

Studies on Metal Complexes in Aqueous Solution by Infrared Spectrophotometry

IV. An Indication of the Existence of Outer-sphere Complexes in some Sulphate Systems

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Infrared spectra in the range 1400–850 K have been recorded for several metal sulphates in aqueous solution. In the case of chromium and indium the same split was clearly observed as has been reported for solid sulphato complexes. For other systems only a broadening of the infrared active ν_3 -band was observed, together with the appearance of a very feeble ν_1 absorption. These two effects have been used for an estimation of the ratio between inner- and outer-sphere complexes for the different systems.

For the trivalent metals this ratio is greater for indium than for cerium. From the broadening of the ν_3 -band the order of the tendency of inner-sphere complexity of two-valent metals increases in the series: Ni < Mn < Co < Zn < Cu < Cd.

From the magnitude of the ν_1 -band the same tendency increases as Mn < Zn \approx Co < Ni < Cu \approx Cd.

Via a comparison of the ν_1 absorption of solid sulphato complexes the absolute ratio between inner-sphere and outer-sphere complexity could be estimated. For cerium and the two-valent metals it was found to be about 0.1 in agreement with the results of Eigen and Tamm,⁵ whereas for the indium system it was about 0.5.

The existence of the second complex, MA₂, for the copper, cadmium, and nickel systems has been confirmed.

The association of sulphate ions with di-, tri-, and tetravalent metal ions has been investigated for many decades with many different techniques. A great number of stability constants have been reported.¹ Much discussion has been devoted especially to the question of the nature and the stability of the sulphato complexes of the divalent transition metals. *E.g.*, it was not until the investigation of Fronæus² with an anion exchanger technique, that the existence of anionic copper(II) and cadmium complexes was definitely established.

Even if the stoichiometry of such complexes now seems to be established or is possible to establish, the question of their molecular structure in aqueous solution still remains to be answered.

Duncan and Kepert³ have suggested that the association of divalent transition metal sulphates should take place *via* two or more interposed water molecules. This suggestion was based on the constancy of the light absorption in the visible part of the spectrum for nickel sulphate solutions of varying composition.

In the same way Smithson and Williams⁴ considered the optical constancy of cobalt(II) sulphate solutions to indicate "ion-pair" formation, whereas a shift of the $d-d$ transition of the copper(II) ion (800 $m\mu$) should indicate a closer interaction between copper(II) and sulphate ions.

In the present paper the term "ion-pair" will not be used. Instead the term "outer-sphere complex" will be used to designate complexes where the ligand is separated from the metal ion by one or two molecules (*e.g.* water). "Inner-sphere complex" then means a complex where the ligand is in direct contact with the metal ion.

The strongest evidence hitherto for the transition metal sulphato complexes to be at least partly of the outer-sphere type comes from the relaxation measurements of Eigen and coworkers.⁵ From a determination of velocity constants of the association and dissociation reactions they could distinguish not only between inner-sphere complexes and outer-sphere ones with one interposed water molecule but also between different types of outer-sphere complexes, namely, complexes with one and two interposed water molecules. The ratio between inner- and outer-sphere complexes was found to be about 1:10. It is interesting to note in this connection that in order to explain their proton relaxation data of magnesium sulphate solutions, Lindner and Pfeiffer⁶ had to use a similar value of the above mentioned ratio.

In a recent review Taube⁷ has suggested that Raman spectroscopic investigations might help to distinguish between ligands bound in the outer coordination sphere of a complex and in the inner ones. Obviously also infrared spectroscopy can be used for this purpose. In a previous paper (Fronæus and Larsson⁸) this technique has been used in an attempt to distinguish between inner- and outer-sphere thiocyanato complexes.

The assumption underlying such investigations is, that the vibration frequencies of the ligands (here denoted by A) bound in the outer sphere of the complex, *i.e.* $M(OH_2)_m A_n$, should be almost the same as those of the free ligand. Ligands bound in direct contact with the metal ion, *i.e.* in the inner-sphere complex MA_n , are supposed to have vibration frequencies different from those of the free ligand.

Thus Raman and infrared spectroscopy yields information about the sum $[A] + \sum_n n[M(OH_2)_m A_n]$, whereas the conventional methods of complex chemistry give the sum $\sum_n n([MA_n] + [M(OH_2)_m A_n])$.

Together with the total concentrations of metal and ligand, C_M and C_A , these two sums can be used for a calculation of the relative proportions of the outer-sphere complexes and of the inner ones.

PRINCIPLE OF INVESTIGATION

The change of the vibration frequencies of the ligand following upon coordination can have two different origins. Firstly, the coordination can cause a rearrangement of the electron distribution within the ligand, resulting in a change of the force constants. Such variations can have drastic effects as for the cyanide ion,⁹ or they can cause only slight shifts as, *e.g.*, in the case of pyridine complexes.¹⁰

Secondly, coordination may annihilate an existing degeneracy of the energy levels of a highly symmetrical ligand. This results in the splitting of an absorption band of the free ligand into two or more bands for the complex.

The sulphate ion is a good example of this effect. The free sulphate ion belongs to the symmetry group T_d . When the ion acts as a unidentate ligand its symmetry is lowered to C_{3v} and when it acts as a bridging or a bidentate ligand its symmetry is further lowered to C_{2v} . Table 1 presents the number

Table 1. Vibration of SO_4^{2-} as a function of symmetry. Abbreviations: A and B, non-degenerate; E, doubly degenerate; T, triply degenerate. Symbols within brackets denote infrared inactive vibrations.

Symmetry	Vibrations			
	SO str ν_1	bend ν_2	SO str ν_3	bend ν_4
T_d	(A ₁)	(E)	T ₂	T ₂
C_{3v}	↓ A ₁	↓ E	↓ A ₁ ↓ E	↓ A ₁ ↓ E
C_{2v}	↓ A ₁	↙ A ₁ ↘ A ₂	↓ A ₁ ↓ B ₁ ↓ B ₂	↓ A ₁ ↓ B ₁ ↓ B ₂

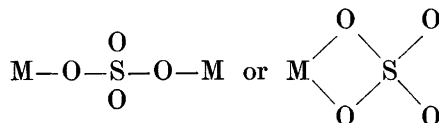
of vibrations of the sulphate ion that according to theory (*cf.* Ref.¹¹, p. 369) are infrared active for the different symmetry groups.

The works on solid sulphato complexes of Nakamoto and coworkers,¹² of Mathieu and coworkers,¹³ and of Barraclough and Tobe¹⁴ confirm these predictions splendidly.

Basing judgement on these results one may anticipate for inner-sphere complexes in aqueous solution a splitting of the ν_3 band and the appearance

of a ν_1 band of moderate intensity. For a $\text{M}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}$ complex we should

thus expect a spectrum with two bands instead of the degenerate band at 1104 K and for a complex of any of the types



we should expect three peaks to appear. In all these cases one more band should be present corresponding to the ν_1 frequency which is known from Raman work to be about 980 K. On the other hand, if only outer-sphere sulphato complexes are formed for a certain system, it is probable that the interaction is so weak that the ν_1 frequency will not appear. (The solid state spectra of $[\text{Co}(\text{HN}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ^{12,13} seem to contradict this assumption insofar as a slight splitting of the ν_3 band is observed as well as a slight ν_1 -peak. This must, however, be due to a perturbation caused by strong electrostatic fields present in this actual substance. In the case of $[\text{Co}(\text{NH}_3)_6]\text{SO}_4$ Br no such effects were observed.¹³)

In an aqueous solution of a metal sulphate, however, there is probably an equilibrium between inner- and outer-sphere complexes. Then the observed spectrum will be a superposition of spectra of the two kinds described above. The integrated absorption of the ν_1 band will be a direct measure of the amount of inner-sphere complexes existing in the solution. If this amount is not too great and if the splitting of the ν_3 band in the pure spectrum of the inner-sphere complexes is not too great, the ν_3 band of the composite spectrum may be expected to appear at about 1104 K and to be somewhat broadened. The increase of the half-width has been regarded in this paper as a measure of the inner-sphere complexity of the system.

EXPERIMENTAL

The spectra were recorded with a Perkin Elmer 221 grating-prism spectrophotometer. In the range of measurement the monochromator is a NaCl-prism. The cells were built up for each time from a pair of IRTRAN-2 glasses and with a platinum foil, usually 8.8 μ thick, as a spacer. A 3 M solution of sodium chloride was kept in the reference cell in order to compensate as closely as possible for the absorption of water.

Only the range between 1400 and 850 K was investigated. In this region where the stretching vibrations of the sulphate ion are to be found, there is a relatively low water absorption. There would be no sense in measuring at lower frequencies as the bending vibrations of the sulphate ion are well outside the spectral range available with the present instrument.

The position of the absorption maxima can be considered accurate to about $\pm 2 \text{ cm}^{-1}$. The extinction coefficients are accurate within about 5 %. The rather large random error is partly caused by difficulties in filling the cell as the IRTRAN plates are not transparent to visible light. One other source of error is the difficulty in estimating a correct base line corresponding to the not completely compensated water absorption. Furthermore, the slight variation of the cell thickness that is inherent in the applied technique, may add to the random error. All chemicals were of analytical grade.

LIST OF SYMBOLS USED IN THIS WORK

C_A, C_M	= total concentration of ligand (metal).
$[\text{A}], [\text{M}]$	= free concentration of ligand (metal).
$[\text{MA}_n]$	= concentration of complexes with the ratio A:M = n .
$[\text{MA}_n]_{\text{in}}$	= concentration of the inner-sphere complex MA_n .
$[\text{MA}_n]_{\text{out}}$	= concentration of the outer-sphere complex $\text{M}(\text{OH}_2)_m\text{A}_n$.
β_n	= $\frac{[\text{MA}_n]}{[\text{M}][\text{A}]^n}$; $\beta_0 = 1$

$\beta_{n, \text{ in}}$	$= \frac{[\text{MA}_n]_{\text{in}}}{[\text{M}] [\text{A}]^n}$
$\beta_{n, \text{ out}}$	$= \frac{[\text{MA}_n]_{\text{out}}}{[\text{M}] [\text{A}]^n}$
\bar{n}	$= \frac{C_A - [\text{A}]}{C_M} = \frac{\sum_{n=0}^N n \beta_n [\text{A}]^n}{\sum_{n=0}^N \beta_n [\text{A}]^n}$
ν_1	= frequency of the band at 975–980 K
ϵ_1	= observed extinction coefficient of that band.
I_1	= observed integrated absorption of that band.
ν_3	= frequency of the band at 1110–1100 K.
ϵ_3	= observed extinction coefficient of that band.
I_3	= observed integrated absorption of that band. (The two bands are many times designated as ν_1 and ν_3 , respectively.)
$(I_k)_{\text{in}}, (\epsilon_k)_{\text{in}}$	= symbols of entities characterizing the inner-sphere complex.
$(I_k)^{(n)}, (\epsilon_k)^{(n)}$	= symbols characterizing the n th complex.
$(\Delta\nu_k)_{\frac{1}{2}}$	= half width of the ν_k band.
d	= thickness of cell.
E	= optical density.

RESULTS

Monovalent ions

The only sulphates of monovalent cations that have been investigated in this work are sodium sulphate and sulphuric acid. The first-mentioned system has been investigated by Jenkins and Monk¹⁴ with a conductometric technique. Their value for the association constant at zero ionic strength is $k_1 \approx 5 \text{ M}^{-1}$, Eigen and Tamm,⁵ too, found evidence of an association process.

We have therefore measured the sulphate spectrum at three different concentrations (Table 2). One can note that there is a definite broadening

Table 2. Spectral data of some sodium sulphate solutions. Only those quantities that could be determined with some accuracy are reported.

$C_{\text{Na}_2\text{SO}_4}$ M	ν_1 K	$(\Delta\nu_1)_{\frac{1}{2}}$ K	ϵ_1 $\text{M}^{-1} \text{ cm}^{-1}$	ν_3 K	$(\Delta\nu_3)_{\frac{1}{2}}$ K	$\epsilon_3 \times 10^{-3}$ $\text{M}^{-1} \text{ cm}^{-1}$
0.03				1104	60 ± 2	
0.3				1104	65 ± 1	2.4 ± 0.2
1.0	980	16 ± 2	35 ± 1			

of the ν_3 band as well as an appearance of the ν_1 absorption band at the highest concentration. Both these facts indicate — according to the discussion above — a slight association of the type where the two ions are in direct contact with each other.

From the association constant quoted above and accounting for the decrease of association constants with ionic strength one can estimate that not more than 5 % of the sulphate ions should be associated at the lowest concentration. The half-width of the ν_3 band for a free sulphate ion should then be 60 ± 2 K.

As an example of a typical inner-sphere complex of the sulphate ion with a monovalent ion, HSO_4^- has been chosen. The spectrum was recorded of a solution of sodium sulphate and hydrochloric acid having such a composition that HSO_4^- should be the dominating sulphate specium. The result is given in Fig. 2 c.

Trivalent ions

The spectra of some sulphates of trivalent metals will be presented before those of the divalent ones as they illustrate some important points of the reasoning above. The following metals were investigated: Co(III) as $\text{Co}(\text{NH}_3)_6^{3+}$, Cr(III), In(III), and Ce(III). Of these metals the first two can form inert complexes, a fact which is very useful in studies on outer-sphere coordination.

The cobalt(III) hexammine system. It has been shown^{16,17} that the $\text{Co}(\text{NH}_3)_6^{3+} - \text{SO}_4^{2-}$ system is rather strongly associated. In a solution of the composition given in Table 5, one can estimate from the association constant reported by Vlcek¹⁶ ($\beta_1 = 125 \text{ M}^{-1}$, $I = 0.1 \text{ M}$) that half the amount of the sulphate ions is bound in a complex with the cobalt ion and that the remaining part is free. When one accounts for this association the ionic strength of the solution is almost exactly 0.1 M, which fact justifies the use of the quoted constant.

As a consequence of the inertness of the cobalthexammine ion, no inner-sphere sulphato complexes can be formed. It is therefore interesting to note (Table 3) that the halfwidth of the ν_3 band is the same as that found for the most dilute sodium sulphate solution (Table 2) and that the ν_1 band does not appear. This is in agreement with the predictions made for a pure outersphere association.

The chromium(III) system. Fig. 1 a represents the spectrum of a solution of chromium(III) sulphate. The colour of the solution was distinctly green. As green chromium(III) complexes are known to be of the inner-sphere type,

Table 3. Spectral data for $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ and $\text{Ce}_2(\text{SO}_4)_3$

	ν_1 K	$(\Delta\nu_1)_{\frac{1}{2}}$ K	ϵ_1 $\text{M}^{-1} \text{ cm}^{-1}$	ν_3 K	$(\Delta\nu_3)_{\frac{1}{2}}$ K	ϵ_3 $\text{M}^{-1} \text{ cm}^{-1}$
$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ 0.018 M				1102	61	1.9×10^3
$\text{Ce}_2(\text{SO}_4)_3$ 0.1 M	975	16 ± 4	80	1107	85	2.7×10^3

we can infer the presence of a large amount of such complexes in the solution. Furthermore, as chromium(III) complexes are rather inert, at room temperature there is a "frozen" equilibrium between these inner-sphere sulphato complexes and the free SO_4^{2-} and HSO_4^- ions. Probably there are some outer-sphere complexes as well. Examining the curve (Fig. 1 a) one observes the existence of a ν_1 band ($\nu \approx 978 \text{ K}$, $\epsilon \approx 300 \text{ M}^{-1} \text{ cm}^{-1}$ and $(\Delta\nu)_\frac{1}{2} = 30 \text{ K}$) and one band at 1130 K which must both be ascribed to $\text{Cr}^{3+}-\text{SO}_4^{2-}$ complexes. The absorption peak at about 1200 K must, however, most probably be ascribed to the HSO_4^- ion whereas the peak at 1040 K may be caused by both $\text{Cr}^{3+}-\text{SO}_4^{2-}$ species and HSO_4^- .

To clarify these matters the solution was percolated through a column of a cation exchange resin in the sodium form. The effluent, which was still very green, should then contain all negatively charged $\text{Cr}^{3+}-\text{SO}_4^{2-}$ -species together with free sulphate ions. As the effluent could not contain any free acid, the concentration of HSO_4^- ions must be expected to be very low. (The acid strength of negatively charged $\text{Cr}(\text{SO}_4)_n(\text{OH}_2)_m$ complexes must be low.) Fig. 1 b represents the spectrum of the effluent. As this solution contains inner-sphere sulphato complexes—indicated by the green colour—and sulphate ions, which may or may not form outer-sphere complexes, it is of great interest to note that only one ν_3 -peak appears (1107 K) but with an appreciable half-width (73 K). This is in agreement with the expected spectrum

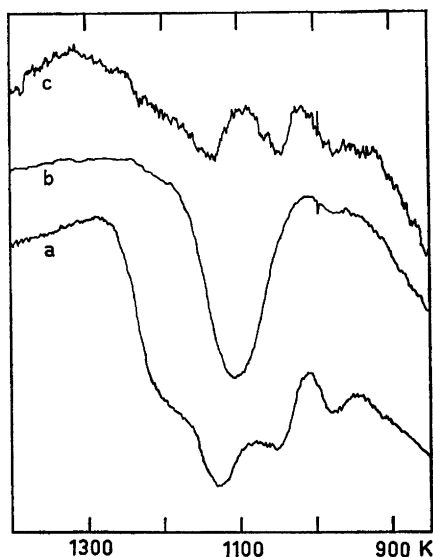


Fig. 1. a. $0.11 \text{ M Cr}_2(\text{SO}_4)_3$ b. Spectrum of solution a, when passed through a cation exchange column. c. Spectrum of the chromium species sorbed on the resin after elution with 3 M NaCl . Scale expansion: $3 \times$.

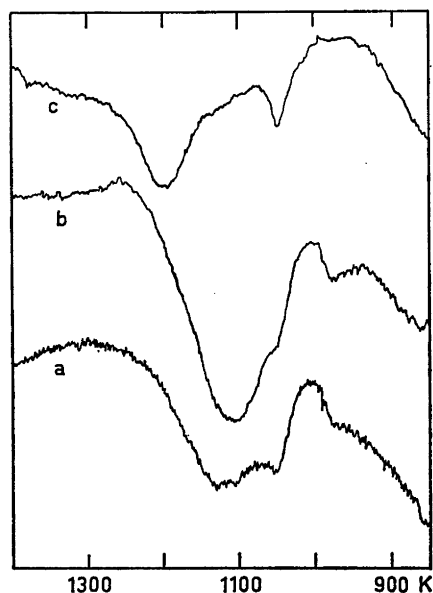


Fig. 2. a. $0.1 \text{ M In}_2(\text{SO}_4)_3$ b. $\text{In}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4$; $C_M = 0.167 \text{ M}$, $C_A = 0.417 \text{ M}$. c. $0.3 \text{ M Na}_2\text{SO}_4 + 1.0 \text{ M HCl}$.

of a solution containing small amounts of inner-sphere complexes together with free or outer-sphere-bound sulphate ions. Furthermore, the presence of a ν_1 -band at 980 K is easily observed. The optical densities (at the peak maximum) of the ν_3 and the ν_1 bands were found to be 0.43 and 0.02, respectively.

The ion-exchange resin was then eluted with a 3 M NaCl solution. The eluate, containing the positively charged chromium species, was still green, a fact that indicates the presence of inner-sphere complexes. The spectrum (Fig. 1 c) shows two well identifiable peaks at 1045 K and one at 975 K. This is a typical spectrum of a sulphate group with C_{3v} symmetry. Hence we can con-

clude that the positive complex is $\text{Cr}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}^+$. If any polynuclear, sulphato-bridged complexes were present in the original solution contributing to the absorption at 1200 K they must have been destroyed during the separation process.

The indium(III) system. The spectra of indium sulphate solution recorded in Fig. 2 are of interest in relation to the work of Hester, Plane and Walrafen.¹⁸ Fig. 2 a gives the spectrum of a solution of 0.1 M $\text{In}_2(\text{SO}_4)_3$, i.e. $C_M = 0.2$ and $C_A = 0.3$ M. The data of Sundén^{19,20} can be used for an estimate of the amount of sulphate complexes present in such a solution. Approximately, one finds that $\bar{n} = 1.2$ and the concentration of free sulphate ions is 0.08 M. Thus conditions for observing the effects of coordination on the sulphate spectrum are good. Three new absorption bands can be observed: 1135 K, 1050 K, and 975 K. Fig. 2 b presents the spectrum of a solution of the composition $C_M = 0.167$ M, $C_A = 0.417$ M. Similarly one obtains $\bar{n} = 1.7$ and $[\text{A}] = 0.13$ M. Here the new band of the highest wave number is obviously hidden by the normal ν_3 -band, but bands at ~ 1050 K and 975 K are easily observed. For the latter one can calculate — taking into consideration only the concentration of bound sulphate ions (0.28 M) — $\varepsilon_1 = 215 \text{ M}^{-1} \text{ cm}^{-1}$ and $\Delta\nu_{\frac{1}{2}} = 25$ K. The calculations above are of course only approximative, because the stability constants used were determined at another ionic strength and because any formation of hydroxo complexes was neglected. Nevertheless, the spectrum expected for a C_{3v} sulphate group is observed.

The Raman spectrum of indium sulphate has been studied repeatedly.^{18,21} The above-mentioned authors¹⁸ claim that in the frequency range studied in this work only two new lines appear, viz. 1125 K and 1000 K. These values may be compared to the 1135 K and 975 K values of this paper. They observe, however, a third line at 1045 K but ascribe this entirely to the presence of HSO_4^- ions. As they use a high concentration of sulphuric acid (2 M) this may be so, but it is difficult to see how these authors can ascribe a C_{3v} symmetry to the complex-bonded sulphate ions. (Both the A_1 and E terms originating from the T_2 term — cf. Table 1 — are Raman active.¹¹) Mc Carroll and Lietzke²¹ on the other hand consider the Raman line at 1045 K as originating from indium-sulphate complexes. Possibly their result can be better interpreted as one 1045 K-line and one weak line at ~ 1120 K.

Irrespective of the contradictory results from Raman investigations, it must be stated here that the infrared absorption at 1050 K must be ascribed

to a complex-bonded sulphate group. Had it been entirely caused by the presence of HSO_4^- , we should also observe a still stronger band at *ca.* 1200 K. This is not the case.

The cerium(III) system. The results of measurements of a thoroughly recrystallized sample of cerium (III) sulphate are represented in Table 3. No fine structure of the ν_3 -band could be observed but a definite broadening as well as the appearance of the ν_1 absorption. From this we can conclude that there is some inner-sphere complexity, but not so strong as in the case of the indium system.

Divalent ions

Spectra of several divalent transition metal sulphates have been recorded (Table 4). For some of these metals, spectra were also recorded for solutions where the quotient $C_A:C_M$ was made >1 by addition of sodium sulphate (Table 5).

In order to be able to interpret the spectra it is necessary to know what species are present in the solutions. Fronæus² has shown that for the copper and cadmium systems, the mean ligand number $\bar{n} = 1$ for $[A] \approx 50$ M. From this it follows that the 0.3 M solutions of cadmium and copper sulphate should have a composition of about $[A] \approx 0.04$ M, $[MA] \approx 0.2$ M, and $[MA_2] \approx 0.04$

Table 4. Spectral data for some transition metal sulphates.

	C_{MSO_4} M	ν_1 K	$(\Delta\nu_1)_{\frac{1}{2}}$ K	ϵ_1 $\text{M}^{-1} \text{cm}^{-1}$	ν_3 K	$(\Delta\nu_3)_{\frac{1}{2}}$ K	$\epsilon_3 \times 10^{-3}$ $\text{M}^{-1} \text{cm}^{-1}$																																																																																																									
Mn	0.3	978		40	1105	70	2.3																																																																																																									
	1.0	978	16	45				Co	0.3				1103	71	2.4 ₅	1.0	980	17	55	Ni	0.3				1105	69	2.1	1.0	977	16	58	Cu	0.3	978		55	1104	75	2.1	0.5	980		69	1106	78	2.0	0.8	980		66	1105			1.0	978	16	67				Zn	0.3				1105	72	2.0	1.0	980	15	54	Cd	0.3	978		56	1104	78	2.4	0.5	977		70	1104	81	2.1	1.0	980		76				1.0*					83		2.0	982	17	76				2.0*			
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* Solutions marked with an asterisk were measured without a spacer in the cell.

Table 5. Optical densities and related data for the ν_1 band for some solutions with $C_A \geq C_M$.
 $C_M = 0.30$ M; $d = 8.8 \mu$

Copper			Nickel			Cadmium		
C_A	E/d	$\frac{E}{d \cdot C_M}$	C_A	E/d	$\frac{E}{d \cdot C_M}$	C_A	E/d	$\frac{E}{d \cdot C_M}$
M	cm ⁻¹	cm ⁻¹ M ⁻¹	M	cm ⁻¹	cm ⁻¹ M ⁻¹	M	cm ⁻¹	cm ⁻¹ M ⁻¹
0.3	16.5	55				0.3	15	50
0.6	33	110				0.6	28	94
0.8	49	164	0.8	36	120	0.8	31	103
1.0	63	210	1.0	45	150	1.0	40	133

M, *i.e.* $\bar{n} \approx 0.87$. In other words, 87 % of the sulphate ions are bound as complexes. From this and assuming that $\varepsilon_1^2 = 2\varepsilon_1^1$, the extinction coefficient that corresponds directly to the first sulphato complexes can be estimated: $\varepsilon_1^1 = \varepsilon_1/0.87$. Then one obtains for copper, $\varepsilon_1^1 = 63$ M⁻¹ cm⁻¹ and for cadmium, $\varepsilon_1^1 = 64$ M⁻¹ cm⁻¹.

In principle, these values should be almost equal to ε_1 determined for the solutions with $C_{\text{MSO}_4} = 1$ M. This seems to be the case for the copper system. For the manganese system a similar relation holds between the values of ε_1 for $C_{\text{MSO}_4} = 0.3$ M and $C_{\text{MSO}_4} = 1$ M, which fact shows that this system has a complexity of the same strength as the copper and cadmium systems. This conclusion agrees with reported values of the first association constant.^{1,22} In the case of the cadmium system, however, there seems to be an increase of ε_1 beyond the expected value. This may be caused either by a formation of polynuclear complexes or by an increase of the ratio between inner- and outer-sphere complexes as the electrolyte concentration increases. The increase of the halfwidth of the ν_3 -band agrees with both these interpretations. Taking all these matters into due consideration, we propose the following values for ε_1^1 (M⁻¹ cm⁻¹): Mn = 45, Co = 55, Ni = 58, Cu = 66, Zn = 54, and Cd = 66.

There is now two ways to compare the degree of inner-sphere complexity in the investigated systems:

Firstly, from the ε_1^1 -values just presented and the constancy of $(\Delta\nu_1)_{\frac{1}{2}}$ (Table 4) one may arrange the metals in order of increasing I_1^1 , where $I_1^1 = \varepsilon_1^1 \cdot (\Delta\nu_1)_{\frac{1}{2}}$:

$$\text{Mn} < \text{Zn} \approx \text{Co} < \text{Ni} < \text{Cu} \approx \text{Cd}. \quad (1)$$

If one assumes the constancy of $(I_1^1)_{\text{in}}$ this series also gives the sequence of increasing inner-sphere complexity. The measured I_1^1 is of course related to the same quantity for the inner-sphere complex, $(I_1^1)_{\text{in}}$, by the relation

$$I_1^1 = \frac{[\text{MA}]_{\text{in}}}{[\text{MA}]_{\text{in}} + [\text{MA}]_{\text{out}}} \times (I_1^1)_{\text{in}} \quad (2)$$

or

$$I_1^1 = \frac{\beta_{1,\text{in}}}{\beta_1} \times (I_1^1)_{\text{in}} \quad (3)$$

The actual magnitude of $(I_1^1)_{\text{in}}$ for a given system is not possible, however, to determine exactly (*Vide infra*).

On the other hand the magnitude of $(\Delta\nu_3)_{\frac{1}{2}}$ may also be used as a measure of inner-sphere complexity. Using the values of Table 4 for $C_{\text{MSO}_4} = 0.3 \text{ M}$ we obtain the sequence:

$$\text{Ni} < \text{Mn} < \text{Co} < \text{Zn} < \text{Cu} < \text{Cd} \quad (4)$$

With the exception of nickel, this agrees rather well with the series (1). The experimental error in the reported values make any closer comparison impossible, however.

One further calculation may be made from the values reported. In Table 5 some values of $E/(d \times C_M)$ for the ν_1 band are given. One may write:

$$E/d = \sum_n \varepsilon_1^n [\text{MA}_n] \quad (5)$$

Thus

$$\frac{E}{d \times C_M} = \frac{\sum_n \varepsilon_1^{(n)} \beta_n [\text{A}]^n}{\sum_n \beta_n [\text{A}]^n} \quad (6)$$

Assuming, that

$$\varepsilon_1^{(n)} = n \times \varepsilon_1^1 \quad (7)$$

we obtain

$$\bar{n} = \frac{E}{d \times C_M \times \varepsilon_1^1} \quad (8)$$

In Table 6, the results of such a calculation of \bar{n} is given together with $[\text{A}]$ from the relation $[\text{A}] = C_A - \bar{n}C_M$.

The E -values should really have been corrected for the $\text{Na}^+ - \text{SO}_4^{2-}$ association effect. However, a crude estimate showed this correction to be so small that it is of no practical consequence for the qualitative deductions that may

Table 6. Mean ligand number, \bar{n} , from formula (8) and subsequent estimation of $[\text{A}]$. $C_M = 0.3 \text{ M}$

Copper			Nickel			Cadmium		
C_A M	\bar{n}	$[\text{A}]$ M	C_A M	\bar{n}	$[\text{A}]$ M	C_A M	\bar{n}	$[\text{A}]$ M
0.3	0.8	0.06				0.3	0.8	0.06
0.6	1.7	0.09				0.6	1.4	0.18
0.8	2.5	0.05	0.8	2.1	0.17	0.8	1.6	0.32
1.0	3.2	0.04	1.8	2.6	0.22	1.0	2.0	0.40

be made from the data. It is obvious from the increase of \bar{n} that a second complex exists in all the three cases. On the other hand one is not allowed to infer the existence of a third complex from the fact that \bar{n} reaches values > 2 . Rather, this means that eqn. (7) is not exactly valid, but $\varepsilon_1^{(2)} > 2\varepsilon_1^1$. That this is so, is drastically shown in the case of the copper system, where the calculated $[A]$ does not increase monotonously with C_A . This effect cannot be observed for the cadmium system.

Assuming that $(I_1^{(2)})_{in} = 2(I_1^1)_{in}$ and that $(\Delta\nu_1)_\ddagger$ does not change, which latter assumption was experimentally found to be reasonable, the relation $\varepsilon_1^{(2)} > 2\varepsilon_1^1$ must mean that $\beta_{2,in}/\beta_2 > \beta_{1,in}/\beta_1$. This relation may be obtained from relations analogous to eqn. (3).

Thus we may conclude that the degree of inner-sphere complexity for the second complex is greater than for the first one, and that this effect increases in the sequence $Cd < Ni < Cu$.

ESTIMATION OF THE DEGREE OF INNER-SPHERE COMPLEXITY

It was pointed out above that for a given labile complex system one cannot determine $(I_1^1)_{in}$. Hence it is impossible, from eqn. (3) to obtain an exact information concerning the ratio $\beta_{1,in}/\beta_1$.

However, an approximative estimation may be made by "borrowing" the I_1^1 value from an inert complex ion such as $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ or $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{SO}_4]^+$. Of course, this is a very crude method, as different central ions must affect the sulphate ion by different amounts. Unfortunately, these complexes hydrolyse in aqueous solution to such a degree, that it proved difficult to obtain good spectra in water. Therefore, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{SO}_4]\text{Cl}$ in solid state was used for this estimation. A spectrum (Fig. 3) obtained with the KBr-pellet technique, showed the same splitting of the ν_3 band into three peaks as reported by Drouin, Mathieu and Poulet. The integrated

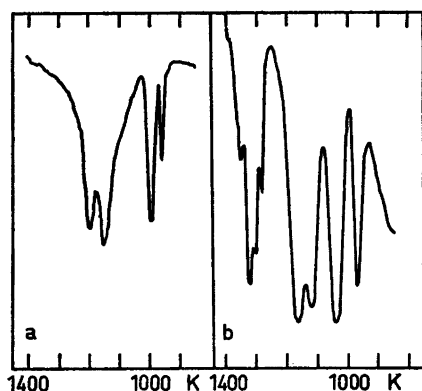


Fig. 3. a. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.3 mg/300 mg KBr). b. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{SO}_4]\text{Cl}$ (1.3 mg/300 mg KBr).

Table 7. Optical densities (E), halfwidths ($\Delta\nu_{\frac{1}{2}}$) and the products of these entities for $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{SO}_4]\text{Cl}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

	ν K	E	$\Delta\nu_{\frac{1}{2}}$ K	$E \cdot \Delta\nu_{\frac{1}{2}}$ K
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{SO}_4]\text{Cl}$	968	0.70	20	14
	1038	1.58	28	44
	1120	1.03	34	35
	1165	1.64	33	54
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	960	0.20	9	1.8
	998	0.41	18	7
	1151	0.53	54	29
	1200	0.43	38	16

absorptions are given below (Table 7) as products of optical density and half-width. From these values a quotient Z was derived,

$$Z = \frac{I_{968}}{I_{1038} + I_{1120} + I_{1165}}$$

Once forced to use solid state measurements, it seemed reasonable to use also the spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. In this crystal it is known that there is a direct contact between the metal and the sulphate ion. The result showed the greatest splitting of the ν_3 band yet observed, (Table 7).

In the same way as above we obtain

$$Z = \frac{I_{960}}{I_{998} + I_{1151} + I_{1200}}$$

The mean value of the two Z -values is 0.07.

With as reasonable accuracy as can be hoped for, we then put $(I_1^1)_{\text{in}} = 0.07 I_3$. If we then use the value of I_3 for the free sulphate ion we obtain $(I_1^1)_{\text{in}} = 0.07 \times 65 \times 2.4 \times 10^3 = 1.1 \times 10^4$ ($\text{M}^{-1} \text{cm}^{-1} \text{K}$).

For 1 M NiSO_4 , *e.g.*, we then obtain from the data of Table 4 and eqn. (3):

$$\beta_{1,\text{in}}/\beta_1 = \frac{16 \times 58}{1.1 \times 10^4} = 8 \times 10^{-2}$$

As the nickel system is a representative case of the two-valent transition metal sulphates, we may conclude that for these systems the degree of inner-sphere complexity is about 10 %. It is pleasing to note that this agrees quite well with the data given by Eigen and Tamm,⁵ although their order between the metals is another than reported above.

If we now turn to the trivalent metals, we obtain for the indium system (p. 1930)

$$\beta_{1,\text{in}}/\beta_1 = \frac{215 \times 25}{1.1 \times 10^4} = 0.5$$

and for the cerium system (Table 3)

$$\beta_{1,\text{in}}/\beta_1 = \frac{16 \times 80}{1.1 \times 10^4} = 0.12$$

There is accordingly a much greater variation of the inner-outer-sphere equilibrium between different trivalent metals than there is for the divalent ones.

As a final remark it must be stressed, that these results illustrate the importance of measuring the intensities of infrared bands. Even if this can be done only with a rather limited accuracy, much information can be obtained that is not easily extracted from measurements of frequencies only.

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