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

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

INTRODUCTION

Previous work in this laboratory dealt with the determination of the composition and thermodynamic stability of complex species formed in CoCl₂-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 (lz) (³). In the present communication attention is focussed upon some noteworthy properties associated with the CoCl₂-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; DMFz, 3,5-dimethyl pyrazole; ε, mean molar absorptivity = \frac{A/b}{\text{cm}^3}; I_z, imidazole; L, ligand; \text{M}, measured conductance (\mu \text{hos}); \lambda, wavelength (nm); \text{M}, molar concentration; P_y, pyrrole; P_z, 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 DMFz were purified as reported[5,6] (m.p. 65.2-66.1°C and 106.0-106.9°C, respectively). Iz ("Fluka", "purum = grade e") 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 instrument 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 \text{cm}^{-1}. Measurements were all carried out in acetone medium at 25.00 ± 0.05°C in a room thermostated at 25 ± 1°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_2Pz_n adducts (1 < n < 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 which is only uncharged adducts seemed to form.

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 decrease continuously from C_l/C_M = 0 (13.6 \mu \text{hos}, corresponding to 1.00 mM CoCl_2 solution) to C_l/C_M = 100 (2.25 \mu \text{hos}); this makes clearly apparent that Pz, even in considerable excess, does not displace chloride ions from the inner coordination sphere of the complexes formed. The above mentioned reproducibility of spectra, obtained through dilution of the C_l/C_M = 100 solution is also observed in connection with the conductance data, i.e., the original values corresponding to C_l/C_M 10, 20 and 50 are recovered within the experimental error.
The properties of CoCl$_2$-Pz system, especially for C$_1$ / C$_{M}$ > 5, are in sharp contrast with the ones displayed by systems involving closely related diazoles. Thus the CoCl$_2$-DMP$_2$ system has been previously investigated (C$_M$ = 1.50-2.00 mM, C$_1$ = 0.22-3.25 mM); the corresponding conductimetric and spectrophotometric data pointed to the formation of four complex species, i.e., CoCl$_2$L$_{2}$$^{	ext{II}}$, where 1 ≤ n ≤ 4 (1,3). The spectral features as well as the conductivity data for this system are summarized in Table I. It can be seen that the band intensities increase with increasing ligand concentration, at least up to C$_1$ / C$_{M}$ = 100. An upward trend in conductance is observed for C$_1$ / C$_{M}$ values higher than ≈ 20; this behavior can be readily understood by considering the ionization scheme previously proposed for various systems in acetonitrile (1,8).

| TABLE I — Characteristic Absorption Bands, Absorption Maxima and Mean Molar Absorptivities for CoCl$_2$ and CoCl$_2$-DMP$_2$ System in Acetone Medium.

<table>
<thead>
<tr>
<th>C$<em>1$ / C$</em>{M}$</th>
<th>λ$_{\text{MAX}}$ (µm)</th>
<th>ε$_{\text{MAX}}$ (mM$^{-1}$cm$^{-1}$)</th>
<th>C$_{\text{MAX}}$ (µm)</th>
<th>ε$_{\text{MAX}}$ (mM$^{-1}$cm$^{-1}$)</th>
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* E values were calculated from absorptions 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 Co (saloph) and Ni (saloph), where saloph = N$_2$N'—bis (salicydene-d-o-phenylene) amidino, in dichloromethane, was investigated through MNIR, calorimetric and visible spectral data by TOVROG et. al (10). 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 DONAN et al. (10), who reinvestigated the named systems and could find no evidence indicating that either Pz or Iz bind Co (saloph) or Ni (saloph) via their N-1 atoms. DONAN 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 ex-aminated 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$_1$ / C$_{M}$ = 4,000 and Ni (saloph)-Py up to C$_1$ / 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 II. The electronic spectral data seem to indicate a free interaction up to C$_1$ / C$_{M}$ = 200; marked changes in intensity and profile of absorption are observed for C$_1$ / 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$_1$ / C$_{M}$ ratios. Confirmation was obtained by detecting free chloride ions in the mentioned solutions through m.f. measurements of the following cell:

$\text{Ag/AgCl} \quad \text{0.100M LiCl} \quad \text{0.100M LiCl}_{10} \quad \text{Test solution} \quad \text{AgCl/Ag}^+$

It was found that for C$_1$ / C$_{M}$ > 100, the increase in free chloride ion concentration was paralleled by the increase in conductivity.

| TABLE II — Characteristic Absorption Bands, Absorption Maxima and Mean Molar Absorptivities for CoCl$_2$ and CoCl$_2$-Py System in Acetone Medium.

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<tr>
<th>C$<em>1$ / C$</em>{M}$</th>
<th>λ$_{\text{MAX}}$ (µm)</th>
<th>ε$_{\text{MAX}}$ (mM$^{-1}$cm$^{-1}$)</th>
<th>C$_{\text{MAX}}$ (µm)</th>
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* The E values were calculated from absorptions taken directly from low resolution spectra and are thus approximate. 
† shoulder.
The properties of the CoCl$_2$-Py system resemble those displayed by 2,6-dimethyl pyridine and 2,4,6-trimethyl pyridine in their reactions with CoCl$_2$.$^9$

No satisfactory explanation can be advanced concerning the behaviour presented by the CoCl$_2$-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.

ACKNOWLEDGEMENT

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

REFERENCES