81. *A Possible Differentiation between Ion-pairs and Complexes.*

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A study has been made of the association between several anions and the cobaltous ion. The absorption spectra of the species involved are discussed as they lead to a possible method for distinguishing between transition-metal cation complexes and ion-pairs.

Ion-pairs and Complex Formation.—A simple theoretical distinction between the complex of a cation M and a ligand L and an ion-pair can be made by looking upon the former as the associated group ML in which L is adjacent to M and the latter as an associated unit M(S)L where S, a solvent molecule such as water, lies between M and L.* The distinction has been of limited use because most methods of examination of a solution containing M and L will not distinguish between the alternatives. However if M is a transition-metal cation, such as cupric, and has two sets of absorption bands, one of high intensity in the ultraviolet and one of much lower intensity in the visible region, as is generally so for such cations, a possible method of differentiation arises. The weak bands in the visible region are forbidden *d–d* transitions and the wavelength of the absorption depends on the separation (splitting) of the *d* states. This splitting is a function of the polarisation of the cation by the ligand. The splitting therefore depends upon a high power of the inverse of the distance of separation, r, between the ligand and the cation, possibly varying[1] as r^{-5}. Ion-pair formation will be expected then to have very little effect on this *d–d* splitting because of the large separation between M and L in ion-pairs. The ultraviolet bands of the solutions of transition-metal cations are considered to be

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* It is not an essential part of this definition that there should be only one solvent molecule between M and L but that there should be at least one.

[1] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 405.

charge-transfer bands.[2] The dependence of the stability of the excited state relative to the ground state upon r therefore must be more nearly as r^{-1} than r^{-5} as the expression for the energy of interaction in one (or both) of the states contains [2] terms in r^{-1}. Both ion-pair and complex formation will be expected to affect the position of the ultraviolet bands, the latter to the greater degree. Naturally changes of extinction coefficient are expected concomitant with changes in the position of the absorption but it has not been possible to develop a generally accepted theoretical discussion.[1,3]

Thus, by observing changes in both ultraviolet and visible spectra in a series of transition-metal complexes we might be able to discover whether ion-pairs or complexes were formed. This examination will be the more thorough if it is made together with studies of activity coefficients. The method of treating association equilibria should be capable of extension to studies of anions in which there are forbidden transitions, *e.g.*, the nitrate ion, for all such transitions depend upon changes in polarisation of one member of the unit ML rather than on changes in the dipole of ML.

As examples we will consider some cobaltic complexes and ion pairs, where the differentiation between the two types of association can be made clearly as the rate of exchange of ligands in the co-ordination sphere is extremely slow. Table 1 lists[4] some spectroscopic observations on pentamminocobaltic complexes in which there is one further ligand. In these associated units the anion is adjacent to the cation. The absorption band referred to in the Table is due to an internal *d–d* transition of the cobaltic ion and is sensitive to the ligand in the complex as expected.

TABLE 1. *Absorption spectra of pentamminocobaltic complexes.*

Ligand in 6th co-ordination place ...	NH_3	H_2O	SCN^-	$S_2O_3^{2-}$	NO_3^-	SO_4^{2-}	Cl
$\lambda_{max.}$	472	490	497	500	500	515	531
$\log \varepsilon_{max.}$	1·74	1·68	2·28	—	1·75	1·75	1·71

In two or three cases the corresponding hexamminocobaltic and aquopentamminocobaltic ion pairs have also been studied, in which it is known from exchange studies that the anion and cation are not adjacent. For example Taube and Posey[5] found that the position and the intensity of the absorption band due to the *d–d* transition of the aquopentamminocobaltic sulphate ion-pair were the same as those of the unassociated perchlorate. Similar observations[6] have been made on the chloride, bromide, and iodide ion-pairs of this cation and of the hexamminochromic cation. Although there are no changes in the *d–d* bands, the ultraviolet absorption spectra, of high extinction, is considerably modified. Bale, Davies, and Monk have shown[7] that on the formation of the hexamminocobaltic sulphate and thiosulphate ion-pairs there is no change in the visible absorption although the ultraviolet absorption changes appreciably. In all these cases the stability of the ion-pairs could be calculated from the changes in the ultraviolet spectra with concentration of the ions. Such observations are in keeping with the theoretical argument made above. In the study[5] of the association of sulphate and the aquopentamminocobaltic ion it was shown that the equilibrium constants for the formation of the ion-pair $[Co(NH_3)_5H_2O]^{3+}SO_4^{2-}$ and for the complex $[Co(NH_3)_5SO_4]^-$ were almost equal. We will show that what we take to be the ion-pair of cobaltous sulphate has almost the same stability as the complex of cobaltous thiosulphate.

The nitrate ion has a forbidden transition which gives rise to absorption around 300 mμ. In organic solvents spectra of solutions of anhydrous nitrates show that this band is considerably modified and it has been generally accepted that the change is brought about

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[2] Orgel, *Quart. Rev.*, 1954, **8**, pp. 424 and 440.

[3] Ballhausen, *Acta Chem. Scand.*, 1955, **9**, 821.

[4] von Kiss and Czegledy, *Z. anorg. Chem.*, 1938, **235**, 407.

[5] Taube and Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.

[6] Linhard and Weigel, *Z. anorg. Chem.*, 1951, **266**, 49.

[7] Bale, Davies, and Monk, *Trans. Faraday Soc.*, 1956, **52**, 816.

by the polarisation of the nitrate anion in complexes with the cations.[8] Supporting this deduction is the fact that the greatest changes in the nitrate band occur in the order of cations of transition metals, A-sub-group metals of high charge or small size, A-sub-group metals of low charge or large radius (*e.g.*, $Li^+ > K^+$, $Mg^{2+} > Ca^{2+}$). In aqueous solutions of the same molarity the order of the effect of different cations is completely altered to $K^+ > Li^+$ and $Ba^{2+} > Ca^{2+} > Mg^{2+}$,[9,10] which suggests that the larger cations form complexes to the greater degree. The study of activity coefficients of nitrates has been taken to show that it is the larger cations which associate with the nitrate ion to the greater extent.[11] In the case of lead nitrate [12] the two methods, studies of absorption spectra changes and of reversible electrode potentials, led to the same association constant. As the spectroscopic method depended on examining the intensity changes of a forbidden transition we consider that a complex is formed. Now if the perchlorates of bivalent cations are taken as a standard of non-associated 1 : 2 electrolytes then the activity coefficients of all nitrates, which are lower, imply some kind of specific interaction. By examining the spectra of solutions of a transition-metal nitrate both in the region of the nitrate absorption and that of the cation absorption, complex formation should be easily detected. Moreover apart from the perchlorate we can use the chloride ion and the iodide ion as reference anions as the activity coefficients of many iodides are very like those of perchlorates and the activities of certain chlorides are very like those of nitrates, *e.g.*, cobaltous. We have chosen the cobaltous cation for this study as the absorption spectra of cobaltous salts are very sensitive, especially in intensity, to changes in the co-ordinating ligands.

EXPERIMENTAL

We studied the changes in absorption spectra of cobaltous ion solutions in media of constant ionic strength. The conditions are given in Table 2. Univalent perchlorates were used to make up the ionic strength.

The measurements were made with the Unicam S.P. 500 and 600 spectrophotometers with matched cells at 20° ± 1°. All absorption spectra were measured against blanks made up in the same manner as the test solution but with the cation omitted. All reagents were " AnalaR." As all previous spectrophotometric measurements on these systems [13-15] were made without a constant ionic-strength background and without appropriate blanks we cannot strictly compare them with our observations nor is it easy to use them to discuss the spectra or stability of individual complexes ML.

Results.—We will take the study of the thiocyanate solutions as a typical example. Two changes in the absorption bands appear on adding thiocyanate to cobaltous perchlorate. One is at 275 mμ where the absorption is of high extinction. This is considered to be a charge-transfer band. The second is a smaller change, being a modification of the *d*–*d* transition, at 575 mμ. The two bands increase proportionately, showing that they belong to species which have the same dependence on thiocyanate concentration. The simplest assumption satisfying this condition is that they belong to the same species, which we take to be an associated unit Co/CNS, leaving it to be decided whether it is a complex or an ion-pair. Making this simplest assumption and observing that neither thiocyanate ions nor cobaltous perchlorate absorbs appreciably at 275 mμ, we derive the following expression

$$K = E_m \,.\, Co_T/\{E_x[Co_T - (E_m \,.\, Co_T/E_x)][T_x - (E_m \,.\, Co_T/E_x)]\} \quad . \quad . \quad . \quad (1)$$

where Co_T is the total cobalt concentration, E_x the (unknown) extinction coefficient of CoSCN for the given Co_T, E_m the measured extinction per mole of cobalt (which varies with

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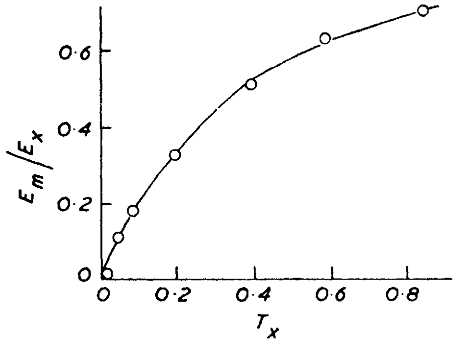
[8] Katzin, *J. Chem. Phys.*, 1950, **18**, 789.
[9] Halban, *Z. Electrochem.*, 1928, **34**, 489.
[10] Kortum, *ibid.*, 1944, **50**, 144.
[11] Williams, *J.*, 1952, 3770.
[12] Hershenon, Smith, and Hume, *J. Amer. Chem. Soc.*, 1953, **75**, 507.
[13] von Kiss and Csokan, *Z. phys. Chem.*, 1940, **186**, *A*, 289
[14] von Kiss and Major, *ibid.*, 1941, **189**, *A*, 364.
[15] von Kiss and Gerendas, *ibid.*, 1937, **180**, *A*, 117.

T_x, the total thiocyanate concentration), and K is the desired equilibrium constant [CoSCN]/([Co][SCN]) for the given ionic strength.

When $T_x \gg \mathrm{Co}_T$, a plot of $1/T_x$ against $1/E_m$ is linear with intercept $-K$ and slope KE_x. Using the values of K and E_x so derived we can test eqn. (1) over the whole range of T_x values; it is obeyed (see Figure). The equations are equally valid with data at a different wavelength. The same equations have been applied to the other systems giving the results in Table 3. The ionic strengths are given earlier, and the conditions in Table 2.

The fact that the equations hold so well supports the assumption that there is only one associated species within the range of the measurement, *i.e.*, Co/SCN in the case of the thiocyanate. The formation constant of the thiosulphate K can be compared with that obtained ($1{\cdot}2 \times 10^2$) by Denney and Monk [16] using a conductivity method. Ours, found by a very lengthy extrapolation by the Davies equation,[17, 18] is 5×10^1. The agreement is as good as can be expected, the known limitations of the extraposition being considered, and is very similar to that found when comparing studies by optical and other methods on the association of cupric sulphate.[19] † A modified procedure was adopted in the treatment of the chloride data for the formation of a second complex, $\mathrm{CoCl_4}^{2-}$, interferes. Allowance was readily made for this complex, however, as its absorption bands are much more intense and at considerably longer wavelength. Our method was to determine the absorption spectrum of the fully formed $\mathrm{CoCl_4}^{2-}$, in the presence of 10M-lithium chloride, and then to use the value of the extinction coefficient so found to determine the amount of cobalt bound as $\mathrm{CoCl_4}^{2-}$ at any chloride concentration. The calculation then proceeded as above and the fact that the equilibrium



Plot of total thiocyanate concentration (M) *against the degree of formation of the thiocyanate complex.*

Full line from eqn. (1), and experimental points by use of data in Table 3. Total cobalt concentration 0·05M.

TABLE 2. *Conditions used in the study of cobaltous complexes.*

Ligand	Cl^-	SCN^-	$\mathrm{S_2O_3}^{2-}$	$\mathrm{SO_4}^{2-}$	I^-	$\mathrm{NO_3}^-$
Concn. (ligand molarity)...	0·40—2·15	0·05—0·85	0·01—0·25	0·01—0·25	0·80—7·00	0·05—0·85
Ionic strength (M)	7·0	1·0	1·0	1·0	7·0	1·0

TABLE 3. *Association constants and absorption spectra of some cobaltous complexes.*

Ligand	K	Species	$\lambda_{\text{max.}}$ (mμ)	$\varepsilon_{\text{max.}}$	$\lambda_{\text{max.}}$ (mμ)	$\varepsilon_{\text{max.}}$
$\mathrm{ClO_4}^-$	—		No measurable association of any kind			
SCN^-	2·5	CoCNS^+	275	1140	516	44·4
Cl^-	0·37	CoCl^+	250	—	529	12·7
$\mathrm{S_2O_3}^{2-}$	2·35	$\mathrm{CoS_2O_3}$	295	620	512	375
$\mathrm{SO_4}^{2-}$	?	$\mathrm{CoSO_4}$ *	No observable change in visible			
$\mathrm{NO_3}^-$	?	$\mathrm{CoNO_3}^+$ *	No observable change in visible			
I^-	—		No measurable association of any kind			
$\mathrm{H_2O}$	—	—	<250	—	512	4·75

* Species presumed present from activity coefficient changes (see text).

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† The association constant for cupric sulphate at ionic strength 1·0 is 4·0 and by ionic-exchange methods 9·0. The association constant quoted by Brown and Prue, determined by two different methods at low ionic strengths, lies in the range 200—300. The measurements for cobalt thiosulphate show a very similar change with ionic strength.

[16] Denney and Monk, *Trans. Faraday Soc.*, 1951, **47**, 992.

[17] Davies, *J.*, 1938, 2093.

[18] Guggenheim, *Phil. Mag.*, 1935, **19**, 588.

[19] Brown and Prue. *Proc. Roy Soc.*, 1955, *A*, 2232320

constant obtained is constant over a wide range of chloride was considered proof that no other complexes needed to be considered:

Chloride concn.	0·41	0·63	0·81	0·98	1·40	1·82
Equilibrium const.	0·41	0·38	0·34	0·38	0·36	0·30

The molar extinction coefficient used for $CoCl_4^{2-}$ was 605 at 690 mμ. The ratio of the extinction coefficients at 690 mμ and 625 mμ, the region of the spectrum in which $CoCl_2$ or $CoCl_3^-$ complexes might be expected to absorb, was constant at 1·55 over a range of approximately 1000-fold change in absorption at these wavelengths. We take it that the amounts of complexes other than $CoCl^+$ and $CoCl_4^{2-}$ are negligible.

DISCUSSION

The formation of thiocyanate, thiosulphate, and chloride complexes is accompanied by a change in the absorption spectra in the visible as well as in the ultraviolet spectrum. The change in position of a *d–d* band of a bivalent cation on complex formation should be about half that of a tervalent cation according to Owen's observations.[20] This relationship is roughly obeyed in a comparison between the data on the cobaltous and cobaltic ions, Tables 1 and 3 confirming that association is as complexes in these cases.

From a study with use of a cryoscopic method depending on the determination of activities, Brown and Prue [19] found that the thermodynamic stability constant of cobaltous sulphate association is $2·3 \times 10^2$. Of course this study did not allow of a distinction between ion-pairs and complexes. The value is very similar to the thermodynamic stability constant found [16] for cobaltous thiosulphate, $1·2 \times 10^2$, and as the two salts are electrolytes of the same charge type the same dependence of the association upon ionic strength is to be expected. Although very considerable changes in the absorption spectra of cobaltous solutions ($\mu = 1·0$) were observed in the presence of thiosulphate, no spectrophotometric changes were found in the cobaltous sulphate solutions at the same ionic strength. We conclude that the association in the sulphate is of the ion-pair rather than the complex type. Confirmation of this can be obtained by studies with other cations.

In cupric perchlorate solutions to which sulphate is added the *d–d* band at ~800 mμ shifts to longer wavelengths and higher extinctions as expected for complex and not ion-pair formation.[22] The strength of this association is, within experimental error, the same as that in cobaltous solutions [19] but the cobaltous and the cupric solutions have different spectroscopic properties. It is interesting that cobaltous sulphate crystallises with an octahedron of water molecules about it whereas cupric sulphate crystallises with a sulphate anion in one of the six positions. The changes in absorption spectrum of the cupric sulphate solutions are towards the spectrum of the crystalline pentahydrate.[21] Only when cobaltous sulphate is in a solution of very strong sulphate concentration does the absorption at 515 mμ shift to longer wavelengths [23, 24] and toward that of anhydrous cobaltous sulphate. We presume that at these concentrations the sulphate anions are adjacent to the cation. Though much of this evidence is circumstantial it points to the first association of cobaltous and sulphate ions as being of the ion-pair type. An entirely comparable series of observations has been made in nitrate solutions and we believe that the low activities of cobaltous nitrate solutions referred to earlier are due to ion-pair formation also as there is no indication of any complex. Earlier [11] we expressed the opinion that small cations form ion-pairs with sulphate and nitrate and that large cations form complexes. This assumption explained the anomalous stability orders of association of Group IIA cations with these anions. The present discussion confirms the earlier impression, cobaltous being considered a small cation. In the same paper we stated that hydration numbers of anions, as given by Stokes and Robinson,[24] must be in error as the

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[20] Owen, *Discuss. Faraday Soc.*, 1955, **19**, 127.

[21] Bjerrum, Ballhausen, and Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1275.

[22] Nasanen, *Acta Chem. Scand.*, 1949, **3**, 179.

[23] Ballhausen and Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 397.

[24] Stokes and Robinson, *J. Amer. Chem. Soc.*, 1948, **70**, 1870.

calculation of them did not take into account the formation of ion-pairs and complexes in concentrated solutions of strong electrolytes. The relative hydration of cobaltous iodide and chloride was a case in point. We have now shown that cobaltous forms halide complexes in the stability order $Cl^- > I^-$. Unless account is taken of this association Stokes and Robinson's calculation leads to an anomalously higher hydration tor iodide than chloride.

Cobaltous Complexes.—During this study interesting information has accumulated about cobaltous complexes. The first point is the stability order of anion complexes $ClO_4^- \leqslant I^- < Br^- < Cl^- < CNS^- < (CN^-)$, which appears to be quite general for first-row transition-metal cations. It is the order of the crystal-field splitting produced by these anions as found from the spectra of the complexes.

A second point concerns the extinction coefficients of the complexes. The extinction coefficient at the absorption maxima (Table 2) has the following values in CoX^- (ultra-violet in parentheses follows visible): Cl^-, 12·7 (?); SCN^-, 44·4 (1140); $S_2O_3^{2-}$, 375 (620).

The very sharp rise in extinction in the visible band of the thiosulphate is observed in ferric thiosulphate complexes too.[25] It does not appear in the nickel complex. We believe that the *d–d* transition has become mixed with a partial charge-transfer to the holes in the d_ϵ states of the cation.[25]

In the study of the cobaltous halides we have shown that although we can detect $CoCl(H_2O)_5^+$ and $CoCl_4^{2-}$ no intermediate complexes could be found spectrophotometrically. This suggests that the change from an octahedral to a tetrahedral complex occurs on the addition of the fourth chloride ion and that the complexes $CoCl_2(H_2O)_4$ and $CoCl_3(H_2O)_3^-$ are unstable as octahedra because of the size of the ligands and unstable as tetrahedra because of the weak polarisability of the water molecules.

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[25] Williams, *J.*, 1956, 8.