Monatshefte für Chemie 118, 1225—1235 (1987)

Monatshefte für Chemie
Chemical Monthly

The Coordination State of $CoCl_2$ in Propylene Carbonate

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(Received 27 May 1986. Accepted 9 June 1986)

The formation of chlorocomplexes of cobalt(II) chloride in propylene carbonate (*PC*) solution has been investigated spectrophotometrically and conductometrically. The influence of the nature of the solvent on the coordination state of cobalt(II) chloride is discussed in terms of donor number (*DN*) and dielectric constant.

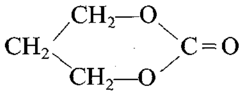
(Keywords: Spectrophotometry; Conductometry; Cobalt(III) chloride: Propylene cabonate; Coordination state)

Der Koordinationszustand von Kobalt(II)-chlorid in Propandiol-1,2-carbonat

Die Bildung von Chlorokomplexen des Kobalt(II)-chlorids in Propandiol-1,2-carbonat (*PC*) wird auf spektrophotometrischem und konduktometrischem Wege untersucht. Die Abhängigkeit des Koordinationsverhaltens von Kobalt(II)-chlorid von der Donorzahl (*DZ*) und der Dielektrizitätskonstante in verschiedenen Lösungsmitteln wird diskutiert.

Introduction

The behaviour of $CoCl_2$ in coordinatively active solvents has been the subject of numerous investigations. It was shown that in systems involving pyridine [1], acetonitrile [2], N,N-dimethylacetamide [3], N-methylformamide [4], N,N-dimethylformamide [5], and dimethylsulphoxide [6] $CoCl_2$ forms mixed complexes of the general formula $CoCl_mL_n$ (L—solvent molecule), the composition and structure of individual complexes in solution as well as their relative amounts being dependent on the nature of the solvent. The purpose of the present work was to establish the coordination state of a $CoCl_2$ solution in propylene carbonate (*PC*). *PC* has been selected for investigation because of its strong ionizing properties, which are associated with its high dielectric constant ($\varepsilon = 69$), and low donor number ($DN = 15.1$).



PC

Experimental

Propylene carbonate AR grade was dried over molecular sieve 4 Å and distilled under reduced pressure through an adiabatic column at 120–122 °C. The specific conductivity of the final product was $4–7 \cdot 10^{-8}\,\mathrm{S\,cm^{-1}}$.

The solution of $CoCl_2$ was obtained by dissolving the anhydrous salts in *PC*. The concentrations of the respective stock solutions were determined by standard *EDTA* titration. The solutions for conductometric and spectrophotometric measurements were prepared from stock solution by weighing. Densities of the solutions were determined using a bicapillary pycnometer calibrated with water at 25.00 ± 0.05 °C.

Conductivities were determined using a Beckman Model RC 18A bridge. All measurements were performed at a constant temperature of 25.00 ± 0.05 °C. Further details have been described previously [6]. Absorption spectra were measured using a Beckman UV 5270 spectrophotometer with a thermostated cell compartment. All operations with anhydrous substances were carried out in a dry box.

Results and Discussion

Ternary system $CoCl_2$—Et_4NCl—*PC*

It usually proves helpful to examine spectral effects induced by variable anion concentration prior to analysing the data for a two-component solution under study. Figure 1 shows the visible absorption spectra of solutions containing $CoCl_2$ at a constant concentration ($c \cong 0.0088\,\mathrm{mol\,dm^{-3}}$) and tetraethylammonium chloride at a variable concentration ($0.0176 < c < 0.590\,M$) in *PC* at 25 °C. The starting point of the analysis of the above mentioned spectra is the assumption that the intensive absorption bands occurring in the spectral range 550–750 nm correspond to tetrahedral complexes of cobalt(II) which is evident in the light of numerous literature data concerning electronic spectra of cobalt complexes. Octahedral complexes of cobalt(II) are characterized by absorption bands of low intensity, usually appearing in the 450–600 nm spectral region.

Figure 1 shows that for the ratio of chloride to cobalt ions below 2.98 the spectrum consists of a broad band with maxima located at 588 nm and 680 nm (curves 1, 2, 3). The band position, contour, and high intensity are typical of cobalt(II) in pseudotetrahedral environment [6, 7]. The

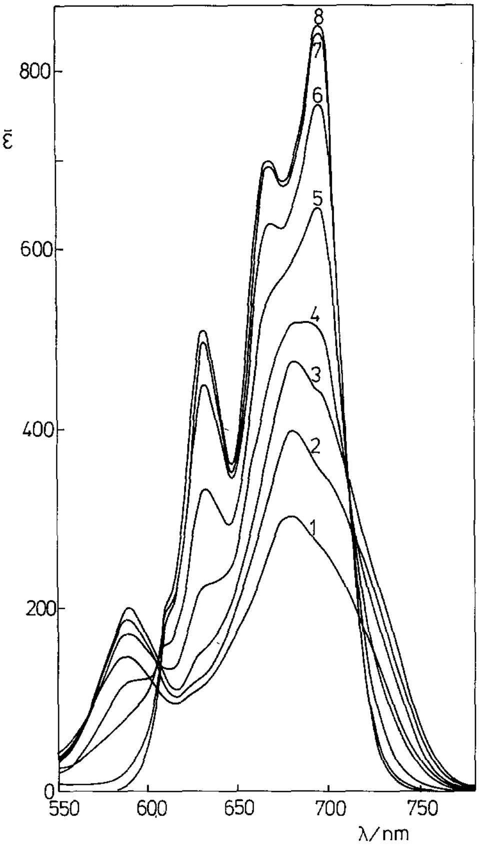


Fig. 1. Absorption spectra of mixed solutions: $CoCl_2$ (constant concentration of ca. 0.0088 mol dm^{-3}) + Et_4NCl (variable concentration) in *PC* at 25 °C. Concentration of Et_4NCl in mol dm^{-3}: *1* 0.0176; *2* 0.0229; *3* 0.0262; *4* 0.0282; *5* 0.0311; *6* 0.0334; *7* 0.0382; *8* 0.0590

similarity of the discussed spectra to the spectra of the $CoCl_3L^-$ complex in such solvents as *DMSO* [6], *DMF* [5] and *DMA* [3] allows to assume that the complex existing in this range of concentrations of chloride anions is the pseudotetrahedral $CoCl_3(PC)^-$ complex. At Et_4NCl to Co(II) ratios exceeding 2.98 an increase of Et_4NCl concentration results in gradual disappearance of the maximum at 590 nm and a simultaneous development of a new spectrum consisting of three bands with maxima at 636, 669 and 696 nm. Subsequently, two isosbestic points can be observed in the spectra at 605 and 712 nm. When the Et_4NCl to Co(II) ratio exceeds 4.24 further increase of chloride concentrations does not affect the spectrum. The limiting spectrum shows the characteristics of the tetrachloro-

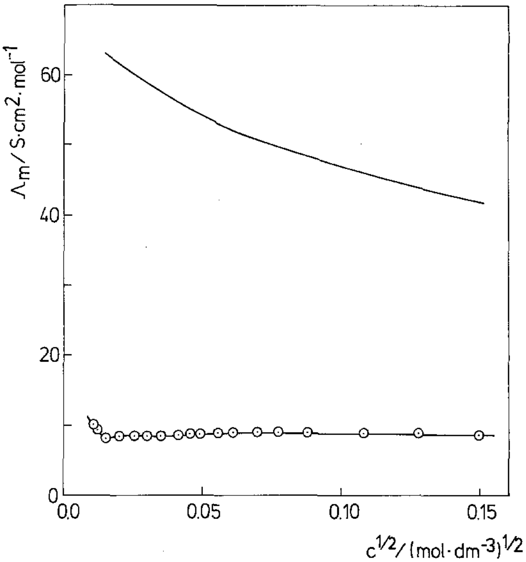


Fig. 2. Dependence of molar conductivity on the square root of concentration for $CoCl_2$ in *PC* at 25 °C. The solid line indicates the conductivities of the corresponding perchlorate [8]

Table 1. *Molar conductivities of* $CoCl_2$ *in PC solution at 25 °C*

c 10^{-4} mol dm^{-3}	Λ S cm^2 mol^{-1}
1.102	10.00
1.440	9.45
2.250	8.34
4.000	8.38
6.503	8.40
9.060	8.44
12.110	8.51
16.974	8.61
20.794	8.65
23.717	8.76
30.581	8.87
36.240	8.95
48.302	8.95
59.290	8.96
76.562	8.92
117.07	8.80
163.33	8.71
223.20	8.59

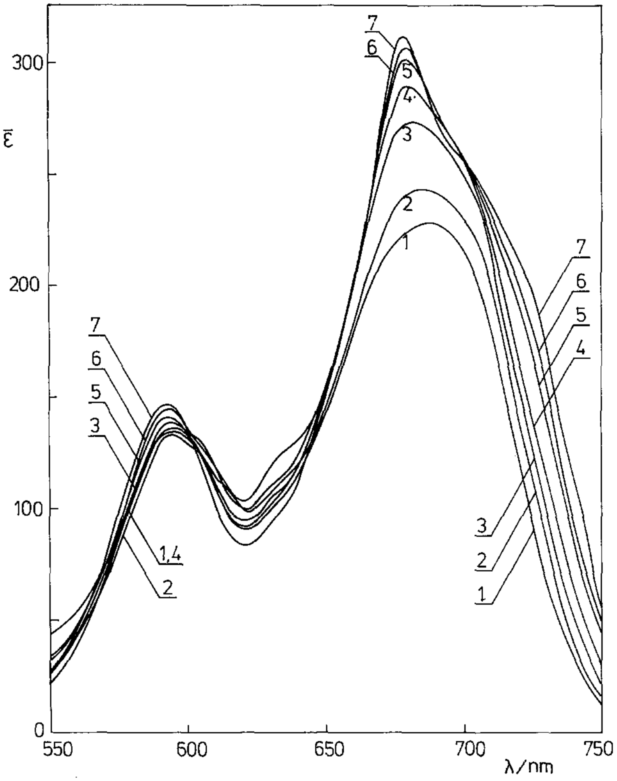


Fig. 3. Absorption spectra of $CoCl_2$ in *PC* at 25 °C. Concentrations (mol dm^{-3}): *1* 0.00067; *2* 0.00132; *3* 0.00281; *4* 0.00568; *5* 0.01119; *6* 0.01686; *7* 0.02238

complexes [5]. These facts indicate a two species equilibrium

$$CoCl_3(PC)^- + Cl^- \rightleftharpoons CoCl_4^{2-} + PC \qquad (1)$$

setting up within the 2.98 to 4.28 range of the Cl^- to Co^{2+} ratio.

Solutions of $CoCl_2$ *in PC*

Figure 2 shows the molar conductance curve of $CoCl_2$ in *PC* solution at 25 °C. The experimental values are listed in Table 1. The molar conductance curve of $Co(ClO_4)_2$ [8] is presented in the same figure. It can be seen that the molar conductance curve of $CoCl_2$ runs well below the respective curve for $Co(ClO_4)_2$ known to exist in the form of $Co(PC)_6^{2+} \cdot 2\,ClO_4^-$-type complex electrolytes, only slightly associated.

Further inspection of the figure shows that the molar conductance curve of $CoCl_2$ exhibits a slight decrease in conductivity with increasing concentration in the lowest concentration region, while the experimental points run almost horizontally at higher $CoCl_2$ concentrations. A relatively low value of the molar conductance indicates a high degree of complex formation. The absorption spectra of $CoCl_2$ in *PC* at 25 °C for

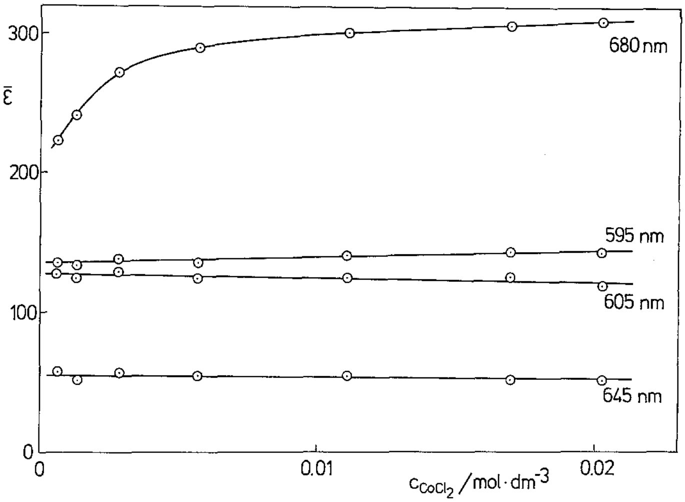


Fig. 4. Dependence of the mean molar absorption coefficient of the $CoCl_2$ solutions in *PC* at 25 °C at selected wavelengths

the concentration ranging from 0.000669 to 0.02238 mol dm^{-3} are presented in Fig. 3. The spectra consist of a broad band having two maxima located at ca. 592 and 680 nm. As follows from the discussion of the ternary system, this spectrum is associated with the presence of the pseudotetrahedral complex $CoCl_3PC^-$ in the investigated systems. However, in the case of existence of only one tetrahedral complex a steady increase of the absorption coefficients should be observed in the range in which tetrahedral complexes absorb. The spectra intersect follow from Fig. 3 yielding not too well defined isosbestic points, which is illustrated by the dependence $\bar{\varepsilon} = f(c_{CoCl_2})$ for selected wavelengths (shown in Fig. 4). This indicates that at least one more tetrahedral complex must coexist in equilibrium with the $CoCl_3PC^-$ complex. Comparison of the spectra of $CoCl_2$ in *PC* with those for the ternary system leads to a conclusion that this complex cannot be tetrahedral complex $CoCl_4^{2-}$. Thus, a hypothesis can be formulated that the complex in question is electrically neutral

$CoCl_2(PC)_2$. Therefore, the presented absorption spectra of $CoCl_2$ in *PC* can be explained on the basis of the following equilibria:

$$2\,CoCl_2(PC)_2 + 2\,PC \rightleftharpoons Co(PC)_5Cl^+ + Co(PC)Cl_3^- \qquad (2)$$

$$3\,CoCl_2(PC)_2 + 2\,PC \rightleftharpoons Co(PC)_6^{2+} + 2\,Co(PC)Cl_3^- \qquad (3)$$

The occurrence of the above equilibria is also confirmed by the experimental electrolytic conductivity curve for $CoCl_2$. Approximate constancy of electrolytic conductivity with concentration, except for the lowest concentrations, is characteristic for systems in which coordination disproportionation equilibria are set up [3, 5].

In order to confirm the occurrence of equilibria (2) and (3) in the solutions of $CoCl_2$ in *PC* the absorption spectra and electrolytic conductivity of the ternary system $CoCl_2$—*PC*-benzene were measured. They are shown in Fig. 5. The absorption spectra and electrolytic conductivity were derived for constant concentration of $CoCl_2$ equal to $0.0012\,mol\,dm^{-3}$ and varying benzene to *PC* ratios. An addition of non-coordinating diluent of low polarity should result in two effects: (a) the decrease in the activity of the coordinating solvent should shift the equilibrium towards release of the solvent molecules and (b) the decrease in the decrease in the dielectric constant of the medium favouring reactions in which neutral species are being formed.

Inspection of the spectra shown in Fig. 5 reveals a drastic change of their shape with the increase in benzene content, resulting in formation of a new absorption band with maxima at 573, 605 and 637 nm. The location of the band and high absorption coefficients are apparently characteristic for tetrahedral complexes of cobalt(II). At the same time, the electrolytic conductivity drops to $0.01\,S\,cm^2\,mol^{-1}$ for $x_{benzene} = 0.970$. Such low conductivity value suggests that practically the sole complex existing in this solution is an electrically neutral complex. The conclusion drawn from absorption spectra and electrolytic conductivity indicate that this is the pseudotetrahedral complex $CoCl_2(PC)_2$. Hence, an additional argument was gained confirming setting up in the solutions of $CoCl_2$ in *PC* of equilibria (2) and (3).

It remains to decide which one of the proposed equilibria predominates in this solution. This is difficult due to the fact that the octahedral complexes present in the investigated system have low absorption coefficients and also owing to superposition of substantially more intense spectra of tetrahedral complexes on the absorption bands of octahedral complexes. Thus, only an analysis of the bands of tetrahedral complexes can be carried out. As mentioned previously, the absorption bands of the system $CoCl_2$-*PC* suggest that the predominating tetrahedral complex is $CoCl_2PC^-$. It follows from the spectra shown in Fig. 3 that the complex

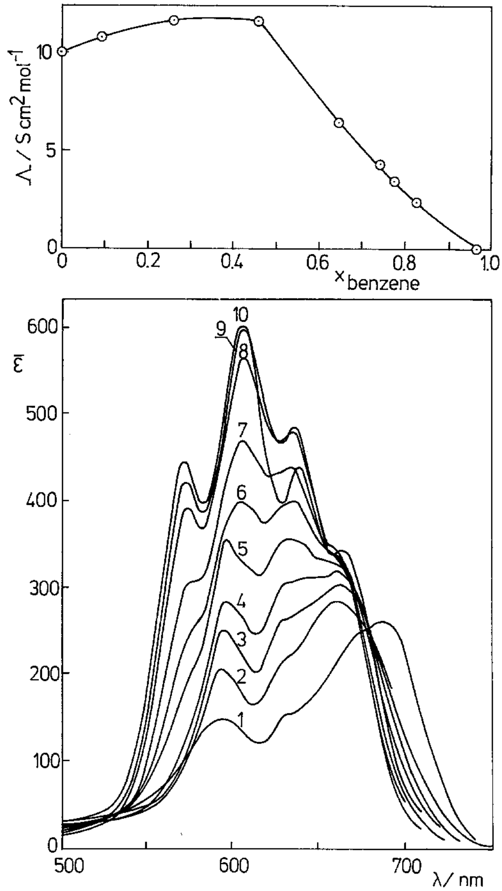


Fig. 5. Absorption spectra and molar conductivities of the $CoCl_2$-*PC*-benzene ternary system of constant $CoCl_2$ concentration (c = 0.00012 mol dm^{-3}) and variable *PC* to benzene ratio. The mole fractions of benzene: *1* 0.0; *2* 0.090; *3* 0.156; *4* 0.258; *5* 0.357; *6* 0.460; *7* 0.563; *8* 0.734; *9* 0.830; *10* 0.972

$CoCl_2(PC)_2$ exists only in small amounts. Therefore, equilibria (2) and (3) are shifted towards the products. In this situation $\bar{\varepsilon}$ should approach 1/2 ε_3 in the case of reaction (2) or 2/3 ε_3 for reaction (3). ε_3 is the molar absorptivity of the $CoCl_3PC^-$ complex and, unfortunately, its value is unknown. However, on the basis of papers published so far [5, 6] it can be estimated that ε_3 for 680 nm should be equal to 600–650. Taking into consideration the dependence $\bar{\varepsilon} = f(c_{CoCl_2})$ (Fig. 4) it can be noticed that $^{-}(\lambda = 680\,\text{nm})$ only slightly exceeds 300 which indicates that the dominating reaction in the system $CoCl_2$-*PC* is reaction (2).

Table 2. *Forms of existence of* $CoCl_2$ *in aprotic polar solvents*

Solvent	*DN*	ε	Dominating coordination forms of $CoCl_2$
N-Methylformamide		182	$CoL_6^{2+} \cdot 2\,Cl^-$, $CoClL_5^+ \cdot Cl^-$
Acetonitrile	14.1	38	$CoCl_2L_2$, $CoL_6^{2+} \cdot 2\,CoCl_3L^-$
Propylene Carbonate	15.1	69	$CoClL_5^+ \cdot CoCl_3L^-$
N,N-Dimethylformamide	26.6	36.1	$CoL_6^{2+} \cdot 2\,CoCl_3L^-$
N,N-Dimethylacetamide	27.8	38.9	$CoCl_2L_2$
Dimethylsulphoxide	29.8	45.0	$CoL_6^{2+} \cdot 2\,CoCl_3L^-$
Pyridine	33.1	12.3	$CoCl_2L_4$

DN Donor Number
ε Dielectric constant

Conclusion

Commenting on the results presented above we should note that the influence of the solvent on complex formation in solution is an effect of great importance. The problem has been discussed in terms of the donor and acceptor numbers, hard and soft donor and acceptors, or dielectric constant [9, 10]. Although many properties of nonaqueous solutions of the divalent transition metal salts may be explained using additional factors such as the relative stability of octahedral and tetrahedral complexes and the *Jahn-Teller* effect, it seems to be difficult to find correlation between the nature of the solvent and the coordination state of dissolved salts.

The diversity of coordination states of $\mathrm{CoCl_2}$ in nonaqueous solutions is the best manifestation of complexity of the problem. It has been shown in present paper that a solution of $\mathrm{CoCl_2}$ in *PC* contains the dissolved salt mainly as the $\mathrm{Co}(PC)_5\mathrm{Cl}^+ \cdot \mathrm{Co}(PC)\mathrm{Cl}_3^-$ complex electrolyte. The principal forms of existence of the solute in other solvents are presented in Table 2 along with the corresponding solvent parameters.

As is seen, in solvent of low polarity such as pyridine only the neutral coordination form is present [1], and the coordination state may be considered as a result of extreme ionic association. A quite opposite effect is responsible for the coordination state of the solute in N-methylformamide. The high polarity results in a high extent of separation of cations and anions. The intermediate dielectric constant favours the coordinative disproportionation equilibria producing the $\mathrm{Co}L_6^{2+} \cdot 2\,\mathrm{CoCl_3}L^-$ and $\mathrm{Co}L_5\mathrm{Cl}^+ \cdot \mathrm{CoCl_3}L^-$ sometimes accompanied by the $\mathrm{CoCl_2}L_2$ neutral coordination forms. However, it seems to be impossible to find a relation between coordinating ability and coordination state of the salt.

Inspection of Table 2 shows that two solvents of very similar parameters, *DMF* and *DMA*, exhibit striking difference of the coordination states of $\mathrm{CoCl_2}$. The dominating form of $\mathrm{CoCl_2}$ in *DMA* is the $\mathrm{CoCl_2}(DMA)_2$ tetrahedral complex [3] while in *DMF* the salt exists exclusively as the $\mathrm{Co}(DMF)_6^{2+} \cdot 2\,\mathrm{CoCl_3}DMF^-$ complex electrolyte. This comparison illustrates the complexity of the problem. The coordination state of the salt in solution should be discussed in terms of stability of individual complexes. The extremal stability of the $\mathrm{CoCl_3}DMF^-$ complex anion [5] results in formation of the $\mathrm{Co}(DMF)_6^{2+} \cdot 2\,\mathrm{CoCl_3}DMF^-$ complex electrolyte. The formation of the $\mathrm{Co}(PC)_5\mathrm{Cl}^+ \cdot \mathrm{CoCl_3}(PC)^-$ complex electrolytes in *PC* solution is due to the relatively high stability of the monochloride complex. Thus, the specific properties of the individual complexes are responsible for the coordination states of the salt in solution.

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