Spectrophotometric and Conductometric Study of Cobalt(II) Bromide–Dimethyl Sulphoxide Solutions

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Visible absorption spectra and the molar conductivities of $CoBr_2$ dissolved in dimethyl sulphoxide (dmso) have been determined. Absorption spectra of the $Co(ClO_4)_2$–LiBr–dmso and $CoBr_2$–chlorobenzene–dmso ternary systems have also been investigated at 25 °C. The results indicate the existence of the $[Co(dmso)_6]^{2+}$, $[CoBr(dmso)_6]^+$, and $[CoBr_3(dmso)]^-$ complexes in dmso solutions of $CoBr_2$ while the $[CoBr_4]^{2-}$ ion exists in the ternary system at high Br^- to Co^{2+} ratios only.

Divalent transition metal halides and pseudohalides dissolved in non-aqueous donor solvents, such as acetonitrile, *N,N*-dimethylformamide (dmf), *N,N*-dimethylacetamide, and dimethyl sulphoxide (dmso), exhibit a variety of electrolytic behaviour. It is obvious that the differences between the systems are due to the nature of the salt as well as the solvent. The present systematic study was undertaken in order to establish the most important factors controlling the electrolytic properties of these non-aqueous systems. However, inspection of the literature shows that there is a divergence of opinion concerning the nature of the species formed in particular systems. The results of studies on the Co^{2+}–Cl^-–dmso system[1–3] are a striking illustration.

The Co^{2+}–Br^-–dmso system was studied qualitatively by Gutmann and Bohunovsky[4] and their results suggested a lack of co-ordination interaction between cobalt(II) and Br^- anion. This is surprising and seems to be questionable in the light of the results obtained for the Co^{2+}–Cl^-–dmso and Co^{2+}–Br^-–dmf systems[5] providing experimental evidence for the existence of tetrahedral bromo complexes of cobalt(II). The donor properties of these solvents are very similar (donor numbers:[6] 26.6 for dmf, 29.8 for dmso) and the drastic difference cannot be attributed to the small difference in density.

In this paper we report conductometric and spectrophotometric measurements carried out in order to determine the nature of complexes formed in the Co^{2+}–Br^-–dmso system, and the ionization equilibria of $CoBr_2$ in dmso.

Experimental

Reagent grade dmso was purified and dried as described previously.[7] The conductivity of the final product was $(3.0–5.0) \times 10^{-8}$ S cm^{-1}. The dmso-solvated $Co(ClO_4)_2$ and $CoBr_2$ were obtained by dissolving the hydrated salts in dmso, followed by distilling off the excess of solvent under reduced pressure at 60 °C. On cooling, the crystalline solids were obtained and recrystallized twice from anhydrous dmso. Lithium bromide was dried under reduced pressure over phosphorus pentoxide and recrystallized three times from acetonitrile.

The stock solutions of the salts were analyzed by standard ethylenediaminetetra-acetate titrations. Solutions for measurement were prepared from weighed amounts of the stock solution and the solvents. Final concentrations were calculated taking into account the densities which were determined independently. The densities of single solutions were measured using a bicapillary pycnometer. Details of the procedures for spectrophotometric and conductometric measurements were identical to those described previously.[8,9] All the preparations and manipulations were performed in a dry-box.

Results and Discussion

Figure 1 shows the visible absorption spectra (600—770 nm) of a series of dmso solutions containing $Co(ClO_4)_2$ at an approximately constant concentration of 0.0024 mol dm^{-3} and LiBr at a number of different concentrations. This spectral range is characteristic for the absorptions of cobalt(II) in an environment of four ligands, *i.e.* for pseudotetrahedral and tetrahedral complexes.[3,10]

Inspection of Figure 1 shows that the spectrum of cobalt(II) obtained at the highest concentration ratio [$c_{Br^-}/c_{Co^{2+}}$ = 2 048, curve (i)] consists of a band with four maxima located at 642, 667, 700, and 724 nm. The contour of the band and positions of the maxima are very close to those obtained for the corresponding Co^{2+}–Br^- systems in propylene carbonate[11] and acetonitrile[12] and are typical of the spectrum of the tetrahedral $[CoBr_4]^{2-}$ complex. Further analysis of the spectral curves shows that a decrease of the concentration of bromide anion results in distinct changes in intensity and contour of the spectrum of cobalt(II), with the disappearance of the maxima due to the $[CoBr_4]^{2-}$ complex, while new maxima at 664, 672, and 704 nm, also characteristic for four-co-ordinated cobalt(II), are observed. These facts are a clear indication of the co-existence of two four-co-ordinated complexes of cobalt(II) in the studied range of concentration of LiBr. One of them is $[CoBr_4]^{2-}$ while the nature of the second complex is at present unclear.

The visible absorption spectra of cobalt(II) in the spectral range characteristic for cobalt(II) in an octahedral environment are presented in Figure 2 which shows the spectra of ternary solutions containing LiBr at $c_{Br^-}/c_{Co^{2+}}$ = 64—186. The known spectrum of the $[Co(dmso)_6]^{2+}$ solvent complex[13] is indicated by a broken line. A detailed analysis of the absorption curves is rather difficult due to overlapping of the octahedral band with the intense band due to the tetrahedral species. However, inspection of the effects related to an increasing concentration of LiBr provides evidence of the formation of some octahedral complex, presumably monobromocobalt(II), in this system. As is seen, the absorption maximum due to the presence of $[Co(dmso)_6]^{2+}$ is gradually shifted towards longer wavelengths. It should be noted that the effect is observed for solutions containing LiBr in relatively large excess, which means that the octahedral bromo complex of cobalt(II) displays low stability with respect to the tetrahedral species.

Figure 3(*a*) shows the visible spectra of a series of dmso solutions of $CoBr_2$ in the concentration range 0.002 491—0.1112 mol dm^{-3} at 25 °C; Figure 3(*b*) shows the spectra obtained

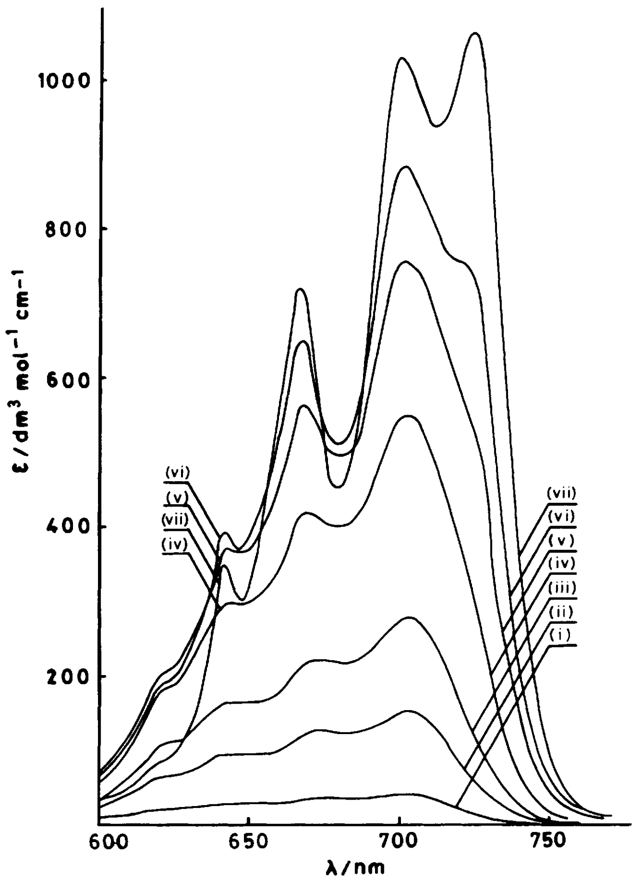

Figure 1. Absorption spectra of $Co(ClO_4)_2$–LiBr solutions in dmso at 25 °C. Concentrations (mol dm^{-3}) of $Co(ClO_4)_2$ and LiBr: (i) 0.002 383, 0.2248; (ii) 0.002 420, 0.4511; (iii) 0.002 640, 0.6586; (iv) 0.002 429, 1.239; (v) 0.002 401, 2.044; (vi) 0.002 495, 3.262; (vii) 0.002 653, 5.434

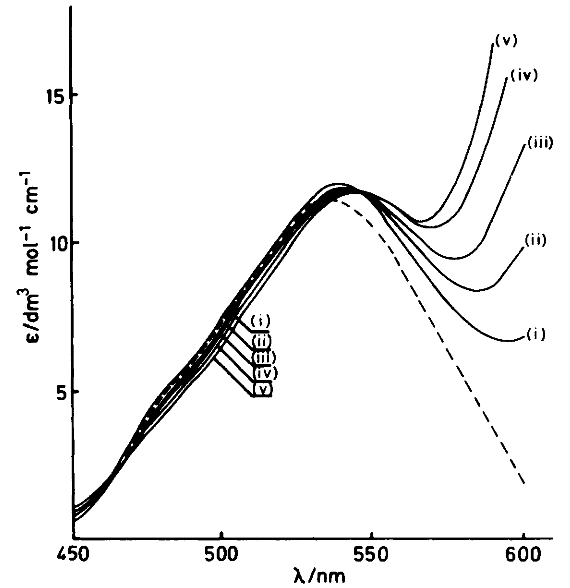

Figure 2. Absorption spectra of $Co(ClO_4)_2$–LiBr solutions in dmso at 25 °C. Concentrations (mol dm^{-3}) of $Co(ClO_4)_2$ and LiBr: (i) 0.002 387, 0.1611; (ii) 0.002 383, 0.2248; (iii) 0.002 389, 0.2938; (iv) 0.002 388, 0.3512; (v) 0.002 420, 0.4511

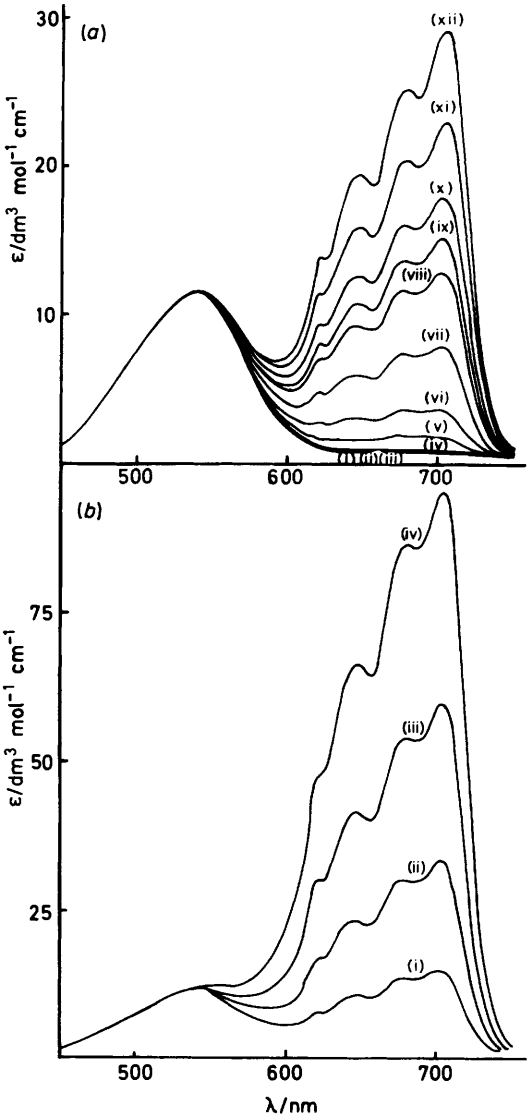

Figure 3. (*a*) Visible absorption spectra of $CoBr_2$ solutions in dmso at 25 °C. Concentrations of $CoBr_2$ (mol dm^{-3}): (i) 0.002 491, (ii) 0.004 4693, (iii) 0.006 806, (iv) 0.011 21, (v) 0.022 67. (vi) 0.033 35, (vii) 0.054 48, (viii) 0.073 83, (ix) 0.077 42, (x) 0.088 64, (xi) 0.099 25, (xii) 0.1112. (*b*) Influence of temperature on the visible absorption spectrum of a $CoBr_2$ (*ca.* 0.0774 mol dm^{-3}) solution in dmso: (i) 25 °C, (ii) 35 °C, (iii) 45 °C, (iv) 55 °C

for one of the solutions at different temperatures. As is seen, the spectra of cobalt(II) obtained for the most dilute solutions of $CoBr_2$ [curves (i), (ii), and (iii)] are identical to the spectrum of dmso solutions of $Co(ClO_4)_2$ (broken line in Figure 2). Thus, the obvious conclusion follows that cobalt(II) exists in this concentration range of $CoBr_2$ as the $[Co(dmso)_6]^{2+}$ solvento cation. Further inspection of Figure 3 shows that an increase of concentration of $CoBr_2$ results in gradual development of the bands with maxima at 644, 672, and 704 nm typical of four-co-ordinated cobalt(II) while the bands due to the octahedral species remain practically unchanged.

The spectrum of the tetrahedral species is similar to that of cobalt(II) obtained for lower concentrations of LiBr. It is obvious that the spectrum is due to a pseudotetrahedral complex of cobalt(II) containing less than four bromide anions. The lack of distinct changes in the octahedral region of the spectrum

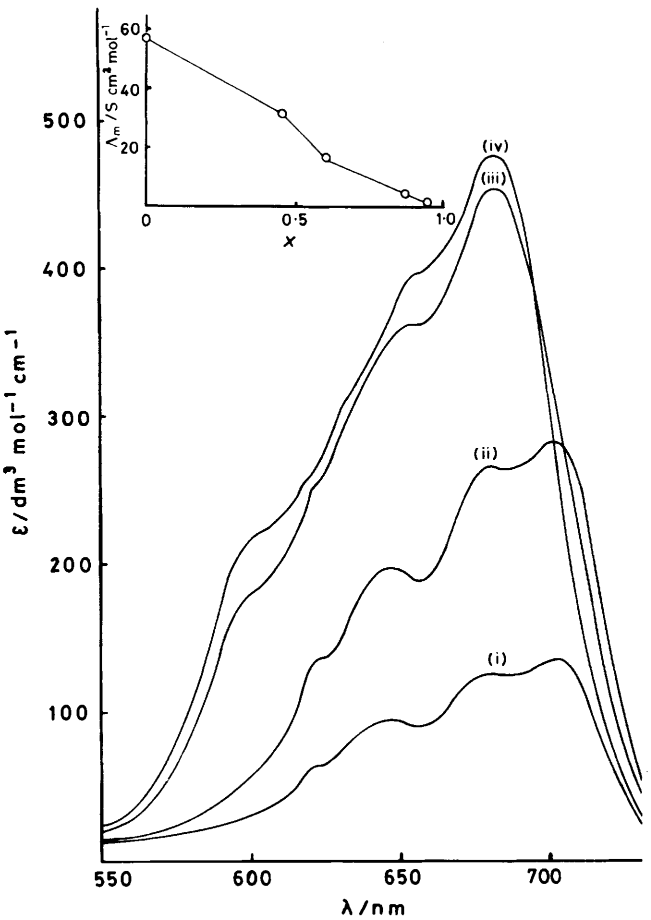

Figure 4. Absorption spectra and molar conductance of the $CoBr_2$–dmso–chlorobenzene system. Concentrations of $CoBr_2$ (mol dm^{-3}) and mole fractions (x) of chlorobenzene: (i) 0.012 19, 0.455; (ii) 0.011 08, 0.603; (iii) 0.001 172, 0.862; (iv) 0.000 482, 0.942

suggests that $[Co(dmso)_6]^{2+}$ is the dominating form of six-co-ordinated cobalt(II) over almost the whole concentration range. However, the existence of outer-sphere ion pairs of the type $[Co(dmso)_6]^{2+}\cdot Br^-$ cannot be excluded.

Similar effects are caused by increasing temperature and the observed increase of the mean molar absorption coefficient of cobalt(II) is obviously related to increasing mole fraction of the pseudotetrahedral bromo complex. The independence of the band contour and position of the maxima on concentration and temperature clearly indicates that only one tetrahedral complex of cobalt(II) is present in the dmso solutions of $CoBr_2$. This conclusion is supported by results of the Coleman's tests[14] for the number of light-absorbing species, carried out for the tetrahedral spectral range. It is clear that the pseudotetrahedral complex of cobalt(II) is either $[CoBr_2(dmso)_2]$ or $[CoBr_3(dmso)]^-$. Thus, the co-ordination state of $CoBr_2$ in dmso is described by one of the equilibria (1) or (2).

$$[Co(dmso)_6]^{2+} + 2\,Br^- \rightleftharpoons [CoBr_2(dmso)_2] + 4\,dmso \quad (1)$$

$$[Co(dmso)_6]^{2+} + 3\,Br^- \rightleftharpoons [CoBr_3(dmso)]^- + 5\,dmso \quad (2)$$

In order to identify which is responsible for the observed spectral changes we have studied the effect which addition of an inert diluent of low polarity exerts on the spectrum and electrical conductivity of $CoBr_2$ in dmso solutions. The spectra and molar conductance of $CoBr_2$ solutions in chlorobenzene–dmso mixed solvent at 25 °C are presented in Figure 4. It can be seen that addition of chlorobenzene causes initially an increase of intensity of the tetrahedral band only. When the mole fraction of chlorobenzene exceeds 0.6 distinct changes in its intensity and shape are observed. The effect consists of the development of a new spectrum with a maximum at 682 nm and two shoulders at *ca.* 653 and 680 nm [curve (iv), mole fraction of chlorobenzene 0.942]. The spectrum differs markedly from the spectra of cobalt(II) described above. Moreover, the spectral changes are accompanied by a distinct decrease in electrical conductance of the solutions. The molar conductance of a 0.000 482 mol dm^{-3}

Table. Molar conductivities of $CoBr_2$ in dmso at 25 °C

10^3c/mol dm^{-3}	Λ_m/S cm^2 mol^{-1}	10^3c/mol dm^{-3}	Λ_m/S cm^2 mol^{-1}
0.4939	74.91	8.024	59.93
0.5836	74.37	10.05	58.37
0.7430	73.36	12.36	56.59
1.013	72.26	13.24	56.13
1.186	71.52	14.93	55.28
1.401	70.57	19.42	52.99
1.800	69.39	22.16	51.67
2.064	68.41	26.62	50.19
2.401	67.80	29.91	49.05
2.860	66.92	31.92	48.50
3.417	65.64	40.98	46.00
4.299	64.29	51.60	43.62
5.418	62.51	63.85	41.16
5.615	62.39	78.96	38.63

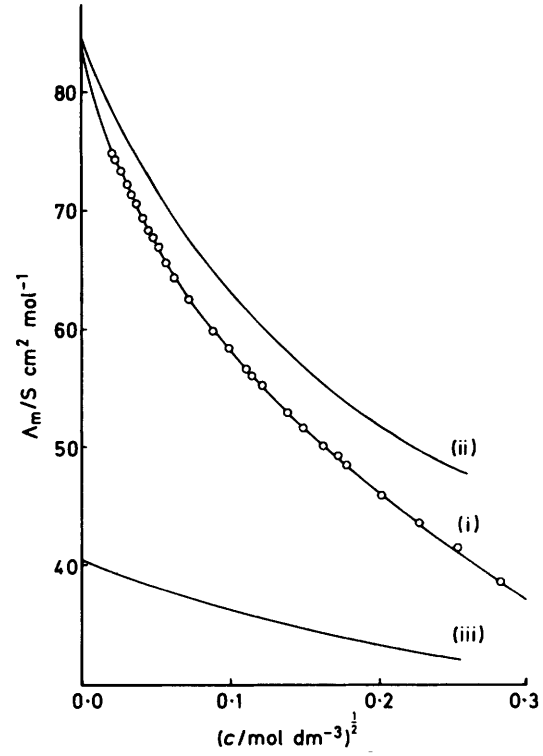

Figure 5. Plot of molar conductivity against the square root of concentration for solutions of $CoBr_2$ in dmso at 25 °C: experimental values (i); predicted for the complex electrolytes $[Co(dmso)_6]^{2+}$,$2Br^-$ (ii); and $[CoBr(dmso)_5]^+$,Br^- (iii)

solution of $CoBr_2$ in chlorobenzene–dmso (0.942:0.058) is only 0.51 S cm^2 mol^{-1}, while the value for the corresponding pure dmso solution is *ca.* 74.5 S cm^2 mol^{-1}, indicating an absence of ionic complexes of cobalt(II) in the former solution. Thus, the corresponding spectrum of cobalt(II) may be considered as the spectrum of the $[CoBr_2(dmso)_2]$ complex. A simple conclusion follows: that the spectrum observed for the pure dmso solutions of $CoBr_2$ is due to the pseudotetrahedral $[CoBr_3(dmso)]^-$ complex anion, and the electrolytic properties of the solution are determined by the equilibrium (2).

Figure 5 shows the molar conductance curve of $CoBr_2$ in dmso at 25 °C; the experimental values are listed in the Table. Also in Figure 5 are the molar conductance curves predicted for the hypothetical completely dissociated electrolytes $[Co(dmso)_6]^{2+}$,2Br$^-$ and $[CoBr(dmso)_5]^+$,Br$^-$ on the basis of known limiting ionic conductances[7,15] and the Robinson-Stokes equation.[16] The molar conductance of the $[CoBr(dmso)_5]^+$ cation was estimated as 80% of the equivalent conductance of the $[Co(dmso)_6]^{2+}$ solvento cation, as discussed in previous papers.[17,18]

The experimental points in Figure 5 run below the curve expected for the completely dissociated $CoBr_2$ and well above that predicted for complete first-step association. However, the data obtained for the most dilute solutions are very close to the values predicted for the fully dissociated salt. This fact indicates that the dominant form of cobalt(II) in the most dilute dmso solutions of $CoBr_2$ is the $[Co(dmso)_6]^{2+}$ solvento cation and complex formation has no significant influence on the electrolytic properties of the studied systems. The same conclusion was drawn from the spectrophotometric studies, as discussed above. The tribromo complex of cobalt(II) exists in more concentrated solution and its formation is responsible for a decrease of the molar conductance over the higher concentration range. The rapid decrease of electrical conductance observed for the dilute solutions seems to be due to an outer-sphere association.

To evaluate the association constant the conductance data for the most dilute solutions were analysed using the Lee-Wheaton conductance equation[19] assuming that only one association step occurs according to equilibrium (3). The

$$[Co(dmso)_6]^{2+} + Br^- \xrightleftharpoons{K_1} [Co(dmso)_6]^{2+}\cdot Br^- \quad (3)$$

calculations were performed by Dr. A. Pethybridge, University of Reading, using his original computer programs and procedures.[20,21] The best-fit parameters obtained for $CoBr_2$ are: $K_1 = 52$ dm^3 mol^{-1} for the first-step association constant [equation (3)], and $\lambda^0(\frac{1}{2}Co^{2+}) = 17.6$ S cm^2 mol^{-1} for the conductivity of the $[Co(dmso)_6]^{2+}$ solvento cation in dmso. However, an estimate of the absolute errors is rather difficult from this method of calculation.

Summarizing, the dominant form of cobalt(II) in dilute dmso solutions of $CoBr_2$ is the $[Co(dmso)_6]^{2+}$ solvento cation coexisting in equilibrium with the $[Co(dmso)_6]^{2+}$,Br$^-$ ion pair. In more concentrated solutions of $CoBr_2$ some mole fraction of cobalt(II) exists as the $[CoBr_3(dmso)]^-$ complex anion. The formation of the latter species is responsible for the decrease of the molar conductance observed over the higher concentration range. A significant fraction of cobalt(II) exists as the tribromo complex in the $Co(ClO_4)_2$–LiBr–dmso solution. Moreover, at the highest LiBr to $Co(ClO_4)_2$ ratios (*ca.* 2 000) formation of the $[CoBr_4]^{2-}$ ion is observed. The effects observed in the octahedral spectrum of cobalt(II) for the higher LiBr to $Co(ClO_4)_2$ ratios (see Figure 2) suggest the presence of an octahedral complex of cobalt(II), presumably the $[CoBr(dmso)_5]^+$ complex cation. It is surprising that formation of the tribromo complex was not detected by Gutmann and Bohunovsky.[4]

It is of interest to compare the present results with those reported previously for analogous cobalt(II) halide systems. It has been shown by Libuś *et al.*[3] that $CoCl_2$ dissolved in dmso exhibits similar behaviour but the respective tri- and tetrahalide complexes exist to a much greater extent. At Cl$^-$ to Co^{2+} ratios > 36, cobalt(II) exists exclusively as an equilibrium mixture of these complexes and at a ratio of 470 only one complex of cobalt(II) exists in solution. The distinct differences in the properties of the Co^{2+}–X$^-$–dmso systems is related to the difference in donor properties of the respective anions. The same was found for the Co^{2+}–X$^-$–dmf systems. The extreme stability of the $[CoCl_3(dmf)]^-$ complex results in formation the $[Co(dmf)_6]^{2+}$,2$[CoCl_3(dmf)]^-$ complex electrolyte in dmf solutions of $CoCl_2$.[22] This means that all chloride anions are consumed in the formation of the respective trichloro complex and *ca.* 66% of cobalt(II) exists as the $[CoCl_3(dmf)]^-$ complex. The $[CoBr_3(dmf)]^-$ complex is the dominant form of cobalt(II) in dmf solutions of $CoBr_2$, but its abundance is only slightly greater than 50%.[5] The pseudo-tetrahedral $[CoX_3L]^-$-type complexes are the most stable species in dmf solution while their stability in dmso is markedly lower. This difference can be easily explained in terms of the donicities of the solvents, which display opposite order.

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