

739. *Stability Constants and Spectra of some Lanthanide Complexes.*

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Formation constants for some europium(III) complexes are reported from measurements on spectra assigned to ligand-to-metal charge transfer. Similar spectra have been observed in samarium, thulium, and ytterbium complexes. The spectrophotometric association constants for the monosulphates of the trivalent lanthanides have been compared with literature values obtained by other techniques, to estimate the formation of inner and outer sphere complexes.

THE purpose of this Paper is primarily to establish the assignment of ultraviolet (u.v.) absorption bands in some lanthanide complexes. Considerable work has already been done on these spectra. In the region 10—50 kK most of the spectra observed in lanthanide(III) perchlorate solutions are sharp, low intensity, Laporte-forbidden transitions inside the $4f$ shell. A few of the spectra show broad bands in the u.v. region with extinction coefficients between 50 and 800. The lanthanides which give these bands are those with an accessible quadrivalent state, cerium, praeaseodymium, and terbium; the spectra have been assigned to $4f-5d$ transitions.¹

¹ Jørgensen and Brinen, *Mol. Phys.*, 1963, **6**, 629.

Those lanthanides which can be reduced to give divalent ions, samarium, europium, thulium, and ytterbium, have solution spectra which rise towards 50 kK, the band maxima lying further into the u.v. region. Jørgensen and Brinen¹ have recently located a band in aqueous europium perchlorate at 53.2 kK and they suggest that the corresponding band in ytterbium solutions lies at about 59 kK. They ascribe those bands to electron-transfer from ligand to metal and this is confirmed by going to more reducing ligands than water, the bands then moving towards the visible region. By examining ethanolic solutions containing lanthanide bromide complexes Jørgensen² found that the order of the energy of the first charge-transfer band is $\text{Eu} < \text{Yb} < \text{Sm} < \text{Tm}$. This corresponds to the order of the solution redox potentials $\text{Ln}^{3+}/\text{Ln}^{2+}$. The extinction coefficients of these bands are similar to those of the $4f-5d$ bands but the half widths to lower energy (δ -) are greater, 2–4 kK compared with about 1 kK for the latter.

The energies of the charge-transfer bands are much more ligand dependent than those of the $f-f$ or $4f-5d$ bands. Aqueous europium(III) has a redox transition at 53.2 kK but in EuSO_4^+ the corresponding band appears at 41.7 kK. This may be compared with the $4f-5d$ band in praseodymium(III) at 46.5 kK which does not shift as the monosulphate complex forms although the extinction coefficient rises from 50 for the aquo-ion to 110 for PrSO_4^+ . Again, two of the $4f-5d$ bands of cerium(III) are found at 47.3 and 45.2 kK in perchlorate solutions, each of these moves by 0.5 kK to higher energy as the sulphate complex forms. Even these changes are large by comparison with those of the $f-f$ bands; when sodium sulphate was added to erbium perchlorate so that about half the metal was complexed the changes in optical density at the 39.3 and 26.4 kK bands were 1 and 0.5%, and the peaks moved by 0.00 and 0.04 kK, respectively.

These differences should make it relatively simple to identify lanthanide charge-transfer bands; but to obtain accurate extinction coefficients the species involved must be identified and their formation constants determined. Jørgensen's work is open to the criticism that the stoichiometry of the complexes was not established. However, detailed spectrophotometric studies have been made of several lanthanide monosulphates in aqueous solution^{3,4} and in this paper we report on europium complexes with sulphate, hypophosphite, and thiocyanate. Additionally the positions of charge-transfer bands are listed for some further complexes of the reducible lanthanides.

All formation constants mentioned in this Paper were measured at 25° and corrected to infinite dilution, unless otherwise stated.

EXPERIMENTAL AND RESULTS

The technique used for precision spectrophotometry and the calculation of the results from constant ionic strength data have been described by Monk.^{4,5} In Tables 1 and 2 the notation used is as follows: $(D_1 - D_2)$ is the optical density difference between two solutions with

TABLE 1.
Data at constant ionic strength for europium sulphate.

240 μ . $10^5 a = 501$.											
10^{5b}	10^{5c}	$10^3(D_1 - D_2)$	$10^5 x$	$10^4 I$	β'	10^{5b}	10^{5c}	$10^3(D_1 - D_2)$	$10^5 x$	$10^4 I$	β'
303	210	126.5	129	524	199	728	123	240	249	495	198
425	170	164	167	498	195	910	90	271	276	498	194
607	150	215	219	501	201	1031	50	288	294	484	193
						1213	0	317	323	470	204

identical stoichiometric metal concentrations a , one of which contains ligand of stoichiometric concentration b . Sodium perchlorate c is added to control the ionic strength. The free ligand

² Jørgensen, *Mol. Phys.*, 1962, **5**, 271.

³ Newton and Arcand, *J. Amer. Chem. Soc.*, 1953, **75**, 2449.

⁴ Barnes and Monk, *Trans. Faraday Soc.*, 1964, **60**, 578.

⁵ Bale, Davies, and Monk, *Trans. Faraday Soc.*, 1956, **52**, 816.

TABLE 2.

Data at constant ionic strength for europium hypophosphite.

217.2 m μ . $10^3a = 580$.									
10^5b	$10^3(D_1 - D_2 - D_L)$	10^5x	10^3I	β'	10^5b	$10^3(D_1 - D_2 - D_L)$	10^5x	10^3I	β'
762	218	156	42	60	1905	415	297	49	65
1143	298	213	44	62	3048	506	362	58	62
1524	357	255	46	62	3810	550	393	65	62

absorption D_L is allowed for, if it is significant. The complex concentration x is calculated from a series of approximations on the equations:

$$\begin{aligned} 1/\beta'(\epsilon_{ML} - \epsilon_M) &= a(b - x)/(D_1 - D_2) - (b - x)/(\epsilon_{ML} - \epsilon_M) \\ x &= (D_1 - D_2)/(\epsilon_{ML} - \epsilon_M) \\ \beta' &= [ML]/[M][L] = x/(a - x)(b - x) \end{aligned}$$

and activity coefficients obtained from the Davies form of the Debye-Huckel equation.⁶

The lanthanides used were 99 or 99.9% pure; no bands from other lanthanides could be seen in the spectra of 0.1M-solutions. Perchlorate solutions were prepared by dissolving the weighed oxides in small volumes of AnalaR 60% perchloric acid and diluting with water or ethanol. Hypophosphorous acid was purified according to Jenkins and Jones⁷ and neutralised with standard sodium hydroxide. All other salts used were AnalaR quality.

Spectra were recorded on a Beckman DK2 spectrophotometer and accurate optical densities measured on a Unicam S.P. 500.

Complex Species and Formation Constants.—Europium sulphate. When sodium sulphate was added to europium perchlorate in aqueous solution one new band was found, at 41.7 kK. Examination of this by a method due to Newton and Arcand⁸ indicated that the only species present was EuSO_4^+ over the concentration range studied. Typical data at constant ionic strength are presented in Table 1. After correction to zero ionic strength the formation constant was found to be 2250 ± 100 . The molar extinction coefficient of the band is 100.

Europium hypophosphite. The addition of sodium hypophosphite to aqueous europium perchlorate produced a new band at 45.8 kK. Analysed as above this proved to belong to $\text{EuH}_2\text{PO}_2^{2+}$ and a formation constant of 186 ± 5 was obtained, with an extinction coefficient of 140. Some data are presented in Table 2, the last two points being used as "variable ionic strength" information.⁵

The only constant in the literature for a metal hypophosphite is 600 for the ferric complex deduced from spectrophotometric work under unspecified conditions.⁹ This does suggest that this ligand forms very much weaker complexes than phosphate.

Europium thiocyanate. Although the interaction spectrum of europium with potassium thiocyanate could be observed the formation constant is too small to be measured with any accuracy. A solution containing 6 mM-metal required 0.2M-ligand to give an optical density of 0.16. We suggest that the formation constant is in the region of 5 under these conditions, and if so the molar extinction coefficient would be 60.

Ultraviolet Spectra.—In Table 3 we report some new absorption bands of reducible lanthanide complexes. The spectra are assigned to charge transfer because they fulfil the criteria mentioned earlier: similar new bands do not appear when the non-reducible lanthanides are complexed with the same ligands; the bands are strongly ligand-sensitive, but the band energies with any one ligand follow the sequence $\text{Eu} < \text{Yb} < \text{Sm} < \text{Tm}$.

For the charge-transfer spectra to be observed with the lanthanides the ligand must either be very reducing, e.g., diethyl dithiocarbamate,² or else transparent well into the ultraviolet region since ligand transitions often have molar extinction coefficients many times greater than the charge-transfer bands. This rules out many of the more familiar ligands, such as β -diketones, which complex strongly with the lanthanides. Some of the weaker complexes required very high ligand-to-metal ratios to observe the spectra, e.g., thiocyanate (see above). The complexes form much more strongly in ethanol; Jørgensen has noted that complexes between Ce^{3+} and Cl^- form much more strongly in 0.001M-ethanolic chloride than in 10M-hydrochloric acid. The

⁶ Davies, J., 1938, 2093.

⁷ Jenkins and Jones, J. Amer. Chem. Soc., 1952, **74**, 1353.

⁸ Banerjee, Science and Culture, 1950, **16**, 115.

TABLE 3.
Lanthanide(III) redox spectra at 18°.
Aqueous solutions.

Ligand	Metal	λ (m μ)	σ (kK)	$\delta(-)$	ϵ
SO ₄ ²⁻	Sm	208	48.1	2.0	60
	Eu	240	41.7	2.8	100
	Yb	225	44.5	1.9	15
		210	47.6	2.1	40
S ₂ O ₃ ²⁻	Eu	280	35.5	3.0	
SeO ₄ ²⁻	Eu	228	44	3.0	
NCS ⁻	Eu	292	34.2	3.2	60
	Yb	270	37	1.6	
H ₂ PO ₃ ⁻	Eu	218	45.8	3.1	140
H ₂ O (Ref. 1)	Eu	188	53.2	5.1	235
	Yb	170			
Ethanolic solutions.					
NCS ⁻	Sm	270	37		
	Eu	346	28.9	2.9	
	Tm	235	42.5		
	Yb	300	33.3	2.5	
Cl ⁻	Sm	219	45.7	2.8	200
	Eu	276	36.2	2.6	200
		240	41.7		
	Yb	244	41.0	2.1	
Br ⁻ (Ref. 2)	Sm	249	40.2	3.3	300
	Eu	320	31.2	3.6	110
		266	37.6		180
		230	43.5		170
	Tm	225	44.5	3.0	140
	Yb	282	35.5	3.2	40
	238	42.0	2.8	90	

spectra of the halide complexes of the reducible lanthanides are readily observed in ethanol but cannot be seen in water. However, the lanthanide sulphates and thiosulphates are insoluble in ethanol and their spectra could only be recorded in water.

Some other ligands were also investigated but no new band was noted with them in aqueous europium solutions, either because no complex formed under the chosen conditions or because the transition would be at too high an energy. These ligands included sulphite, azide, nitrite, cyanide, ascorbate, ammonia, hydroxylamine, and hydrazine.

Jørgensen found that the charge-transfer bands that he observed in europium and ytterbium bromides were split,² and he discusses this in terms of the possible transitions in monobromide complexes. He did not consider the possibility that some of the bands belong to higher species. In our spectra multiple bands were observed only for ytterbium sulphate and europium chloride. No second band could be seen in ethanolic europium thiocyanate although there is a considerable energy gap between the charge-transfer absorption and the edge of the ligand band.

DISCUSSION

Nature of the Species: Inner and Outer Sphere Complexes.—Besides the ligand-to-metal ratio the function of the solvent molecules must be considered in a solvated complex. When formation constants are derived from conductance data it is not possible to distinguish between an outer complex, with the inner co-ordination sphere made up entirely of solvent molecules, and an inner sphere complex where the ligand X has displaced a solvent molecule and taken up a position immediately adjacent to the metal. Usually equilibrium is rapidly established between these two entities but Fogel, Tai, and Yarborough⁹ were able to separate the inner and outer spheres chromium(III) monosulphate complexes on an ion-exchange column. They reported the *d-d* spectra of both species and deduced formation constants.

We have considered the lanthanide charge-transfer spectra and the formation constants

⁹ Fogel, Tai, and Yarborough, *J. Amer. Chem. Soc.*, 1962, **84**, 1145.

of the monosulphate complexes derived from these and other spectrophotometric measurements in terms of inner and outer complex formation. No useful information on these complexes can be obtained from the very small shifts which occur in the $f-f$ bands, but the larger perturbations of the $4f-5d$ bands in Ce^{3+} and Pr^{3+} have yielded formation constants.^{3,4} The first ligand transition of sulphate lies just beyond 50 kK and shifts to higher energy when the anion is complexed; at 51.6 kK free sulphate has an extinction coefficient of 30 but HSO_4^- does not absorb appreciably. (The wavenumber quoted represents the instrumental limit, not the band maximum.) From measurements of this shift Barnes and Monk¹⁰ estimated the formation constant of HSO_4^- to be 95 ± 1 , in reasonable agreement with the accepted value of 98 which derives from a spectrophotometric pH indicator study.¹¹ Although the shift in the ligand band can be seen with all the trivalent lanthanide ions an attempt to study $LaSO_4^+$ yielded only an order of magnitude answer, 5000 ± 4000 , because of an unfavourable combination of parameters.

Charge transfer between an adjacent ligand and a metal would be expected at much lower energy than that across a solvent sheath with the same ligand. Instead of solvent molecules forming the sheath other groups may do so, for instance ammonia in the cobaltic hexa-ammine ion. The removal of one of the ammonia molecules leaves room for a different ligand adjacent to the metal atom in the cobaltic penta-ammine salts. In water the first band associated with charge transfer from iodide to cobalt(III) in $[Co(NH_3)_6]^{3+} I^-$ is found at 35.8 kK compared with 26.1 kK for $[Co(NH_3)_5I]^{2+}$. Similarly the bromide complexes have their bands at 42.6 and 31.8 kK, respectively.¹²

The lanthanides would be expected to form both inner and outer complexes; the first intense bands having their origin in the inner species. This assignment is confirmed by the plots in the following Paper where the charge-transfer energies of one metal with a series of ligands are related to those of another metal with the same ligands. Fig. 1 in that Paper includes the europium data plotted against that for cobaltic penta-ammine. Water must appear as an inner ligand with both cations, and it can be seen that a line through the points denoting the other ligands also passes through that for the aquo-complexes. If any one of the other ligands formed only an outer complex with europium but an inner complex with cobalt penta-ammine this would appear as a marked deviation from the straight-line plot, and if no ligand except water formed an inner complex then the straight line would not include the point for water.

Thus the first charge-transfer bands in the lanthanide spectra originate in species where a ligand X has replaced a solvent molecule. Although the spectra originate in the inner complexes the formation constants calculated from them represent the sum of inner and outer complexes.¹³ The formation constants derived from conductance measurements also represent the sum of the inner and outer complexes; and so K_{spect} should equal K_{cond} . This seems to hold for systems containing cations of low charge, *e.g.*, the bisulphate ion mentioned above and the alkali metal thiosulphates.¹⁴ For triply charged cations, such as the lanthanides and the cobaltic amines, the spectrophotometric formation constants are frequently smaller than those from conductance. At the moment there seems to be no obvious reason for this, unless it be that some outer complexes which appear in the conductance measurements do not affect the concentration terms in the spectrophotometric method. These might possibly be interactions in which the ligand is separated from the metal by several layers of solvent.

For inner and outer complexes of the same ligand-to-metal ratio formation constants are additive, so that the difference between the spectrophotometric and conductance constants has the dimensions of a formation constant, although we are not clear at present just

¹⁰ Barnes and Monk, unpublished observations.

¹¹ Klotz and Singleterry, quoted by Klotz, *Chem. Rev.*, 1947, **41**, 373.

¹² Jørgensen, *Mol. Phys.*, 1963, **6**, 43.

¹³ Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.

¹⁴ Bjerrum, Schwartzenbach, and Sillen, "Stability Constants," *Chem. Soc. Special Publ. No. 7*, Part 2.

what it refers to. Table 4 contains the constants available for the lanthanide monosulphates from various methods and their differences. The latter remain similar throughout. The ratio of the difference to the larger constant is similar to that obtained by Fogel, Tai, and Yarborough⁹ for the chromium(III) monosulphate system, where the difference was 16 and the larger constant 66 at 60°.

TABLE 4.

Formation constants of lanthanide(III) monosulphate complexes in water at 25°, corrected to zero ionic strength.

Metal	K_{spect}	$K_{\text{cond.}}$	Difference
Ce.....	2330 ^a	3850 ^c	1500
Pr.....	2180 ^b	4200 ^c	2000
Sm.....	3450 ^b	4550 ^c	1100
		4250 ^d	800
Eu.....	2250	3630 ^e	1400

^a Ref. 3. ^b Ref. 4. ^c Conductance data from Spedding and Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 882. ^d Data from (c), recalculated in Ref. 4. ^e Solvent extraction data, Manning and Monk, *Trans. Faraday Soc.*, 1962, **58**, 938.

Reducing Power of the Ligands.—The order of the charge-transfer bands with a given metal gives a sequence of increasing ease of electron removal from the ligand: $\text{H}_2\text{O} < \text{H}_2\text{PO}_2^- < \text{SeO}_4^{2-} < \text{SO}_4^{2-} < \text{S}_2\text{O}_3^{2-} < \text{CNS}^-$ in water and $\text{Cl}^- < \text{Br}^- < \text{CNS}^-$ in ethanol. It appears that thiocyanate will reduce metal ions under these conditions almost as well as iodide.

Hypophosphite is usually classified as a strong reducing agent. Its position so early in the series is surprising until it is recalled that in this case the oxygen $p\pi$ orbitals of the ligand are transferring an electron into the lowest lying empty $4f$ orbital of the metal, whereas in the oxidation of hypophosphite in solution a hydride bonded to the phosphorus atom is replaced by oxygen.

Sulphate and selenate are seldom regarded as reducing agents but the evidence is clear that electron transfer from the anion is occurring in the excited state since new bands are seen only with those metal ions that can be reduced most readily. Once again the electron must come from oxygen $p\pi$ orbitals.

The sequence, then, is not one of reducing power in the sense of solution redox potentials. It reflects the ease of transfer of an electron in forming an excited state of the complex; in the case of the halides this is the same process as is measured by the redox potential, but for the other ligands the formation of a charge-transferred excited state is only one step in the reaction described by the half cell potential of the ligand.

It has come to our notice that Professor K. W. Sykes of Queen Mary College, London, has observed bands in the u.v. region in some complexes of samarium, europium, and ytterbium. He also assigns these to charge transfer.

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