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