ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS. XCV. NEW IODO-AMINO-BIS-DIMETHYLGLYOXIMATO-COBALT(III)-NONELECTROLYTES

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Abstract

New nonelectrolytic type chelate compounds of cobalt(III) with the general formula [Co(DH)₂IA] (DH – monodeprotonated dimethylglyoxime, A – different aromatic and heterocyclic amines and tertiary phosphines) were obtained by means of a substitution reaction from the diiodo-bis-dimethylglyoximato-cobaltiat and the corresponding amines and phosphines in alcoholic-aqueous media. The nonelectrolytes are sparingly soluble in water and soluble in some organic solvents, e.g. CHCl₃, DMFA, DMSO, etc. These derivatives were characterized by IR and electronic spectra, and in several cases by derivatographic measurements.

Keywords: iodo-amino-bis-dimethyl-glyoximato-cobalt(III)-complexes.

Introduction

In the presence of monodentate ligands the coordination of the iodo-ligand to cobalt(III) is difficult to achieve, probably due to redox interactions. The synthesis of iodo-amino-cobalt(III) complex was first reported by YALMAN [1] in the case of $[Co(NH_3)_5I]^{2+}$. The iodo-derivatives of the frequently studied complexes of the type: $[Co(NH_3)_4X_2]^+$, $[Co(en)_2X_2]^+$, $[Co(en)_2X(amine)]^{2+}$ (X = Cl, Br, 'en' – ethylene-diamine) were not reported in the literature. Iodo-complexes with more than one iodo-ligand are characteristic of platinum ($[PtI_6]^{2-}$) and rhenium ($[ReI_6]^{2-}$).

ABLOV [2] obserced that the diiodo-derivative of cobalt(III) can be obtained easily when cobalt(II) salts are dioxidized in the presence of KI and dimethylglyoxime.

$$2\ Co^{2+} + 4\ DH_2 + 4\ I^- + 1/2\ O_2 = 2[Co(DH)_2I_2]^- + H_2O + 2\ H^+.$$
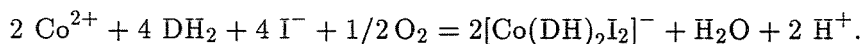
One iodo-ligand in this complex can be easily replaced by other mono- and divalent anions with strong nucleophilic properties (NCS^-, $NCSe^-$, N_3^-, SO_3^{2-}, $S_2O_3^{2-}$ [3, 4] and by neutral molecules, e.g. H_2O, NH_3, different amines, etc.

The kinetics and mechanism of the aquation of $[Co(DH)_2I_2]^-$ was studied in our previous paper [5].

In the first step of these substitution reactions nonelectrolytes of the $[Co(DH)_2IA]^\circ$ type are formed (A – various neutral molecules with donor properties).

Besides the diiodo-derivatives, various iodo-acido-bis-dimethyl-glyoximato-cobalt(III) complexes, e.g. $[Co(DH)_2ClI]^-$, $[Co(DH)_2BrI]^-$, $[Co(DH)_2(NO_2)I]^-$, $[Co(DH)_2(NCS)I]^-$ form also iodo-nonelectrolytes of the above mentioned type by interaction with neutral ligands [6, 7]. E. g. the ammonia derivative: $[Co(DH)_2I(NH_3)]$ can be obtained by the interaction of these monobasic mixed complex acids with equimolecular amount of ammonia in the cold [8].

The oxidation of a mixture of CoI_2 (or $Co(acetate)_2 + 2\,KI$), dimethyl-glyoxime and amines (molar ratio 1:2:2) leads also to the formation of impure $[Co(DH)_2I(amine)]$ [9].

Instead of dimethylglyoxime also other α-dioximes can be used for the synthesis of $[Co(Diox.H)_2I\,A]$ derivatives. (E.g. 1,2-cyclohexane dione dioxime: $[Co(Niox.H)_2I\,A]$ [10].

We observed that the $[Co(DH)_2I\,A]$ type complexes react with free amines in boiling alcoholic solutions and binary complex salts: $[Co(DH)_2(amine)_2]I$ are formed.

The reverse reaction, viz. the partial deamination process

$$[Co(DH)_2(amine)_2]I = [Co(DH)_2(amine)I] + amine$$
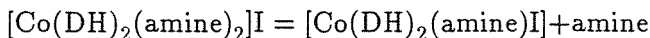
was accomplished in the solid state between 150–220 °C, depending on the nature of the coordinated amine, under the conditions of thermogravimetric analysis [11, 12]. This process was studied also from the kinetic point of view.

Results and Discussion

In this paper the formation of nonelectrolytes of the type $[Co(DH)_2I\,A]^\circ$ was studied, starting from the potassium salt of the diiodo-acid. We observed that dilute alcoholic solution of the $K[Co(DH)_2I_2]$ reacts easily with a series of aromatic and heterocyclic amines having pK_b values between 6 and 13. Very weak bases ($pK_b = 14$–16) are not suitable for this purpose (nitro-anilines, sulphanilic acids, etc.).

Table 1
New nonelectrolytes of the type $[Co(DH)_2I(amine)]$

amine	Mol. wt. calcd.	Yield (%)	Appearance		Analysis	
					Calcd.	Found
m-Br-aniline	588.1	70	dark brown	Co	10.03	9.88
			dendrites	N	11.90	11.42
2-4-dimethoxy-aniline	569.2	75	irregular,	Co	10.35	10.10
			brown plates	N	12.31	12.18
2-amino-thiazole	516.2	50	sparkling yellow-	Co	11.41	11.34
			brown prisms	N	16.28	16.40
pyridine	495.2	85	gold-yellow	Co	11.90	11.58
			sparkling plates	N	14.14	14.32
4-ethyl-pyridine	523.2	80	yellow-brown	Co	11.26	11.19
			irregular plates	N	13.30	13.11
β-picoline	509.2	90	gold-yellow	Co	11.57	11.38
			sparkling plates	N	13.76	13.30
γ-picoline	509.2	80	light brown	Co	11.57	11.66
			sparkling dendrites	N	13.76	13.50
				C	33.01	33.42
				H	4.14	4.30
3,4-lutidine	523.2	85	thin, brown plates	Co	11.26	11.17
				C	34.44	34.66
				N	13.30	12.93
3,5-lutidine	523.2	90	dark brown	Co	11.26	11.10
			dendrites	N	13.38	13.60
imidazole	484.2	60	dark yellow	Co	12.17	12.18
			microcryst.	N	17.36	17.06
2-methyl-imidazole	498.17	55	dark yellow	Co	11.83	11.60
			microcryst.	N	16.87	16.49
benzimidazole	534.2	75	brown	Co	11.03	11.25
			microcryst.	N	15.73	15.40

This reaction was carried out in warm dilute alcoholic solutions in the presence of ammonium acetate buffer, which promotes the formation of the nonelectrolytes.

In addition to these reactions the interaction of the diiodo-salt with tertiary phosphines was also studied. The alkyl-aryl-phosphines with weaker basic, but stronger nucleophilic properties than those of the amines (due to the greater size of the phosphorus atom as compared to that of the nitrogen atom and the vacant 3 d orbitals of the phosphorus atom being capable of interacting with the filled nonbonding d orbitals of the cobalt atom).

Contrasting with the dioximine chelates of iron(II), the Co(III) dioximine moiety coordinates also triaryl-phosphines with very weakly basic properties.

The new nonelectrolytes obtained are characterized in *Tables 1* and *2*.

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Table 2

New nonelectrolytes of the type $[Co(DH)_2I(phosphine)]$

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Phosphine	Mol. wt. calcd.	Yield (%)	Appearance		Analysis Calcd.	Found
diethyl-phenyl-phosphine	582.3	85	sparkling yellow-brown prisms	Co N	10.12 9.62	10.35 9.50
diethyl-p-tolyl-phosphine	594.3	85	sparkling yellow-brown prisms	Co N	9.90 9.41	9.46 9.30
dibutyl-phenyl-phosphine	638.3	90	brown prisms	Co N	9.23 8.77	9.40 8.90
diphenyl-ethyl-phosphine	630.3	90	brown microcryst.	Co N C H	9.35 8.88 41.93 4.64	9.05 8.72 41.68 4.90
tributyl-phosphine	618.3	70	yellow square plates	Co N C H	9.53 9.06 38.84 6.68	9.22 9.12 39.14 6.91
triphenyil-phosphine	678.3	90	dark brown microcryst.	Co N	8.69 8.26	8.58 8.05
tris-p-tolyl-phosphine	720.4	90	dark brown microcryst.	Co N C H	8.18 7.77 48.35 4.89	7.95 7.50 48.85 4.98
triphenyl-phosphine-oxide	694.3	75	dark brown prisms	Co	8.48	8.35

These chelate compounds are very sparingly soluble in water (the phosphine-derivatives are insoluble in water). They are soluble in alcohols, $CHCl_3$, CCl_4, in aromatic hydrocarbons, etc.

The nonelectrolytic character was proved in several cases by means of electrical conductivity measurements. Molar electric conductivity: 2–15 ohm^{-1} cm^2 measured 10–30 minutes after dissolution at a dilution of V = 1000 1/mole.

By boiling an aqueous suspension of $[Co(DH)_2I\ A]$ with $AgNO_3$ solution AgI precipitate is formed slowly.

IR spectra. In the IR spectra of $[Co(DH)_2\ I\ A]$ complexes the coordinated dimethylglyoxime frequencies are the most characteristic of the $Co(DH)_2$ moiety. The $\nu C = N$, $\nu N-O\ldots$ and $\nu N-OH$ frequencies appear at

1550–1560 cm^{-1} (s), 1240 cm^{-1} (v.s.) and 1090 cm^{-1} (v.s.), respectively, not influenced by the nature of the axial ligands. The νO–H at 2300–2400 cm^{-1} (m) and βO–H...O at 1680–1730 cm^{-1} (w) prove the existence of very short O–H...O intramolecular hydrogen bondings, which stabilize the coplanar Co(DH)$_2$ moiety [13].

The νN–H frequencies at 3200 cm^{-1} (s) and 3080–3100 cm^{-1} (s) of the coordinated primary amines show the existence of strong Co–N(amine) covalent bonds. The appearance of the νCo–I valence vibrations, sensitive to the nature of the axial amine and phosphine ligands is expected at 80–140 cm^{-1}, in the far infrared region, which was not available with the spectral apparatus used.

Electronic spectra were recorded for 11 complexes studied. The position of the absorption bands together with the molar absorption coefficients are given in *Table 3*.

Table 3

Wavelength (λ) and molar absorption coefficient (ε) values for the electronic transition bands of Co(DH)$_2$I A type nonelectrolytes

| band | A | | B | | C | | D | | E | |
A	λnm	lg ϵ	λnm	lg ϵ	λnm	lg ϵ	λnm	lg ϵ	λnm	lg ϵ
β-picoline	780	1.81	420	3.32	303	4.18	250	4.36	215	4.15
γ-picoline	750	1.88	421	3.20	306	3.98	247	4.00	220	3.70
4-ethyl-pyr	760	1.78	420	3.30	303	4.13	250	4.32	218	3.98
3,4-lutidine	750	1.70	417	3.23	305	4.09	250	4.24	217	3.90
3,5-lutidine	750	1.88	420	3.30	303	4.11	250	4.30	215	3.93
3-Br-aniline	700	2.08	425	3.08	296	3.96	242	4.11	215	3.45
2-NH$_2$-thiazole	760	1.85	451	3.02	305	3.98	245	4.32	218	3.94
imidazole	680	1.90	400	3.30	296	4.00	244	4.30	—	—
(Bu)$_3$P	600	2.78	426	3.98	320	4.20	250	4.28	226	4.09
(Et)$_2$Ph.P	615	2.98	405	4.20	322	4.33	248	4.36	214	4.00
(Et)$_2$(p-tolyl).P	620	2.84	400	4.08	329	4.30	250	4.30	215	4.35

The spectra of some derivatives are shown in *Fig. 1*.

In the spectra of both the amine and phosphine derivatives 5 bands are observed.

Bands C and D are characteristic of the Co(DH)$_2$ moiety and were reported for many complexes [14–17]. They are thought to be due to the electronic transitions of the coordinated DH ligand, since in the spectrum of free DH$_2$ two bands are observed at 265 nm and at about 312–317 nm, respectively [18]. Nevertheless, these transitions may imply also Co–DH (band C) and DH–Co (band D) charge transfer [17]. Band C appears at
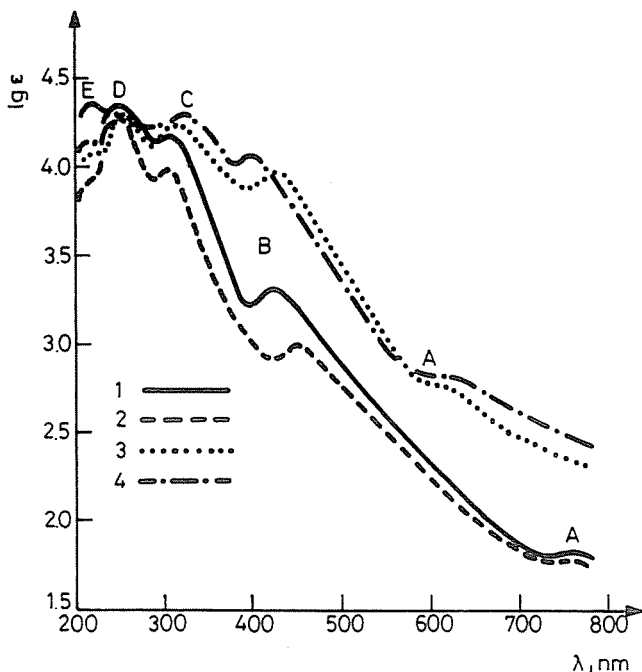
Fig. 1. The absorption bands A, B, C, D and E in the UV and visible spectrum of [Co(DH)$_2$I A] type complexes, the '*A*' being:
1 — β-picoline; 2 — 2-aminothiazole;
3 — tributylphosphine; 4 — diethyl-p-tolyl-phosphine.

higher wavelengths with phosphine derivatives as compared to the amine ones. This effect is similar to that observed in the case of the analogous [Co(Diph.H)$_2$(amine)$_2$]$^+$ (Diph.H$_2$ – diphenylglyoxime) complexes, which exhibit band C at 310–335 nm [19, 20]. In the case of these diphenylgly-oxime complexes also band D is shifted to 265 nm.

Bands A and B in the visible region might be assigned to crystal field, i.e. Laporte forbidden d–d transitions. Since the local symmetry near the cobalt atom is C$_{4v}$, the single T$_{2g}$ →E$_g$ transition, occurring in O$_h$ field, is splitted, involving presumably an E→A, and an E→B$_1$ transition. In the case of band A the ε values are consistent with this presumption, but with band B the intensity of the band is too high. Presumably, the crystal field band is partially overlapped by an amine – Co CT band, as suggested also for the other similar complexes [17].

In the case of the phosphine derivatives, band A is shifted towards lower wavelengths, suggesting an increase in the strength of the crystal field. An increase in ε is also observed, which might be due to the increased covalent character of the Co-ligand bonds, reducing the d character of

the terms A_1 and B_1. Generally, the intensity of band E is less that the intensity of band D and in the spectra this band appears as an inflexion point. Band E might be assigned to a Co→ligand CT transition, involving the axial amine and phosphine ligand, respectively.

The *thermal behaviour* of some $Co(DH)_2I(amine)$ type complexes was studied by derivatography. The thermal curves indicate no weight loss up to 190 °C or even 225 °C, depending on the nature of the amine component. This phenomenon shows the absence of crystallization water. Unlike the binary salts of the type $[Co(DH)_2(amine)_2]I$, the thermal curves of the $[Co(DH)_2I(amine)]°$ nonelectrolytes do not exhibit any partial de-amination step with an endothermal peak on the DTA curve. Over 190–225 °C takes place the thermal decomposition of the nonelectrolytes with a complicated simultaneous de-amination, partial oxidation and decomposition of the coordinated oxime and amine ligands. Generally, these superimposed processes have strong exothermic character. The formation of a stoichiometric intermediate in this decomposition process was not evidenced. The final product at 850–900 °C is Co_3O_4 in stoichiometric amount.

Experimental

Preparation of $K[Co(DH)_2I_2]$-solution

A mixture of 25 g of cobalt(II) acetate (0.1 mole) and 48 g of KI (0.3 moles) in 200 ml water and 23.2 g of finely powdered dimethylglyoxime (0.2 moles) in 800 ml methanol was oxidixed by air bubbling during 6–8 hours. The dark red–brown solution formed was filtered off and used for substitution reactions with amines and phosphines.
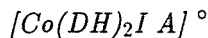
$[Co(DH)_2I\ A]°$

10 mmoles $K[Co(DH)_2I_2]$ in 100 ml aqeous alcoholic solution were treated with 5 g of ammonium acetate and 10–12 mmoles of the corresponding amine or phosphine in 50–100 ml methanol. The dark brown solution was warmed on a water bath for 20–45 minutes. Characteristic crystalline products were formed. These were filtered off after cooling, washed with dilute alcohol and dried in air.

Analysis. The purity of the products was checked by the determination of the Co (complexometrically) and N (gas volumetric) content.

IR-spectra were recorded in KBr pellets by a UR 20 spectrophotometer (Carl Zeiss Jena, Germany) from 400 to 3500 cm $^{-1}$.

The *electronic spectra* were recorded in methanol with a Specord spectrophotometer (Carl Zeiss Jena) (conc. $1-2\times10^{-3}$ mol/l in the visible and $1-2\times10^{-5}$ mol/l in the UV region).

The *thermal measurements* were carried out with a MOM derivatograph (Budapest). Sample weight 100 ± 1 mg; heating rate: 10 °C/min.

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