

Preliminary Note
EQUILIBRIA IN ACETONE MEDIUM, IX.*
THE PECULIAR
BEHAVIOUR OF THE COBALT (II)
CHLORIDE-PYRAZOLE SYSTEM.

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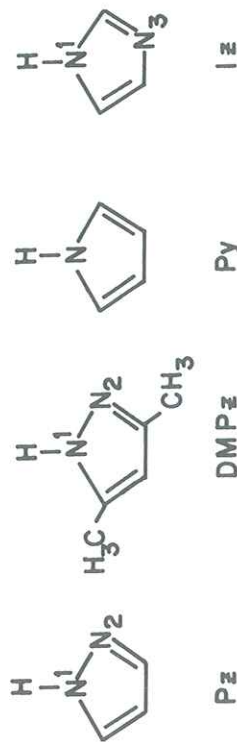
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KEY-WORDS: Cobalt (II) chloride, pyrazole, conductivity, spectrophotometry.

INTRODUCTION

Previous work in this laboratory dealt with the determination of the composition and thermodynamic stability of complex species formed in $\text{CoCl}_2\text{-L}$ systems in acetone medium, at 25°C , where L stands for pyrazole (Pz)⁽¹⁾, 3,5-dimethyl pyrazole (DMPz)⁽¹⁾, 3,5-

dimethyl-1-phenyl pyrazole (2) and imidazole (Iz)⁽³⁾. In the present communication attention is focussed upon some noteworthy properties associated with the $\text{CoCl}_2\text{-Pz}$ system. These properties are compared with those displayed by binary systems comprising the same metal salt and related ligands, i.e., DMPz, Iz and pyrrole (Py) in the aforementioned medium and temperature.



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LIST OF MAIN SYMBOLS AND ABBREVIATIONS

A, measured absorbance; b, length of the optical path; C_L , total concentration of ligand; C_M , total concentration of CoCl_2 , DMPz, 3,5-dimethyl pyrazole; ϵ , mean molar absorptivity = $A/b \cdot C_M$ ($M^{-1} \cdot \text{cm}^{-1}$); Iz, imidazole; L, ligand; λ , wavelength (nm); M, molar concentration; Py, pyrrole; Pz, pyrazole.

EXPERIMENTAL PART

Acetone was purified and dehydrated as previously mentioned⁽⁴⁾. The preparation and standardization of anhydrous stock solution of CoCl_2 was described elsewhere⁽⁴⁾. Pz and DMPz were purified as reported^(5,6) (m. p.'s. 65.2-66.1°C and 106.0-106.9°C, respectively). Iz ("Fluka", "purum = grade) was recrystallized as recommended by PERRIN *et al.*⁽⁷⁾ (m.p. 87.8-88.1°C) Py ("C.Erba") was stored over KOH pellets for 12 hr. and fractionally distilled from KOH in the dark. All other reagents used were of analytical purity. Electronic spectra were recorded on a "Varian" mod. 635 instru-

ment using matched silica cell of 1.00 cm optical path. Conductances were measured with a "Metrohm" mod. E527 apparatus using a cell with a constant of 0.78 cm^{-1} . Measurements were all carried out in acetone medium at $25.00 \pm 0.05^\circ\text{C}$ in a room thermostated to $25 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

The absorption spectra of CoCl_2 -Pz mixtures (C_L/C_M ratios from 0 to 10) at constant C_M are given in Fig. 1. These spectra show a quite usual pattern up to $C_L/C_M = 5$ indicating complex formation. It has been shown that for solutions in which $C_M = 1.50 - 2.00$ mM and $C_L = 0.31 - 2.80$ mM, the conductimetric and spectrophotometric data are consistent with the formation of CoCl_2L_n adducts ($1 < n \leq 4$), whose stability constants have been determined⁽¹⁾. The spectrum associated with $C_L/C_M = 10$ is less intense than that for $C_L/C_M = 5$; in fact it is very nearly coincident with the $C_L/C_M = 3$ spectrum, especially in the vicinity of the main peak. This decrease in intensity with increasing ligand to metal ratio is an unusual feature for a system in which only uncharged adducts seemed to form.

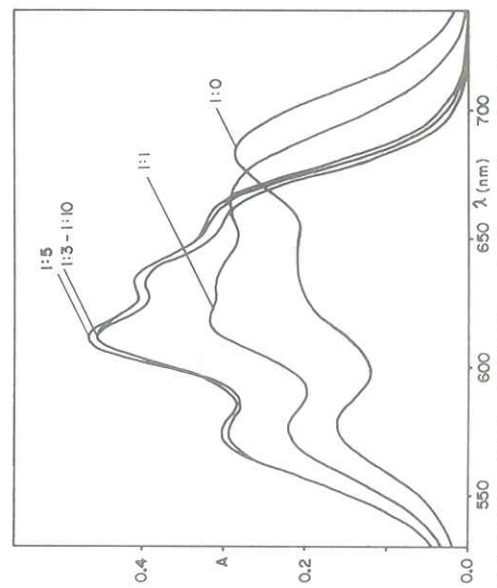


Fig. 1 — CoCl_2 -Pz system, in acetone medium, at 25°C . Absorption Spectra of metal salt: ligand mixtures in different proportions. $C_M = 0.95$ mM.

The system was further investigated with C_L/C_M ranging from 10 to 100; the corresponding spectra (Fig. 2) show a definite decrease in band intensity with increasing ligand concentration. The band maxima remain essentially unchanged. When aliquots of the $C_L/C_M = 100$ solution are diluted yielding solutions with C_L 10, 20 and 50 mM and CoCl_2 is conveniently added so as to maintain $C_M = 1.00$ mM in each of these solutions, the corresponding spectra in Fig. 2 could be reproduced indicating that the process is completely reversible. On the other hand, the conductances of these solutions de-

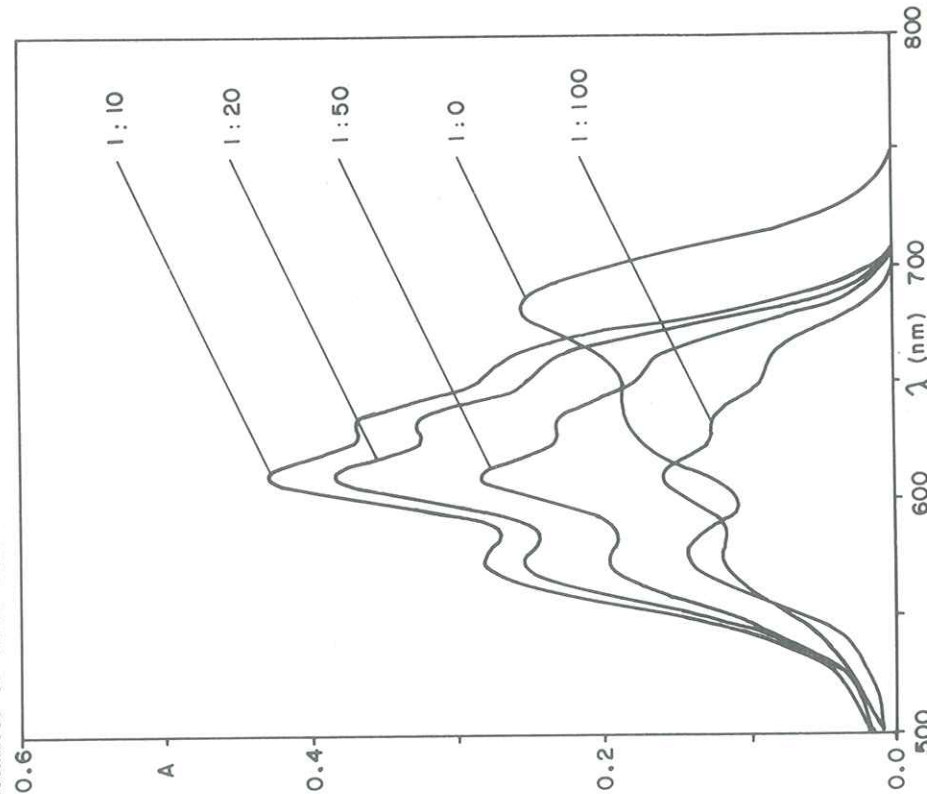


Fig. 2 — CoCl_2 -Pz system, in acetone medium, at 25°C . Absorption Spectra of metal salt: ligand mixtures in different proportions. $C_M = 1.00$ mM.

The properties of $\text{CoCl}_2\text{-Pz}$ system, especially for $C_L/C_M > 5$, are in sharp contrast with the ones displayed by systems involving closely related diazoles. Thus the $\text{CoCl}_2\text{-DMPz}$ system has been previously investigated ($C_M = 1.50\text{-}2.00$ mM, $C_L = 0.22\text{-}3.25$ mM); the corresponding conductimetric and spectrophotometric data pointed to the formation of four complex species, i.e., CoCl_2L_n , where $1 \leq n \leq 4$ (1). The

TABLE 1 — Characteristic Absorption Bands, Absorption Maxima and Mean Molar Absorptivities for CoCl_2 and $\text{CoCl}_2\text{-DMPz}$ System in Acetone Medium. $C_M = 1.00$ mM

C_L/C_M	A		B		C		Λ_m (μmho)
	λ_{max}	ϵ^*_{max}	λ_{max}	ϵ^*_{max}	λ_{max}	ϵ^*_{max}	
0	680	290	640	223	575	164	13.6
1	665†	338	635-620	403	577	246	4.90
3	630	597	620	595	580	363	—
5	635	599	620	597	580	365	1.58
10	635	607	620	605	580	371	1.36
20	—	—	—	—	—	—	1.38
50	635	626	620	626	580	379	1.60
100	635	632	620	632	580	382	2.00

* — ϵ values were calculated from absorbances taken directly from low resolution spectra and are thus approximate.

† — shoulder.
Iz behaves much like DMPz toward CoCl_2 ; a survey of conductivity and electronic spectral data for the $\text{CoCl}_2\text{-Iz}$ system is given in Table II. The upward trend in conductance is more pronounced than that observed for the DMPz system. This difference between the two systems can be explained by taking into account that Iz is stronger than DMPz ligand(1,3). The Iz system has also been quantitatively studied ($C_M = 0.50\text{-}1.50$ mM, $C_L = 0.20\text{-}2.45$ mM); only two CoCl_2L_n adducts were found to exist and their stability constants have been determined (3).

TABLE 11 — Characteristic Absorption Bands, Absorption Maxima and Mean Molar Absorptivities for CoCl_2 and $\text{CoCl}_2\text{-Iz}$ System in Acetone Medium. $C_M = 1.000$ mM

C_L/C_M	A		B		C		Λ_m (μmho)
	λ_{max}	ϵ^*_{max}	λ_{max}	ϵ^*_{max}	λ_{max}	ϵ^*_{max}	
0	680	290	640	223	575	164	13.6
1	660†	325	630	380	577	243	10.7
3	630	545	610	555	577	365	3.58
5	630	545	610	555	577	365	3.51
10	630	535	610	544	577	358	3.89
15	630	535	610	544	577	358	4.34
20	630	535	610	544	577	358	5.03
50	630	545	610	555	577	365	8.54
100	630	545	610	555	577	365	17.0

* — ϵ values were calculated from absorbances taken directly from low resolution spectra and are thus approximate.

† — shoulder.

The mode of bonding of Pz and Iz to the square planar Schiff base complexes of Co (saloph) and Ni (saloph), where saloph = $\text{N,N}'\text{-bis}$ (salicydene-o-phenylene) diamino, in dichloromethane, was investigated through MNR, calorimetric and visible spectral data by TOVROG *et al.*(9). The authors concluded that both Pz and Iz behave as ambidentate ligands towards the above mentioned complexes, i.e., they may coordinate through either of their nitrogen atoms. The work of TOVROG *et al.* was severely criticized by DOONAN *et al.*(10), who reinvestigated the named systems and could find no evidence indicating that either Pz or Iz bind to Co (saloph) or Ni (saloph) via their N-1 atoms. DOONAN *et al.*(10) stated that the N-1 positions of Pz and Iz should be very nearly equivalent to the nitrogen of Py in their reactions with Lewis acids and examined the ability of Py to coordinate

Ni (saloph) or Co (saloph). No evidence of interaction was produced for Co (saloph) - Py mixtures up to $C_L/C_M = 4,000$ and Ni (saloph)-Py up to $C_L/C_M = 1,238$.

Similar experiments were performed to determine the effect of Py on CoCl_2 in acetone medium. Our results are summarized in Table III. The electronic spectral data seem to indicate a feeble interaction up to $C_L/C_M = 200$; marked changes in intensity and profile of absorption are observed for C_L/C_M 500 and 1,000, making clearly apparent that interaction takes place. The conductivity data suggest that chloride is displaced from the inner coordination sphere of the complex (es) formed, even for low C_L/C_M ratios. Confirmation was obtained by detecting free chloride ions in the mentioned solutions through e.m.f. measurements of the following cell:



It was found that for $C_L/C_M > 100$, the increase in free chloride ion concentration was paralleled by the increase in conductivity.

TABLE III — Characteristic Absorption Bands, Absorption Maxima and Mean Molar Absorptivities for CoCl_2 and $\text{CoCl}_2\text{-Py}$ System in Acetone Medium. $C_M = 1.00$ mM

C_L/C_M	A		B		C		Λ_m (μmho)
	λ_{max}	ϵ^*_{max}	λ_{max}	ϵ^*_{max}	λ_{max}	ϵ^*_{max}	
0	680	290	640	223	575	164	13.6
10	680	292	640	224	575	165	14.6
15	680	285	640	217	575	163	15.0
20	679	284	640	216	575	160	15.7
50	679	281	640	213	575	159	19.2
100	678	278	640	210	575	157	25.3
200	677	275	640	208	575	159	37.5
500	664	267	640†	225	575	159	59.4
1.000	660†	314	635	357	612†	310	63.3

* — ϵ values were calculated from absorbances taken directly from low resolution spectra and are thus approximate. — † shoulder.

The properties of the $\text{CoCl}_2 \cdot \text{Py}$ system resemble those displayed by 2,6-dimethyl pyridine and 2,4,6-trimethyl pyridine in their reactions with $\text{CoCl}_2^{(8)}$.

No satisfactory explanation can be advanced concerning the behaviour presented by the $\text{CoCl}_2 \cdot \text{Pz}$ system. It is felt that more data for tendencies and modes of bonding of various bases to cobalt(II) salts or complexes must be accumulated

to enable generalizations to be made concerning the essential factors leading to the different kinds of resulting complexes.

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UNITERMOS: Cloreto de cobalto (II); pirazol; condutometria; espectrofotometria.

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