Chlorides Specie of Cobalt(II) Sorbed on Ion Exchangers

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The spectra of cobalt ions sorbed on a cation and anion exchanger from different equilibrating solutions were recorded. Under various conditions different absorption spectra were obtained in the visible and near infrared region. An assignment of the spectra of the individual sorbed species was possible by comparing these spectra to those of known species in other media, and by taking into account the properties of the various ion-exchangers used.

Introduction

The system cobalt(II)-solvent-cloride is one of the most studied systems due to its striking colour change from pink to blue.[1] This colour change is caused mainly by a change from an octahedral to a tetrahedral configuration.[2-4] A series of papers[5-15] especially those of the groups of Libus[8-11] and Gutmann,[12-15] deal with the composition and the configuration of the various chloride species in aqueous and in non-aqueous solvents, studying at the same time also the influence of an excess of chloride ions on their formation. These studies were mainly done by spectrophotometry and evidence has been found for species containing 2, 3 and 4 chloride ions per cobalt ion, while at least in the aqueous phase there has been no evidence for a 1:1 complex. The papers which deal with the determination of the stability constants of these species mention the existence of the very unstable $CoCl^+$.[16-17] Several additional papers deal with the origin of the spectral bands,[18-27] but as could well be expected, they are mainly concerned with the

cases in which the compounds are $Co(H_2O)_6^{2+}$ or $Co(solv)_n^{2+}$ and $CoCl_4^{2-}$.

The aim of the present paper was to characterise the absorption spectra of the intermediate compounds, using various ion-exchangers and equilibrating solutions, which can sorb selectively some of the species, and thus may cause a partial separation of the mixture. From equilibrium studies carried out on anion-exchangers,[28-33] the assumption was made that mainly $CoCl_3^-$ is sorbed, while Coleman[29] and Rutner[28] conclude by the measurement of the spectra of the exchanger that the $CoCl_4^{2-}$ is sorbed.

The absorption spectra of the exchangers were measured mainly in the visible and near infrared region. More information may also be obtained by comparing the relative absorption heights of the peaks in the visible and near infrared spectra.

Experimental Section

Equipment and materials. The spectra were recorded on the Cary Model 14 recording spectrophotometer. The $CoCl_2$ used was c.p. $CoCl_2 \cdot 6H_2O$. The ion-exchangers Dowex 1 X 8 and Dowex 50W X 8 were of analytical grade supplied by Fluka, the mesh size used was 50-100.

Preparation of samples. The loaded resins were prepared by equilibrating with the appropriate solutions for about 6 hours at room temperature and filtering through a porous glass crucible. Longer contact times between resin and solution had no effect on the spectra. No washing agent was employed after the filtration, as none of the agents tried were really adequate; they interfere with the equilibrium, sometimes interacting with the sorbed species,

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changing its nature and its configuration. For this reason, the samples were just vacuum dried at room temperature; microscopic measurements did not show any physical absorption or any impurities among the beads.

Samples for the spectrophotometric determinations were prepared by introducing a suspension of the exchanger beads with nujol into 1 mm quartz cells and centrifuging to obtain a homogeneous layer.

The appropriate exchanger equilibrated with the same solutions except the cobalt salt served as a reference. The spectra of the various solutions were also measured in 1 mm cells, occasionally placing metal screens in the reference beam path to lower its intensity (as attenuators).

Results and Discussion

In order to define the species sorbed on the cation and anion exchanger under varying conditions, comparisons of their absorption spectra with those well known as $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$ in aqueous solutions and other media were made.

Those comparisons were mostly made in the visible region (around 20000 cm^{-1} and between 16600 and 14300 cm^{-1}) and in the NIR region. Numerous splittings of the main absorption bands are observed; these are due mainly to spin-orbit couplings which are not negligible in the case of the cobalt ions and to transition to doublet states.[34] The interpretation of the NIR spectra is even more complicated by the fact that water itself shows a series of absorption bands in these regions. Even when using a rigorously controlled reference sample of the exchanger, in most of the examined cases the water content could not be exactly balanced. Therefore in most of the spectra measured a deep minimum of absorption has been found at the respective water peaks, or a slight maximum showing definitely that the sample generally contained more or less water than the reference*.

It can also be assumed from the present study and from studies done on cobalt ions in solids and non-aqueous phases,[26] that in the region of the strong water bands no cobalt bands are obscured. According to Yamatera et al[35] the absorption bands of water in NIR are at 5160, 5620, 6880 and 8310 cm^{-1}. The absorption regions of water observed in the present study were at 5300 and about 7100 cm^{-1}.

The criteria used for the determination of the geometrical arrangement (octahedral, distorted or tetrahedral) was the relative ratio of absorbancies between the NIR and visible region. No molar extinction coefficients were determined but for each spectrum the flat part of the curve between 9000 and 11000 cm^{-1} was taken as the base-line, and to this line the absorbancies of NIR and visible were related.

Figure 1 shows the absorption bands of cobalt ions in aqueous solutions in the NIR in the presence and

in the absence of chloride ions. (The spectra of the solutions in the visible region are well known and are only summarised in the first part of Table 1). The two minima in the NIR spectra are due to the strong water peak of the reference sample. The $Co(H_2O)_6^{2+}$ presents a relatively strong absorption band at 8000 cm^{-1} as already measured and found by Ballhausen et al.[19] This species was not yet measured at lower frequencies (apparently because of technical reasons and difficulties in interpretation). Not much more can be said about the NIR region other than that upon addition of chloride the whole absorption region is shifted to lower frequencies, increasing very strongly in absorption, showing definitely the formation of a tetrahedral chloride species. Comparing these spectra to the tetrahedral tetrachloro complex measured by Fine,[6] and Cotton and Goodgame[22] it is clear that the tetrahedral tetrachloro complex is not formed in aqueous solutions. The absorption spectra of concentrated $CoCl_2$ and $Co(NO_3)_2$ solutions without addition of chloride ions show a very similar pattern, excluding the formation of a chlorinated cobalt species. However the peak at 6060 cm^{-1} in $CoCl_2$ solution shows that a small amount of some chloride species is already formed. Lawson[26] did not assign this band to the cobalt ion, while Ludi and Feinknecht[25] and Ferguson et al.[24] assigned it to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ for the octahedral $CoCl_2$ (6 Cl$^-$ ions around the central Co^{2+} ion).
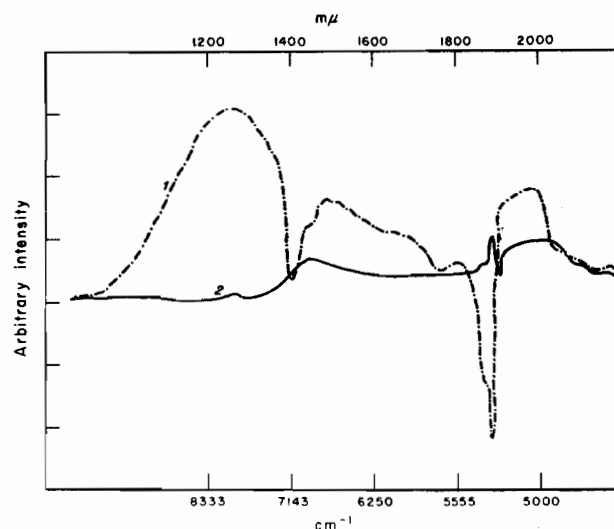

Figure 1. Near infrared absorption spectra of cobaltous ions in aqueous solution 1) 2m $CoCl_2$; 2) 0.01m $Co(NO_3)_2$ in 12m LiCl.

The spectra of cobalt ions sorbed on ion exchangers. Figure 2 and 3 show the absorption bands of cobalt species sorbed on cation and anion exchangers from different equilibrating solutions.

Three different spectra are obtained by sorbing cobalt solutions on a cation exchanger in the absence and in the presence of LiCl. If cobalt ions are sorbed from a dilute cobalt nitrate or cobalt chloride solution the spectra obtained is the same as that of $Co(H_2O)_6^{2+}$ in aqueous solution showing the weak broad absorption peak of the aqueous solution at

(*) Similar spectra measured in non-aqueous media have shown that the same Cobalt peaks occur also in the absence of water.
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Table I. Absorption bands of cobalt ions in cm⁻¹ in aqueous solutions and sorbed on ion exchangers

Resin	Equilibrating media	ν_1	ν_3	Assigned species
	2m CoCl₂ in water	5440(0.17)* 6660(0.27) 6890(0.23) 7300 (sh) 8000(0.31)	15000 (sh) 19410(1.27)	$Co(H_2O)_6^{2+}$
	1m Co(NO₃)₂ in water	5440(0.07) 6060(0.10) 7000(0.10) 8000(0.21)	19410(0.58) 21300 (sh)	$Co(H_2O)_6^{2+}$
	0.2m Co(NO₃)₂ in 12m LiCl	5440(0.65) 6060(0.063) 6890 7300(0.18)	14480(6.4) 15050(6.0) 15530 (sh) 16000(3.9) 16380 (sh) 18880(0.12)	mixture of species
Dowex 50	0.01m CoCl₂(Co(NO₃)₂) in water	5440(0.18) 5950(0.14) 6450 (sh) 7700(0.18)	19230(0.52) 24400(0.4) 31750(0.4)	$Co(H_2O)_6^{2+}$
Dowex 50	0.01m CoCl₂ in 1m LiCl	5470(0.14) 5975(0.17) 6450 7230(0.08)	14930(0.66) 15880 (sh) 16400 (sh) 19230 (sh) 25650(0.02) 31240(0.21)	$[Co(H_2O)_5Cl]^-$
Dowex 50	0.01m CoCl₂ in 3m LiCl	55430(0.1) 6060(0.1) 723?(0.03)	14380(0.51) 15050(0.5) 15620 (sh) 16000(0.36) 16380 (sh) 31750(0.17)	$CoCl_2(H_2O)_4$ or/and $CoCl(H_2O)_5^+$
15.3	0.01m CoCl₂ in water	4770 vw 5500(0.77) 5980(0.05) 7580(0.04)	14400(0.49) 15120(0.47) 15900(0.45) 16260 (sh) 20000	$Co(H_2O)_4Cl_2^-$
1 hr	0.002m CoCl₂ in 12m LiCl	4720 5000(0.26) 5180 5350(0.12) 5460(0.11) 6140(0.09) 6670 6900(0.08)	14400(1.07) 15120(1.02) 15500 (sh) 15900(0.8) 16400 (sh)	$CoCl_4^{2-}$

* Values in parentheses are relative absorption values (cf. page 5).

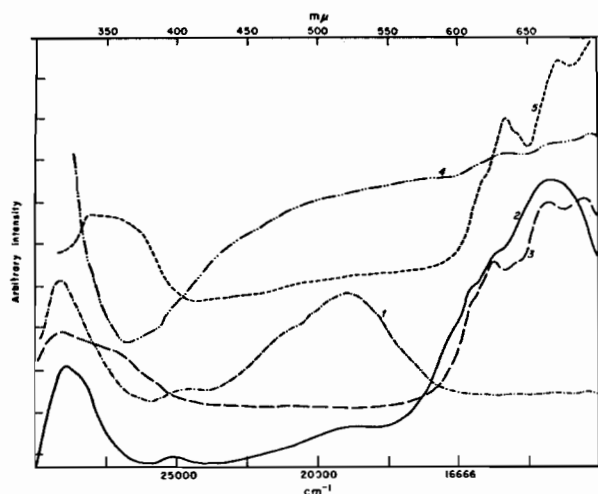about 20000 cm⁻¹ (Figure 2). If the sorption is done from solutions containing 1 mole LiCl the main ab-

Figure 2. Visible absorption spectra of cobalt(II) species sorbed on ion exchangers: 1) 0.01m CoCl₂ on Dowex 50W X8 Li⁺; 2) 0.01m Co(NO₃)₂ in 1m LiCl on Dowex 50W X8 Li⁺; 3) 0.01m CoCl₂ in 3m LiCl on Dowex 50W X8 Li⁺; 4) 0.01m CoCl₂ on Dowex 1 X8 Cl⁻; 5) 0.002m Co(NO₃)₂ in 12m LiCl on Dowex 1 X8 Cl⁻.
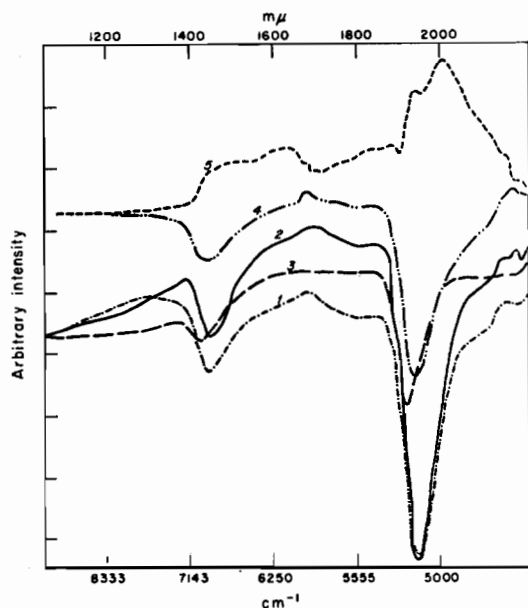

Figure 3. Near infrared absorption spectra of cobalt(II) species sorbed on ion exchangers: 1) 0.01m CoCl₂ on Dowex 50W X8 Li⁺; 2) 0.01m Co(NO₃)₂ in 1m LiCl on Dowex 50W X8 Li⁺; 3) 0.01m CoCl₂ in 3m LiCl on Dowex 50W X8 Li⁺; 4) 0.01m CoCl₂ on Dowex 1 X8 Cl⁻; 5) 0.002 m Co(NO₃)₂ in 12m LiCl on Dowex 1 X8 Cl⁻.

sorption band is displaced to lower energy at 14930 cm⁻¹, also increasing strongly in intensity.

A further gradual shifting to lower energies is to be found in the spectrum of cobaltous ions sorbed from 3m LiCl solution and in the spectra of the anion exchanger. The absorption spectra of cobalt sorbed on the anion exchanger from a 12m LiCl solution is similar to this of $CoCl_4^{2-}$ measured on the solid.[22] As may be seen from Table I and Figure 3 a similar shift of the absorption bands in NIR may be observed.

Some conclusions on the intermediate species may be drawn by considering the individual properties of the two exchangers and by comparison with known spectra in various phases. The spectrum of CoCl₂ or Co(NO₃)₂ sorbed on Dowex 50 are very similar to the one obtained in aqueous solution and should be assigned to the $Co(H_2O)_6^{2+}$ ion. The main transitions ν_2 and ν_3 are very slightly shifted to lower energies in the ion exchanger, the ratio of the intensities of the two bands remaining the same (about 1:4). In the presence of 1m LiCl solution the two bands are considerably red shifted and the ratio of their intensities changes to about 1:8. The red shift must be connected with a replacement of some water molecules by chloride ions, according to the spectrochemical series. The increase in intensity is not big enough for a change in configuration to the tetrahedral symmetry caused by the chloride replacement. As this species is sorbed in appreciable amount on the cation exchanger it must be assumed that this is a cationic species, which can only be $[CoCl(H_2O)_5^+]$. This species is not formed (or is very unstable) in aqueous or nonaqueous media. Some evidence was found for its existence on a cation exchanger by Tremillon[16] who calculated its stability constant as $k_1 = 4.07$. From Beavers' et al.[5] study it may be assumed that such a species has an absorption band at 14900 cm⁻¹. Not very clear is the assignment for the spectra of the cation exchanger from 3m LiCl solutions. While some red shifting may be observed, the absorption bands especially in the visible range suggest the formation of some tetrahedral species. However a further replacement of chloride ions does not appear very probable as a further addition of cloride ions assumes the formation of a neutral or anionic species, $[CoCl_2(H_2O)_2]$ or $[CoCl_3H_2O]^-$. The formation of the anionic species may be excluded according to Kraus'[36] studies; furthermore the two spectra recorded on anion exchangers imply the same. There is a possibility of a physical sorption of the

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neutral species, though a microscopic analysis of the beads did not show it.

Together with this neutral species or by itself could also be formed some tetrahedral mono-chloride species $CoCl(H_2O)_3^+$ which could explain the fact that a homogeneous sorption on a cation exchanger is obtained with a tetrahedral red shifted spectra. The selective sorption of $CoCl(H_2O)_3^+$ could be explained in this case by the presence of a higher chloride concentration and consequently a reduction of the number of available water molecules.

Much easier are the interpretation and the assignment of the spectra obtained on the anion exchanger. It is sufficient to compare two spectra, one obtained by sorption from a cobalt chloride solution and the other obtained by addition of a very concentrated LiCl solution (12m); as may be well seen from Figure 3 a further slight red shift is obtained (compared to the spectra of the cation exchanger) in both regions, the intensity ratios going up to 1:12. The spectra of the species sorbed from a concentrated LiCl solution is identical to that known from solid spectrum (Cotton and Goodgame[22]) and can definitely be assigned to the tetrahedral $CoCl_4^{2-}$ species. The spectra of $CoCl_2$ itself on the anion exchanger is more similar to that obtained in aqueous solutions contai-

ning chloride salts. These spectra should be connected with the sorption of $CoCl_3(H_2O)^-$. No big changes in the spectra would be expected by the replacement of one mole H_2O by a Cl^- ion.

Concluding this study it may be said that the two final species, the hexahydrate and tetrachloro cobalt sorbed on ion exchangers are very similar to those known from other media, the spectra obtained agree in details (NIR and Vis regions) with those obtained by Cotton et al.[22] No such comparison can be drawn for the intermediate species mainly because no definite spectra are known. Studies which assume the formation of such species were made in various organic media with increasing chloride concentrations. No similarity were expected to the spectra obtained in the present study as the intermediate species will obviously contain the organic solvent.[37,6] The spectra attributed to $CoCl_2$ and $CoCl_3^-$ in acetone media[6] are not recorded spectra but graphically computed by the mole ratio method. Taking even into account that more than one species may be sorbed on the ion exchanger in some cases, the selectivity of the ion exchanger provides the necessary condition for one species only to be sorbed in major amounts.

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