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ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS,

Part XC

NEW AZIDO–COMPLEX ACIDS OF COBALT(III) WITH ALICYCLIC α-DIOXIMES

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Abstract

Four new diazido-complex acids of the type $H[Co(Diox.H)_2(N_3)_2]$ ($Diox.H_2$ = alicyclic α–dioximes: $Cpdox.H_2$, $Niox.H_2$, $Heptox.H_2$ and $Octox.H_2$) and the $H[Co(Niox.H)_2(N_3)(NO_2)]$ were obtained by air oxidation of the components and by substitution reactions. The free acids and their salts were characterized by IR and electronic spectra and by potentiometric measurements. The composition of the azido-derivatives was proved also by isolation of 30 new salts with cobalt(III)- and chromium(III)- amine bases.

Keywords: azido-complex acids of cobalt(III), alicyclic α–dioxime complexes.

Introduction

The formation of complex metal-azides in various solvents has been investigated by means of electrochemical and spectroscopic methods and the existence of some azido-aquo specia $[M(H_2O)_n(N_3)_{6-n}]^m$ ($m = +2, +1, 0, -1, -2, -3$) was demonstrated [1–3]. Homogeneous $[M(N_3)_4]^{-p}$ and $[M(N_3)_6]^{-r}$ ($p = 2, 4, r = 2, 3, 4$) with various transition metals were also isolated in the solid state as alkaline salts. These derivatives are generally slightly explosive.

Their explosive character can be diminished by 'dilution' of the azide, e. g. by formation of tetraphenylarsonium and phosphonium salts and mixed complexes [4–9].

The azide ion easily enters the inner coordination sphere of transition metal complexes in various substitution, anation, etc. reactions and due to the π–donor properties of this ligand, overlapping of its occupied π orbitals with the d–orbitals of the corresdponding metal ion also occurs.

'Mixed' classical azido-complexes and chelate compounds of rhodium(III) $[Rh(NH_3)_5(N_3)]^{2+}$, $[Rh(en)_2(N_3)_2]^+$, [10],

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chromium(III) $[Cr(NH_3)_5(N_3)]^{2+}$, $[Cr(en)_2(N_3)_2]^+$ [11], iron(II) $[Fe(o\text{-}phen)_2(N_3)_2]$ [12], and especially cobalt(III), $[Co(en)_2(N_3)_2]^+$, $[Co(en)_2(N_3)(NO_2)]^+$ [13], etc. may enter various types of substitution reactions. The kinetics of some azido-derivatives was also investigated. It is worth mentioning that the explosive character of the azide is diminished in these mixed complexes, too.

Results and Discussion

In previous papers [14–17] some anation reactions of the aquo-acido-bis-dimethylglyoximato-cobalt(III)- nonelectrolytes with NaN_3 were studied:

$$[Co(DH)_2(H_2O)X] + N_3^- = [Co(DH)_2(N_3)X]^- + H_2O\,,$$

$$(X = Cl,\ NO_2,\ NCO,\ NCS,\ etc.)$$

New complex acids of the type $H[Co(DH)_2(N_3)X]$ were obtained and characterized by preparative and physico-chemical methods.

In the present paper the formation conditions and the characterization of some new mixed azido-acids of cobalt(III) with alicyclic α–dioximes

(1,2–cyclopentane dione dioxime) Cpdox.H_2,
1,2–cyclohexane dione dioxime (Nyoxime) Niox.H_2,
1,2–cycloheptane dione dioxime (Heptoxime) Heptox.H_2, and
1,2–cyclooctane dione dioxime (Octoxime) Octox.H_2,
were investigated.

We have observed that the diazido-acids of the type:

$$H\,[Co(Diox.H)_2(N_3)_2]$$

are easily formed by the oxidation of the components (Co(II)-salt, dioxime, NaN_3 molar ratio 1:2:2.2) in aqueous alcoholic solutions (air, H_2O_2, etc.)

$$2Co^{2+} + 4Diox.H_2 + 4N_3^- + \frac{1}{2}O_2 = 2\,[Co(Diox.H)_2(N_3)_2]^- + 2H^+ + H_2O\,.$$

The anation reaction of

$$[Co(Diox.H)_2(H_2O)X] \qquad (X = Cl,\ Br,\ I)$$

with an excess of NaN_3 leads also to the formation of diazido-complexes. In cases where $X{=}NO_2$, NCS, NCSe, the substitution product is only a monoazido derivative, e. g.

$$[Co(Diox.H)_2(H_2O)(NO_2)] + N_3^- = [Co(Diox.H)_2(N_3)(NO_2)]^- + H_2O\,.$$

The free acids

$$H\,[Co(Diox.H)_2(N_3)_2] \quad \text{and} \quad H\,[Co(Diox.H)_2(N_3)(NO_2)]$$

can be separated from their aqueous solutions with an excess of diluted sulphuric acid.

The free acids are characterized in *Table 1.*

Table 1
New azido-complex acids of the type $H[Co(Diox.H)_2X(N_3)]$

Formula	Mol. wt. calcd.	Yield (%)	Appearance	Analysis (%)		
					Calcd.	Found
$H[Co(Niox.H)_2(N_3)_2]$	426.3	75	sparkling, brown dendrites	Co	13.82	13.79
				N	32.86	32.57
$H[Co(Niox.H)_2(NO_2)(N_3)] \cdot H_2O$	448.3	60	yellow rhomb. plates	Co	13.15	13.33
				H_2O	4.02	3.65
				N	25.00	25.25
$H[Co(Heptox.H)_2(N_3)_2]$	454.3	80	sparkling, red-brown plates	Co	12.97	12.94
				N	30.84	31.10
$H[Co(Octox.H)_2(N_3)_2]$	482.4	80	thin, brown dendrites	Co	12.21	12.56
				N	29.04	29.22

Like the other

$$[Co(Diox.H)_2XY]^-$$

type anions, the azido-nitro- and diazido-complexes readily form slightly soluble precipitates with monovalent metal ions (Cu^+, Ag^+, Tl^+) and with diacido- tetramine type complexes of cobalt(III) and chromium(III), e. g.

$$[M(NH_3)_4X_2]^+\,, \quad [M(en)_2X_2]^+\,,$$

etc; M=Co, Cr.

The formation of crystalline products of the type:

$$[Co(Diox.H^{x})_2(amine)_2] \cdot [Co(Diox.H^{xx})_2(N_3)X]$$

Table 2
New derivatives of the H[Co(Cpdox.H)$_2$(N$_3$)$_2$] complex acid

Formula	Mol. wt. calcd.	Appearance	Analysis		
				Calcd.	Found
[Co(DH)$_2$(pyridine)$_2$]·A	844.6	dark yellow, sparkling rhomb. plates	Co	13.96	13.97
			N	26.54	26.40
[Co(DH)$_2$(m-xylidine)$_2$]·A	928.7	brown rhomb. plates	Co	12.69	12.84
			N	24.13	24.25
[Co(DH)$_2$(aniline)$_2$]·A	872.6	brown rhomb. sparkling plates	Co	13.51	13.46
			N	25.68	25.45

Cpdox.H: $C_5H_7N_2O_2$
DH = dimethylglyoximate monoanion: $C_4H_7N_2O_2$
Yield: 80–90%

A = [Co(Cpdox.H)$_2$(N$_3$)$_2$]

is characteristic also in this case (Diox.H^x, Diox.H^{xx} different α–dioximes).

Data for 30 new derivatives of the mentioned azido-acids are given in *Tables 2–6.*

H [Co(Diox.H)$_2$(N$_3$)$_2$] and H [Co(Diox.H)$_2$(N$_3$)(NO$_2$)] are medium strong monobasic acids. With 0.1 mol/l KOH neutralized aqueous $2 \cdot 10^{-3}$ mol/l complex acids have pH values between 2.92–3.07 (potentiometric titration).

The free acids liberate HCN and CO$_2$ from aqueous KCN and NaHCO$_3$ solutions.

The azido-acids and salts show stability towards mechanical shocks and decompose rapidly on heating over 150 – 250°C. The *infrared spectra* of some H[Co(Diox.H)$_2$(N$_3$)$_2$] free acids are presented in *Fig. 1.*

The spectral data show the presence of strong intramolecular O–H ... O hydrogen bridges, similar to those observed in the case of the analogous dimethylglyoximine derivatives: H[Co(DH)$_2$Cl$_2$], H[Co(DH)$_2$Br$_2$], etc. $\left(\nu_{\text{O-H}}: 2300\text{–}2350\,\text{cm}^{-1}\ (w),\ \delta_{\text{O-H...O}}: 1680\text{–}1750\,\text{cm}^{-1}\ (w)\right)$. These hydrogen bridges stabilize the coplanar Co(Diox.H)$_2$ ring system, i. e. the trans geometric configuration of the azido-acids [14, 18].

The important stretching vibrations and the δ_{N_3}, $\delta_{\text{Co-N}_3}$ deformation vibrations of the coordinated azido-group appear at $\nu^{as}_{\text{N}_3}$: 2030–2050 and 2120–2140 cm^{-1} (v. s.), $\nu^{s}_{\text{N}_3}$: 1320–1340 cm^{-1} (m), δ_{N_3}: 610–630 cm^{-1} (m) and $\delta_{\text{Co-N}_3}$: 400–410 cm^{-1} (m–s) .

Table 3

New salts of the $H[Co(Niox.H)_2(N_3)_2]$ complex acid

Formula	Mol. wt. calcd.	Appearance	Analysis		
				Calcd.	Found
trans-$[Co(en)_2Cl_2] \cdot B \cdot H_2O$	693.1	sparkling green-yellow needles	Co H_2O N	17.00 2.60 28.29	17.50 2.50 28.45
trans-$[Cr(en)_2(NCS)_2] \cdot B \cdot H_2O$	731.4	sparkling brown rhomb. plates	Co+Cr S	15.16 8.77	15.67 9.00
$[Co(pyridine)_4Cl_2] \cdot B$	871.6	yellow short irreg. prisms	Co N	13.52 22.50	13.40 22.75
$[Co(DH)_2(NH_3)_2] \cdot B$	748.5	dark yellow, long needles	Co	15.74	15.49
$[Co(DH)_2(pyridine)_2] \cdot B$	872.6	yellow-brown rhomb. plates (from dil. soln.)	Co N	13.51 25.68	13.39 25.45
$[Co(DH)_2(aniline)_2] \cdot B$	900.7	sparkling, brown irreg. plates	Co	13.08	12.93
$[Co(DH)_2(\alpha - naphthylamine)_2] \cdot B$	1000.9	dark brown irreg. cryst.	Co N	11.78 22.39	11.55 22.60

$B= [Co(Niox.H)_2(N_3)_2]$;
$Ag= [Co(Niox.H)_2(N_3)_2]$ (dark yellow microcryst. mass)
and $Tl= [Co(Niox.H)_2(N_3)_2]$ (dark yellow microcryst. not analysed)

The values $\nu^{as}_{N_3}$ and δ_{N_3}, as compared to those of NaN_3 $\nu^{as}_{N_3}$: 2120–2140 cm^{-1} (v.s.), and δ_{N_3}: 645 cm^{-1} (s) show the strong covalent character of the Co-azide bond.

In the IR spectra of the azido-complexes of Co(III) there appear more than 5 azide absorption bands, and this means a decreasing symmetry and the appearance of non linear Co-azide bonding Co–N–N–N with various N–N atomic distances. (In the free, non coordinated N_3^-–ion these distances are equal.) With increasing π– interaction between the p–orbitals of the N–atom and the d–orbital of the metal ion both the N–N atomic distance and the energy of the $\nu^{as}_{N_3}$ vibration increase [19–24].

In the IR spectra of the monoazido-derivatives $\nu^{as}_{N_3}$ appears as a very strong band at 2020–2050 cm^{-1}. For the free diazido-acids this band is split in two strong bands (2030–2050 and 2120–2140 cm^{-1}) due to the non-equivalence of the $Co–N_3$ –bondings ($Co–N_3$ and $Co–N_3H$, the latter with the acidic proton). The other azido-bands ($\nu^{s}_{N_3}$, δ_{N_3}, $\delta_{Co\text{-}N_3}$) are generally overlapped by various stretching and deformation vibrations of the other ligands.

Table 4

New salts of the $H[Co(Niox.H)_2(N_3)(NO_2)]$ complex acid

Formula	Mol. wt. calcd.	Appearance	Analysis	Calcd.	Found
trans-$[Co(en)_2Cl_2]\cdot C$	679.1	yellow-brown plates	Co	17.35	17.28
			N	24.75	24.90
$[Co(DH)_2(aniline)_2]\cdot C$	904.7	gold yellow sparkling prisms	Co	13.03	12.90
			N	21.68	21.99
$[Co(DH)_2(pyridine)_2]\cdot C$	876.6	yellow-brown dendrites	Co	13.44	13.18
			N	22.37	22.70
$[Co(DH)_2(p\text{-}phenetidine)_2]\cdot C\cdot 2H_2O$	1028.8	brown needles	Co	11.45	11.05
			H_2O	3.50	3.60
			N	24.75	24.63
trans-$[Cr(en)_2(NCS)_2]\cdot C$	717.4	yellow irreg. cryst.	Co+Cr	15.45	15.56
			S	8.93	9.15

$C=[Co(Niox.H)_2(N_3)(NO)_2]$;
Co determined complexometrically, S as $BaSO_4$, Co+Cr as sum of the Co_3O_4+Cr_2O_3 (900°C, 2–3 hrs);
Yields: 80–90%.

$Ag[Co(Niox.H)_2(N_3)(NO)_2]$ (yellow microcryst.)
$Tl[Co(Niox.H)_2(N_3)(NO)_2]$ yellow microcryst. not analysed.

The $\nu_{N\text{-}O}$ stretching vibrations of the nitro-group in the case of $H[Co(Niox.H)_2(NO_2)(N_3)]$ appear at 1440 and 1380 cm^{-1}, showing the formation of a nitro-acid with $Co\text{–}NO_2$–bonding through the nitrogen atom [18].

The $\nu_{C=N}$ and $\nu_{N\text{-}O}$ (oxime) frequencies of the coordinated alicyclic dioximes appear at 1550–1570 cm^{-1} (m-s) and at 1235–1240 cm^{-1} (s), 1080–1095 cm^{-1} (s), not influenced by the coordination effect. An analogous phenomenon can be observed also in the case of the $\nu_{C\text{-}H}$ and δ_{CH_2} frequencies of the alicyclic rings $\nu_{C\text{-}H}$: 2950, 2870 cm^{-1} (s, v.s.) and δ_{CH_2}: 1460–1470 cm^{-1} (m-i), 1350–60 cm^{-1}). (*Table 7*).

The absorption band at 39–41 kK appears in the spectra of the majority of the dioximino-complexes of cobalt(III) $[Co(Diox.H)_2X_2]^-$,

The *electronic spectra* of the azido-acids were recorded in methanol. The spectral data are presented in *Table 8*. The absorption curves of $H[Co(Niox.H)_2(N_3)_2]$ and $H[Co(Heptox.H)_2(N_3)_2]$ are shown in *Fig. 2*.

$[Co(Diox.H)_2X(amine)]$, $[Co(Diox.H)_2(amine)_2]^+$ and is due probably to the presence of the $Co(Diox.H)_2$ moiety [25]. In our cases this band is overlapped with charge transfer bands of the ligands. In the case of the diazido-acids two bands appear in the visible region at 14–16 kK, and at

Table 5

New salts of the $H[Co(Heptox.H)_2(N_3)_2]$ complex acid

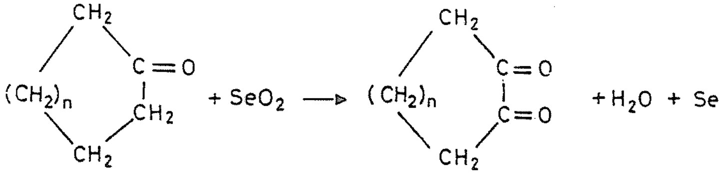
Formula	Mol. wt. calcd.	Appearance	Analysis		
				Calcd.	Found
trans-$[Co(en)_2Cl_2]\cdot D$	703.2	yellow, long needles	Co	16.76	16.73
trans-$[Co(en)_2(NCS)_2]\cdot D$	741.5	dark yellow irregular cryst.	Co+Cr	14.96	15.15
			S	8.69	8.77
$[Co(DH)_2(NH_3)_2]\cdot D$	776.5	yellow square plates	Co	15.18	15.23
			N	28.86	29.03
$[Co(DH)_2(aniline)_2]\cdot D\cdot H_2O$	946.7	light brown needles	Co	12.45	12.75
			H_2O	1.90	2.13
			N	23.67	23.49
$[Co(DH)_2(m\text{-xylidine})_2]\cdot D$	984.8	brown prisms	Co	11.97	11.80
			N	22.76	22.97
$[Co(DH)_2(pyridine)_2]\cdot D$	900.7	short, yellow-brown prisms	Co	13.08	13.11
			N	24.88	24.64

D–$[Co(Heptox.H)_2(N_3)_2]$;
$Ag[Co(Heptox.H)_2(N_3)_2]$ (orange microcryst.)
$Tl[Co(Heptox.H)_2(N_3)_2]$ (yellow microcryst.) not analysed.

Heptox.H: $C_7H_{11}N_2O_2$;
Yields: 70–80%.

19 kK, respectively. By substitution of an N_3–ligand with other groups, the band at 14–16 kK disappears and the second one is shifted towards higher frequencies (20–21 kK). These bands have a ligand field character.

Experimental



The alicyclic α–dioximes were obtained by the selective oxidation of the corresponding alicyclic monoketones with selenium dioxide in boiling alcoholic solution (4–6 hours) followed by the oxidation of the distilled α-diketones(10–12 mm Hg) with an excess of hydroxylamine (2 moles) $NH_2\text{–}OH\cdot HCl+2$ moles KOH by warming on a water bath in aqueous-

Table 6

New salts of the $H[Co(Octox.H)_2(N_3)_2]$ complex acid

Formula	Mol. wt. calcd.	Appearance	Analysis		
				Calcd.	Found
$[Co(DN)_2(thiourea)_2] \cdot E$	922.8	brown irregular cryst.	Co S	12.77 6.95	12.85 7.23
$[Co(DH)_2(2\text{-amino-thiazole})_2] \cdot E$	970.8	dark brown irregular cryst.	Co	12.14	12.29
$[Co(DH)_2(p\text{-chlor-aniline})_2] \cdot E$	1025.7	brown stars	Co N	11.49 21.85	11.25 21.66
$[Co(DH)_2(aniline)_2] \cdot E$	956.8	short, brown prisms	Co N	12.30 23.42	12.10 23.66
$[Co(DH)_2(p\text{-phenetidine})_2] \cdot E$	1044.9	sparkling brown desks	Co N	11.28 21.45	11.10 21.15
$[Co(pyridine)_4Cl_2] \cdot E \cdot H_2O$	945.7	yellow-brown thin needles	Co H_2O	12.46 1.90	12.20 1.87
trans-$[Cr(en)_2(NCS)_2] \cdot E$	769.6	dark orange needles	Co+Cr S	14.41 8.33	14.75 8.65
trans-$[Co(en)_2Cl_2] \cdot E$	731.2	yellow short prisms	Co N	16.12 26.82	16.50 26.48
trans-$[Co(pn)_2Cl_2] \cdot E \cdot H_2O$	777.5	yellow irregular plates	Co H_2O N	15.16 2.31 25.22	14.90 2.28 25.19

E–$[Co(Octox.H)_2(N_3)_2]$ (Octox.H: $C_8H_{13}N_2O_2$)
Yields: 70–85%.

alcoholic solution. The crude products were recrystallized from hot water [26].

$H[Co(Diox.H)_2(N_3)_2]$ free acids

0.1 mole of cobalt(III) acetate in 200 ml water were treated with 0.2 mole alicyclic dioxime in 200–250 ml alcohol. The mixture was oxidized by air bubbling for 3–4 hours. Then 0.22 mole of NaH_3 in 50–60 ml water were added. After 40–50 min of air bubbling the reddish-violet solution was ice cooled and filtered from the separated $[Co(Diox.H)_2(N_3)(H_2O)]$ nonelectrolytic byproduct and the free acids were precipitated with a large excess of 30–35% sulphuric acid. The crystalline precipitates were filtered off after 10–15 min. standing, washed with a small amount of ice cold water and with a mixture of ether-alcohol (10:1) and dried in air.

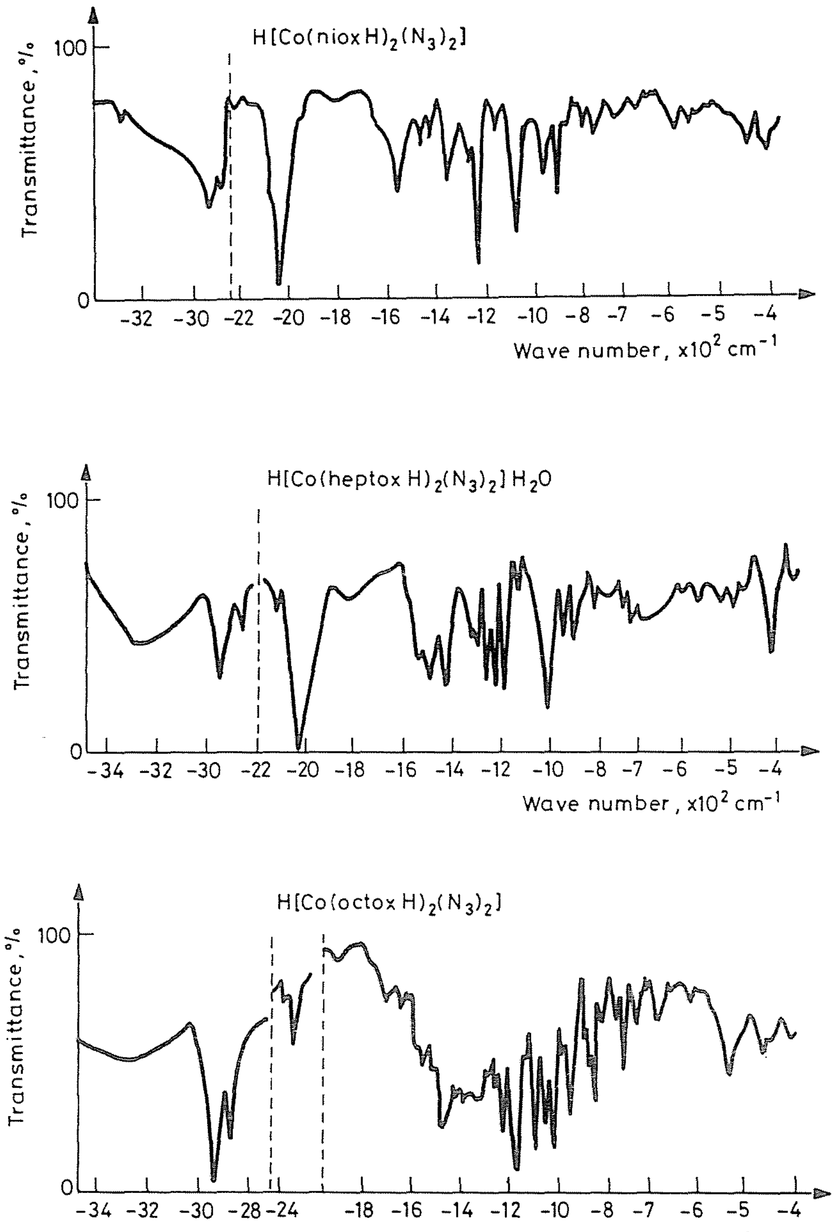


Fig. 1. Infrared spectrum of $H[Co(Niox.H)_2(N_3)_2]$, $H[Co(Heptox.H)_2(N_3)_2]$ and $H[Co(Octox.H)_2(N_3)_2]$

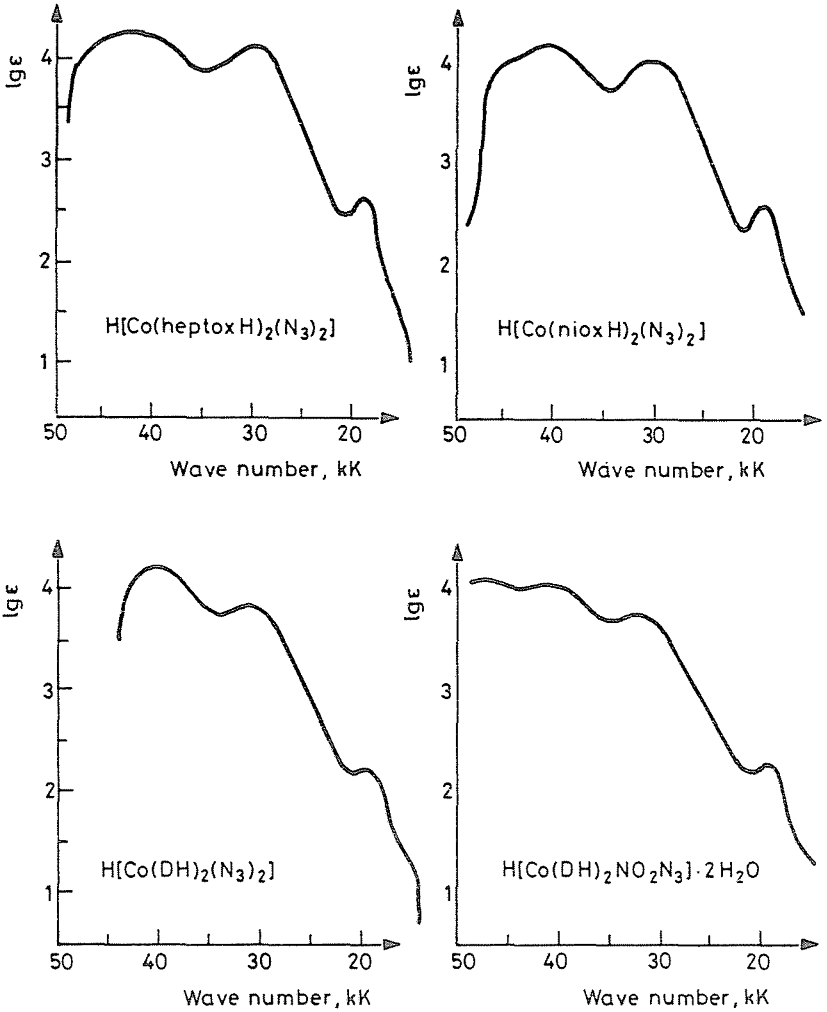


Fig. 2. Electronic spectrum of $H[Co(Heptox.H)_2(N_3)_2]$, $H[Co(Niox.H)_2(N_3)_2]$, $H[Co(DH)_2(N_3)_2]$ and $[Co(DH)_2(NO_2)(N_3)]H_2O$

$H[Co(Diox.H)_2(N_3)(NO_2)]H_2O$

50 mmoles of $[Co(Niox.H)_2(NO_2)(H_2O)]$ in 100 ml dil. alcoholic suspension were treated with 50 mmoles of NaN_3 in 25 ml aqueous solution. The nitro-aquo nonelectrolyte dissolves after 10–15 min stirring on a water bath. The free nitro-azido acid was separated with dil. sulphuric acid.

Table 7
Infrared spectral data of some azido-complexes

Vibration	I.	II.	III.	IV.	V.
ν_{C-H}	2950 – 2970 m 2870 m	2950 – 2970 m 2975 m	2950 s 2870 m	2950 – 2980 m 2870 m	–
$\nu_{as_{N_3}}$	2025 v.s. 2130 s	2050 v.s.	2040 – 2060 v.s. 2140 s	2050 v.s. 2130 s	2120 – 2160 v.s.
ν_{O-H}	2340 m	2340 – 2350 m	2350 – 2370 m	2350 – 2370 m	–
$\delta_{O-H\ldots O}$	1720 – 1800 w	1720 – 1780 w	1750 – 1850 w	1730 – 1840 w	–
$\nu_{C=N}$	1570 m	1560 m	1560 s	1560 s	
δ_{CH_2}	1475 m 1425 m	1470 m 1360 m	1460 s 1430 m 1350 m	1460 m 1420 m 1360 m	–
$\nu_{N-O(NO_2)}$	–	1440 s 1380 m	–	–	–
$\nu_{s_{N_3}}$	1330 – 1350 m	1330 s	1330 s	1335 s	–
$\nu_{N-O(oxime)}$	1235 v.s. 1075 v.s.	1240 v.s. 1085 v.s.	1235 v.s. 1100 m	1245 v.s. 1095 s	
γ_{C-H}	765 m 740 m	740 m	740 m 700 m	740 m	
δ_{N_3}	630 w	630 w	615 w	620 w	645 s
δ_{Co-N_3}	420 w	425 w	400 s	410 s	

I. $H[Co(Niox.H)_2(N_3)_2]$;
II. $H[Co(Niox.H)_2(N_3)(NO_2)]$;
III. $H[Co(Heptox.H)_2(N_3)_2]$;
IV. $H[Co(Octox.H)_2(N_3)_2]$;
V. NaN_3.

Synthesis of $[M(amine)_4X_2] \cdot [Co(Diox.H)_2X(N_3)]$ and

$[Co(DH)_2(amine)_2] \cdot [Co(Diox.H)_2X(N_3)]$

5 mmoles of the corresponding diacido-teramine salt (chlorides or acetates) in 80–100 ml water, or in dil. alcohol (1:2), respectively, were treated with 5 mmoles of $H[Co(Diox.H)_2X(N_3)]$ in 30–50 ml dil. alcohol (1:2). The crys-

Table 8
Electronic spectral data of some azido-complexes

Complex	ν_1^*	$\log \varepsilon_1$	ν_2^*	$\log \varepsilon_2$	ν_3^*	$\log \varepsilon_3$	ν_4^*	$\log \varepsilon_4$	ν_5^*	$\log \varepsilon_5$
$H[Co(Niox.H)_2(N_3)_2]$	15.8	1.72	19.0	2.67	30.5	4.12	40.0	4.19	42.5	4.20
$H[Co(Heptox.H)_2(N_3)_2]$	15.5	1.6	19.0	2.68	30.5	4.13	40.0	4.20	43.0	4.23
$H[Co(Octox.H)_2(N_3)_2]$	15.7	1.75	19.2	2.70	30.5	4.20	40.5	4.30	43.0	4.30
$H[Co(Niox.H)_2(N_3)(NO)_2]$	—	—	21.0	2.9	31	4.30	41.0	4.40	—	—

(ν^* wave number in kK)

talline precipitate is filtered after 1/3–1/2 h, washed with water and dried in air.

The *IR spectra* of the azido-acids have been recorded in KBr pellets, by means of a UR 20 Carl Zeiss–Jena spectrophotometer in the spectral range 400–3600 cm^{-1}.

The *electronic spectra* were recorded by means of a Specord recording spectrophotometer in methanol. Conc. VIS: $1\text{–}2 \cdot 10^{-3}$ mol/l, UV: $1\text{–}3 \cdot 10^{-5}$ mol/l.

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