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EQUILIBRIA IN ACETONE MEDIUM. VII[*]. CONDUCTIMETRIC AND SPECTROPHOTOMETRIC STUDIES ON BINARY SYSTEMS OF COBALT(II) HALIDES WITH DIAZOLES. A PRELIMINARY SURVEY.

M. MOLINA [**]
M. DE MORAES [***]
C. MELIOS [****]
J. O. TOGNOLLI [*****]

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MOLINA, M.; MORAES, M.; MELIOS, C.; TOGNOLLI, J. O. Equilibria in acecone medium VII. Conductimetric and spectrophometric studies on binary systems of Cobalt(II) halides with diazoles. A preliminary survey. *Ecl. Quím.*, São Paulo, **4:** 47-53, 1979.

SUMMARY: The equilibria involved in binary systems of Cobalt(II) halides and some diazoles in acetone, at 25.00 ± 0,05°C were investigated through conductometric and spectrophotometric measurements. These systems are: a) $CoCl_2$-L, in which L = pyrazole (Pz), 3,5 dimethyl pyrazole (DMP), 1-phenyl-3,5 dimethyl pyrazole (PDMP), 1-phenyl-3--methyl-5-pyrazole (PMP) and imidazole (Iz), b) CoX_2–L (X = Br–, I–; L = Pz, DMP and PDMP). The obtained results in connection with available stability constants for certain concerned $CoCl_2$–L (L = Pz, DMP and PDMP) and CoX_2–L (X = Br–, I–; L = PDMP) systems, suggested the same stability order for each CoX_2–L (X = Cl–, Br–, I–) series, namely:

DMP > Pz > PDMP > PMP

The available data did not allow a clear conclusion concerning the location of Iz in the above stability order.

UNITERMS: Cobalt(II) Halides; Diazoles; Acetone; Conductimetry; Spectrophotometry; Stability Constants.

INTRODUCTION

A set of earlier papers from this laboratory dealt with complex species of the type CoX_2L_n formed in binary systems comprising cobalt(II) halides (CoX_2, where X = Cl–, Br–, I–) and some unidentate organic ligands (L = phosphine oxides, sulfoxides, pyrazole and pyridine derivatives etc.) in anhydrous

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[**] Professor Titular junto ao Departamento de Química Analítica do Instituto de
[*] Part VI: *Ecl. Quím*, São Paulo, **4:** 39, 1979.
Química da UNESP.

[***] Bolsista da FAPESP.

[****] Professor Assistente Doutor junto ao Departamento de Química Analítica do Instituto de Química da UNESP.

[*****] Professor Assistente junto ao Departamento de Química Analítica do Instituto de Química da UNESP.

acetone medium, at 25ºC(1–6). In an endeavour to extend the previous work, the behaviour of binary systems incorporating cobalt(II) halides and pyrazole, 3,5 dimethyl pyrazole, 1-phenyl-3,5 dimethyl pyrazole, 1-phenyl-3-methyl-5--pyrazolone and imidazole, in the referred solvent and temperature, have been comparatively examined through conductimetric and spectrophotometric data.

LIST OF MAIN SYMBOLS AND ABBREVIATIONS

A, measured absorbance; b, length of the optical path; β_n, overall stability or formation constant of CoX_2L_n M^{-n}; C_L, total concentration of ligand; C_M, total concentration of CoX_2; DMP, 3,5 dimethyl pyrazole; ε, mean molar absorptivity $= A/b.C_M$ ($M^{-1}.cm^{-1}$); Iz, imidazole; L, ligand; Λ_m, measured conductance (μmho); Λ_m, molar conductance ($mho.cm^2.mole^{-1}$); λ, wavelenght (nm); M, molar concentration; PDMP, 1-phenyl-3,5 dimethyl pyrazole; PMP, 1-phenyl-3-methyl-5-pyrazolone; Pz, pyrazole.

EXPERIMENTAL PART

Grade A glassware was employed for all volumetric work. Acetone was purified and dehydrated as previously mentioned(1, 7). Anhydrous solutions of the cobalt(II) halides were prepared and standardized as reported(7). DMP was prepared from hydrazine sulphate and acetylacetone(8); PDMP was synthesized and purified as described elsewhere(7). Pz ("Eastman", m.p. 65.2-66.1ºC), PMP and Iz, both from "Fluka", "purum" grade, m.p's. 126.6-127.5 and 86.8-88.2ºC, respectively, were used without further purification. The purity of Pz, DMP and PDMP was checked by potentiometric titration with $HClO_4$ in anhydrous acetic acid(8). Acetone solutions of known concentrations of all mentioned ligands were assessed by direct weighing of the products.

Eletronic spectra were recorded on a "Varian" model 635 spectrophotometer. Conductances were measured with a "Metrohm" model E527 apparatus using a cell with a constant of $0.78 cm^{-1}$. Measurements were all carried out in acetone medium, at 25.00 ± 0.05ºC in a room thermostated to 25 ± 1ºC.

RESULTS AND DISCUSSION

Each system was investigated by fixing the metal salt concentration while C_L was allowed to vary. The first evidence of complex formation in all the investigated systems was provided by the absorption spectra (range: 500-800 nm) of metal salt-ligand mixtures in different proportions. These mixtures exhibit absorption maxima and/or associated mean molar absorptivities quite distinct in comparison with the corresponding metal salts, in identical experimental conditions. The absorption maxima are collected in Table I. The quoted λ_{max} were obtained for C_L:C_M proportions (at constant C_M) in which the CoX_2 were almost entirely present as the highest CoX_2L_n complexes (*i.e.*, the spectra remained unchanged with further addition of ligand). For the $CoCl_2$ – – PMP system no saturation was attained at least up to C_L:C_M = 50; the absorption maxima given for this system are those displayed for C_L : C_M = 100. Hyperchromic effect is associated with all bands (relative to the ones given by CoX_2). Complex formation is evidenced also by hypsochromic effect revealed in connection with the B and C bands (Table I). Moreover, the solid complexes $CoX_2(Pz)_4$, $CoX_2(Iz)_2$, $CoX_2(DMP)_2$ and $CoX_2(PDMP)_2$ have been isolated and characterized(10–14).

TABLE I — Characteristic Absorption Bands and Absorption Maxima of CoX_2 and CoX_2 — Diazole Systems in Anhydrous Acetone. t = 25.00 ± 0.05ºC.

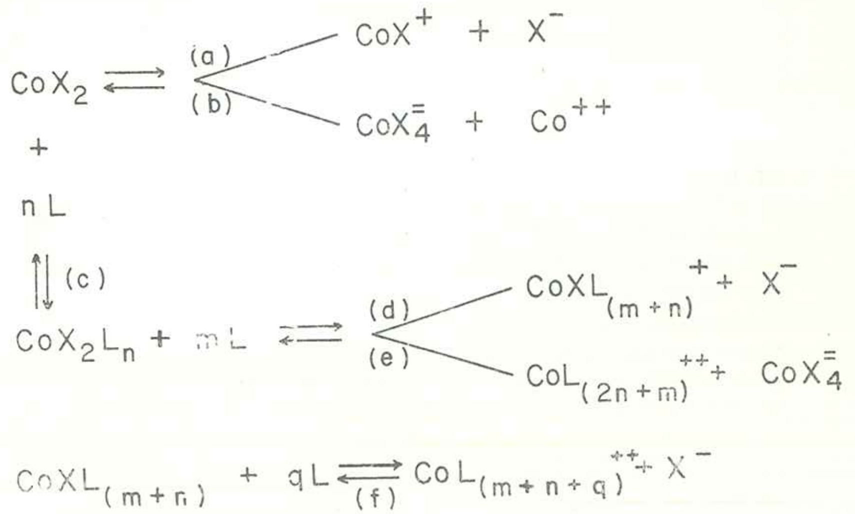
System	λ_{max} (nm) A*	B*	C*
$CoCl_2$	**575**	**640**	**677**
" -DMP	580	620	635
" -Pz	575	610	635
" -PDMP**	570	620	665
" -PMP	580	615 (sh)***	660
" -Iz	580	610	630
$CoBr_2$	**590**	**640** (sh)	**670**
" -DMP	600	630	650
" -Pz	590	630	650
" -PDMP**	590	640 (sh)	670
CoI_2	**615**	**666,700**	**740**
" -DMP	620	655	695
" -Pz	620	650	685
" -PDMP**	615	665	700

* — absorption band;
** — ref. 9;
*** — shoulder

Results from conductimetric measurements are given in Tables II, IV and V. It can be seen that for the $CoCl_2$ complexes (Table II) the decrease of conductance with increasing amounts of the ligands is more pronounced in the sequence:

DMP > Pz > PDMP > PMP . . . (1)

A somewhat different behaviour is presented by the system involving imidazole; for low C_L values it is placed approximately together with Pz in sequence (1); for C_L > 5.00mM, a continuous increase in conductance takes place. A slight increase of conductance as a function of C_L is also revealed by the PDMP and DMP systems but at much smaller extent and at significantly higher C_L values. In acetone, 1.000mM solutions of $CoCl_2$, $CoBr_2$ and CoI_2 present Λ_M values of 9.5 ± 1.5, 17.0 ± 2.0 and 31.0 ± 4.0, respectively. The mean Λ_M given for 1:1 electrolytes in the mentioned solvent is 137 (range: 100-160)(15). The cobalt(II) halides are therefore weak electrolytes in anhydrous acetone and the low conductance values sistematically found can be attributed (without taking into account the solvation of the involved species) to equilibria (a) and/or (b) in the following scheme:



The continuous decrease of conductance with increasing C_L (observed for all the systems considered in this work) may be ascribed to the occurrence of equilibria indicated by (c), with repression of the ionizations represented in (a) and/or (b) and formation of the uncharged adducts CoX_2L_n. For some systems (*e.g.*, $CoCl_2$-Iz, $CoBr_2$-PDMP and CoI_2-DMP) the conductance values reach a minimum for a certain ligand concentration; further addition of ligand results in a continuous increase in conductance. This behaviour could be explained taking into account the simultaneous participation of one or more of the equilibria represented by (d), (e) and (f) in the above scheme. For C_L/C_M ratios in which a clear decrease in conductance is depicted the exclusive occurrence of equilibria (c) was assumed(1–4, 6) and the determined overall stability constants were thus defined by : $\beta_n = [CoX_2L_n] / [CoX_2] \cdot [L]^n$. Stability constants have already been determined for systems involving $CoCl_2$ and some of the ligands considered in this work(4, 16). A comparison of the stability and conductivity data for the $CoCl_2$ systems (Tables II and III) shows that the stability order found is in line with sequence (1) *i.e.*, the more pronounced the decrease of conductance with increasing ligand content, the more stable the system. This correlation between conductivity and stability data has also been observed for other $CoCl_2$-L systems(6); furthermore, the conductimetric approach has already been applied for establishing relative donor strenghts of ligands towards various Lewis acids in nonaqueous media(17, 18). From the presented reasoning it follows that the PMP system should be the least stable within the sequence of the chloro complexes. The particular behaviour associated with the $CoCl_2$-Iz interaction does not allow a safe location of this system in the stability series. However, the strong nucleophilic character of Iz seems evident.

TABLE II — Conductimetric Data for $CoCl_2$ — Diazole Systems in Anhydrous Acetone.
$t = 25.00 \pm 0.05°C$.
$C_M = 1.00$ mM
Λ_m (μmho)

C_L (mM)	DMP	Pz	PDMP*	PMP**	Iz***
0	13.6	13.6	13.6	13.6	13.6
1.00	4.90	8.55	—	—	10.7
3.00	—	4.16	—	—	3.58
5.00	1.58	3.14	5.10	—	3.51
10.0	1.36	2.93	3.95	11.9	3.89
15.0	1.52	2.97	3.65	—	4.34
20.0	1.38	2.80	3.70	—	5.03
25.0	—	—	—	9.97	—
50.0	1.60	2.78	3.90	9.25	8.54
100	—	—	4.40	9.97	17.0
200	—	—	5.50	—	—

Λm (ligands) < 0.4 μmho, except for PMP (see bellow)

* — ref. 9.

** — A 100mM solution of the pure ligand gave $\Lambda_m = 4.35$ μmho. This small conductance is probably due to keto-enol tautomerism (known to occur with pyrazolones) with subsequent dissociation of the enol form. Conductances ascribed to this effect were proportionally deducted from the measured conductances. The resulting Λ_m values are the ones shown in this Table.

*** — System investigated by fixing $C_M = 0.40$ mM. For this system the C_L values given actually correspond to C_L/C_M ratios. Precipitation was found to occur for the listed C_L/C_M, at C_M values higher than the one mentioned above. In order to permit comparison with the other systems, the experimental Λ_m values were converted to $C_M = 1.00$ mM by assuming direct proportionality between C_M and Λ_m.

TABLE III — Overall Stability Constants for Binary Systems Involving CoX_2 and Some Pyrazoles, in Anhydrous Acetone.
$t = 25.00 \pm 0.05°C$.

System	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
$CoCl_2$-DMP*	4.53	8.78	12.69	17.02
$CoCl_2$-Pz*	3.69	7.07	10.24	13.54
$CoCl_2$-PDMP**	3.33	3.85	7.30	9.24
$CoBr_2$-PDMP**	3.56	6.05	7.60	10.80
CoI_2-PDMP**	3.58	5.65	—	—

* — ref. 16.
** — ref. 4.

Stability constants for the $CoBr_2$-PDMP and CoI_2-PDMP have been determined(4). The obtained values are given in Table III. These results, in connection with the conductimetric data given in Tables IV and V, seem to indicate that in acetone medium, the following stability order (considering the same CoX_2 series) should hold:

$$CoX_2(DMP)_n > CoX_2(Pz)_n > CoX_2(PDMP)_n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

This order is the one encountered for the analogous $CoCl_2$ complexes. It is perhaps worth noting that a direct correlation has been found between the stabilities (and predicted stabilities) of the considered systems and the intensity of the *C* absorption band for each CoX_2-L series; the more stable the system, the higher the molar absorptivity at the associated with the named band. Further work is currently in progress with the aim of confirming sequence (2) through formation constant values.

An exploratory investigation on complexes of cobalt(II) fluoride with the ligands mentioned in this work was tried.

TABLE IV — Conductimetric Data for Binary Systems Involving $CoBr_2$ and Some Pyrazoles, in Anhydrous Acetone. $t = 25.00 \pm 0.05°C$.
$C_M = 1.00$ mM

DMP		Pz		PDMP*	
C_L (mM)	Λ_m (μmho)	C_L (mM)	Λ_m (μmho)	C_L (mM)	Λ_m (μmho)
0	17.6	0	17.6	0	17.6
1.00	7.30	1.00	10.7	5.04	6.39
2.00	2.72	2.00	6.57	10.1	4.89
3.00	2.36	3.00	5.26	15.1	4.29
5.00	2.27	4.00	4.82	20.2	4.14
8.10	2.26	5.00	4.72	49.9	4.36
10.0	2.32	10.0	4.45	101	5.19
				200	6.62

Λ_m (ligands) < 0.4 μmho; * — ref. 9.

Unfortunately, the concerned experiments could not be performed owing to the very low solubility of CoF_2 in anhydrous acetone.

TABLE V — Conductimetric Data for Binary Systems Involving CoI_2 and Some Pyrazoles, in Anhydrous Acetone. t = 25.00 ± 0.05°C.

C_M = 1.00 mM

DMP		Pz		PDMP*	
C_L (mM)	Λ_m (μmho)	C_L (mM)	Λ_m (μmho)	C_L (mM)	Λ_m (μmho)
0	40.0	0	40.0	0	40.0
1.00	18.6	1.00	25.3	5.04	15.8
2.00	6.70	2.00	13.0	10.1	11.7
3.00	5.60	3.00	8.81	15.1	10.6
4.00	6.52	4.00	8.09	20.2	10.8
5.00	7.46	5.00	8.04	49.9	10.9
10.0	11.0	10.0	9.79	101	15.4
				200	31.5

Λ_m (ligands) < 0.4 μmho; * — ref. 9.

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MOLINA, M.; MORAES, M.; MELIOS, C.; TOGNOLLI, J. O. Equilíbrios em meio acetônico. VII. Estudo condutométrico e espectrofotométrico de sistemas binários de haletos de cobalto(II) com diazóis. Resultados preliminares. *Ecl. Quím.*, São Paulo, 4: 47-53, 1979.

RESUMO: Os equilíbrios envolvidos em sistemas binários contendo haletos de Cobalto(II) e alguns diazóis, em acetona, a 25,00 ± 0,05°C, foram investigados através de dados condutométricos e espectrofotométricos. Esses sistemas são:

a) $CoCl_2$-L, onde L = pirazol (Pz), 3,5 dimetilpirazol (DMP), 1-fenil-3,5 dimetilpirazol (PDMP), 1-fenil-3 metil-5-pirazolona (PMP) e imidazol (Iz);

b) CoX_2-L (X = Br−, I−, L = Pz, DMP e PDMP). Os resultados obtidos, em conexão com dados de constantes de estabilidade disponíveis para alguns dos sistemas considerados ($CoCl_2$−L, onde L = Pz, DMP e PDMP; CoX_2−L, onde X = Br−, I− e L = PDMP), sugerem a seguinte ordem de estabilidade, que é a mesma para cada série CoX_7—L (X = Cl—, Br—, I—):

DMP > Pz > PDMP > PMP

Os dados disponíveis não permitem situar precisamente o Iz na seqüência acima.

UNITERMOS: Haletos de Cobalto(II); Diazóis; Acetona; Condutometria; Espectrofotometria; Constantes de Estabilidade.

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