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Complexes of Cobalt(II) with Chloride and Thiocyanate Ions in Dimethyl Sulfoxide

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The important cobalt(II)-chloride ion complexes which form in dimethyl sulfoxide solutions are $Co(DMSO)Cl_3^-$ *and* $CoCl_4^{2-}$ *and their overall formation constants are* $(4.21\pm0.58)\times10^8$ M^{-3} *and* $(1.12\pm0.16)\times10^9$ M^{-4}*, respectively, at 25°C. The important cobalt(II)-thiocyanate ion complexes which form in dimethyl sulfoxide solutions are* $Co(DMSO)_5(NCS)^+$*,* $Co(DMSO)_4(NCS)_2$*, and* $Co(NCS)_4^{2-}$ *and their overall formation constants are* (465 ± 72) M^{-1}*,* $(5.12\pm0.48)\times10$ M^{-2} *and* $(5.79\pm0.55)\times10^6$ M^{-4}*, respectively, at 25°C. A value of* 20 ± 4 M^{-1} *was found for the* $Co(DMSO)_6^{2+}.ClO_4^-$ *ion pairing constant. Molar absorptivities of the complexes are reported for selected wavelengths.*

Introduction

Qualitative studies of cobalt(II)-chloride equilibria have been made in dimethyl sulfoxide (DMSO) solutions.[1-6] There is some disagreement on the nature of the species present. Buffagni and Dunn[1] believed that $Co(DMSO)_6^{2+}$, $Co(DMSO)Cl_3^-$ and $CoCl_4^{2-}$ were the main species, depending on the Cl^- concentration, with possibly some $Co(DMSO)_5Cl^+$ whereas Gutmann and Bohunovsky[3] concluded that $Co(DMSO)_6^{2+}$, $Co(DMSO)_2Cl_2$, $Co(DMSO)Cl_3^-$ and $CoCl_4^{2-}$ were the main species to be found. It was pointed out[1] that the cobalt(II) was incompletely converted to $CoCl_4^{2-}$ at the highest chloride concentrations used and that the molar absorptiviies which had been reported were not true molar absorptivities but were average absorptivities for the mixture of species existing in solution at arbitrary chloride concentrations. Likewise, only qualitative studies have been made of the cobalt(II)-thiocyanate equilibria in DMSO solutions[7] and it was concluded that only $Co(DMSO)_6^{2+}$, $Co(DMSO)_5(NCS)^+$ and $Co(NCS)_4^{2-}$ were present in significant amounts. Here we report the results of quantitative studies of cobalt(II)-Cl^- and cobalt(II)-NCS^- equilibria in DMSO solutions.

Experimental Section

Mallinckrodt A. R. grade DMSO was dried and stored over Linde 4A molecular sieves. All solutions were made with dried, filtered DMSO under nitrogen atmosphere in a dry box and were stored over Linde 4A molecular sieves. All solutions were filtered through a fine fritted glass filter in a dry atmosphere before use.

The salts $[Co(H_2O)_6](ClO_4)_2$, $[Co(DMSO)_6](ClO_4)_2$[8], and $[Co(DMSO)_6][CoCl_4]$[6,8] were used to prepare cobalt(II) solutions in DMSO. The latter salt was, of course, not used in the thiocyanate studies. The data obtained were not dependent on the salt used. Anhydrous $LiClO_4$, dissolved in dry DMSO and stored over molecular sieves, was used to maintain constant ionic strength when desired. Anhydrous LiCl, dried orvenight at 120°C, was used to vary chloride ion concentration and anhydrous KNCS, dried overnight at 150°C, was used to vary thiocyanate ion concentration. The KNCS solutions in dry DMSO were prepared just before use.

All cobalt(II) salts were analyzed by EDTA titration using murexide as indicator.[9] The Cl^- and NCS^- solutions were analyzed gravimetrically as AgCl and AgNCS. Water determination was made with Karl Fischer reagent; in no case did the water content exceed 0.02 percent.

Absorbance measurements were made and spectra were determined with either a Beckman DU or a Cary Model 14 spectrophotometer. Both instruments were equipped with thermostated cell compartments maintaining the temperature at 25.0±0.2°C.

Results and Discussion

Cobalt(II)-Chloride Ion System. In Figure 1 are shown the spectra obtained at concentrations of chloride ion equal to or greater than 0.027 *M* in the presence of 1.1×10^{-3} *M* cobalt(II). Three well-developed isosbestic points were found at 622, 644 and 655 nm which indicated strongly that only two cobalt species of any importance existed at these concentrations. One of these two species was tetrahedral $CoCl_4^{2-}$ be-

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(1) S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961).

(2) V. Gutmann and L. Hübner, *Monatsh. Chem.*, *92*, 1261 (1961).

(3) V. Gutmann, and O. Bohunovsy, *ibid.*, *99*, 740 (1968).

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(6) D. W. Meek, D. K. Straub and R. S. Drago, *J. Amer. Chem Soc.*, *82*, 6013 (1960).

(7) V. Gutmann and O. Bohunovsky, *Monatsh. Chem.*, *99*, 751 (1968).

(8) F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, *82*, 2986 (1960).

(9) P. F. J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic Acid, D. Van Nostrand Company, Princeton, N. J., 1958. p. 230.

cause of the location and intensity of its absorption and because it is the limiting species formed at high chloride ion concentrations. Gutmann and Bohunovsky[3] stated that $CoCl_4^{2-}$ was formed quantitatively with a 200-fold excess of Cl^- but we found, with Buffagni and Dunn,[1] that $CoCl_4^{2-}$ was not quantitatively formed at the highest Cl^- concentration used (0.9 *M*). Hence it was not possible to obtain the molar absorptivities directly.

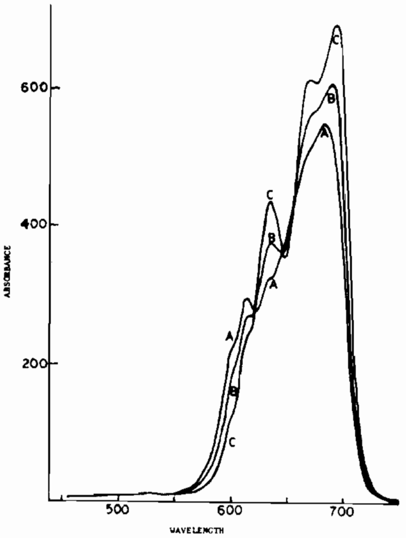

Figure 1. Spectra of cobalt(II)-chloride ion solutions in DMSO at high chloride ion concentrations. 1.1×10^{-3} *M*Co^{II}. (A) 0.027*M*Cl^-. (B) 0.10*M*Cl . (C) 0.30*M*Cl^-.

The second species present at the concentrations under consideration was tetrahedral $Co(DMSO)Cl_3^-$ for the following reasons. The position and intensity of the absorption of the species from which $CoCl_4^{2-}$ was being formed suggest strongly that the species is tetrahedral, rather than octahedral, because cobalt(II) is attached to chloride ions and the oxygen atom of DMSO. This tetrahedral species is $Co(DMSO)Cl_3^-$, rather than $Co(DMSO)_2Cl_2$, because at low Cl^- concentrations the spectrum obtained by subtracting the $CoCl_4^{2-}$ absorbance from the observed absorbance, resembled the spectrum attributed to $CoCl_3^-$ in dimethylformamide[1] rather than the spectrum attributed to $CoCl_2$.[1] If $Co(DMSO)Cl_3^-$ was formed in preference to $Co(DMSO)_2Cl_2$ at low Cl^- concentrations (0.0057 *M*) then it was formed preferably at high Cl^- concentrations. The spectra attributed to $Co(DMSO)Cl_3^-$ and $CoCl_4^{2-}$ are shown in Figure 2.

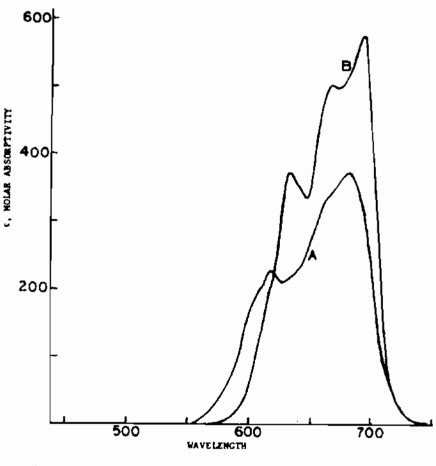

Figure 2. The spectra of cobalt(II)-chloride ion complexes in DMSO. (A) $Co(DMSO)Cl_3^-$. (B) $CoCl_4^{2-}$.

Molar absorptivities and complex ion formation constants were calculated for various models using two computer programs,[10] one written initially by Z Z. Hugus and one written by Peter J. Lingane. The Davies equation [11] for the activity coefficients:

$$-\log f_i = AZ_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad (1)$$

where I is the ionic strength and A = 1.12 at 25°C for DMSO, was used to calculate the activity coefficients f_i of the ionic species with charge Z_i. This equation was selected because it contains no arbitrary constants and because its use by Peterson, Lingane and Reynolds[12] proved quite satisfactory for the mercury(II)-iodide ion equilibria in DMSO solutions. For 91 solutions at 1.00 *M* ionic strength covering the concentration range of 1.1×10^{-4} to 9.4×10^{-3} *M* for cobalt(II) and of 3.5×10^{-3} to 0.946 *M* for Cl^-, the model which best satisfied the data was the one for $Co(DMSO)_6^{2+}$, $Co(DMSO)Cl_3^-$ and $CoCl_4^{2-}$ in agreement with the conclusion reached by Buffagni and Dunn[1] on more qualitative grounds. Use of $Co(DMSO)_2Cl_2$ or $Co(DMSO)_5Cl^+$ in place of $Co(DMSO)Cl_3^-$ gave unacceptable results; in case of $Co(DMSO)_2Cl_2$ large negative molar absorptivities were obtained for $Co(DMSO)_2Cl_2$ at the higher cobalt(II) concentrations whereas in the case of $Co(DMSO)_5Cl^+$ the molar absorptivities were unacceptably large for an octahedral species. Use of four species, namely, $Co(DMSO)_5^{2+}$, $Co(DMSO)_3^-$, $CoCl_4^{2-}$ and a dichloro species or a monochloro species gave essentially zero formation constants for the dichloro and the monochloro species indicating that postulating their presence was not necessary.

For 99 solutions of variable ionic strength with no added $LiClO_4$ similar results were obtained. However the values of β_3 and β_4, the overall formation constants of $Co(DMSO)Cl_3^-$ and $CoCl_4^{2-}$, in the variable ionic strength media were larger than those for constant ionic strength by a factor of approximately 10. The use of activity coefficient expressions other than equation (1) did not give agreement between the β-values for the two different media; the reasons why are discussed in Appendix I. Assumption of ion pair formation between Li^+ and Cl^-, which reduces the activity of Cl^- in the presence of $LiClO_4$, gave agreement between the β_3 values but not between the K_4 values because the β_3 value has a much higher dependence on the activity of Cl^-. The existence of $Li^+ . Cl^-$ ion pairs in DMSO has been suggested by Pool[13]

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(10) Kenneth R. Magnell Ph.D. thesis, niversity of Minnesota, 1970.

(11) C. W. Davies, Ion Association, Butterworths and Company, Ltd., London, 1962.

(12) R. J. Peterson, P. J. Lingane and W. L. Reynolds, *Inorg. Chem.*, 9, 680 (1970).

(13) K. H. Pool, *J. Polargr. Soc.*, *13*, 23 (1967).

Table I. Molar Absorptivities of Cobalt(II)-Cl^- Complexes in DMSO Solutions.

	Molar Absorptivities ($M^{-1}cm^{-1}$)					
Species	600 [a]	613	635	665	680	694
$Co(DMSO)Cl_3^-$	248±3	317±3	312±3	495±3	550±3	461±3
$CoCl_4^{2-}$	42±3	168±3	488±3	621±3	644±3	795±5

[a] *All wavelengths in nm.*

from conductance data but Dunnett and Gasser[14] found that the conductance data could be completely explained by correcting for viscosity effects. Griffiths and Scarrow[15] concluded from spectral behavior of mixtures of nickel(II) salts and various chlorides that there was little, if any, ion pairing between Li^+ and Cl^- in DMSO.

Assumption of the $Co^{2+} . ClO_4^-$ ion pair in the constant ionic strength $LiClO_4$ media gave agreement between the β's for the two different kinds of media. Ion pairing between Co^{2+} and ClO_4^- reduced the $Co(DMSO)_6^{2+}$ activity and gave agreement for the β_3 and β_4 values simultaneously. Because $\beta_4 = K_4\beta_3$ and because K_4, the stepwise formation constant for $CoCl_4^{2-}$, was very insensitive to change of $Co(DMSO)_6^{2+}$ activity, increasing β_3 by a factor of 10 increased β_4 simultaneously by a factor of 10 so as to give agreement between the β_3 values and between the β_4 values for the two different kinds of media. Burrus[16] suggested $Co^{2+} . ClO_4^-$ ion pairs in DMSO to explain polarographic results.

The molar absorptivities and their errors obtained for a best fit at selected wavelengths over the region where $Co(DMSO)Cl_3^-$ and $CoCl_4^{2-}$ absorb strongly are listed in Table I. The best value of β_3 was $(4.21\pm0.58)\times10^8$ M^{-3}, that of β_4 was $(1.12\pm0.16)\times10^9$ M^{-4}, and that of the $Co^{2+} . ClO_4^-$ ion pair formation constant was 20 ± 4 M^{-1}.

The distribution diagram for the cobalt(II)-chloride ion system in DMSO is shown in Figure 3.

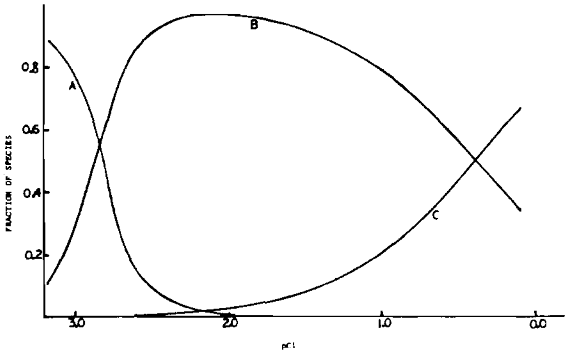

Figure 3. The distribution diagram for cobalt(II)-chloride ion complexes in DMSO solution for Co^{II} concentrations in the range 1.0×10^{-4} to 9.0×10^{-3} M. (A) $Co(DMSO)_5^{2+}$, (B) $Co(DMSO)Cl_3^-$, (C) $CoCl_4^{2-}$.

Cobalt(II)-Thiocyanate Ion System. When KNCS was added to a 3×10^{-3} M solution of $Co(DMSO)_6^{2+}$ in DMSO up to NCS^- concentrations of 3×10^{-3}, the maximum at 535 nm, due initially to $Co(DMSO)_6^{2+}$, increased in intensity and shifted very slightly to longer wavelengths; clearly another octahedral cobalt(II) species or two was being formed. At NCS^- concentrations approximately equal to 4.5×10^{-3} M, an absorption at 625 nm was noticeable which increased in intensity with increasing NCS^- concentration. This absorption peak had a shoulder at 587 nm and was due to only one tetrahedral species because, at increasing NCS^- greater than 0.1 M where the octahedral species did not absorb appreciably at 587 and 625 nm because of small molar absorptivities, the ratio of the intensities at the maximum and at the shoulder remained constant at 1.86 although the two intensities increased considerably with further increase of NCS^- concentration. If two tetrahedral species had been present it is unlikely that this ratio would have remained constant.

The model which gave the best results for molar absorptivities and for the complex ion formation constants was the one for the presence of the four species $Co(DMSO)_6^{2+}$, $Co(DMSO)_5(NCS)^+$, $Co(DMSO)_4(NCS)_2$ and $Co(NCS)_4^{2-}$. The final refined values of the molar absorptivities for the $Co(DMSO)_x(NCS)_2$ species were 29.4, 18.6, and 13.9 at 535, 587, and 625 nm, respectively; these values are more typical of those for an octahedral complex than of those for a tetrahedral complex and these values were obtained whether the initial estimates used for the computer program were typical of the values expected for a tetrahedral or for an octahedral complex.

When only the species $Co(DMSO)_6^{2+}$, $Co(DMSO)_5(NCS)^+$ and $Co(NCS)_4^{2-}$ were used, as suggested by the results of Gutmann and Bohunovsky,[7] the refined parameters resulted in the calculated absorbances at the larger NCS^- concentrations being consistently too low. Lingane and Hugus[17] observed this tendency when the refinement of the iron(III)-Cl^--DMSO system was attempted with a species missing.

When all species, $Co(DMSO)_6^{2+}$, $Co(DMSO)_5(NCS)^+$, $Co(DMSO)_x(NCS)_2$, $Co(DMSO)_y(NCS)_3^-$ and $Co(NCS)_4^{2-}$, were used, three of six molar absorptivities for $Co(DMSO)_y(NCS)_3^-$ were significantly negative and the remaining three were typical of an octahedral complex. In this model $Co(NCS)_4^{2-}$ was the only species having molar absorptivities typical of those expected for a tetrahedral complex in agreement with the conclusion reached on the basis of the ratio of the absorbances at 587 and 625 nm. This model does not give acceptable results because of the negative molar absorptivities and octahedral geometry for $Co(DMSO)_y(NCS)_3^-$.

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(14) J. S. Dunnett and R. P. H. Gasser, *Trans. Faraday Soc.*, *61*, 922 (1965).
(15) T. R. Griffiths and R. K. Scarrow, *J. Chem. Soc.* (A), 827 (1970).
(16) R. T. Burrus, Ph.D. Dissertation, University of Tennessee, 1962.
(17) P. J. Lingane and Z Z. Hugus, Jr., *Inorg. Chem.*, *9*, 757 (1970).

Table II. Molar Absorptivities of Cobalt(II)—NCS— Complexes in DMSO Solutions.

Species	Molar Absorptivities ($M^{-1}cm^{-1}$) 485 [a]	535	540	587	610	625
$Co(DMSO)_5(NCS)^+$	$12.2 \pm .6$	23.1 ± 1.0	23.5 ± 1.0	$6.8 \pm .5$	$8.6 \pm .4$	$-0.4 \pm .4$
$Co(DMSO)_4(NCS)_2$	$13.0 \pm .4$	$29.4 \pm .8$	$30.0 \pm .8$	18.6 ± 1.4	15.1 ± 1.7	13.9 ± 1.8
$Co(NCS)_4^{2-}$	$16.8 \pm .4$	$25.9 \pm .4$	$36.0 \pm .4$	969 ± 4	1550 ± 5	1796 ± 5

[a] All wavelengths in nm.

When the species $Co(DMSO)_6^{2+}$, $Co(DMSO)_5(NCS)^+$, $Co(DMSO)_y(NCS)_3^-$ and $Co(NCS)_4^{2-}$ were used the refined final values of the molar absorptivities for $Co(DMSO)_y(NCS)_3^-$ were those for an octahedral complex whether the initial estimates used were those for a tetrahedral or for an octahedral complex. Since only tetrahedral trithiocyanatocobalt(II) complexes have been observed in other solvents[7] it is reasonable to expect this complex to be tetrahedral in DMSO. Furthermore, the computed errors in the parameters were significantly larger for this model than for the one with $Co(DMSO)_x(NCS)_2$ in place of $Co(DMSO)_y(NCS)_3^-$.

It was assumed in all cases that $Co(NCS)_4^{2-}$ was the terminal species because of the similarity of its spectrum with that attributed to $Co(NCS)_4^{2-}$ in other non-aqueous solvents.[18]

The molar absorptivities and their errors obtained for a best fit of the data from 99 solutions covering the concentration ranges of 2.4×10^{-5} to 5.6×10^{-3} M for cobalt(II) and of 7.7×10^{-4} to 0.8 M for NCS^- are given in Table II for 6 wavelengths. The best values of the overall formation constants at 25°C were 465 ± 72 M^{-1} for β_1, $(5.12 \pm 0.48) \times 10^4$ M^{-2} for β_2 and $(5.79 \pm 0.55) \times 10^6$ M^{-4} for β_4. The Davies equation was used to calculate all activity coefficients. No perchlorate salt was used to maintain constant ionic strength because the NCS^- solutions were too unstable in DMSO perchlorate solutions.

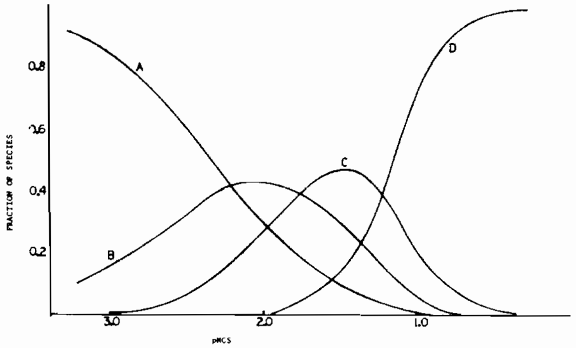

Figure 4. The distribution diagram for cobalt(II)-thiocyanate complexes in DMSO solutions for Co^{II} concentrations in the range 2.4×10^{-5} to 5.6×10^{-3} M. (A) $Co(DMSO)_6^{2+}$, (B) $Co(DMSO)_5(NCS)^+$, (C) $Co(DMSO)_4(NCS)_2$, (D) $Co(NCS)_4^{2-}$.

The distribution diagram for the cobalt(II)-NCS^- system in DMSO is given in Figure 4.

Appendix I

Attempts were made to obtain agreement of the β_3 values and of the β_4 values between constant ionic strength and variable ionic strength media by changing the relationship between the activity coefficient and ionic strength rather than by introducing ion pairing. The activity coefficient-ionic strength relationship was expressed as

$$-\log f_i = AZ_i^2\left(\frac{\sqrt{I}}{1+b\sqrt{I}} - CI\right) \qquad (A)$$

When expression A was substituted into the equation for log β_3 and the partial derivatives of log β_3 taken with respect to the parameters b and C, it was readily shown[10] that increasing values of b caused the β_3 values to diverge and that no positive values of C could make the β_3 values agree if β_3 for 1.00 M ionic strength was smaller than β_3 for the smaller, variable ionic strengths, as was the case.

For $b = 1$, as in the Davies equation, the β_3 values for 1.00 M ionic strength and variable ionic strength could be made to agree for $C = -1.18$. However, this value for C is unacceptable for three reasons: First, the K_4 values differ by 300 percent for $C = -1.18$ although they were essentially in agreement for $C = 0.3$. This large difference in K_4 values for the two kinds of media is not acceptable. Second, for $C = -1.18$ the value of β_3 is 1.6×10^{17} M^{-3} for both kinds of media. The value of β_3 cannot be this large because spectra show that, at Cl^- concentrations slightly greater than 3 times the Co^{II} concentration, the cobalt(II) is incompletely complexed. Third, the use of a positive linear term in equation (A) is contrary to the reason for the addition of the linear term; this reason is to account for an increase in f_i at high ionic strengths. Hence no acceptable variation of equation (A) can give agreement for the β_3 and K_4 values between the two different kinds of media.

(18) A. Turco, C. Percile and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).