STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIII, 1-2, 1998

ELECTRONIC SPECTRA OF SOME bis-DIOXIMINO-COMPLEXES OF Co(III) WITH ALICYCLIC α-DIOXIMES

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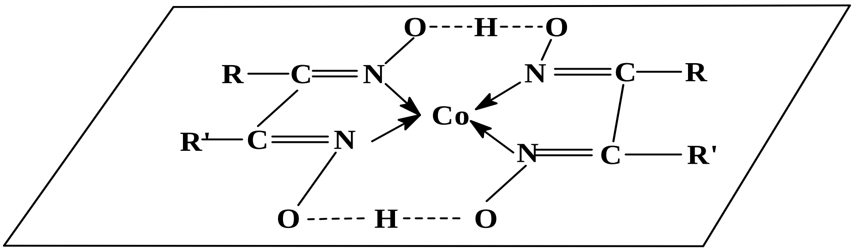
ABSTRACT. Electronic spectra of 22 [$Co(Diox.H)_2X_2$] and of 26 [$Co(Diox.H)_2XY$] type complexes (Diox.H - deprotonated alicyclic α-dioxime: 1,2-cyclopentane-, -cyclohexane-, -cycloheptane- and cyclooctane-dione dioxime) are compared and discussed. Mean values of the wave numbers are calculated for complexes containing a given ligand. An attempt is made to assign the absorption bands to crystal field transitions and electronic transitions in the co-ordinated ligand.

INTRODUCTION

Visible and UV spectra of [$Co(Diox.H)_2XY$] type complexes (where $Diox.H_2$ stands for dimetylglyoxime) were studied first by Ablov and Filippov [1]. These authors have found an absorption band at about 40 kK, assigned by them to the common moiety of all bis-dioximino-cobalt(III) complexes, viz. to

The charge transfer (CT) bands of some bis-dioximino-complexes of Co(III) have been studied by Matsumoto and al. [2 - 4].

In the last 20 years we found no spectral data of bis-dioximato-Co(III) complexes in the literature.



In our earlier papers [5] an attempt was made to study the ligand field transition bands of several dimetylglyoximato- and diphenylglyoximato-Co(III) derivatives and to derive Racah parameters, tetragonal perturbation parameters and nephelauxetic ratio from the position of these bands.

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[**] *Part of the PhD thesis.*

In the case of alicyclic dioximes as 1,2-cyclopentane-dione-dioxime (Cpdox.H_2), 1,2-cyclohexane-dione-dioxime (Niox.H_2), 1,2-cycloheptane-dione-dioxime (Heptox.H_2) and 1,2-cyclooctane-dione-dioxime (Octox.H_2) electronic spectra have been recorded for many [Co(Diox.H)$_2$X$_2$] and [Co(Diox.H)$_2$XY] type complexes [6 - 12]. In the present paper these results are discussed.

EXPERIMENTAL

The spectra were recorded in aqueous or diluated alcoholic solutions (1:3) with SPECORD Spectrophotometer. Conc. of samples: 1 - 3•10^{-3} M/l in visible and 1 - 2•10^{-4} - 10^{-5} M/l in UV region.

DISCUSSIONS

Electronic spectral data of some compounds and those reported in [6 - 12] are presented in Tables 1 and 2. viz. in Table 1 for 22 complexes of [Co(Diox.H)$_2$X$_2$] type, corresponding to a D_{4h} local symmetry and in Table 2 for 26 complexes of [Co(Diox.H)$_2$XY] type, of C_{4h} symmetry.

As seen the number of absorption bands found varies between 2 and 5, and they are situated in 8 spectral regions, denoted as A, B, C, D, E, F, G and H. Bands A and B appear in the visible region and have relatively small molar absorption coefficients. Therefore, these bands may be considered to correspond to crystal field transitions, i.e. to Laporte forbidden d - d transitions. Since band A is reported only for 3 complexes, and B for 14 ones, their interpretation is rather difficult. Nevertheless, one may observe that generally the wave number of B is higher with X ligands situated in the second part of the spectrochemical series, i.e. creating a strong crystal field. This observation is in agreement with the above presumption that B is a ligand field transition band.

Table 1.

Absorption bands of the [Co(Diox.H)$_2$L$_2$]$^+$ and [Co(Diox.H)$_2$X$_2$]$^-$ type complexes (Wave numbers - $\overline{\nu}$, in kK).

Diox.H	L or X	$\overline{\nu}_A$	$\overline{\nu}_B$	$\overline{\nu}_X$	$\overline{\nu}_\Delta$	$\overline{\nu}_E$	$\overline{\nu}_\Phi$	$\overline{\nu}_\Gamma$	$\overline{\nu}_H$	Ref.
	α-naphtylamine	-	20.0	24.4	-	32.3	39.2	-	-	4
	β-naphtylamine	-	19.2	25.0	-	31.2	42.6	-	-	4
Niox.H	aniline	-	20.0	23.8	-	31.2	40.3	-	-	7
	o-ethylaniline	-	19.2	24.4	-	31.7	40.0	-	-	7
	p-ethylaniline	-	18.9	25.0	-	32.3	40.5	-	-	7
	4-amino-m-xylene	-	20.6	26.3	28.2	32.3	40.5	-	-	7
	o-toluidine	-	20.8	23.5	26.7	33.3	40.0	-	-	8
Cpdox.H	p-toluidine	-	20.8	23.5	26.7	32.8	40.0	-	-	8
	aniline	-	20.0	23.8	-	31.3	40.3	-	-	
	NH_3	-	-	23.5	-	35.0	39.5	46.0	-	
	β-picoline	-	-	23.5	-	33.5	39.0	48.0	-	
Heptox.H	Et_2PhP	-	-	-	-	31.0	40.5	45.0	-	
	Bu_2PhP	-	-	-	-	31.0	41.0	46.0	-	
	Ph_2EtP	-	-	-	29.5	-	41.0	46.0	-	
	NO_2	-	-	-	28.6	35.1	40.0	-	-	5
	CN	-	-	-	30.5	36.0	40.0	-	-	
Niox.H	NCSe	-	20.0	26.0	-	33.0	40.0	-	-	

Diox.H	L or X	$\overline{\nu_A}$	$\overline{\nu_B}$	$\overline{\nu_X}$	$\overline{\nu_\Delta}$	$\overline{\nu_E}$	$\overline{\nu_\Phi}$	$\overline{\nu_\Gamma}$	$\overline{\nu_H}$	Ref.
	N_3	15.8	19.0	-	30.5	-	40.0	42.5	-	
	S_2O_3	-	-	-	29.5	-	39.5	48.0	-	9
Cpdox.H	NO_2	-	-	24.4	29.9	34.2	39.2	-	-	
Heptox.H	N_3	15.5	19.0	-	30.5	-	40.0	43.0	-	
Octox.H	N_3	15.7	19.2	-	30.5	-	40.5	43.0	-	

Table 2.

Absorption bands of the [Co(Niox.H)$_2$XY] type complexes.

Ξ	Ψ	$\overline{\nu_A}$	$\overline{\nu_B}$	$\overline{\nu_X}$	$\overline{\nu_\Delta}$	$\overline{\nu_E}$	$\overline{\nu_\Phi}$	$\overline{\nu_\Gamma}$	$\overline{\nu_H}$	Ρεφ.
	pyridine	-	-	-	29.5	33.5	39.7	44.8	48.8	10
	β-picoline	-	-	-	28.5	34.0	39.2	45.0	48.4	10
	NH_3	-	-	-	28.0	33.5	39.5	-	48.3	10
	o-ethyl-aniline	-	-	-	29.2	33.1	38.9	-	48.5	10
	m-xylidine	-	-	-	28.1	33.2	39.8	-	47.6	10
NO_2	o-anisidine	-	-	-	27.8	33.4	39.3	45.5	48.1	10
	p-anisidine	-	-	-	26.8	32.5	39.5	45.2	48.6	10
	p-phenetidine	-	-	-	27.5	33.0	39.2	-	48.7	10
	p-Cl-aniline	-	-	-	29.5	33.2	39.5	-	48.5	10
	p-Br-aniline	-	-	-	29.5	33.5	39.6	-	48.5	10
	thiourea	-	-	-	30.0	36.0	40.8	-	49.0	10
	p-anisidine	-	-	25.6	-	31.9	39.1	-	-	6
	m-toluidine	-	-	25.0	28.9	32.3	39.2	-	-	6
	o-phenetidine	-	-	26.0	-	32.7	38.6	-	-	6
I	p-Cl-aniline	-	-	24.1	28.9	32.1	39.4	-	-	6
	p-toluidine	-	-	-	30.6	-	39.4	-	-	6
	aniline	-	-	26.7	30.3	33.3	39.5	-	-	6
	α-naphtyl-amine	-	-	23.7	30.8	32.3	39.1	-	-	6
NCS	aniline	-	-	-	30.7	-	39.1	-	-	6
N_3	NO_2	-	21.0	-	31.0	-	41.0	-	-	
	allil-thiourea	-	-	27.0	30.0	-	40.0	-	48.0	9
	p-toluidine	-	-	-	33.0	35.0	40.0	-	47.0	9
SO_3	p-I-aniline	-	-	-	-	32.0	39.8	-	49.0	9
	β-picoline	-	-	-	-	32.0	40.5	-	-	9
	aniline	-	-	-	-	32.0	40.0	-	-	9
S_2O_3	pyridine	-	-	-	-	32.0	39.2	-	48.0	9

Band C is situated at the limit of the visible region and it might imply also a ligand field transition, but the high molar extinction coefficient values indicate a CT transition, which masks the crystal field transition if there is such one.

Bands D, E, F, G, H are presumed to imply CT transitions. Band F is present in all spectra investigated and this is in agreement with Ablov's hypothesis, that this band is due to the Co(Diox.H)$_2$ moiety.

In order to clear up the nature of the transitions implied in the appearance of the CT bands, mean values of the wave numbers ($\bar{\nu}$) have been calculated and presented in Table 3.

Table 3.

Mean values of the wave numbers in kK.

Ligand	$\bar{\nu}_{B}$	$\bar{\nu}_{\mathrm{X}}$	$\bar{\nu}_{\Delta}$	$\bar{\nu}_{E}$	$\bar{\nu}_{\Phi}$	$\bar{\nu}_{\Gamma}$	$\bar{\nu}_{\mathrm{H}}$
Niox.H	19.86	24.96	29.83	32.77	39.79	44.60	48.30
Heptox.H	19.00	23.50	30.00	32.62	40.17	45.67	-
X = Y = amine	20.02	24.25	27.20	32.45	40.16	47.00	-
X = Y = phosphine	-	-	29.50	31.00	40.83	45.67	-
X = Y = amine + phosphine	20.02	24.25	27.78	32.24	40.29	46.20	-
X = Y = anion	19.30	25.20	29.92	34.57	39.90	42.83	-
X = Y (D_{4h})	19.84	24.39	29.16	32.76	40.18	44.94	-
X = NO_2; Y = amine	-	-	28.58	33.54	39.55	45.12	48.45
X = I; Y = amine	-	25.22	29.90	32.43	39.17	-	-
X = SO_3; Y = amine	-	27.00	(33.00)	32.60	39.17	-	48.00
X ≠ Y (L) (C_{4h})	21.00	25.52	29.40	33.02	39.58	-	48.30
General mean	19.89	24.75	29.32	32.91	39.82	45.00	48.30

With respect to band B, one may observe that in the case of diamino-derivatives (X = Y = amine), the wave number $\bar{\nu}_B$ is higher than with the diacido-complexes, with ligands situated at the beginning of the spectrochemical series. This phenomenon pleads for the importance of the cristal field strength, i. e. for the cristal field transition character of band B.

Band C may be presumed to imply a Co → X charge transfer transition. As seen from Table 3, $\bar{\nu}_C$ is 24.25 for diamino- and 25.2 for the diacido-derivatives, in perfect agreement with the above assignment, since the negative charge of the acido X ligand requires a higher energy for this transition. Further, one can observe that $\bar{\nu}_C$ is higher for the polar acido- amino-complexes of C_{4h} simmetry, as compared to the D_{4h} type diamino ones. This also agrees with the above assignment of the transition.

In the case of band D the relatively high difference in $\bar{\nu}_D$ between the phosphine and amine derivatives, and between the iodo- and nitro-nonelectrolytes, respectively suggests the idea that also Co → X CT transition occurs.

Bands E and F seem to imply transition in the $Co(Diox.H)_2$ moiety. Practically the axial ligands X and Y have no influence upon $\bar{\nu}_F$ and also $\bar{\nu}_E$ [15] are very close to the general mean values indicated in Table 3.

On the contrary, with the bis-diphenylglyoximato-Co(III) complexes an important shift of band E and especially of band F is observed [14]. The corresponding mean wave numbers are the following: $\bar{\nu}_E = 31$ kK, $\bar{\nu}_F = 37.7$ kK [15]. Since this shift is due to the electron withdrawing effect of the phenyl groups, the transition may be presumed to consist of Co → Diox.H charge transfer.

Bands G and H are situated at the boundary of the spectral region investigated, where the absorption is very high. Therefore their determination is rather difficult. This is why for the majority of the complexes these bands are not reported in Table 1 and 2.

Up to now we discussed only the crystal field transitions and the CT transitions, but in the electronic spectra absorption bands may be due also to electronic transitions in the co-ordinated ligands. The chelating agents, i. e. the dioximes and the amino (phosphine) ligands have several absorption bands in the UV region comprized between 25 and 50 kK. Therefore the above discussed bands may have a complex character, i. e. the overlap of CT and ligand transition bands may occur.

Thus, the free dimethylglyoxime has two absorption bands at 31.5 and at 37.7 kK, respectively [16] and the pure α-diphenylglyoxime absorbs at 28.5 and 34.5 kK [17]. One cannot exclude the possibility, that bands E and F of the bis-dioximino-Co(III)-complexes are due to the same electron transitions occurring in the co-ordinated dioxime. Both wave numbers are shifted towards higher values, as compared to the free dioximes, which might be due to the relatively strong covalent character of the Co–N bonds.

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