1012. *The Spectra of Inorganic Complexes in Non-aqueous Solvents. Part I. Chlorocobaltate Ion and Cobalt Chloride.*

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The spectra of $CoCl_2$ and the $[CoCl_4]^{2-}$ ion have been examined in various non-aqueous solvents, particularly nitromethane and *NN*-dimethylformamide. The results show that there is a considerable amount of interaction between the " solute " and the " solvent " and that species postulated as $[CoCl_2S_2]$, $[CoCl_3S]^-$, $[CoS_6]^{2+}$, and $[CoS_5Cl]^+$ occur in varying, but appreciable, amounts.

NN-DIMETHYLFORMAMIDE (DMF), dimethylacetamide (DMA), dimethyl sulphoxide (DMS), formamide, nitromethane (NM), and similar substances are frequently used as solvents for both organic and inorganic compounds; in particular, the first four are optically " transparent " to about 2800 Å when pure and can thus be used for spectroscopic purposes. The extent to which these solvents react with the solute has been underestimated in the past, especially with respect to inorganic complexes. In view of their increasing use, in both kinetics and spectroscopy, it seemed desirable to examine the spectrum of some well-characterised species and, for reasons which will be discussed by one of us elsewhere, the essentially tetrahedral cobalt halides were chosen for the study, the chloride ion $[CoCl_4]^{2-}$ being studied in detail.

Crystallographically authentic samples of this ion are now obtainable in the solid state combined with one of three different cations, as Cs_3CoCl_5,[1,2] Cs_2CoCl_4,[2] $[Et_4N]_2[CoCl_4]$,[3] and $[Ph_3MeAs]_2[CoCl_4]$.[4] The last two, being more soluble in organic solvents, have been

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[1] Powell and Wells, *J.*, 1935, 359.
[2] Porai-Koshits, *Kristallografiya*, 1956, **1**, 291.
[3] Gill and Nyholm, *J.*, 1959, 3997.
[4] Gill, Nyholm, and Pauling, *Nature*, 1958, **182**, 168.

used to the largest extent in this investigation, but the cæsium salts have been used for single-crystal absorption and diffuse reflectance spectra of the solids since their crystallography is known more accurately.[2]

The visible spectra of the chlorocobaltate ion and of cobalt chloride have been extensively investigated in aqueous [5,6] and alcoholic solutions,[7,8] some non-hydroxylic solvents,[8] and nitromethane.[3] Re-examination of the spectrum in purified and dried nitromethane showed [9] that the solutions gave small but consistent departures from Beer's law and that the apparent maximum molar extinction coefficient of the solute was raised from the quoted values of 653 in nitromethane [3] and 603 in water [5a] by saturation of the solutions with chloride ion. The chloride was introduced as tetramethyl- or tetraethyl-ammonium or methyltriphenylarsonium chloride, inorganic halides (*e.g.*, LiCl) being avoided on account of their known tendency to form ion pairs in non-aqueous solvents.[6] Also, since the methyltriphenylarsonium salt is not easily obtainable in large quantities and because it is easier to dry the tetramethylammonium salt to the degree required, most of the work was carried out with this. The tetramethylammonium salt has the disadvantage that its solubility is much lower (about 100 times) than that of its tetraethyl analogue or methyltriphenylarsonium salt, but this is not of importance except in studies at high chloride concentrations, where indeed the other salts were used.

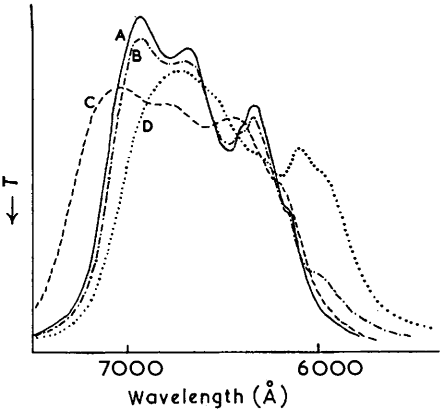

FIG. 1. Absorption spectra of (A) $[CoCl_4]^{2-}$ in nitromethane containing 0·1M-$Ph_3MeAsCl$, (B) $[CoCl_4]^{2-}$ in nitromethane solution, (C) Diffuse reflectance spectrum of Cs_3CoCl_5, and (D) $[CoCl_4]^{2-}$ in dimethylformamide.

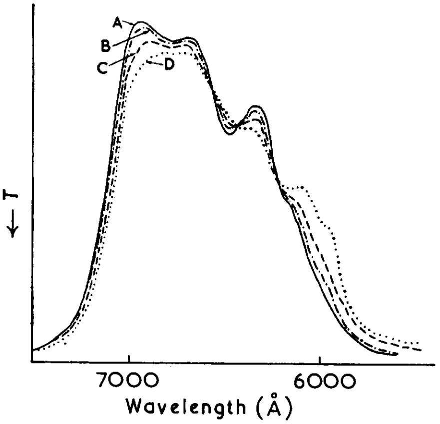

FIG. 2. $[CoCl_4]^{2-}$ in solution in 4 : 1 nitromethane–dimethylformamide, containing added chloride of concentrations (A) 0·2, (B) 0·4, (C) 0·6, and (D) $0{\cdot}6 \times 10^{-2}$M.

In nitromethane the increase in molar extinction coefficient is accompanied by the disappearance of a weak band at 5940 Å and the more intense features of the spectrum of $[CoCl_4]^{2-}$ in nitromethane are finally obtained [9] as shown in Fig. 1A. (Fig. 1B shows the spectrum before chloride addition.) Comparison with the diffuse reflectance spectrum of Cs_3CoCl_5 given in Fig. 1C confirms the supposition that the spectrum obtained in the presence of excess of chloride ion is the spectrum of the authentic $[CoCl_4]^{2-}$ ion. Since, as

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[5] (*a*) Kiss and Gerendas, *Z. phys. Chem.*, 1937, *A*, **180**, 117; (*b*) Dreisch and Trommer, *ibid.*, 1937, *B*, **37**, 37; Robinson and Brown, *Trans. Proc. Roy. Soc.* (*N.Z.*), 1948, **77**, 1; Katzin, *J. Amer. Chem. Soc.*, 1954, **76**, 3089.

[6] Smithson and Williams, *J.*, 1958, 457.

[7] Libus, Ugniewska, and Minc, *Roczniki Chem.*, 1960, **34**, 29; Barbinok, *J. Phys. Chem.* (*U.S.S.R.*), 1948, **22**, 1100.

[8] Katzin and Gebert, *J. Chem. Soc. Amer.*, 1950, **72**, 5464.

[9] Buffagni and Dunn, *Nature*, 1960, **188**, 937.

will be reported elsewhere, the diffuse reflectance curve is the same as the single-crystal absorption spectrum of Cs_3CoCl_5 and, in addition, the spectrum in chloride-saturated nitromethane is independent of the nature of the cation and obeys Beer's law over a concentration range of 50 (from $0{\cdot}5 \times 10^{-4}$M to $2{\cdot}5 \times 10^{-3}$M), the spectrum in Fig. 1A is undoubtedly that of $[CoCl]_4]^{2-}$.

In dimethylformamide solution the spectrum is very different and is given in Fig. 1D for absence of chloride; the spectrum in the presence of chloride assumes the contour of Fig. 1A but with rather different $\varepsilon_{max.}$ values. Similar spectra have previously been obtained by Katzin and Gebert [8] for solutions of cobalt chloride in some organic solvents, such as benzene, quinoline, and chloroform. The $\varepsilon_{max.}$ values obtained for nitromethane and dimethylformamide solutions seem to depend only on the solubility limit of the arsonium chloride $Ph_3MeAsCl$ which, being more soluble than either of the ammonium salts, yields the highest value. The values obtained are given in the Table, and it must be emphasized that they are not necessarily the usual *molar* extinction coefficients since, as will be seen below, not all the absorption arises from a single absorbing species. For this reason, all the figures have been presented with an arbitrary ordinate of percent transmission *T*. Also, the solutions do not obey Beer's law in the absence of chloride and the values in the Table are for 1 cm. of solution having an optical density about 0·3, *i.e.*, 50% transmission.

	Peak 1		Peak 2		Peak 3		Peak 4	
Solvent	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
NM	6940	622	6690	555	6350	418	5950	100
NM + Me_4NCl	6950	705	6680	606	6340	440		
NM + $Ph_3MeAsCl$............	6950	750	6680	630	6340	465	6150s	200
DMF	6780	490			6100	295		
DMF + Me_4NCl	6890	600	6740	590	6350	392	6120	282
DMF + $Ph_3MeAsCl$	6950	820	6680	688	6350	513	6150s	215
H_2O + 12M-HCl	6970	620	6625	576	6233	385		

The ε values have been calculated on the basis that all the absorption is caused by a single species, and so the concentration of cobalt ion is the only value used. These "effective" extinction coefficients are useful since many of the spectra of the different species are superposed, making it impossible to disentangle them completely. A Beer's law check on the solutions of $[CoCl_4]^{2-}$ ions in dimethylformamide in the absence of added chloride shows a decrease of about 15% in ε on ten-fold dilution over the concentration range 10^{-4} to 10^{-5}M, so that it is clear that the solvent is involved in some rôle other than that of "passive" solvation. To ascertain the nature of the species present in the solutions, various procedures have been used and these will be discussed in turn.

(a) *Addition of Chloride Ion to a Solution of* $[CoCl_4]^{2-}$ *Ion.*—The solutions of $[CoCl_4]^{2-}$ ion in nitromethane and dimethylformamide have been studied spectrophotometrically over the range 8000—3500 Å at varying chloride concentrations. The method of continuous variations was not used since it can lead to incorrect conclusions, as has been pointed out by Libus, Ugniewska, and Minc.[7] Since the spectrum in dimethylformamide is different from that in nitromethane at low chloride concentrations ($\sim 10^{-2}$M), dimethylformamide was added to the chloride-saturated nitromethane solution to observe the interconversion. No change was found up to 30% of added dimethylformamide and above this limit there was a gradual change to the spectrum observed in pure dimethylformamide. The effect of changing the chloride concentration is, however, much more drastic and is used here to illustrate the differences between, as well as the interconversion of, the two species. A solution of $[CoCl_4]^{2-}$ ion in 4 : 1 nitromethane–dimethylformamide shows three isosbestic points as the chloride concentration is varied and this is illustrated in Fig. 2. Small amounts of water were also added: spectra taken during 48 hours then showed only a very small instantaneous decrease in ε of the tetrahedral species with no important changes with time. In fact, if cobalt chloride hexahydrate is dissolved in dimethylformamide directly,[10] the solution is blue and contains about 30% of tetrahedral species. From what follows it is clear that any added water forms a small amount of octahedral complex of the type $[Co(H_2O)_x(DMF)_yCl]$ and/or $[Co(H_2O)_p(DMF)_qCl_2]$ where $x + y = 5$ and $p + q = 4$.

The presence of three isosbestic points proves that essentially only two species are present. One of these has been identified beyond doubt as $[CoCl_4]^{2-}$. It is postulated that the other is $[CoCl_3(DMF)]^-$ on grounds of previous work,[8] and of probability, and from other evidence which follows. Conductivities have yielded no unambiguous information as to the nature of the species present since the solutions are never obtained with, beyond doubt, only two interconverting ions.

(b) *Addition of Chloride Ion to the Complex* $[Co(DMF)_6][ClO_4]_2$.—When a $[CoCl_4]^{2-}$ salt is dissolved in dimethylformamide, a weak band appears at about 5300 Å which is usually associated with an octahedral species. This band disappears when chloride is added to the solution, the octahedral being transformed into a tetrahedral form. In an endeavour to examine this equilibrium, the complex $[Co(DMF)_6[ClO_4]_2$ was prepared; its solution in dimethylformamide has a single broad band, with some structure, and a maximum at 5250 Å (ε 21) (Fig. 3A). Curves 3B—D show the effect of added chloride ion, the final species being $[CoCl_4]^{2-}$ (not shown in Fig. 3). A finely graded series of spectra with respect to changing chloride concentration shows that in the Cl : Co range from 0 : 1 up to 7 : 1, the species previously postulated as $[CoCl_3(DMF)]^-$ exists in equilibrium with the octahedral complex, as shown by the presence of an isosbestic point. For ratios $\geqslant 8 : 1$ the same isosbestic points as are shown in Fig. 2 again appear, corresponding finally to conversion into $[CoCl_4]^{2-}$. In fact, there is never 100% conversion into $[CoCl_4]^{2-}$ in dimethylformamide when fully saturated tetramethylammonium chloride solutions are used, and it is not certain whether complete conversion is obtained even in the saturated solutions of the more soluble chlorides. The spectra overlap considerably and an exact estimate of the amounts of the individual species present cannot be made.

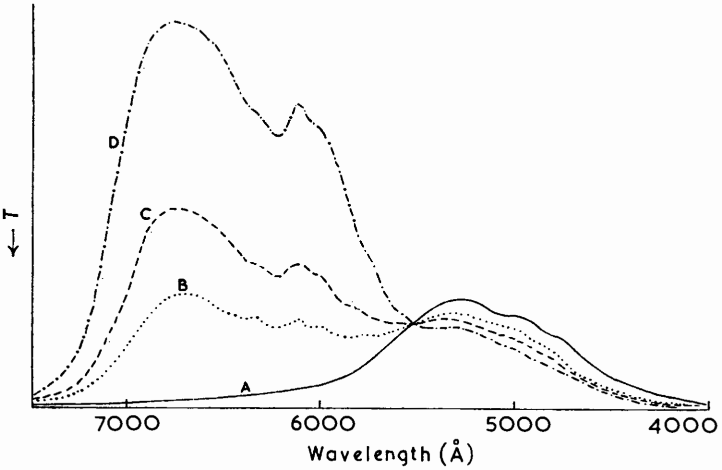

FIG. 3. Absorption spectrum of $4{\cdot}4 \times 10^{-3}$M-$[Co(DMF)_6](ClO_4)_2$ in 9 : 1 dimethylformamide–nitromethane containing added chloride of concentrations (A) 0, (B) 1·2, (C) 1·8, and (D) $4{\cdot}2 \times 10^{-3}$M.

It seems certain also that more than one octahedral species is present at low Cl : Co ratios, since there are small but consistent shifts of the octahedral band maximum on the

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[10] Pflaum and Popov, *Analyt. Chim. Acta*, 1955, **13**, 165; Dunn, Proc. Internat. Conf. Spectroscopy, Bologna, 1959, in the press.

addition of chloride. One additional species is certainly formed, and perhaps also a second. By analogy with the behaviour of $[Mn(H_2O)_6](ClO_4)_2$ on addition of chloride,[11] it is assumed that the second species is $[Co(DMF)_5Cl]^+$, the doubtful one being $[Co(DMF)_4Cl_2]$. The isosbestic point is not much affected by this multiplicity of octahedral species since the extinction coefficient at the crossing point is almost identical for both (or all) of them. There are, however, small departures from a strict " point " crossing which confirm the presence of more than two interconverting species (this is also true of the tetrahedral form—see below).

At the highest chloride concentrations attainable with the methylammonium salt, it is found that the dimethylformamide solutions obey Beer's law to within experimental error over a dilution range from 10^{-3} to 5×10^{-5}M, chloride-saturated dimethylformamide being the diluent; and the ratios of the individual peak heights also remain constant within experimental error. Unfortunately it is not possible to determine the equilibrium constants of the various reactions taking place during the octahedral–tetrahedral conversion since, apart from activity considerations,[6] up to a Cl : Co ratio of about 8 : 1 there are probably five species present, namely, $[CoCl_4]^{2-}$, $[CoCl_3(DMF)]^-$, $[Co(DMF)_4Cl_2]$, $[Co(DMF)_5Cl]^+$, and $[Co(DMF)_6]^{2+}$. If the presence of $[Co(DMF)_4Cl_2]$ is ignored, analysis of the results shows that at the concentration represented by curve 3C (*i.e.*, a Cl : Co ratio of 0·27 : 1) the solution contains $[Co(DMF)_6]^{2+}$ 72%, $[Co(DMF)_5Cl]^+$ 21%, $[CoCl_3(DMF)]^-$ 6·5%, and $[CoCl_4]^{2-}$ 0·5%. The analysis holds good below Cl : Co ratios of about 0·5 : 1, but above this value there seems to be a change in mechanism of formation and the concentration of $[CoCl_4]^{2-}$ rises quickly with respect to that of $[CoCl_3(DMF)]^-$ and there is also a change in the ratio of $(Co(DMF)_6]^{2+}$ to $[Co(DMF)_5Cl]^+$. The set of equilibria is now being studied in much more detail.

(c) *Addition of Chloride Ion to Solutions of Anhydrous Cobalt Chloride.*—Anhydrous cobalt chloride was dissolved severally in nitromethane and dimethylformamide in an endeavour to confirm the nature of the species postulated above.

(i) *Nitromethane solution.* The spectra obtained can be explained on the basis of the following equilibria:

$$CoCl_2 + NM \rightleftharpoons [CoCl_2(NM)_2]$$

$$[CoCl_2(NM)_2] + Cl^- \rightleftharpoons [CoCl_3(NM)]^- + NM$$

$$[CoCl_3(NM)]^- + Cl^- \rightleftharpoons [CoCl_4]^{2-} + NM$$

Experimentally, three distinct spectra (Fig. 4) were observed depending on the concentration of added chloride. Curve 4A is obtained only when the nitromethane and cobalt chloride are dried to the practical limit and addition of chloride, or water in small amounts, converts it into 4B, which is then converted into 4C by further addition of chloride. It is clear that curve 4C is the spectrum of $[CoCl_4]^{2-}$ and 4B is that of the species which occurs when $[CoCl_4]^{2-}$ is simply dissolved in pure dry nitromethane (see Fig. 1B). The species giving rise to curve 4B is here formulated as $[CoCl_3(NM)]^-$, and that giving rise to 4A as $[CoCl_2(NM)_2]$. The latter assignment is supported by the fact that this solute is a non-electrolyte. No evidence of an octahedral species was found in these dry solutions, although it was carefully looked for. There does not seem, therefore, to be an equilibrium of the octahedral–tetrahedral type in a solution of cobalt chloride in nitromethane and this possibly explains the appearance of the $[CoCl_2(NM)_2]$ which has no analogue in the dimethylformamide solution (see below). In view of the *a priori* possibility [12] of the loss of Cl^- from cobalt chloride the solution was examined for traces of chloride down to about 10^{-5}M; that none was found seems to eliminate the possibility that the *aci*-nitromethane negative ion is the co-ordinating species rather than nitromethane itself. The true molar extinction coefficient of the $[CoCl_3(NM)]^-$ species lies in the range 300—400 and that of

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[11] Schlafer, *Z. phys. Chem.*, 1956, **6**, 201; Jörgensen, *Acta Chem. Scand.*, 1957, **11**, 53.

[12] Pocker, *J.*, 1958, 240.

$[CoCl_3(NM)_2]$ in the range 65—75, but it is difficult to determine them with certainty, since there is always enough water present in the solutions to allow some " disproportionation " of $[CoCl_2(NM)_2]$ into $[CoCl_4]^{2-}$ and $[CoCl_3(NM)]^-$, with probably some $[Co(H_2O)_5Cl]^+$ or $[Co(H_2O)_6]^{2+}$. Again, however, the concentration of these octahedral species is too small to be detected spectroscopically since the total cobalt concentration of the solution is only about 10^{-3}M.

(ii) *Dimethylformamide solution.* The situation here is somewhat different from that of nitromethane solutions, and the spectra can be explained on the basis of the equilibria:

$$2CoCl_2 + DMF \rightleftharpoons [CoCl_4]^{2-} + [Co(DMF)_6]^{2+}$$

$$[CoCl_4]^{2-} + DMF \rightleftharpoons [CoCl_3(DMF)]^- + Cl^-$$

$$[Co(DMF)_6]^{2+} + Cl^- \rightleftharpoons [Co(DMF)_5Cl]^+ + DMF$$

Both in the presence and in the absence of extra chloride, only two tetrahedral species need be postulated to explain the spectra, *viz.*, $[CoCl_4]^{2-}$ and $[CoCl_3(DMF)]^-$, the former to an extent of about 15—20%. The tri- and the tetra-chloride are readily formed in dimethylformamide since the octahedral species discussed in section (*b*) are formed readily in dimethylformamide and, since the Cl : Co ratio is only 2 : 1, the spectrum obtained is similar to one of those given already in Fig. 3. The molar extinction coefficient of the $[CoCl_3(DMF)]^-$ species is not known with certainty, but seems to be about 350. This has been estimated by subtracting curves corresponding to known amounts of $[CoCl_4]^{2-}$ from the experimental curve and can be done more readily here than for nitromethane solutions since no other tetrahedral species corresponding to $[CoCl_2(NM)_2]$ has been found in quantity.

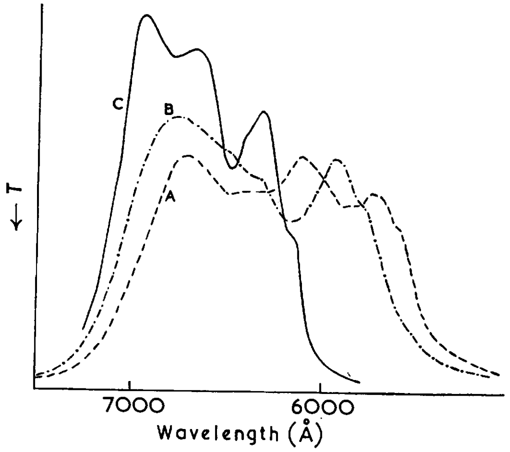

FIG. 4. Absorption spectrum of anhydrous cobalt chloride in dry nitromethane. (A) No added chloride; (B) 10^{-4}M in chloride, 10^{-4}-M in Me_4NCl; (C) 10^{-2}M in chloride.

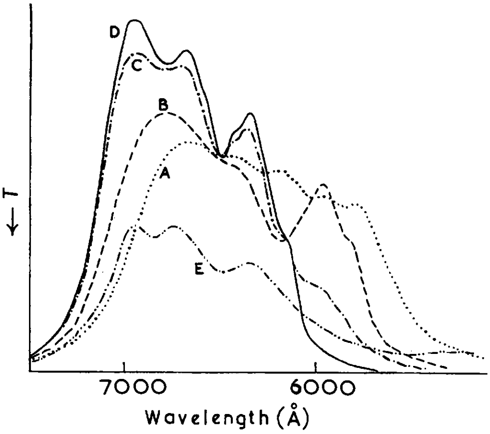

FIG. 5. Absorption spectra of $CoCl_2(DMF)_2$ in dry nitromethane, containing added chloride in concentrations (A) 0, (B) 10^{-4}, (C) 10^{-3}, and (D) 10^{-2}M. (E) Diffuse reflectance spectrum of solid $CoCl_2(DMF)_2$.

These subtractions were, in fact, done with the reference cell in a double-beam spectrophotometer containing various amounts of $[CoCl_4]^{2-}$ in a $Ph_3MeAsCl$-saturated dimethylformamide solution. The difference curve is plotted by the spectrophotometer and it is relatively easy to observe the cross-over point from too much $[CoCl_4]^{2-}$ to too little. Since the total cobalt concentration is known it is possible to find the amount locked in the octahedral forms, and the concentration of $[CoCl_3(DMF)]^-$ in the original solution can thus be determined. In this way it has been established that a solution of cobalt chloride in dimethylformamide contains, approximately, $[CoCl_4]^{2-}$ 10%, $[CoCl_3(DMF)]^-$ 35%, and 55% of various octahedral species. It is interesting that these values allow exactly one chloride ion per octahedral species and so the predominant ion is probably $[Co(DMF)_5Cl]^+$, although some $[Co(DMF)_4Cl_2]$ and some $[Co(DMF)_6]^{2+}$ may be present.

(d) *Isolation of a " Tetrahedral " Cobalt Complex of* DMF *and* Cl^-.—A complex with the empirical formula $CoCl_2(DMF)_2$ has been isolated and its spectrum measured both in nitromethane and as a solid by diffuse reflectance. The two spectra are completely different and the original hope that the solid would be the analogue of $[CoCl_2(NM)_2]$ was vain.

The spectra in nitromethane solution are interesting and have been studied with respect to both chloride and dimethylformamide addition. The spectrum for nitromethane solution given in Fig. 5A and its similarity to that of the postulated species $[CoCl_2(NM)_2]$ and $[CoCl_3(NM)]^-$ in Figs. 4A and B should be noted. It is, however, slightly different and this cannot be due simply to its being a superposition of various amounts of these two species, since there are small differences in $\lambda_{max.}$, particularly in the longest wavelength band. The spectrum does not obey Beer's law and appears to be brought near that of $[CoCl_2(NM)_2]$ by changing the relative intensities and positions of its bands; it is therefore suggested that the original spectrum arises from either $[CoCl_2(DMF)_2]$ or $[CoCl_2(NM)(DMF)]$; it is clearly never free from large amounts of $[CoCl_3(NM)]^-$.

Addition of chloride (curves 5B—D) seems to give anomalous results in that the spectrum of the species $[CoCl_3(NM)]^-$ appears first, to be followed by that of $[CoCl_4]^{2-}$. It seems that the addition results in replacement of dimethylformamide in the complex by Cl^-. Addition of dimethylformamide in small amounts (<5%) to the original solution (without addition of Cl^-) does not produce marked changes, but merely depresses the short-wavelength bands and increases the intensity of the band in the region of 6800 Å. This is almost certainly due to formation of small amounts of $[CoCl_3(DMF)]^-$.

The diffuse reflectance spectrum of the solid $CoCl_2(DMF)_2$ is shown in curve 5E. It is not identical with any of the solution spectra but, because of its contour and position, it could be present up to 20% concentration without being observed. This spectrum shows marked similarities with that of Cs_3CoCl_5 (Fig. 1C) and, in addition, has a weak band at about 5250 Å which is where $[Co(DMF)_6]^{2+}$ absorbs. On these grounds, the complex has been formulated tentatively as $[Co_2Cl_6][Co(DMF)_6]$, *i.e.*, as containing a dimeric tetrahedral cobalt chloride anion.

(e) *Diffuse Reflectance Spectra.*—The diffuse reflectance spectra have been discussed briefly above but it is important to emphasize that the present work has confirmed the essential identity of the diffuse reflectance, Nujol mull, and single-crystal measurements on the salts Cs_3CoCl_5, $[Et_4N]_2[CoCl_4]$, and $[Ph_3MeAs]_2[CoCl_4]$. The contours are identical within experimental error, even though there are slight differences (~200 cm.$^{-1}$) in the wavelengths of the maxima obtained by the different methods. It is then difficult to understand the spectra of $[CoCl_4]^{2-}$ in bromide discs at —196° (see Katzin[5]), and some of the bands in the aqueous solution measurements[5a] (in 13N-hydrochloric acid). Since it seems that only about two-thirds of the cobalt is present as tetrachlorocobaltate under these conditions it might well be that some of the bands are caused by the species $[CoCl_3(H_2O)]^-$.

(f) *Spectra in Other Non-aqueous Solvents.*—The spectra of cobalt(II) chlorides have also been examined for solutions in dichloromethane, ligroin, tetramethylene sulphone, dimethylacetamide, dimethyl sulphoxide, and ethyl acetate. In all cases, except dichloromethane, a solution of $[Ph_3MeAs]_2[CoCl_4]$ has much the same spectrum as in dimethylformamide. The spectrum in dichloromethane is identical in contour with that of $[CoCl_4]^{2-}$ in nitromethane, although the $\varepsilon_{max.}$ value is 675 compared with 705 for tetramethylammonium chloride-saturated nitromethane solution. The dimethyl sulphoxide solution contains only a relatively small amount of tetrahedral species (~20%), and most of the solute is present as various octahedral forms; the spectra of these solutions are given in Fig. 6.

The order of the solvents with respect to preservation of the original tetrahedral species is $CH_2Cl_2 > NM > DMA > DMF > DMS > EtOAc$, and the lack of co-ordinating power of dichloromethane appears to suggest its use as a convenient solvent for inorganic spectroscopy.

The spectrum of anhydrous cobalt chloride in each of these solvents has also been obtained and, in most cases, the effects of added chloride observed. The curves for ligroin solution are shown in Fig. 7, since one of the many coincidences which are a feature of the tetrahedral cobalt solutions is here apparent. Thus the spectrum at lowest chloride concentration shows little evidence of $[CoCl_4]^{2-}$ (<10% must be present, as seen from the changing peak height of the 5850 Å band) and yet there are already three bands (those at 6680, 6400, and 6280 Å) which are common to both the initial and the final species (the presence of exceptionally sharp isosbestic points proves there to be only two species).

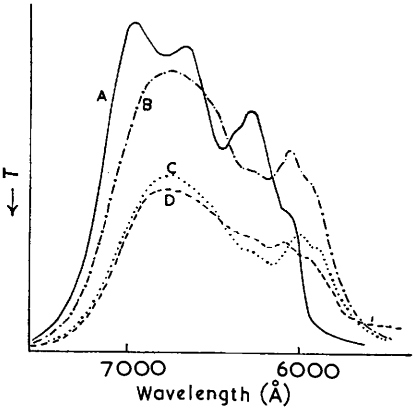

FIG. 6. Absorption spectrum of $[CoCl_4]^{2-}$ in (A) dichloromethane, (B) dimethylacetamide, (C) dimethylformamide, and (D) dimethyl sulphoxide.

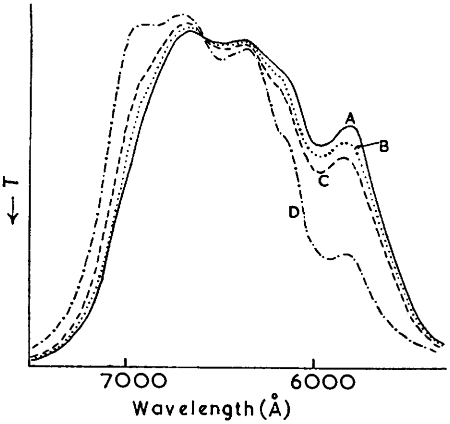

FIG. 7. Absorption spectrum of anhydrous cobalt chloride in ligroin solution containing 1% of dimethylformamide: (A) pure solvent; (B—D) added chloride, (B) 10^{-5}M, (C) 10^{-4}M, (D) 10^{-3}M.

Of the other spectra it suffices to say that all have the contours of the various tetrahedral species $[CoCl_3S]^-$ (where S = solvent), thereby showing the capacity of the solvents to disproportionate the solute and to form octahedral and tetrahedral species. Only with ethyl acetate is it by no means clear that a tetrahedral species is involved, since the spectrum is sufficiently different to make it impossible to claim definitely a tetrahedral or a square planar form (or a badly distorted form between the two). The solubility of cobalt chloride in nitromethane is unfortunately too low to allow accurate magnetic moment measurements as a check on the assumption [13] that the species giving rise to the spectra is spin-free planar cobalt. The spectra obtained are not discussed individually since the general principles of their reactions with the solvent seem to be those discussed above.

Conclusions.—Three different spectra have been found for solutions of cobalt chloride in nitromethane, including those containing added chloride ion. The first of these species (see Fig. 4A) is a non-electrolyte, and this supports its formulation as $[CoCl_2(NM)_2]^0$. It retains some features of the $[CoCl_4]^{2-}$ spectrum, but it is not impossible for it to be badly distorted from a perfect tetrahedron towards a square shape, as are the copper tetrahalides.[14] The second species (see Fig. 4B) is very similar in spectrum to $[CoCl_4]^{2-}$, and it seems that its distortion is not much larger than that for $[CoCl_4]^{2-}$, although if the distance between

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[13] Cotton and Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 2979.

[14] Helmholz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

the 6800 and the 5940 Å peaks is taken as a measure of distortion, then it is more distorted than $[CoCl_4]^{2-}$ by somewhat less than 1000 cm.$^{-1}$ energetically. This second species is never obtained on its own, but always accompanied by $[CoCl_4]^{2-}$, estimated at 10—20%, so that it is not possible to get absolutely unique isosbestic points for its conversion into $[CoCl_4]^{2-}$. It seems likely, however, that, being intermediate between a non-electrolyte of formula $[CoCl_2(NM)_2]$ and the ion $(CoCl_4]^{2-}$, it is to be identified as $[CoCl_3(NM)]^-$.

As has been observed above, the same species appears when $[CoCl_4]^{2-}$ is dissolved in dry nitromethane and the suggested assignment thus appears highly probable. Conductivity data do not unambiguously assign the species as a mononegative ion, since there are at all times two other species present, one a non-electrolyte and the other doubly charged, and both are present in unknown amounts (since all three spectra overlap badly) so that the results are not definitive. Efforts to obtain the material as a solid have failed, but there seems little doubt as to its nature.

In a dimethylformamide solution of $[CoCl_4]^{2-}$ salts it can be shown that there is about 30% of $[CoCl_4]^{2-}$ present, together with some other species which it has been suggested is $[CoCl_3(DMF)]^-$. The figure of 30% is reasonably certain, since a fair estimate of the true molar extinction coefficient has been obtained from experiments of the type described in sections (b) and (c). The coefficient is ~350, and curve 8A shows a solution of $[CoCl_4]^{2-}$ in dimethylformamide, while 8B is a curve obtained by subtracting 30% of $[CoCl_4]^{2-}$ from A. The latter curve bears a strong resemblance in contour to curve 4B for $[CoCl_3(NM)]^-$ and it seems safe to conclude that both of these species are of the type $[CoCl_3S]^-$. The similarity, and yet difference, between the nitromethane and dimethylformamide species provide evidence that the spectra observed in non-aqueous solvents are not due to a simple polymerisation or association of the solute (since the spectra would be the same in that case, apart from a small solvent shift). The value of the molar extinction coefficient for the species $[CoCl_2(NM)_2]$ is worthy of comment. The very low value found (65—75) strongly suggests a large distortion towards a square-planar shape or at least some species possessing a pseudo-centre of symmetry. Such square-planar forms have been postulated by Cotton and Holm,[13] and their spectra are not dissimilar to that given in Fig. 4A—Cotton and Holm's $\varepsilon_{max.}$ are somewhat lower, but this is unimportant in view of the difficulty experienced in measuring this value and it should be taken as indicating only the correct magnitude.

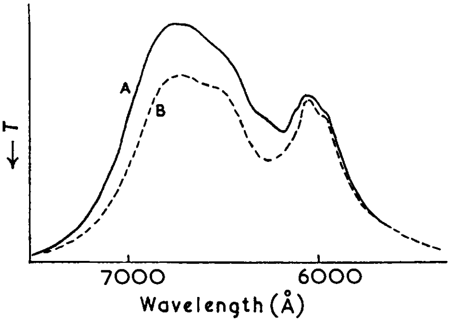

FIG. 8. (A) Absorption spectrum of $[CoCl_4]^{2-}$ in dimethylformamide solution. (B) The same curve after subtraction of that for 30% of $[CoCl_4]^{2-}$.

All the spectra of solid $CoCl_2(DMF)_2$ in nitromethane solution can be explained in terms of superposition of varying amounts of the species $[CoCl_2(NM)(DMF)]$ and $[CoCl_2(NM)_2]$, together with $[CoCl_3(NM)]^-$, and justify confidence in the correctness of the assignments made.

It has not proved possible to obtain the equilibrium constants of the many equilibria involved, but it is hoped that this can be done by other methods. In addition, the equilibria of the tetrabromocobaltate ion and of the nickel tetrahalides have been examined and will be discussed elsewhere.

EXPERIMENTAL

Purification of Solvents.—(a) *Nitromethane.* Two methods of preparing pure dried nitromethane were used since that using phosphorus pentoxide [12] was not suitable for spectroscopic work because of the fine suspended solid material present even after distillation. Nitromethane was refluxed with active charcoal for 24 hr., a current of oxygen-free nitrogen being bubbled through the liquid. The suspension was then filtered, dried (Na_2SO_4), and distilled, the fraction of b. p. 101—102°/760 mm. being collected. This was twice passed through an alumina column and redistilled. The method for the solvent used in conductivity measurements is that described by Pocker.[12] It was never found possible to obtain a water content below about 0·02% ($\sim 10^{-2}$M).

(b) NN-*Dimethylformamide.* Benzene (5% by volume) was added to the solvent, and the azeotrope over the range about 85—120° collected and then distilled twice; the fraction boiling at 155·0—155·2°/760 mm. was redistilled at about 5 mm., the final solvent having b. p. 50—51°. It was stored out of contact with oxygen and tested with 1-fluoro-2,4-dinitrobenzene for traces of colour indicating the presence of free amine. The water content of these solutions was usually in the range 0·05% ($\sim 2 \times 10^{-2}$M).

Preparation of Complexes.—(*a*) The tetrahedral cobalt complexes used were either kindly supplied by Dr. N. S. Gill [3] or prepared according to the literature.[3]

(*b*) The complex $[Co(DMF)_6](ClO_4)_2$ was prepared by stoicheiometric addition of silver perchlorate to a solution of anhydrous cobalt chloride in dimethylformamide. Silver chloride was filtered off and the complex precipitated by dried ether. The *complex* is a pale pink, very hygroscopic solid (Found: C, 31·4; H, 6·5; Cl, 10·2; N, 12·3. $C_{18}H_{42}Cl_2CoN_6O_{14}$ requires C, 31·0; H, 6·1; Cl, 10·2; N, 12·1%). The magnetic moment of the solid was determined at 297° K as 5·03 B.M., this being normal for an octahedral complex of the suggested type.

(*c*) The *complex* $CoCl_2(DMF)_2$ was precipitated from dimethylformamide solutions of anhydrous cobalt chloride by an excess of ether. It separates as a dark blue microcrystalline solid which is extremely hygroscopic and must be kept over P_2O_5 (Found: C, 27·0; H, 5·35; Cl, 26·25; N, 10·5. $C_6H_{14}Cl_2CoN_2O_2$ requires C, 26·1; H, 5·1; Cl, 25·7; N, 10·15%).

Conductivities.—These measurements were definitive only for nitromethane solutions. A saturated nitromethane solution of cobalt chloride at 20° gave a conductivity of $3{\cdot}20 \times 10^{-6}$ ohm^{-1} cm.^{2}, compared with a value of $2{\cdot}03 \times 10^{-6}$ ohm^{-1} cm.^{2} for pure nitromethane (which rises to $2{\cdot}40 \times 10^{-6}$ ohm^{-1} cm.^{2} after 10 min.). These solutions are about 10^{-3}M in $CoCl_2$, so that the molar conductance is about unity compared with about 100 for a uni-univalent electrolyte, 175—200 for a uni-bivalent electrolyte, and 250 for a uni-tervalent electrolyte.[3] The results confirm the non-electrolyte character of the solute.

The solutions were examined for traces of free hydrogen chloride by streaming a current of dry nitrogen through them, condensing any volatile material in a liquid-oxygen trap, and titrating the condensed liquid. Addition of hydrogen chloride to pure nitromethane showed that it could be detected in concentrations as low as about 10^{-5}M. None was detected in the solution described above.

Spectral Data.—Solution spectra were done both with a Cary model [10] and a Unicam S.P. 500 instrument. The solid spectra were examined by using the Unicam diffuse reflectance apparatus attached to a normal Unicam S.P. 500 instrument.

Anhydrous Chemicals.—Anhydrous cobalt chloride was obtained by drying the hexahydrate at 130° for 4 hr. and allowing it to cool over P_2O_5. Methyltriphenylarsonium, tetraethylammonium, and tetramethylammonium chloride were dried under reduced pressure at 100°.

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