

Chloride Species of Cobalt(II) Sorbed on Ion Exchangers. II. Non-aqueous Media¹

C. Heitner-Wirguin and N. Ben-Zwi (Liebling)

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The spectra of cobalt species sorbed on Dowex 1X8 Cl⁻ and Dowex 50WX8 Li⁺ from acetone and ethanol solutions containing various concentrations of chloride ions were measured and interpreted. These spectra were compared to the spectra obtained by sorption of cobalt ions from aqueous solutions of similar composition. From these studies an assignment of species sorbed from the non aqueous media was possible.

Introduction

A series of papers deals with the Co^{II}-solvent-chloride system. The spectral behaviour and character are explained as being mainly due to configurational change, *i.e.* from octahedral to tetrahedral.²⁻⁶ In non aqueous solutions as well as in water the most commonly mentioned species are the symmetrical CoCl₄²⁻, Co(Solv)_n²⁺, and Co(H₂O)₆²⁺. However some mixed intermediate species containing chloride ions and solvent molecules^{3-6a} have also been studied.

The aim of the present work was to try to separate and to characterise the different Co-chloride-solvent species, using ion exchangers in non aqueous solutions. Ion exchangers are capable of sorbing selectively individual species from the non aqueous media (and excluding others), thus having an advantage over work in non aqueous media by itself.

Experimental Section

In order to obtain anhydrous CoCl₂, the hydrated salt was dried at 135 °C for several hours. LiCl was dried at 110 °C.

All organic solvents were of analytical grade and were not distilled any further, as the water contents of the ion exchangers could not be controlled or reduced to zero.¹ The ion exchanger was equilibrated with the appropriate solvent for several hours before loading of the cobalt solutions.

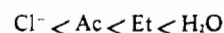
Other materials and procedures used were the same as those previously described.¹

- (1) C. Heitner-Wirguin and N. Ben-Zwi, *Inorg. Chim. Acta*, **4**, 517 (1970).
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Results and Discussion

The various species were defined and their spectra interpreted according to the same criteria as in the aqueous solutions.¹ However when working in non aqueous media one must take into account the spectrochemical effects of the solvents, in this case ethanol (Et) and acetone (Ac) (as compared to the effect of water and chloride ions).

From the studies of Katzin *et al.*^{2,7} it may be inferred that the Δ values in the spectrochemical series slightly increase in the following way⁸:



The interpretation of the near infrared spectrum remains complicated for the same reasons mentioned before¹, (even in these media the water content of the various samples of exchangers could not be balanced) yet no obscuring of the cobalt bands was observed.^{9,10}

The spectra of cobalt ions in solutions. Figure 1 shows the near infrared spectra of cobaltous ions in

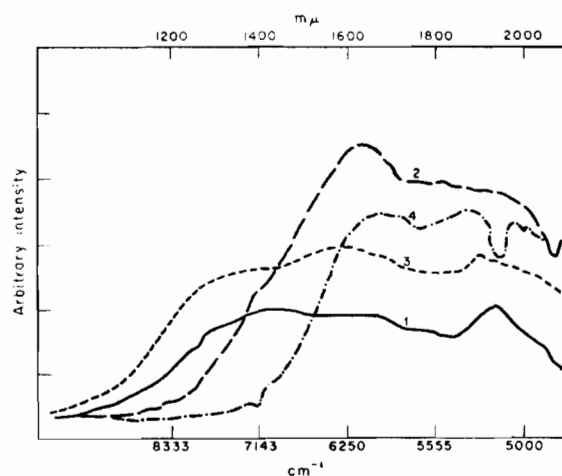


Figure 1. Near infrared absorption spectra of cobaltous ions in non aqueous solutions: (1) CoCl₂ 0.10 m in ethanol; (2) CoCl₂ 0.10 m + LiCl 5.5 m in ethanol; (3) CoCl₂ 0.01 m in acetone; (4) CoCl₂ 0.01 m + LiCl 0.9 m in acetone

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Table I. Absorption bands of cobalt ions in cm^{-1} in ethanol and sorbed on ion exchangers

Resin	Equilibrating media	ν_2	ν_3	Assigned species
1.	CoCl_2 0.1 m	5180, 6140, 6940	19230	$\text{Co}(\text{Et})_6^{2+}$
2.	CoCl_2 0.1 m + LiCl 5.5 m	4650, 5260, 6140, 7140 sh	15040, 16530 sh	mixture of species
3. Dowex 50	CoCl_2 0.01 m	7270	19230	$\text{Co}(\text{Et})_6^{2+}$
4. Dowex 50	CoCl_2 0.01 m + LiCl 0.1 m	6990, 7270	19230	$\text{Co}(\text{Et})_6^{2+}$
5. Dowex 50	CoCl_2 0.01 m + LiCl 1.0 m	6990	15040, 19230	$\text{Co}(\text{Et})_6^{2+} + \text{CoCl}(\text{Et})_5^+$
6. Dowex 1	CoCl_2 0.01 m	5180, 6025	14410, 15000, 15830 16180 sh	$\text{CoCl}_3(\text{Et})^-$
7. Dowex 1	CoCl_2 0.01 m + LiCl 5.5 m	5100, 5320, 5650	14410, 14980, 15830 16270 sh	CoCl_4^{2-}

Table II. Absorption bands of cobalt ions in cm^{-1} in acetone and sorbed on ion exchangers.

Resin	Equilibrating media	ν_2	ν_3	Assigned species
1.	CoCl_2 0.01 m	5190, 6250, 7270	18850	$\text{Co}(\text{Ac})_6^{2+}$
2.	CoCl_2 0.1 m + LiCl 0.9 m	5100, 5180, 5420, 6140	14390, 15030, 15620 sh, 15920, 16320	mixture of species
3. Dowex 50	CoCl_2 0.01 m	5130, 5810, 6990	14920, 18850, 26650	$\text{Co}(\text{Ac})_6^{2+}$
4. Dowex 50	CoCl_2 0.1 m + LiCl 0.4 m	5180, 5720, 6890	14480, 15030, 15920, 16320 sh, 26650	$\text{CoCl}(\text{Ac})_5^+$
5. Dowex 1	CoCl_2 0.01 m	5050, 5465, 6060	14500, 15300, 15880, 16270 sh, 18860, 32250	$\text{CoCl}_3(\text{Ac})^-$
6. Dowex 1	CoCl_2 0.01 m + LiCl 0.9 m	4880, 5620, 6130	14360, 14980, 15260 sh, 15830, 16200 sh, 26060	CoCl_4^{2-}

ethanol and acetone; the visible spectra is not shown as it is already known from previous studies.^{2,3,4,6}

Tables I and II summarize both regions of the spectra. The spectra of cobaltous chloride in acetone shows a clear shift to lower energies compared with the aqueous solution.¹ This is in good agreement with the spectrochemical series.⁸ This energy shift is not accompanied by a marked change in absorption intensity. The presence of one or even two chloride ions in this species must be excluded because they would lower the symmetry of the species formed (and thus increase the absorption intensity). The above mentioned fact imply that an octahedral species with acetone molecules serving as ligands is formed. It may also be expected that the formation of a mixed chloride-solvent species would lead to a bigger red shift than was observed in the present case. When an excess of chloride ions is added to the cobalt salt in acetone solution the whole absorption region is shifted to lower frequencies and the absorptions are strongly increased. Comparing the values given in Table II with Finés work⁶ it is evident that in acetone solution containing a large excess of chloride ions mainly the tetrahedral CoCl_4^{2-} exists probably in equilibrium with some other tetrahedral species as $[\text{Co}(\text{Ac})\text{Cl}_3]^-$.

Similar behaviour is observed in the spectra of ethanol solutions containing cobaltous salt. The spectral shift in absence of chloride ions (compared to aqueous solutions) is smaller than that in the case of acetone solution. This spectra may be assigned to the species $\text{Co}(\text{Et})_6^{2+}$.

When an excess of chloride ions is added to the cobalt solution in ethanol there is a shift of the absorption band to lower energies, but the spectra characteristic to the tetrahedral species (Table II) in the visible region is not obtained. This leads to the conclusion that there is a mixture of species in the ethanol solution which are mainly octahedral.

The spectra of cobalt ions sorbed on ion-exchangers. Table I and II Figures 2 and 3 give information about

the absorption of cobalt ions sorbed on cation and anion exchangers from various ethanol and acetone equilibrating solutions.

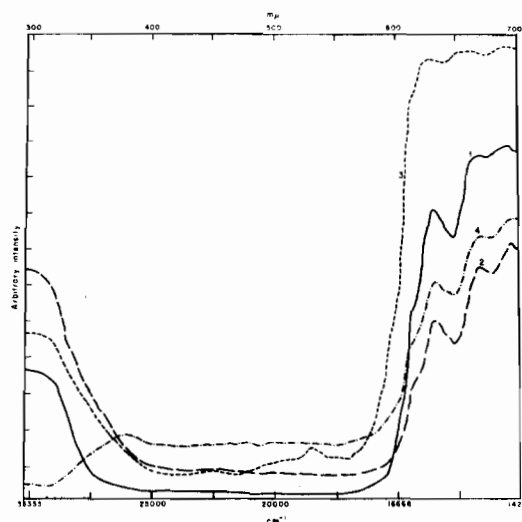


Figure 2. Visible absorption spectra of cobalt(II) species sorbed on Dowex 1X8 Cl^- in non aqueous solutions: (1) CoCl_2 0.10 m in ethanol; (2) CoCl_2 0.10 m + LiCl 5.5 m in ethanol; (3) CoCl_2 0.01 m in acetone; (4) CoCl_2 0.01 m + LiCl 0.9 m in acetone.

By changing the chloride ion concentration in aqueous solutions three different spectra were obtained¹ when these solutions were sorbed on a cation exchanger. Here in both media only two different species were recognized both octahedral ones. This fact can be attributed most probably to the smaller difference in Δ values between acetone, ethanol and chloride ions as compared with the difference in Δ values between water and chloride ions. Another reason may be the limited maximum solubility of LiCl in these

media (6.1 m in ethanol, 0.97 m in acetone¹¹) as compared with its high solubility in water (14.7 m), which prevents the possibility to change too much the ratio of the $\text{Cl}^-:\text{Co}^{2+}$ concentrations. (The cobalt ion concentration could not be reduced, as even in the cases examined in this work the relative absorptions were very low).

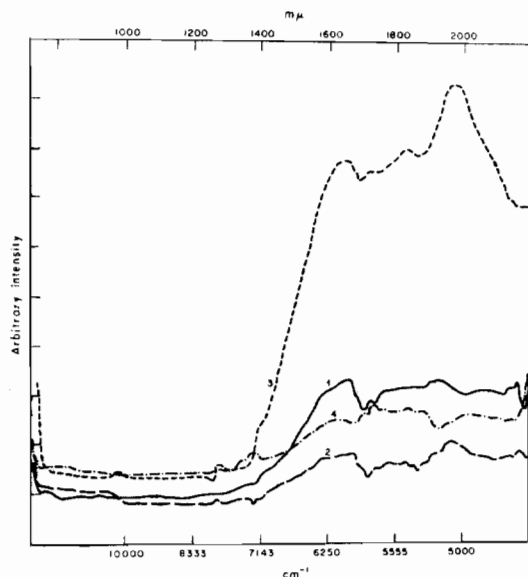


Figure 3. Near infrared absorption spectra of cobalt(II) species sorbed on Dowex 1X8 Cl^- in non aqueous solutions; (1) CoCl_2 0.10 m in ethanol; (2) CoCl_2 0.10 m + LiCl 5.5 m in ethanol; (3) CoCl_2 0.01 m in acetone; (4) CoCl_2 0.01 m in LiCl 0.9 m in acetone.

From acetone solutions two different types of species were sorbed on the cation exchanger depending on the composition of the original solutions. When working with an initial solution of CoCl_2 0.01 m the only species obtained is $\text{Co}(\text{Ac})_6^{2+}$, upon addition of LiCl 0.40 m the character of the species becomes that of $\text{CoCl}(\text{Ac})_5^+$ (a clear shift of the bands to lower energies in the visible and in the near infrared regions, cf. Table II); any further addition of chloride ions to the solution causes a desorption from the exchanger and no further spectral measurements were possible.

In the case of the ethanol — CoCl_2 — LiCl — cation exchanger system the interpretation of the spectra obtained is more complicated. In the absence of excess chloride ions the species sorbed is analogous to that sorbed from acetone (*i.e.* $\text{Co}(\text{Et})_6^{2+}$). The presence of excess chloride ions did not cause the sorption of the $\text{CoCl}(\text{Et})_5^+$ ion by itself as in the acetone media but instead a mixture of $\text{Co}(\text{Et})_6^{2+}$ and $\text{CoCl}(\text{Et})_5^+$ species was sorbed. Upon a further addition of chloride ions a sharp decrease in sorption is observed.

Working with anion exchanger the same types of species are formed in both media under analogous conditions as were obtained in aqueous solutions.

Here too upon addition of chloride ions in excess to the CoCl_2 solution, the spectrum of the species sorbed is similar to that observed in the solid state¹² indicating clearly the formation of CoCl_4^{2-} . The spectra of the species sorbed on the anion exchanger from CoCl_2 solutions (without addition of chloride ions) show in both media a slight shift to higher energies compared to CoCl_4^{2-} , and a marked increase in absorption compared to CoCl_4^{2-} .

This behaviour can only be attributed to the replacement of one mole of chloride ions by one mole of solvent, giving rise to the species $\text{CoCl}_3(\text{solv})^-$. The higher absorption of this species may be due to a decrease in symmetry by the replacing of a chloride ion by a solvent molecule, or simply by the fact that this species being monocharged is sorbed in much higher amounts than the double charged CoCl_4^{2-} .

The results obtained in the present study can be compared to studies of CoCl_2 in ethanol and acetone solutions. The absorption spectra observed by Katzin³ are shown to be ascribable to several entities which are in equilibrium with each other. In Libus' works⁴ as well there exist several tetrahedral chloro complexes, CoCl_2L_2 , CoCl_4^{2-} , and CoCl_3L^- , which could not be separated. Fine⁶ could measure only the spectra of the tetrachloro complex from concentrated chloride solutions, computing the spectra of the dichloro and the trichloro complexes graphically by the mole ratio method.

The use of two different ion exchangers in this study (cation and anion exchanger) made it possible to obtain a selective sorption of one of the species existing in the mixture in the liquid phase and thus allowing a better characterisation of it.

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