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VARIATION OF THE PARAMETERS  
OF ELECTROSTATIC INTERACTION  $F_k$   
DERIVED FROM ABSORPTION SPECTRA  
OF LANTHANIDE COMPLEXES

BY

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## Synopsis.

The narrow  $f^n$ -absorption bands of *Pr* (III), *Nd* (III), *Sm* (III), and *Gd* (III) are shown to be shifted  $\sim 1\%$  towards lower wave numbers in anion complexes, compared to the aquo ions. This effect is interpreted as a decrease of the parameters  $F^k$  of electrostatic interaction between electrons in a partly filled shell. The ratios  $F^2:F^4$  and  $F^4:F^6$  are not freely adjustable, but slightly depend on the radial wave function. It is possible to extrapolate from the values of  $F^k$  to the average radius  $r_0$  of the partly filled shell, which is somewhat smaller than the ionic radii of trivalent lanthanides. The decrease of  $F^k$  is shown to be caused by partly covalent bonding. The broad  $4f \rightarrow 5d$  transitions of *Ce* (III), which occur at lower wave number in the aquo ion than in gaseous  $Ce^{+3}$  is further shifted in anion complexes where the crystal field also gives varying splittings of  $5d$ . A weak band of the *Ce* (III) aquo ion possibly originates from a rare geometrical configuration. The absorption spectra of *CeCl*<sub>3</sub> in *C*<sub>2</sub>*H*<sub>5</sub>*OH* and *HCl* are reported, and the complex equilibria discussed.

The absorption spectra of transition group complexes with partly filled  $d$ -shells can be described by crystal fields of different strength and symmetry, acting on the terms of the gaseous ion, known from atomic spectroscopy.<sup>50</sup> TANABE and SUGANO,<sup>88</sup> OWEN,<sup>67</sup> and ORGEL<sup>66</sup> introduced the idea that the term differences are smaller in complexes than in the gaseous ions. This is equivalent to a decrease of the parameters of electrostatic interaction  $F_k$  as defined by CONDON and SHORTLEY.<sup>9</sup> SCHÄFFER<sup>77</sup> and the present author<sup>48,50</sup> found that  $F_k$  decreases more in anion complexes such as tris-oxalato or hexa-chloro complexes than in complexes with neutral ligands such as water and amines. Representative values of the decrease of  $F_k$  are 8–12 % in manganese (II), 15–30 % in nickel (II), 20–50 % in chromium (III), and even more in cobalt (III) and rhodium (III) complexes. There is a rough correlation between the decrease of  $F_k$  and the crystal field strength ( $E_1 - E_2$ ) in octahedral complexes,<sup>49</sup>—about 2 % for each 1000 K.\* The present paper is a report on investigations into the much smaller decrease of  $F_k$  in complexes with partly filled  $f$ -shells and the behaviour of  $[Xe] 4f \rightarrow [Xe] 5d$  transitions in cerium (III) complexes. Absorption spectra of complexes in solution at room temperature are measured.

### Praseodymium (III) Complexes.

The four visible band groups<sup>32</sup> of  $Pr$  (III) are caused by transitions from  $^3H_4$  to  $^1D_2$ ,  $^3P_0$ ,  $^3P_1$ , and  $^3P_2$ , respectively. The first group is rather broad in solution, while the three other groups in the blue are each represented by a single maximum of the

\* The unit of wave number  $\text{cm}^{-1}$  will be called  $K$  (= Kayser) in this paper in accordance with the proposal made by the Joint Committee for Spectroscopy, 1952.

TABLE I : The shift of absorption bands of Praseodymium (III) complexes.

Excited level:	$^3P_0$	$^3P_1$	$^3P_2$	Average shift	Ref. no.
Aquo ion .....	4822 Å	4675 Å	4430 Å	0.0 % <sub>0</sub>	
Acetate .....	4830 — 35	4695 — 90	4446 — 80	0.3	13
Ethylenediaminetetraacetate .....	4878 — 240	4730 — 250	4478 — 245	1.2	13
Nitrogenetriacetate.....	4855 — 145	4720 — 205	4455 — 130	1.2	13
	(4895) — 310	(4770) — 430	(5110) — 410		
Tartarate .....	4854 — 140	4724 — 220	4463 — 170	0.8	13
	4830 — 35	(4648) — 120	(4410) — 100		
Citrate.....	4861 — 170	4712 — 170	4475 — 230	1.1	13
	4890 — 290	4732 — 260			
$Pr^{+++}$ in 10 M HCl .....	4835 — 55	4687 — 55	4444 — 70	0.3	13
$PrF_3$ .....	4803 — 80	4680 — 20	4425 — 25	0.1	13
$PrCl_3$ .....	4898 — 315	4755 — 360	4503 — 370	1.6	13
$PrBr_3$ .....	4930 — 450	4788 — 510	4532 — 510	2.2	13
$PrJ_3$ .....	4959 — 570	4821 — 650	4565 — 680	2.9	13
$PrCl_3$ , 7 $H_2O$ .....	4828 — 25	4727 — 240	4462 — 160	0.4	13
$PrCl_3$ , 8 $NH_3$ .....	4867 — 190	4732 — 260	4480 — 250	1.1	12
$PrBr_3$ , 6 $H_2O$ .....	4845 — 95	4718 — 195	4462 — 160	0.3	13
$PrJ_3$ , 6 $H_2O$ .....	4855 — 140	4737 — 280	4484 — 270	1.1	13
$PrJ_3$ , 9 $H_2O$ .....	4845 — 95	4708 — 150	4452 — 110	0.5	13
$Pr_2(O_3)_3$ .....	4840 — 75	4720 — 200	4445 — 75	0.6	14
$Pr(NO_3)_3$ , 6 $H_2O$ .....	4841 — 80	4705 — 135	4445 — 75	0.4	14
$(NH_4)_2Pr(NO_3)_5$ , 4 $H_2O$ .....	4810 — 50	4640 — 160	4390 — 205	-0.6	14
$Pr(OH)_3$ .....	4849 — 110	4749 — 340	4460 — 150	1.0	14
$Pr_2O_3$ , ignited 550° C. ....	4882 — 250	4850 — 770	4585 — 670	3.1	15
$Pr_2O_3$ , ignited 900° C. ....	4960 — 570	4948 — 1170	4790 — 1220	5.7	15
$Pr(JO_3)_3$ , 4 $H_2O$ .....	4847 — 110	4720 — 200	4475 — 230	0.9	16
$Pr_4O_{13}$ .....	4850 — 120	4737 — 280	4450 — 100	0.8	16

aquo ion. These bands are shifted  $\sim 1\%$  towards lower wave numbers in the anion complexes in solution as seen from Table 1. The absorption bands of the nitrogentriacetate and citrate complexes are split into several components (but it is not certain that

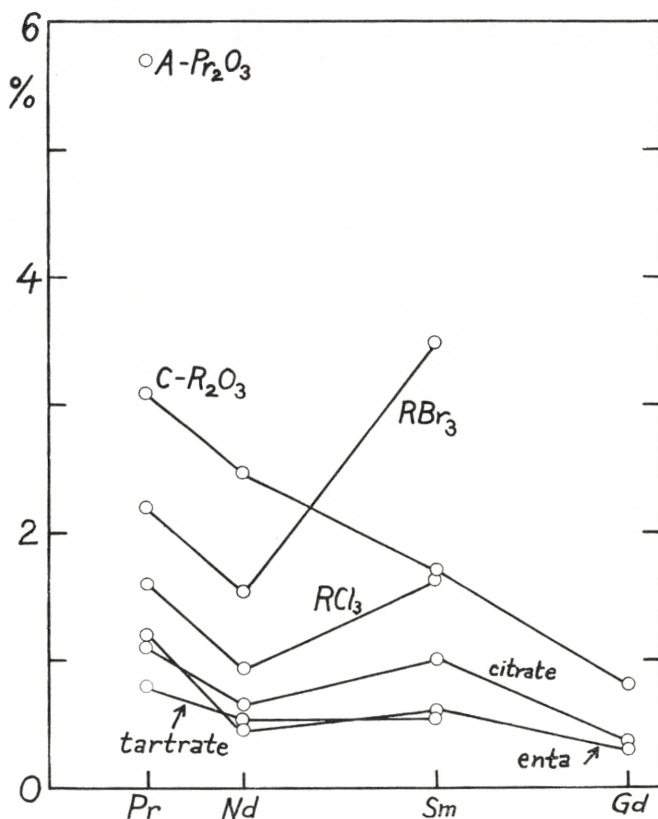


Figure 1. Decrease of the term distances in lanthanide complexes, relative to the aquo ions. The percentage decrease is given as a function of the atomic number for  $A-Pr_2O_3$ , the  $C$ -oxides, anhydrous bromides and chlorides, and the solutions of citrates, tartrates, and ethylenediaminetetraacetates studied here.

these spectra correspond to a single complex, with a definite geometrical configuration, even though the spectra are independent of the concentration of the ligand, when it is present in a large excess). However, average shifts  $\sim 1\%$  can also be estimated in these complexes. BIRMINGHAM and WILKINSON<sup>4</sup> found a larger shift,  $\sim 3\%$ , relative to the aquo ion in the strongly split band groups of praseodymium (III) tris (cyclopentadienide). Figure 1 illustrates the relative decrease of this red shift of the

absorption bands of several compounds with increasing atomic number in the series *Pr*(III), *Nd*(III), *Sm*(III), and *Gd*(III). EPHRAIM and BLOCH<sup>12-15</sup> studied the absorption spectra of solid praseodymium (III) salts and found in the anhydrous halides a red shift, amounting to  $\sim 2\%$  of the wave number, while the solid hydrates and ammoniacates exhibited much smaller red shifts. In only one case, the ammonium double nitrate, the shift was found towards higher wave numbers (and the percentage is then reckoned as negative in Table 1). Most other praseodymium (III) salts with oxy-anions exhibit moderate shifts towards the red. An extreme case is represented by  $Pr_2O_3$ , where the shift can exceed  $5\%$ . BOULANGER<sup>7</sup> later studied *Pr*(III) and found a similar large shift in some forms of  $Pr_2(MoO_4)_3$ . The existence of more crystal forms of  $Pr_2O_3$  (*A*-type stable at high temperatures, *C*-type at low) was established by GOLDSCHMIDT.<sup>26</sup> Since the local environment of oxygen atoms around a praseodymium (III) ion in *C*- $Pr_2O_3$  consists of two types of defect cubes<sup>97</sup> (two of the eight places are empty) and in *A*- $Pr_2O_3$  consists of seven irregularly arranged oxygen atoms,<sup>97</sup> the low co-ordination numbers 6 and 7 can be said empirically to produce decreased term differences, relative to the ordinary 9-co-ordinated lanthanide complexes.<sup>34, 36, 68</sup> As discussed by ZACHARIASEN,<sup>81</sup> the ionic distances increase by  $0.11 \text{ \AA}$  for the co-ordination number  $N = 9$  and by  $0.19 \text{ \AA}$  for  $N = 12$ , as compared with cations with  $N = 6$ . The values given by ZACHARIASEN for the ionic radii of 6-co-ordinated lanthanides (see Table 8) perhaps deviate from those given by GOLDSCHMIDT due to this effect.

EPHRAIM explained the shift in wave number as a contraction of the lanthanide ion, when influenced by many ligand atoms, as found in solvates and in solution. In partly covalent compounds, such as  $Pr_2O_3$ ,  $PrJ_3$ ,  $PrBr_3$ , and  $PrCl_3$ , the  $4f$ -shell was assumed to have a larger radius, corresponding to lower wave numbers. It is interesting that the acetylacetonate  $Pr\text{ acac}_3$  is not very covalent according to this criterion (Table 1). As discussed below, Ephraim's hypothesis is qualitatively correct, if restricted to the dilatation in covalent compounds. The high wave numbers found of the absorption bands of aquo ions and double nitrates do not in the author's opinion depict an active

influence of the environment; rather the conditions of the free, gaseous ion with the highest wave numbers are approached.

Even before the crystal field theory of BETHE,<sup>30</sup> BRUNETTI<sup>8</sup> assumed the observed band shifts of praseodymium(III) salts to be due to the strong intermolecular electrostatic fields. However, while the sub-levels of each level have different energy caused by this Stark-effect, the levels can only be moved by variation of the central field, as shown below from the theory of perturbations.

The shifts found at room temperature are composed of changes in the energy differences between the levels  $2^{S+1}L_J$  and changes of the sub-levels of the excited levels and the ground level, due to the influence of crystal fields. The sub-levels of a given level are usually distributed over a range  $\sim 200 K$ . The absorption spectra of solids cooled to low temperatures (e. g. in liquid helium) are caused by transitions from the lowest sub-level of the ground-level, since other sub-levels are not sufficiently populated in the Boltzmann distributions. Even though the lowest sub-level was situated some  $50 K$  lower in the anion complexes relative to the aquo ion, it could not explain the observed red shifts between  $100$  and  $1000 K$ .

### Neodymium (III) Complexes.

The excited level  $2P_{1/2}$ , which cannot split into sub-levels due to the Kramers degeneracy, corresponds to a very narrow band in  $Nd(III) \sim 23400 K^{44}$ . The shift observed of this band is given in Table 2a, while the shift of some other band groups are shown for a few anion complexes in Table 2b. The results are scattered around  $1 \text{ }^0/0$  shift and seem to be smaller than in the corresponding praseodymium(III) complexes (cf. Fig. 1).

LIVELING<sup>55</sup> discovered that the absorption bands of  $NdCl_3$  and  $Nd(NO_3)_3$  are shifted towards lower wave numbers for organic solvents than for aqueous solutions. JONES et al.<sup>39, 40, 41</sup> thoroughly investigated these effects and especially the intermediate spectra of solutions with a few volume  $^0/0$  water. The exchange process of water, alcohols, and anions will be discussed below in a separate section. SCHÄFFER<sup>78</sup> and UZUMASA<sup>91, 92</sup> also studied

TABLE 2 a. The shift of absorption bands of Neodymium (III) complexes.

a: The excited level	${}^2P_{1/2}$		Shift	Ref. no.	
Aquo ion .....	4273 Å	23400 K	0.00 %		
Ethylenediaminetetraacetate ...	4292	— 105	0.44		
Nitrogenetriacetate.....	4293	— 110	0.47		
Tartrate .....	4296	— 125	0.54		
Citrate.....	4301	— 150	0.65		
$Nd^{+++}$ in 12 M HCl.....	}	4330	— 310	1.33	}
		4297	— 130	0.56	
		4271	+ 10	— 0.05	
		4328	— 285	1.24	
		4291	— 100	0.41	
		4272	+ 5	— 0.02	
$NdCl_3$ in $CH_3OH$ .....	4295	— 120	0.52	6,39	
$Nd(NO_3)_3$ in $CH_3OH$ .....	4280	— 40	0.16	39	
3 M $Nd(NO_3)_3$ in $H_2O$ .....	4280	— 40	0.16	41,82	
Didymium glass .....	4312	— 210	0.94		
$Nd\ aca_3$ , anhydrous .....	4305	— 170	0.75	21	
$Nd\ aca_3$ , $2H_2O$ .....	4301	— 150	0.65	21	
$Nd\ aca_3$ in $C_6H_6$ , $CCL_4$ , $CS_2$ , or $C_2H_5J$ .....	}	4310	— 200	0.87	}
		4303	— 160	0.70	
		4297	— 130	0.56	
$Nd\ aca_3$ in $CH_3OH$ .....	4302	— 160	0.68	73	
$Nd(BrO_3)_3$ , 9 $H_2O$ .....	4273.8	— 5	0.02	11	
$Nd(C_2H_5SO_4)_3$ , 9 $H_2O$ .....	4279.7	— 36	0.14	11	
$NdCl_3$ , 6 $H_2O$ (in La-salt) .....	4283.6	— 58	0.23	11	
$NdF_3$ .....	4265	+ 45	— 0.11	17	
$NdCl_3$ .....	4313	— 215	0.94	17	
$NdBr_3$ .....	4334	— 330	1.53	17	
$Nd_2(C_2O_4)_3$ , 10 $H_2O$ .....	4299	— 140	0.61	17	
$(NH_4)_2 Nd(NO_3)_5$ , 4 $H_2O$ .....	4261	+ 65	— 0.28	17	
$Nd_2O_3$ .....	4378	— 560	2.46	17,96	

this phenomenon and HARTMANN and LORENZ<sup>28</sup>  $NdCl_3$  in mixtures of water and formamide.

The acetylacetonate  $Nd\ aca_3$  has been studied in a solid state<sup>21</sup> and in many different solvents.<sup>73</sup> Since the dihydrate is rather stable,<sup>21</sup> and since  $Nd\ aca_3$  seems\* to dimerize<sup>38</sup> in  $CCL_4$  and  $CS_2$ ,

\* Note added in Proof: However, MOELLER and ULRICH<sup>61a</sup> detected no dimerization by cryoscopy. These authors compare the solvent effects on acetylacetonates thoroughly and find much higher intensity of some bands of  $Nd\ aca_3$ ,  $Ho\ aca_3$ , and  $Er\ aca_3$  than of the corresponding aquo ion bands, while other bands of these complexes, and all bands of  $Pr\ aca_3$ , do not exhibit increased intensities.



TABLE 2 b. The shift of absorption bands of Neodymium (III) complexes.

The excited levels:	Aquo ion		Ethylenediamine-tetraacetate		Nitrogentriacetate		Tartrate		Citrate	
Two sub-levels of $4F_{7/2}$	7422 Å	13470 K	7470 Å	— 85 K		7450 Å	— 50 K	7475 Å	— 95	
	7340	13620	7370	— 55		7370	— 55	7385	— 85	
Sub-levels of $4G_{9/2}$ (?)	5220	19160	5265	— 170	5260 Å	— 140 K	— 130	5255	— 135	
	5215	19180	5250	— 120	5250	— 120	— 130	— 135		
	5125	19510	5145	— 125	5160	— 130	— 110	5135	— 90	
	5100	19610			5130	— 110		5135	— 90	
Three levels of $4D$ . . .	3539	28260	3576	— 295	3568	— 230	— 240	3576	— 295	
			3551	— 95			— 255	3531	— 190	
	3507	28530	3536	— 235	3533	— 210	— 235	3501	— 280	
	3468	28830	3496	— 235	3493	— 210	3496	— 235		
Average shift . . . . .		0.0 %		0.7 %		0.7 %			0.7 %	0.8 %

there seems to be a considerable rest affinity in the 6-co-ordinated  $Nd\text{ }aca_3$ .

Recently, ethylenediaminetetraacetate and nitrogentriacetate have been discussed by MOELLER and BRANTLEY<sup>60</sup> and VICKERY<sup>94</sup> as a mean for splitting of the absorption bands of lanthanides. The low symmetry of the crystal field produces  $2J + 1$  distinct sub-levels from each level in the case of an even number of  $4f$ -electrons and  $J + \frac{1}{2}$  sub-levels for an odd number of  $4f$ -electrons. However, in many cases, such as  $Pr\text{ }enta^-$  and  $Gd\text{ }enta^-$  studied here, the absorption bands are not conspicuously more split than for the aquo ions. Actually, the red shift is the most prominent difference between the spectra of  $Nd(III)$  anion complexes (such as  $Nd(SO_3)_3^{---}$ ) and the aquo ion.<sup>95</sup>

If  $\delta$  denotes the distance from a maximum with the molar extinction coefficient  $\varepsilon_n$  to the wave number  $\sigma$ , where  $\varepsilon = \frac{\varepsilon_n}{2}$ ,  $\delta$  is only 16  $K$  for the  ${}^2P_{1/2}$  of the neodymium(III) aquo ion, exemplifying the sharpness of transitions between two single sub-levels (cf. Fig. 4). The somewhat broader band at 23090  $K$  cannot be re-found in the other complexes and is perhaps caused by an excited sub-level at 320  $K$  over the ground-level.

SATTEN<sup>75</sup> found the five sub-levels of the ground-level  ${}^4I_{9/2}$  at 0,115,184,363, and 384  $K$  in  $Nd(BrO_3)_3, 9H_2O$ , while SATTEN and YOUNG<sup>76</sup> found the sub-levels at 0,76,226,263, and 301  $K$  in  $Nd_2(SO_4)_3, 8H_2O$ .

### Samarium (III) Complexes.

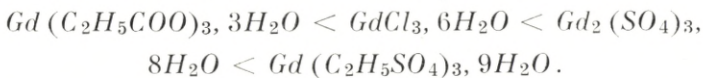
Only the band slightly below 25000  $K$  has been measured here. It is presumably<sup>44</sup> due to a transition from  ${}^6H_{5/2}$  to a level of  ${}^6P$ . In the aquo ion, the band is symmetrical with  $\delta = 100$   $K$ , while it develops a shoulder towards the red in some of the anion complexes. The shifts are somewhat smaller than found for the soluble complexes of  $Nd(III)$ , while the anhydrous solid compounds<sup>17</sup> such as  $SmCl_3$  and  $SmBr_3$  exhibit a rather large shift towards lower wave numbers (cf. Fig. 1).

TABLE 3. The shift of an absorption band of Samarium (III) complexes.

				Shift	Ref.
Aquo ion .....	4012 Å	24920 K		0.0 %	
Ethylenediaminetetra- acetate .....	4036 (4060)	24780 24630	-140 K -290	0.6	
Nitrogentriacetate.....	4036	24780	-140	0.6	
Tartrate .....	4034	24790	-130	0.55	
Citrate.....	4051	24690	-230	1.0	
<i>Sm</i> <sup>+++</sup> in 12 <i>M HCl</i> .....	4017	24890	-30	0.1	
<i>SmCl</i> <sub>3</sub> .....	4080	24510	-410	1.7	17
<i>SmCl</i> <sub>3</sub> , 8 <i>NH</i> <sub>3</sub> .....	4037	24770	-150	0.6	17
<i>SmBr</i> <sub>3</sub> .....	4156	24050	-870	3.5	17
<i>Sm</i> <sub>2</sub> <i>O</i> <sub>3</sub> .....	4082	24500	-420	1.7	17

### Gadolinium (III) Complexes.

The *Gd*(III) aquo ion exhibits a rather complicated spectrum in the ultraviolet<sup>61,87</sup> consisting of bands with  $\delta \sim 10\text{--}15 K$ . The band groups are assumed<sup>44</sup> to have the multiplets <sup>6</sup>*P* and <sup>6</sup>*I* as the excited levels. The spin-forbidden character of the transition from <sup>8</sup>*S*<sub>7/2</sub> is not evident in the four intense bands. As appears from Table 4 and Figure 2, these bands are regularly shifted in the ethylenediaminetetraacetate and citrate, while the fine structure is somewhat blurred out. NUTTING and SPEDDING<sup>64</sup> investigated many solid gadolinium(III) salts and found a series of increasing wave numbers of the band groups:



BERTON and BOULANGER<sup>3</sup> found the band groups of *Gd*<sub>2</sub>*O*<sub>3</sub> shifted much more (0.8 %) towards lower wave numbers than the other anion complexes (~ 0.3 %) as seen from Table 4 and Fig. 1. Thus, the general trend of strongest red shift of the oxides is common to all the lighter lanthanides.

### Erbium (III) Complexes.

SELWOOD<sup>82</sup> found that for strong nitrate solutions, the bands of *Nd*(III) are shifted towards lower wave numbers, but of *Ho*(III) and *Er*(III) towards higher wave numbers. Thus, the

TABLE 4. The shift of absorption bands of Gadolinium (III) complexes.

Group no.	Aquo ion	Ethylenediaminetetraacetate		Citrate		$Gd_2O_3$ (ref. 3)				
		Shift	Shift	Shift	Shift					
1.....	3118 Å	32030 K	—	3130 Å	31950 K	80 K	3140 Å	31850 K	180 K	
2.....	3060	32680	—	—	—	—	3082	32450	230	
	2792	35820	2800 Å	35710 K	110 K	2804	35660	160	—	
3.....	2789	35860	2798	35740	120	2799	35730	130	—	
	2765	36170	2772	36070	100	2777	36010	150	2789	
	2760	36230	2767	36140	100	2769	36120	110	2784	
4.....	2759	36240	—	—	—	2766	36150	120	—	
	2757	36270	—	—	—	—	—	—	—	
	2744	36450	2751	36350	120	2756	36280	170	2769	
5.....	2740	36500	—	—	—	2750	36360	140	—	
	2735	36560	2740	36500	100	2742	36470	90	2759	
	(2734)	36580	—	—	—	2740	36500	100	2755	
6.....	2732	36600	—	—	—	2737	36550	90	2751	
	(2729)	36640	—	—	—	—	—	—	—	
7.....	2522	39650	2530	39530	120	2532	39500	150	—	
8.....	2461	40630	(2470)	40490	140	—	—	—	—	
Average shift.....	—	0.00 % <sub>0</sub>	—	—	0.30 % <sub>0</sub>	—	—	0.36 % <sub>0</sub>	—	0.8 % <sub>0</sub>

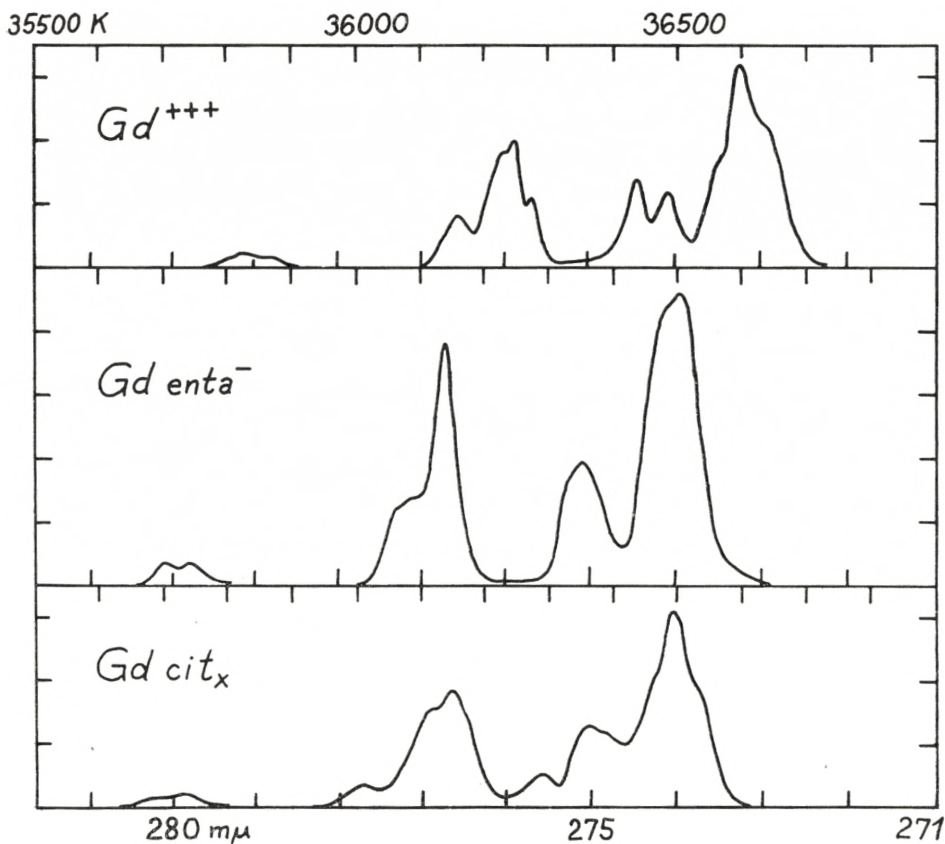


Figure 2. The absorption spectra of Gadolinium (III) complexes. The aquo ion, the ethylenediaminetetraacetate and the citrate are measured as described in the experimental section. The unit of the molar extinction coefficient scale is 1.

decreasing red shift in anion complexes with increasing atomic number seems to be reversed in this case. EPHRAIM, JANTSCH, and ZAPATA<sup>18</sup> still observed a small red shift in the anhydrous halides of holmium (III) and erbium (III). VICKERY<sup>94</sup> did not detect any systematic trend in the wave numbers of  $Er\ enta^{-}$  and  $Er(H_2O)_N^{+++}$ . Table 5 gives some of the strongest bands of these two complexes. BIRMINGHAM and WILKINSON<sup>4</sup> did not observe a shift in erbium(III) tris(cyclopentadienide) either.

A similar result is found by HELLWEGE et al.<sup>31,33</sup> for  $EuCl_3 \cdot 6H_2O$  and  $Eu_2Zn_3(NO_3)_{12} \cdot 24H_2O$ , where the centres of gravity of  ${}^5D_0$ ,  ${}^5D_1$ , and  ${}^5D_2$  only deviate 0.012, 0.014, and 0.017 % respectively.

TABLE 5. The strongest absorption bands of Erbium (III) complexes.

Group no.	Aquo ion		Ethylenediaminetetraacetate	
	1.....	6650 Å 6520	15040 K 15340	6560 Å 6540 6505
2.....	5230 (5210)	19120 19190	5210 5195 5185	19190 19250 19290
3.....	4915 4875 (4855)	20350 20510 20600	4885	20470
4.....	4535 4500	22050 22220	4505	22200
5.....	4070 4055	24570 24660	4075 4055	24540 24660
6.....	3795	26350	(3804) 3788 3780 3776	26290 26400 26460 26480
7.....	3645 (3640)	27440 27470	3664 3653 3607	27290 27380 27720

### Ytterbium (III) Complexes.

Since there is only one hole in the  $4f$ -shell, only one term exists of  $[Xe]4f^{13}$ , and the parameters of electrostatic interaction  $F_k$  cannot be determined. The band group<sup>60</sup> with maxima at 10,250 K ( $\epsilon = 1.7$ ) and 10,620 K ( $\epsilon = 0.6$ ) of the aquo ion is therefore caused by the spin-reversing transition  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ . The ethylenediaminetetraacetate is not very different with maxima at 10,220 K ( $\epsilon = 1.8$ ) and 10,640 K ( $\epsilon = 0.9$ ). All four bands have  $\delta = 150$  K.

FREED and MESIROW<sup>20</sup> reported broad bands of Yb(III) in the ultraviolet. Even though the bands were weaker than those of Ce(III), they were believed to be  $[Xe]4f^{13} \rightarrow [Xe]4f^{12}5d$  transitions. However, the solution of ytterbium(III) perchlorate measured here does not show any sign of these bands, and  $\epsilon$  is below 0.1 in the range 25,000—40,000 K. Probably, traces of

iron(III) or organic materials are responsible for the frequent observation of broad ultraviolet absorption bands of lanthanides with higher atomic number than cerium.

### Actinide Complexes.

The anion effect seems to be somewhat larger and more varying in the actinides than in the lanthanides. The present author<sup>43</sup> reported the bands of the uranium(IV) tetraoxalate ion with  $\sim 2\%$  lower wave numbers than of the aquo ion. Similar results have been obtained from the solutions in strong hydrochloric acid, while the effect is negligible in the ethylenediaminetetraacetate. The spreading of the sub-levels of U(IV) is rather large as evident from GRUEN'S study of fluorides.<sup>27</sup> In the chloride and nitrate complexes of plutonium(III) and plutonium(IV), the bands are shifted towards higher wave numbers.<sup>81</sup> In a note in *Acta Chem. Scand.*, it will be discussed, how the absorption spectrum of grey U(III) in  $HClO_4$  or 2-6  $MHCl$  is changed in 11  $MHCl$ , corresponding to the dark red colour.<sup>44</sup>

### Cerium (III) Complexes.

FREED<sup>19</sup> discovered three high and broad bands of  $Ce(III)$  in the ultraviolet, which by cooling of  $Ce(C_2H_5SO_4)_3 \cdot 9H_2O$  from 300° K to 20° K were shifted only 400 K towards higher wave numbers. Besides these bands,  $CeCl_3 \cdot 6H_2O$  was found to exhibit a weak band at 33,100 K at room temperature only.

LANG<sup>54</sup> found the energy levels of gaseous  $Ce^{+++}$ :

$$\begin{array}{l}
 [Xe] 4f: \quad {}^2F_{5/2} \quad 0 K \\
 \quad \quad \quad {}^2F_{7/2} \quad 2253 \\
 [Xe] 5d: \quad {}^2D_{3/2} \quad 49737 \\
 \quad \quad \quad {}^2D_{5/2} \quad 52226 \\
 [Xe] 6s: \quad {}^2S_{1/2} \quad 86602.
 \end{array}$$

The internal  ${}^2F$ -transition has not yet been identified in cerium(III) complexes, even though the reflection spectrum of an anhydrous compound such as  $CeF_3$  probably would show it. KRÖYER and BAKKER<sup>53</sup> estimate the splitting of the doublet as 1900 K from the emission spectrum of fluorescent cerium(III) compounds.

The strong bands have as excited levels the term  ${}^2D$ , split by the crystal field. Due to KRAMERS' degeneracy, no more than five levels are possible for any symmetry of the complex. Five bands are known of the aquo ion, according to STEWART<sup>87</sup> and HEIDT and BERESTECKI<sup>29</sup> (see Table 6 and Fig. 3). It is evident that the centre of gravity of these levels are situated some thousand  $K$  below 51,230  $K$  from the gaseous ion.

Table 6 demonstrates that the anion effect in  $Ce(III)$  complexes is composed of two phenomena: the average distance between the electron configurations  $[Xe] 4f$  and  $[Xe] 5d$  is decreased, and the crystal field splitting of  $[Xe] 5d$  is changed with resulting variation of the relative positions of the strong absorption bands.

The two strongest absorption bands of the cerium(III) aquo ion are shifted  $\sim 4000 K$  towards lower wave numbers in the case of ethylenediaminetetraacetate, nitrogentriacetate, and acetate complexes (Table 6). Thus, in the latter complexes, the distance between the electron configurations  $[Xe] 4f$  and  $[Xe] 5d$  is roughly 72 % of the distance in the gaseous ion, while in the aquo ion the value is 83.5 %, if the band at 39,500  $K$  is assumed to be doubly degenerate, and the small band at 33,700  $K$  is not reckoned, as rationalized below.

FRIED and HINDMAN<sup>22</sup> found a close analogy between the absorption spectra of protactinium(IV) and cerium(III), implying the ground state  $[Em] 5f$  of the former ion. Thus, the two aquo ions have probably the same co-ordination number, 8 or 9. There does not seem to be a small band of  $Pa(IV)$  at a lower wave number than the strong bands, which are situated<sup>22</sup> at 36,300  $K$ , 39,200  $K$ , and 44,800  $K$  with  $\epsilon_n \sim 1500, 1000, \text{ and } 400$ , respectively. Thus, the spreading of the three bands in  $Pa(IV)$  is 8600  $K$ , while the analogous distance in  $Ce(III)$  is 5600  $K$ . This increase in the crystal field strength, amounting to 54 % from 5 $d$ - to 6 $d$ -electrons, can be compared with the crystal field strength, denoted by  $(E_1 - E_2)$  in octahedral  $d^n$ -complexes, which have the ratios 1.00:1.45:1.75 for 3 $d$ -, 4 $d$ -, and 5 $d$ -electrons, respectively.<sup>47, 50</sup> The absolute value of the crystal field splitting of  $[Xe] 5d$  in  $Ce(III)$  and of  $[Em] 6d$  in  $Pa(IV)$  is rather low, as compared with  $(E_1 - E_2) \sim 20,000 K$  of titanium(III) and other trivalent hexaquo ions. The small values found for cerium(III) may be explained by three causes: the symmetry



TABLE 6. The shift of absorption bands of Cerium (III) complexes. Wave length  $\lambda_n$ , wave number  $\sigma_n$ , and molar extinction coefficient  $\epsilon_n$  of the band maxima.

	$\lambda_1$	$\sigma_1$	$\epsilon_1$	$\lambda_2$	$\sigma_2$	$\epsilon_2$	$\lambda_3$	$\sigma_3$	$\epsilon_3$	$\lambda_4$	$\sigma_4$	$\epsilon_4$	$\lambda_5$	$\sigma_5$	$\epsilon_5$
Aquo ion*	2970 Å	32700 K	16	2525 Å	39600 K	710	2395 Å	41700 K	600	2215 Å	45100 K	380	2110 Å	47400 K	270
CeCl <sub>3</sub> in 6 M HCl	3005	33300	32	2525	39600	680	2405	41600	560	2225	44900	380			
CeCl <sub>3</sub> in 12 M HCl	3090	32400	430	2555	39100	570	(2445)	40900	—						
CeCl <sub>3</sub> in conc. HCl, ref. 10	3100	32300	—	2585	38700	—	2480	40300	—	2415	41400	—			
CeCl <sub>3</sub> in C <sub>2</sub> H <sub>5</sub> OH:															
C <sub>2</sub> H <sub>5</sub> O															
0.0004 M 0.3 M	3090	32400	700	2505	39900	580									
0.0004	3000	33300	210	2505	39900	760									
0.002	3055	32700	480	2505	39900	450	(2250)	44400	—						
0.002	3025	33100	360	2505	39900	600	(2410)	41500	550	(2220)	45000	700	(2110)	47400	—
0.002	2995	33400	160	2520	39700	710	2400	41700	660	2225	44900	560	2115	47300	660
0.002	2990	33400	100	2530	39500	760	2400	41700	690	2225	44900	560	2120	47200	660
0.002, 1 M HCl, 7 M H <sub>2</sub> O.	2985	33500	100	2525	39600	720	2400	41700	670	2230	44800	540	2115	47300	610
Ce <sup>+++</sup> in 0.1 M Na <sub>2</sub> SO <sub>4</sub>	2965	33700	33	2545	39300	650	2410	41500	600	2230	44800	400	2110	47400	400
0.1 M Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , ref. 74	2960	33800	36	2540	39400	740	2400	41700	630						
Acetate				2740	36500	600									
Tartrate	(3330)	30000	—	2810	35600	—									
Citrate	3260	30700	150	2785	35900	600									
Ethylenediaminetetraacetate															
Nitrogeniacetate				2810	35600	480	2610	38300	450						
				2960	33800	550	2750	36400	450						

\* 0,002 M CeCl<sub>3</sub> in H<sub>2</sub>O, 1 M, 3 M, and 5 M aqueous HCl give identical values for  $\lambda_2$ ,  $\lambda_3$ ,  $\lambda_4$ ,  $\epsilon_2$ ,  $\epsilon_3$ , and  $\epsilon_4$  within the experimental uncertainty (10 Å and  $\sim$  10 in  $\epsilon$ ).

of the crystal field may produce a low over-all splitting (especially, if it approximates spherical symmetry); and ions with no crystal field stabilization of the ground state usually have comparatively small values of the crystal field strength. This may be ascribed to the decreased distances to the ligands in the stabilized complexes and perhaps also to partly covalent bonding, i. e. inter-mixing of molecular orbitals. Thus, the  $d^5$ -systems with  $S = \frac{5}{2}$  are not stabilized, and  $(E_1 - E_2)$  is only 7800  $K$  for manganese (II) and 13,700  $K$  for iron (III) hexaquo ions.<sup>50</sup> Finally, the ionic radius of  $Ce(III)$  is considerably larger than that of most other trivalent ions with partly filled shells.

### The Possibility of an Equilibrium between Cerium (III) Aquo Ions with Different Co-Ordination Number, and the Absorption Spectra of Lanthanide Chlorides in Aqueous and Alcoholic Solutions.

The band at 33,700  $K$  of cerium(III) aquo ions has only an intensity  $\sim 3 \text{ }^0/0$  of the other bands. It may be caused by a comparatively rare geometrical configuration in equilibrium with the other  $Ce(III)$  complexes. J. BJERRUM<sup>5</sup> suggested that aquo ions with different co-ordination number  $N$  can be in equilibrium in solution, e. g. zinc(II) with four or six water molecules. Analogously, the common form of cerium(III) aquo ions might have  $N = 9$  (as found<sup>34</sup> in  $Nd(BrO_3)_3 \cdot 9H_2O$ ) and the rare form might be octahedral with  $N = 6$ . HEIDT and BERESTECKI<sup>29</sup> studied the spectra of  $Ce(ClO_4)_3$  in solutions of  $HClO_4$  and  $NaClO_4$ .  $\epsilon_1$  of the small band at 33,700  $K$  is further diminished, and the presence of an isosbestic point supports the formation of only one complex  $Ce(ClO_4)_x(H_2O)^{3-x}$ . However, a surprising effect was reported:  $\epsilon_1$  of the aquo ion is raised from 18 to 26 by warming the solution from 16° C. to 54° C., while the intensity of the strong bands is not noticeably changed. The present author has found a similar result for 0.03  $M$   $CeCl_3$  in  $H_2O$ .

If the oscillator strength of the small band does not vanish for accidental reasons such as a selection rule for transitions in the crystal field,<sup>30</sup> the temperature effect is almost a proof of the existence of an equilibrium, where the complex giving the small

band is formed under absorption of heat, probably with a lower co-ordination number than the common form. SPEDDING et al.<sup>84, 85, 86</sup> assume that the lighter lanthanides may have a higher co-ordination number in solutions than the heavier lanthanides, since the ionic conductances and thermodynamic functions are not monotonous functions of the atomic number, and since<sup>36</sup>  $La^{+++}$  in  $La_2(SO_4)_3, 9H_2O$  has partly  $N = 9$ , partly  $N = 12$ .

The small band of  $CeCl_3$  in  $6M HCl$  is  $\sim 2$  times higher than the band of the aquo ion, analogously to the result of NEWTON and ARCAND<sup>63</sup> for  $CeSO_4^+$ . In  $12M HCl$ , the small band has increased to be as intense as the other bands, and it is shifted  $1300 K$  towards lower wave numbers (Figure 3 and Table 6). Since the second band has had no large tendency to move, the chloro complexes in strong  $HCl$  can be assumed to have the low co-ordination number.  $0.002M CeCl_3$  in ethanolic solutions exhibit a similar development when the water content is removed. Thus 10 volume % water produces  $\epsilon_1 = 100$ , rather independently of the chloride concentration, if added in excess, while the absorption spectrum of  $0.002M CeCl_3$  in 2 %  $H_2O$ \* much resembles the spectrum of  $CeCl_3$  in aqueous  $12M HCl$ . It might seem reasonable to ascribe the variations of absorption spectrum of ethanolic  $CeCl_3$  by addition of small quantities of water to the exchange of  $C_2H_5OH$  and  $H_2O$  in the first co-ordination sphere without the interference of chloride ions. However, since  $Ce(ClO_4)_3$  exhibits a much smaller band at  $33,400 K$  in 98 %  $C_2H_5OH$ , the ethanol solvate of  $CeCl_3$  must be assumed to contain at least one chloride ion.

KATZIN<sup>51, 52</sup> discovered anion complexes (in organic solvents) the formation of which is much more dependent on the absence of water than on the presence of a considerable excess of the free anion. The system  $CeCl_3, C_2H_5OH, H_2O$  is a new member of this class. Thus,  $0.0004M CeCl_3$  in 99.5 %  $C_2H_5OH$  is seen from Table 6 to form the chloride-ethanol complex to a high extent, while in aqueous  $0.6M HCl$ , the formation constant<sup>57</sup> of  $CeCl^{++}$  is only 3.

The situation cannot be described only on the assumption that the order of bonding to metal ions is

\* This is the explanation of the new band reported of  $PrCl_3$  in absolute ethanol.<sup>39</sup>

alcohol < anion < water,

since alcohol distinctly is not 1000 times more weakly bound to metal ions than water, but only ~ 10 times more weakly bound

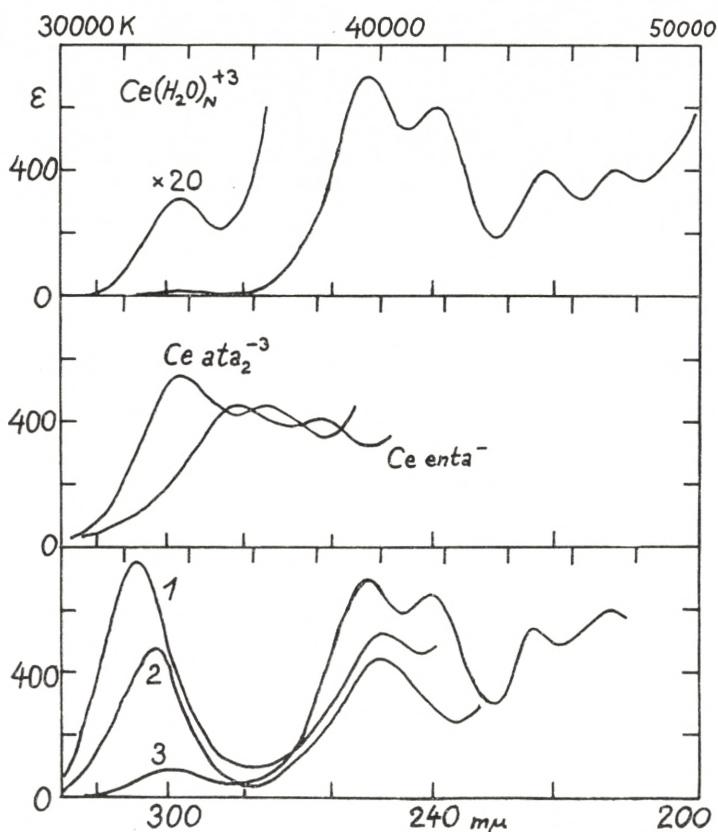


Figure 3. The absorption spectra of Cerium (III) complexes. The first part gives the spectrum of the aquo ion, the second part the nitrogentriacetate and the ethylenediaminetetraacetate. The third part gives the spectra of the following solutions in aqueous ethanol:

- Curve 1: 0.0004 M  $CeCl_3$ , 0.3 M  $H_2O$
- 2: 0.002 M  $CeCl_3$ , 1 M  $H_2O$
- 3: 0.002 M  $CeCl_3$ , 5 M  $H_2O$ .

per molecule.<sup>6,45,51</sup> Rather, the formation of anion complexes serves as indicator for the ethanol solvation, since the pure ethanol solvate is much more unstable towards uptake of anions, relative to the aquo ion. In the case of cerium(III) the high coordination number (nine?) cannot be obtained with ethanol

molecules alone. The characteristic property of water as an ionizing solvent is its ability to replace all the anions in the first co-ordination sphere of a metal ion in solution or in salt hydrates, rather independently of the dielectric constant.

In the case of  $NdCl_3$  in alcohols with a small content of water<sup>6,39,40,41</sup> it cannot be excluded that the anhydrous form is actually a mixed chloride-alcohol complex. Thus, the behaviour of  $Nd(NO_3)_3$  and  $NdCl_3$  in ethanol highly resembles the solutions in concentrated  $HNO_3$  and  $HCl$ , respectively. Thus, QUILL and SELWOOD<sup>71</sup> found a shift 30  $K$  and broadening of the  ${}^2P_{1/2}$  band of  $Nd(III)$  in 16  $M HNO_3$ , while three bands with a larger distance are exhibited in 12  $M HCl$  (Table 2 and Figure 4).

The somewhat narrower band of the  $Nd(III)$  aquo ion is not changed in 6  $M HCl$ , while the effect of nitrate is observed in much more dilute solutions. It is rather surprising that the neodymium(III) spectrum is not changed until two or three chloride ions are taken up, as extrapolated from the equilibrium constant for  $CeCl^{++}$  (if the latter does not refer to some association of chloride ions\* in the second co-ordination sphere). Thus, the spectral change may very well be connected with a dehydration, leading to a lower co-ordination number. The third band of  $NdCl_3$  in 12  $M HCl$ , which has a wave number even 80  $K$  below the band of anhydrous  $NdCl_3$ , can of course belong to an excited sub-level of the ground-level. Figure 4 gives the absorption bands of  $Nd(III)$  in aqueous hydrochloric acid of varying concentration.

The reflection spectra<sup>2</sup> of  $Na_2Ce(NO_3)_5$  and  $Mg_3Ce_2(NO_3)_{12}$ , 24  $H_2O$  exhibit absorption edge at 27,000  $K$ , while the edge in the corresponding lanthanum(III) compounds is situated at 33,000  $K$ . Even though the nitrate ion has a band at the latter position, there seems to be a specific cerium(III) nitrate absorption band. A similar case is encountered<sup>2</sup> in the oxalate  $Ce_2(C_2O_4)_3$ , 9  $H_2O$  with the edge 27,200  $K$ , while the other lanthanide oxalates have edges above 37,000  $K$ .

\* as suggested by the fact (Table 6) that the high  $Ce(III)$  bands are identical in aqueous 0-5 M hydrochloric acid.

## Red Shifts of Emission Bands of Fluorescent Cerium (III) and other Lanthanide Compounds.

ORGEL<sup>66</sup> explained the shift of emission bands of fluorescent and phosphorescent manganese(II) compounds to lower wave numbers than those of the absorption bands by means of the FRANCK-CONDON principle. The excited levels have another equilibrium distance of the ligands than the ground level, if the two levels have a different crystal field stabilization, and therefore the transition by emission from the excited level corresponds to an energy difference  $\sim 2000 K$  too small.

GOBRECHT<sup>25</sup> and MUKHERJEE<sup>62</sup> observed fluorescence of cerium(III) in crystals and in solutions. The emission band is rather broad, with the maximum at 28,000  $K$ . If the corresponding absorption band is the small band discussed above, the red shift is  $\sim 5000 K$ . KRÖYER and BAKKER<sup>53</sup> investigated the fluorescence of many other cerium(III) compounds and found two exciting wave number ranges.

Also the other  $[Xe] 4f^{n-1} 5d$  states of the lanthanides can decay with emission of light, which is shifted towards lower wave numbers. PRZIBRAM<sup>69, 70</sup> recognized these excited electron configurations in divalent lanthanides, which occur as traces in fluorite. Thus,  $Sm^{++}$  gives an emission maximum at 15,900  $K$ ,  $Eu^{++}$  at 23,800  $K$ , and  $Yb^{++}$  at 17,500  $K$ . This is in all cases  $\sim 6000 K$  below the corresponding absorption maxima.

On the other hand, the fluorescence of gadolinium(III) salts<sup>3, 89</sup> occurs at almost the same wave number as the absorption, because neither the ground state nor the excited level is stabilized by the crystal field. In the case of  $Sm^{+++}$ ,  $Eu^{+++}$ , and  $Dy^{+++}$ , the emission ends with excited multiplets of the configuration  $[Xe] 4f^n$ .

## The Integrals of Electrostatic Interaction between Electrons.

In the theory of SLATER, CONDON, and SHORTLEY<sup>9</sup> the distances between the centres of gravity of the different terms (with a definite  $S$  and  $L$ ) of a given electron configuration can be expressed as multiples of the integrals  $F^k$ , which can be written for equivalent electrons:<sup>9</sup>

$$F^k = e^2 \int_0^\infty \left[ \int_0^{r_2} \frac{r_1^k}{r_2^{k+1}} R^2 dr_1 + \int_{r_2}^\infty \frac{r_2^k}{r_1^{k+1}} R^2 dr_1 \right] R^2 dr_2. \quad (1)$$

$e$  is the electronic charge and  $R$  is the radial wave function. For the energy differences of  $f^n$ -systems, the integrals with  $k = 2, 4,$  and  $6$  are of consequence.

For isomorphous radial wave functions, which can be transformed to each other by change of the unit of distance  $r$ , the ratios between  $F^2:F^4:F^6$  will be identical, and the integrals  $F^k$  will be inversely proportional to a characteristic radius, e. g.  $r_{\max}$  with the maximum value of  $R^2$ .

If the electron was concentrated on the surface of a sphere with radius  $r_0$ , the integrals  $F^k$  would all be identical and equal to the integral

$$W = e^2 \int_0^\infty \frac{R^2}{r} dr; \text{ in casu } W = \frac{e^2}{r_0}. \quad (2)$$

For all other radial functions  $R$ , a set of inequalities will be valid:

$$W > F^0 > F^2 > F^4 > F^6 > \dots \quad (3)$$

However, for reasonable functions  $R$ , the decrease of  $F^k$  with  $k$  will not be very great. Therefore, the present author<sup>44</sup> and JUDD<sup>42</sup> emphasized that the ratios  $F^2:F^4$  and  $F^4:F^6$  are only semi-adjustable parameters; it is objectionable to admit  $F^2 \simeq F^4 \simeq 10 F^6$  as maintained for the configuration  $[Xe] 4f^2$  of  $La^+$ , which must be strongly perturbed by electron configuration interactions.<sup>9</sup> TREFFTZ<sup>90</sup> calculated for hydrogen-like  $4f$ -wave functions

$$F^2 = 0.45 W; F^4 = 0.30 W; \text{ and } F^6 = 0.22 W. \quad (4)$$

As shown below, this slow decrease of  $F^k$  with increasing  $k$  is present for most radial functions  $R$  rather independently of the shape. Thus, the observed values of  $F^k$  can be translated to characteristic values of radii  $r_0 = \frac{e^2}{W}$  by extrapolation to  $W$ .

We consider the "rectangular" function

$$R^2 = \frac{1}{n-1} \text{ for } 1 \leq r \leq n, \text{ and elsewhere } R^2 = 0. \quad (5)$$

The integrals  $F^k$  are then for  $k > 0$ :

$$\begin{aligned}
 F^k &= \frac{1}{(n-1)^2} \int_1^n \left[ \int_1^{r_2} \frac{r_1^k}{r_2^{k+1}} dr_1 + \int_{r_2}^n \frac{r_2^k}{r_1^{k+1}} dr_1 \right] dr_2 \\
 &= \frac{1}{(n-1)^2} \int_1^n \left[ \frac{1}{k+1} - \frac{1}{r_2^{k+1}(k+1)} + \frac{1}{k} - \frac{r_2^k}{k \cdot n^k} \right] dr_2 \\
 &= \frac{1}{(n-1)^2} \left[ \frac{2n}{k+1} - \frac{2}{k} + \frac{2}{n^k k(k+1)} \right],
 \end{aligned} \tag{6}$$

while for  $k = 0$

$$F^0 = \frac{2}{(n-1)^2} (n-1 - \ln n) \tag{7}$$

and

$$W = \frac{\ln n}{n-1}. \tag{8}$$

For the limiting case,  $R^2$  a delta function as discussed above,  $n$  can be set  $= 1 + \delta$ . Then the series, valid also for  $k = 0$ , is:

$$F^k = 1 - \frac{k+2}{3} \delta + \frac{(k+2)(k+3)}{3 \cdot 4} \delta^2 - \dots \tag{9}$$

Table 7 gives the numerical results for  $n = 2, 3, 5$ , and 10 for several of these integrals. It is seen from Table 7 that the decrease, represented by the inequality signs in eq. 3 is more prominent, the higher  $n$ , i. e. the broader the wave function. The values in eq. 4 for hydrogen-like  $4f$ -wave functions correspond rather closely to a value of  $n = 3.1$  for the „rectangular” approximation of eq. 5, while hydrogen-like  $3d$ -wave functions with  $F^2 = 0.41 W$  and  $F^4 = 0.27 W$  (see ref. 4) correspond to  $n = 4$ . For hydrogen-like  $l$ -wave functions, the integrals  $F^k$  diverge for  $k \geq 2l + 2$ , while  $F^k$  is defined for all  $k$  in eq. 6. However, this does not seem to be of consequence for the allowed ratios between  $F^k$ . If the radial wave function has maxima for two or more values of  $r$ , the decrease of  $F^k$  relative to  $W$  will generally be more pronounced. This case is realized<sup>46</sup> for  $4d$ -,  $5d$ -, ...  $5f$ -, ... electrons, since the number of maxima of a hydrogen-like  $(nl)$ -wave function is  $n - l$ ; and for covalent bonding, where the linear combination of atomic orbitals have



TABLE 7. Numerical values of the integrals  $F^k$  and  $W$ , derived in eqs. 6, 7, and 8 for the rectangular wave function, defined in eq. 5.

$n =$	2	3	5	10
$W$ .....	0.6932	0.5493	0.4024	0.2558
$F^0$ .....	0.6137	0.4507	0.2988	0.1654
$F^2$ .....	0.4167	0.2593	0.1467	0.0700
$F^4$ .....	0.3062	0.1753	0.0938	0.0432
$F^6$ .....	0.2388	0.1310	0.0686	0.0312
$F^8$ .....	0.1945	0.1042	0.0538	0.0243
$F^{10}$ .....	0.1637	0.0864	0.0433	0.0200
$F^2/W$ ....	0.602	0.472	0.366	0.274
$F^4/W$ ....	0.442	0.320	0.234	0.169
$F^6/W$ ....	0.345	0.238	0.171	0.122

maxima both in the central ion and in the ligands. If the square of the radial function  $R^2$  is distributed on several peaks with the areas  $A_n$ , arranged according to increasing values of  $r_n$ , an approximate expression will be:

$$F^k = \sum_n \frac{A_n^2}{r_n} \left[ 1 - \frac{k+2}{3} \delta_n + \dots \right] + \sum_{m>n} \frac{2A_n A_m r_n^k}{r_m^{k+1}}. \quad (10)$$

The first part of eq. 10 is derived from the series in eq. 9 for a peak with width  $\delta_n$ , while the second part can make the further approximation of assigning the width  $\delta_n = 0$  to the individual peaks  $A_n$ .

CONDON and SHORTLEY<sup>9</sup> divide the integrals  $F^k$  by denominators  $D^k$  in order to get integral values of the multiples of the new integrals  $F_k = \frac{F^k}{D^k}$ . Thus, these authors define for  $f$ -electrons

$$F^2 = 225 F_2; \quad F^4 = 1089 F_4; \quad \text{and} \quad F^6 = 7361,64 F_6, \quad (11)$$

while for  $d$ -electrons

$$F^2 = 49 F_2 \quad \text{and} \quad F^4 = 441 F_4. \quad (12)$$

### The Decrease of $F^k$ in Complexes.

According to eq. 1, the observation of different values of  $F^k$  in various complexes of the same central ion can easily be interpreted as a variation of the average radius of the electron cloud. This can either be caused by a general expansion of the electron cloud, conforming to some sort of „electroneutrality” principle,<sup>50</sup> or to a transport of a certain amount of the wave function into the region of the ligands.<sup>67</sup>

Actually, some kind of covalent bonding is present if defined as more negative charge being present between the nucleus of the central ion and the electron considered than in the corresponding gaseous ion. This follows from the theory of perturbation: The electrostatic potential  $U$  from a spherical surface with radius  $r_0$  and charge  $e$  is constant inside the sphere, and continuously approaching zero outside the sphere:

$$U = \frac{e}{r_0} \text{ for } r < r_0 \text{ and } U = \frac{e}{r} \text{ for } r > r_0. \quad (13)$$

Thus, if any wave function is totally imbedded in the sphere, i. e.  $R = 0$  for  $r > r_0$ , the perturbation energy delivered by the potential of eq. 13 will be a constant. Only if the wave function slightly penetrates into the volume with  $r > r_0$ , the perturbation energy will decrease, if the charge  $e$  is negative.

SCHLÄFER<sup>79</sup> observed that the term differences in the spectra of manganese(II) chloride solutions decrease for increasing chloride concentrations. The present author<sup>49</sup> maintains that these phenomena can rather be ascribed to formation of complexes  $Mn(H_2O)_5Cl^+$  and  $Mn(H_2O)_4Cl_2$  than to a physical salt effect. However, SCHLÄFER<sup>79</sup> investigates an electrostatic model for this variation of the term differences, which is quite interesting. For numerical calculations, he uses the  $ns$ -levels of a hydrogen atom. This choice is provoked by the results, valid for crystal fields which have no spherical symmetry: The crystal field from a distribution of electrical charges is generally expanded in a series<sup>37</sup>:  $G_0$ , representing the action on a charged sphere,  $G_2$ , and  $G_4$ . The first contribution is very large, but not measurable,

because it appears identically in the energy of any level of the central ion. The parameters  $G_2$  and  $G_4$  have the weighted average contribution zero for the levels, split by the crystal field. Thus,  $G_2$  and  $G_4$  are of no consequence for the  $ns$ -levels, which cannot be split.

The result of SCHLÄFER that a Debye-Hückel potential of the type

$$U = -a \cdot \frac{1 - e^{-br}}{r} = -a \left[ b - \frac{b^2 r}{2} + \dots \right] \quad (14)$$

and a crystal lattice with the anions nearest to the central ion both decrease the energies of the excited hydrogen levels, and most for the highly excited levels, is a paraphrase of the action of negative charge between the nucleus and the electron. The Debye-Hückel potential of eq. 14 can only be created by a charge distribution, which partly presents also small values of  $r$ , cf. eq. 13.

Now, the observed decrease of  $F^k$  can be formulated in two ways: either the electron considered is partly present in the domain of the ligands, or electrons from the ligands have partly invaded the central ion.

The first possibility has been discussed as formation of molecular orbitals  $\gamma_3$  by linear combination of  $d$ -orbitals from the central ion and some distinct orbitals from the ligands.<sup>67, 88, 93</sup> If the intermixing of  $d$ -orbitals is so great that the part  $x$  of the anti-bonding orbital occurs in the ligands and the part  $(1 - x)$  in the central ion, then  $F^k$  will to a first approximation be multiplied by  $(1 - x)^2$ , according to eq. 10, since  $r_m$  is much larger than  $r_1$ . Thus, the most complete intermixing with  $x = 0.5$  (when the unperturbed orbitals have the same energy) will imply  $F^k$  slightly over 25 % of the value, found in the gaseous ion. These conditions hardly prevail even in  $Co(CN)_6^{4-}$  or  $RhCl_6^{3-}$ . The latter arguments are not changed much<sup>49</sup> by the consideration of the large overlap integrals 0.4–0.7, which occur between the  $d$ -electron and the orbitals of the ligands, if the Pauling case is approached.

The second possibility does not necessitate that the covalent bonding occurs in the  $\gamma_3$ -orbitals in the case of  $d$ -electrons. Any other kind of bonding, e. g. of even  $\gamma_1$  and odd  $\gamma_4$ -orbitals, forming the  $s$ - and  $p^3$ -parts of Pauling's  $sp^3d^2$ -hybridization,<sup>47</sup> can

increase the electron density, producing the central field in the theory of CONDON and SHORTLEY.<sup>9</sup> ORGEL<sup>65</sup> compared the screening effects of  $s$ -electrons in the electron configurations of gaseous ions  $[A] 3d^n 4s$  and  $[A] 3d^n 4s^2$  relative to  $[A] 3d^n$  with the analogous effect of covalent bonding. Thus, the small decrease of  $F^k$  in  $[Xe] 4f^n$ -complexes do not necessarily imply the beginning presence of  $4f$ -electrons out in the ligands, but can as well be ascribed to the effective charge of the central ion being diminished by more conventional forms of covalent bonding. Since  $F^k$  is roughly proportional in the lanthanides to  $Z_0$ , the external charge plus one,<sup>46</sup> a decrease in  $F^k$  amounting to 1 0/0 corresponds to an effective charge 2.96. It would be interesting to extrapolate to the value of  $F^k$  in the gaseous ions of the lanthanides from the observed differences for aquo ions and anion complexes. It would not be expected from the  $d^n$ -systems that the shift gaseous ion  $\rightarrow$  aquo ion would be more than three times as large as the shift aquo ion  $\rightarrow$  anion complex. The diminished term differences between  $[Xe] 5d$  and  $[Xe] 4f$  in cerium(III) complexes reported above disclose a similar effect.

In the theory of absorption spectra of the transition group complexes, the interest has been concentrated much more on the energy levels than on the wave functions. However, in the discussion of covalent bonding, evidence from paramagnetic resonance and its hyperfine structure\*, due to the ligands' nuclei, can be very valuable.<sup>67</sup> A very interesting discovery was made by SHULL, STRAUSSER and WOLLAN,<sup>83</sup> who found the  $3d$ -wave function of manganese(II) compounds from the neutron diffraction of these paramagnetic materials. The wave function has  $r_{\max} = 0.6 \text{ \AA}$  and vanishes more rapidly for large values of  $r$  than HARTREE'S self-consistent  $3d$ -wave function.

### Actual Values of $F^k$ in the Lanthanides.

The absorption spectra of trivalent lanthanides<sup>44, 75</sup> have provided values of  $F^k$  for the  $[Xe] 4f^n$ -systems, which according to eq. 4 and Table 7 can give information about the average radius (or rather the average reciprocal distances) of the  $f$ -shell. The distances between the terms with the maximum value of  $S$ ,

\* cf. the recent study<sup>88a</sup> of  $Mn(II)$ ,  $Fe(II)$ ,  $Co(II)$ , and  $Cr(III)$ , imbedded in  $ZnF_2$ .

TABLE 8. Observed values of  $F^k$  and crystallographic radii of the trivalent lanthanide ions. The average radius of the 4  $f$ -shell  $r_0$  derived from eq. 2 and the assumption  $W = 2 F^2$ .

	$F^2$	$r_0$	Ionic radius	
			ZACHARISEN <sup>81</sup>	GOLDSCHMIDT <sup>26</sup>
$f^2 La^+ \dots\dots\dots$	21000 $K$	2.8 Å	1.6 Å extrapolated from $Cs^+$	
$f^2 Pr^{+++} \dots\dots\dots$	69000	0.84	1.00 Å	1.16 Å
$f^3 Nd^{+++} \dots\dots\dots$	72000	0.80	0.99	1.15
$f^5 Sm^{+++} \dots\dots\dots$	72000	0.80	0.97	1.13
$f^7 Gd^{+++} \dots\dots\dots$	76000	0.76	0.94	1.11
$f^9 Dy^{+++} \dots\dots\dots$	78000	0.74	0.91	1.07
$f^{12} Tm^{+++} \dots\dots\dots$	98000	0.59	0.86	1.04

giving the strongest absorption bands, are multiples<sup>72, 80</sup> of  $5 F_2 + 6 F_4 - 91 F_6$ . However, there is no doubt<sup>44</sup> that the single parameters can reliably be isolated by assuming eq. 4 or slightly higher values of  $F_6:F_2$ . Thus, the terms with lower  $S$  in praseodymium(III) and neodymium(III) can then be explained, and the sextet terms in gadolinium(III) also imply a value of  $F_2$ , which agrees with the neighbouring lanthanides.<sup>42, 44</sup> Table 8 gives the values of  $F^2$ , which probably are not 10 % in error. It is remarkable that  $F^k$  does not increase much in the range from  $Pr$ (III) to  $Dy$ (III). If  $W$  is assumed to equal  $2 F^2$ , values of  $r_0$  can be inferred as given in Table 8. The value of  $r_0 \sim 0.8 \text{ Å}$  is somewhat smaller than the crystallographic radii, as given in Table 8. Thus, the  $f$ -electron can be said to be mainly incorporated in the kernel,<sup>46</sup> while<sup>4</sup>  $La^+$  with  $F^2 = 21,000 K$  under the same assumptions corresponds<sup>1</sup> to  $r_0 = 2.8 \text{ Å}$ . GOEPPERT MAYER<sup>56</sup> predicts a rather drastic change of the screening conditions for 4 $f$ -electrons at the beginning of the lanthanide group. The position calculated of the "inner"  $f$ -electron at  $0.22 \text{ Å}$  in  $La$  and  $0.17 \text{ Å}$  in  $Nd$  is undoubtedly too small. The values observed of  $F^k$  are not compatible with a smaller  $r_0$  than  $0.5 \text{ Å}$  in the trivalent lanthanides. Since the 4 $f$ -wave functions in complexes cannot be as broad as the hydrogen-like ones, where  $R^2$  has half the maximum value for  $r = 1.5 r_{\text{max}}$ , lower values of  $n$  from Table 7

<sup>1</sup> A hydrogen-like 4 $f$ -electron with  $Z_0 = 2$  has  $r_0 = 4.23 \text{ Å}$ .

are suggested for the complexes supporting this conclusion. In the first transition group  $F^2$  and  $F^4$  are approximately proportional<sup>9</sup> to  $Z_0$ , the external charge plus one, in the  $d^2$ -systems from  $Sc^+$  to  $Ni^{+8}$ . The values observed are  $F^2 = Z_0 \cdot 17,000 K$  and  $F^4 = Z_0 \cdot 13,500 K$ , while a hydrogen-like  $3d$ -electron has  $F^2 = Z_0 \cdot 9950 K$ ,  $F^4 = Z_0 \cdot 6490 K$ , and  $W = Z_0 \cdot 24,390 K$ . In gaseous ions such as  $Cr^{+++}$  or  $Ni^{++}$ , the value of  $F^2$  is  $\sim 70,000 K$ . If  $W$  is assumed to be  $150,000 K$ , the effective radius  $r_0$  will be  $116,000/150,000 = 0.77 \text{ \AA}$ . Since  $F^2$  is decreased in nickel(II) and chromium(III) complexes, the corresponding values of  $r_0 > 1 \text{ \AA}$  are definitely larger than the crystallographic radii, suggesting a partly covalent bonding of the type described by eq. 10.

### Experimental.

**Cerium (III) solutions.**  $CeCl_3$ ,  $6 H_2O$  was recrystallized by saturation of the solution with hydrogen chloride gas at  $0^\circ C$ . This removes iron(III) efficiently, while considerable amounts of other lanthanides were present in the crystals. However, the latter do not influence the spectrum in the ultraviolet. Solutions of tartrates and citrates in aqueous ammonia are rapidly oxidized to yellow cerium (IV) complexes, while ethylenediaminetetraacetates and nitrogentriacetates (made from  $0.2 M Na_4 \text{ enta}$  and  $0.2 M Na_3 \text{ ata}$ , both of "Komplexon" quality) are much more slowly oxidized. The acetate complex was measured in  $2 M CH_3COONH_4$ ,  $2 M CH_3COOH$ .

The consecutive formation constants of the cerium(III) sulphate complexes<sup>23</sup> in  $1 M NaClO_4$  are:  $CeSO_4^+ : 43$ ,  $Ce(SO_4)_2^- : 5$ , and  $Ce(SO_4)_3^{-3} : 6$ , while in dilute solutions the first formation constant<sup>86</sup> is 2600. The consecutive formation constants of acetate complexes<sup>24</sup> are 48, 10, 3.2, and 2.

Since the neutral cerium(III) citrate is feebly soluble, the easily soluble complex in alkaline solution probably contains two citrate groups.<sup>1</sup> BOULANGER<sup>7</sup> demonstrated the formation of lanthanide complexes with two nitrogentriacetate groups, while the ethylenediaminetetraacetates do not seem to react with excess of the reagent.<sup>59</sup>

**Praseodymium (III) solutions.**  $Pr_6O_{11}$  was supplied by Thorium Ltd., London. From the absorption bands at 7400 and 2540  $\text{\AA}$

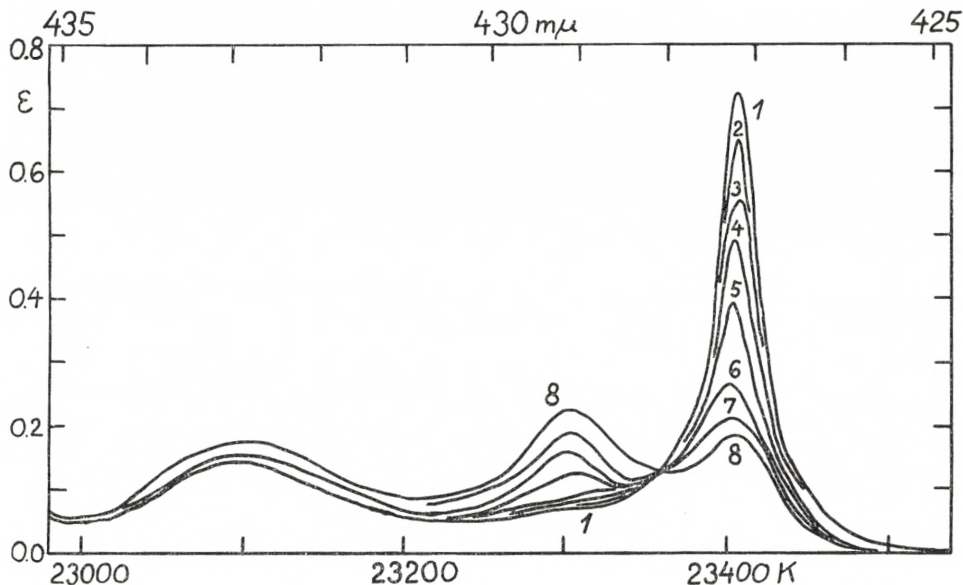


Figure 4. The absorption spectra of Neodymium (III) in hydrochloric acid. 0.38 *M* didymium chloride, as described in the experimental section, dissolved in the following solutions:

Curve 1	$H_2O$	Curve 5	9.5 <i>M HCl</i>
- 2	6.2 <i>M HCl</i>	- 6	10.3 <i>M</i> -
- 3	7.4 <i>M</i> -	- 7	11.0 <i>M</i> -
- 4	8.9 <i>M</i> -	- 8	11.3 <i>M</i> -

1.9 *M* didymium chloride in  $H_2O$  gives in 2 cm cells a spectrum identical with Curve 1, which was measured as the other curves on the figure of solutions in 10 cm cells. The neodymium content is 54% of the didymium mixture.

it was found to contain less than 0.7% *Nd* and 0.015% *Ce*. The double band in the far ultraviolet, reported by STEWART,<sup>87</sup> was observed as a single band at 2148 Å. A solution was prepared, 0.2 *M Pr(ClO<sub>4</sub>)<sub>3</sub>*, 0.4 *M HClO<sub>4</sub>*, and added to solutions of organic acids in  $NH_3$  and  $Na_2CO_3$ , as described above.

**Neodymium (III) solutions.** Technical Didymium Oxide B, as supplied by Thorium Ltd., London, was used for most measurements, because the *Nd*(III) bands studied are free from interference with bands of the other lanthanides. The lanthanide composition is 1% *Ce*, 10% *Pr*, 54% *Nd*, and 11% *Sm*, as estimated from spectrophotometry. The rest is mainly *La*. The absorption spectrum of the ethylenediaminetetraacetate was shown to be independent of addition of aqueous ammonia, when *pH* was higher than 8. But the solid salts, which can be crystal-

lized and which dissolve in water, giving  $pH \sim 5$ , show a different spectrum with more lines, which is changed on addition of base. Probably, the latter solution contains a mixture of complexes, i. e. some carboxyl groups are not co-ordinatively bound and have taken up protons.

BERZELIUS observed that didymium tartrate, dissolved in aqueous ammonia, by evaporation of the highly viscose solution at room temperature forms a transparent, glassy material. If the latter is dissolved in some water, it gives the same absorption spectrum of a mixed solution of  $DiCl_3$ ,  $NH_3$ , and ammonium tartrate.

Solid  $Diac_3$  was precipitated from the stoichiometric amounts of acetylacetone, didymium chloride and aqueous ammonia in 90 volume % ethanol. It was observed that the oscillator strength of the peak at  $5710 \text{ \AA}$  and the broad band  $\sim 5800 \text{ \AA}$  is roughly 10 times that of the band group  $\sim 5750 \text{ \AA}$  of the aquo ion. Else, the oscillator strengths\*, i. e. the areas of the bands, do not vary much for various neodymium(III) complexes.

Two crystals of the size  $3 \times 3 \times 2 \text{ cm}^3$ , of  $(NH_4)_2 Di(NO_3)_5 \cdot x H_2O$  were measured in the spectrophotometer. They both confirmed the blue shift of the  $4265$  and  $4255 \text{ \AA}$  band group.<sup>17</sup> However, some other band groups were different in the two crystals. Thus, bands were found at  $7310$  and  $7440 \text{ \AA}$ ; and  $7310$  and  $7470 \text{ \AA}$ , respectively.

The bathochromic effect of the decreased  $F^k$  in  $Nd_2O_3$  is clearly demonstrated by the bright blue colour<sup>96</sup> in contrast to the other pink neodymium(III) complexes.

**Samarium (III) solutions.** 99 %  $Sm_2O_3$  from Thorium Ltd., London, and a fraction from re-crystallization of magnesium double nitrates (Miss MERETE WICHFELD assisted in its preparation) were used for some measurements. However, for the study of the strong band at  $4020 \text{ \AA}$  the didymium solutions mentioned above were sufficient, because the other lanthanides do not disturb this band.

**Gadolinium (III) solutions.** 200 mg  $Gd_2O_3$  (from Universitetets Institut for teoretisk Fysik) was dissolved in 2.5 ml 2 M  $HClO_4$  and diluted to 3.1 ml in the absorption cell. The ethylenediamine-

\* MERZ<sup>58</sup> reports that the oscillator strength of the bands of  $Mg_3Pr_2(NO_3)_{12} \cdot 24 H_2O$  is  $\sim 20$  times smaller than of  $Pr_2(SO_4)_3 \cdot 8 H_2O$ , and  $Pr(C_2H_5SO_4)_3 \cdot 9 H_2O$ . Cf. the foot-note p. 8.



tetraacetate was prepared by neutralization of a part with  $NH_3$  and addition of a slight excess of  $Na_4enta$ , while another part was added to aqueous ammonia and citrate. It was not possible to dissolve  $Gd(OH)_3$  to a large extent in  $NH_3$  and tartrate.

**Erbium (III) solutions.** A sample of  $Er_2O_3$ ,  $Y_2O_3$  etc. from S. M. JØRGENSEN, and some fractions prepared by Miss KAREN JENSEN (now Mrs. KÜMMELE) from gadolinite supplied by Konservator K. KRISTOFFERSEN, Norges mineralogiske Museum, were used for the measurements.

**Ytterbium (III) solutions.** 200 mg  $Yb_2O_3$  (from Universitetets Institut for teoretisk Fysik) was boiled with 3 ml 2 M  $HClO_4$  for several minutes, until it suddenly passed into a clear solution. It was diluted to 3.1 ml in the absorption cell and later also measured as  $Yb\ enta^-$ .

**The spectrophotometer** was the Cary recording model 11 MS-50. For standardization of the wave-length scale, the  $^2P_{1/2}$  band of the neodymium(III) ion was assumed to be situated at 4273 Å in general agreement with the literature. In the ultraviolet, mercury vapour (in a 10 cm cell at room temperature) was found to give the 2536.5 Å line very sharply. The measurements of the narrow bands were made with the lowest possible scanning speed and recorded with the tungsten lamp 8000—3250 Å (12.5 Å per division = 0.83 cm of paper) and with the hydrogen lamp 4000—2050 Å (5 Å per division). The slit control was set at 10. The relative shifts of the narrow bands can be measured with an uncertainty  $\sim 1$  Å. The shift 23 Å of the narrowest band of neodymium(III) tartrate was also found with a Beckman DU spectrophotometer. The latter instrument was used for the measurement of  $Yb$ (III) in the infra-red.

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## Summary

The narrow bands caused by internal  $f^n$ -transitions in  $Pr(III)$ ,  $Nd(III)$ ,  $Sm(III)$ , and  $Gd(III)$  are shown to be shifted  $\sim 1\%$  towards lower wave numbers in complexes with ligands such as ethylenediaminetetraacetate, nitrogentriacetate, tartrate, and citrate, relative to the aquo ions. EPHRAIM et al. have previously demonstrated even larger shifts in the reflection spectra of oxides and anhydrous halides. Even though the sub-levels of the ground levels can be distributed in a different way for the complexes, the main part of the red shift is due to a decrease of term differences. These can be interpreted as multiples of the parameters of electrostatic interaction between electrons,  $F^k$ , as defined by SLATER, CONDON, and SHORTLEY.

The high and broad absorption bands of cerium(III) complexes, due to  $4f \rightarrow 5d$  transitions, are shifted much more in anion complexes. One of these bands is comparatively low, and its change with temperature suggests the presence of a  $Ce(III)$  aquo ion with a low co-ordination number in equilibrium with the more common form.  $CeCl_3$  in anhydrous ethanol develops a new band, which disappears by addition of water. Since  $Ce(ClO_4)_3$  exhibits another behaviour, the new band is presumably due to a complex with chloride and ethanol whose formation is much more sensitive to addition of water to the solvent than to the chloride concentration. (Thus, the absorption spectrum of  $0.0004 M CeCl_3$  in ethanol resembles that of  $Ce(III)$  in  $12 M HCl$ ).

It is further shown that the fluorescence of excited  $[Xe] 4f^{n-1} 5d$  levels in the lanthanides exhibits the red shift discussed by ORGEL in the case of manganese(II) complexes.

The  $F^k$  integrals are shown to decrease smoothly with increasing  $k$ , rather independently of the wave function assumed for the electron in the partly filled shell. Thus, the ratios  $F^2:F^4$  and  $F^4:F^6$  are only semiadjustable parameters, as previously maintained. From the observed values of  $F^k$  in transition group complexes, the average radius of the wave function can be estimated. In trivalent lanthanides this radius varies slowly around  $0.8 \text{ \AA}$  in the series from  $Pr(III)$  to  $Dy(III)$ , approaching  $0.6 \text{ \AA}$  in  $Tm(III)$ . This is somewhat less than the crystallographic

radii of trivalent lanthanides, indicating no large screening. In  $La^+$ , the  $4f$ -electrons with radius =  $2.8 \text{ \AA}$  are distinctly external electrons. Since the ionic radii are particularly small in  $Pr_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ , and  $Gd_2O_3$  with the low co-ordination number, this may explain the large decrease of  $F^k$  in these solids. In all cases, the decrease of  $F^k$  is most conspicuous in  $Pr(III)$ , where the two  $4f$ -electrons are least shielded.

The increased effective radii of the  $d$ -shell in  $d^n$ -complexes due to covalent bonding do not necessarily imply the intermixing of the  $d$ -electrons with the electrons of the ligands, since the central field can be changed by filling of bonding molecular orbitals of other symmetries. However, the values of  $F^k$  are so small, even in the gaseous ions, that the  $d$ -shell must penetrate into the domain of the ligands, thus forming partly covalent bonds.

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### References.

1. BERTIN-BATSCH, C., *Ann. Chim.* [12] **7** (1952) 481.
2. BERTON, A., *Compt. rend.* **213** (1941) 653 and 1001.
3. BERTON, A. and BOULANGER, F., *Compt. rend.* **224** (1947) 1153.
4. BIRMINGHAM, J. M. and WILKINSON, G., *J. Am. Chem. Soc.* **78** (1956) 42.
5. BJERRUM, J., *Metal Ammine Formation . . . Thesis.* Copenhagen 1941.
6. BJERRUM, J. and JØRGENSEN, C. KLIXBÜLL, *Acta Chem. Scand.* **7** (1953) 951.
7. BOULANGER, F., *Ann. Chim.* [12] **7** (1952) 732.
8. BRUNETTI, R., *Nuovo Cimento* **5** (1928) 391 and **6** (1929) 347.
9. CONDON, E. U. and SHORTLEY, G. H., *Theory of Atomic Spectra.* Cambridge 1953.
10. DATTA, S. and DEB, M., *Indian J. Phys.* **10** (1936) 163.
11. DIEKE, G. H. and HEROUX, L., Johns Hopkins University, Baltimore, NYO — 3977. 1955.
12. EPHRAIM, F. and BLOCH, R., *Ber.* **59** (1926) 2692.
13. EPHRAIM, F. and BLOCH, R., *Ber.* **61** (1928) 65.

14. EPHRAIM, F. and BLOCH, R., Ber. **61** (1928) 72.
15. EPHRAIM, F., Ber. **61** (1928) 80.
16. EPHRAIM, F. and RÂY, P., Ber. **62** (1929) 1509.
17. EPHRAIM, F. and RÂY, P., Ber. **62** (1929) 1520 and 1639.
18. EPHRAIM, F., JANTSCH, G. and ZAPATA, CL., Helv. Chim. Acta **16** (1933) 261.
19. FREED, S., Phys. Rev. **38** (1931) 2122.
20. FREED, S. and MESIROW, R. J., J. Chem. Phys. **5** (1937) 22.
21. FREYMAN, M. and FREYMAN, R., Compt. rend. **211** (1940) 785.
22. FRIED, S. and HINDMAN, J. C., J. Am. Chem. Soc. **76** (1954) 4863.
23. FRONÆUS, S., Svensk Kem. Tidskr. **64** (1952) 317.
24. FRONÆUS, S., Svensk Kem. Tidskr. **65** (1953) 19.
25. GOBRECHT, H., Ann. Physik [5] **31** (1938) 181.
26. GOLDSCHMIDT, W. M. et al., Geochemische Verteilungsgesetze der Elemente, IV, V and VII, Oslo 1925 and 1926.
27. GRUEN, D. M. and FRED, M., J. Am. Chem. Soc. **76** (1954) 3850.
28. HARTMANN, H. and LORENZ, E., Z. Elektrochem. **54** (1950) 341.
29. HEIDT, L. J. and BERESTECKI, J., J. Am. Chem. Soc. **77** (1955) 2049.
30. HELLWEGE, K. H., Ann. Physik [6] **4** (1948) 95, 127, 136, 143, 150, and 357.
31. HELLWEGE, K. H. and KAHLE, H. G., Z. Physik **129** (1951) 62.
32. HELLWEGE, A. M. and HELLWEGE, K. H., Z. Physik **130** (1951) 549.
33. HELLWEGE, K. H. and SHRÖCK-VIETOR, W., Z. Physik **138** (1954) 449.
34. HELMHOLZ, L., J. Am. Chem. Soc. **61** (1939) 1544.
35. HOFFMANN, K. A. and HÖSCHELE, K., Ber. **47** (1919) 240.
36. HUNT, E. B., RUNDLE, R. E. and STOSICK, A. J., Acta Cryst. **7** (1954) 106.
37. ILSE, F. E. and HARTMANN, H., Z. Physik. Chem. **197** (1951) 239.
38. JANTSCH, G. and MEYER, E., Ber. **53** (1920) 1577.
39. JONES, H. C. and ANDERSON, J. A., Carnegie Inst. Publ. No. 110. Washington 1909.
40. JONES, H. C. and STRONG, W. W., Carnegie Inst. Publ. No. 130, Washington 1910.
41. JONES, H. C. and STRONG, W. W., Carnegie Inst. Publ. No. 160, Washington 1911.
42. JUDD, R. B., Proc. Roy. Soc. (London) **A 228** (1955) 120.
43. JØRGENSEN, C. KLIXBÜLL, Mat. Fys. Medd. Dan. Vid. Selsk. **29**, (1955) no. 7.
44. JØRGENSEN, C. KLIXBÜLL, Mat. Fys. Medd. Dan. Vid. Selsk. **29**, (1955) no. 11.
45. JØRGENSEN, C. KLIXBÜLL, Acta Chem. Scand. **8** (1954) 175.
46. JØRGENSEN, C. KLIXBÜLL, J. Inorg. Nucl. Chem. **1** (1955) 301.
47. JØRGENSEN, C. KLIXBÜLL, Acta Chem. Scand. **10** (1956) 500, 518.
48. JØRGENSEN, C. KLIXBÜLL, Acta Chem. Scand. **9** (1955) 1362 and **10** (1956) 887.

49. JØRGENSEN, C. KLIXBÜLL, *Acta Chem. Scand.* **10** (1956)
50. JØRGENSEN, C. KLIXBÜLL, Reports of X'th Solvay Conference, Bruxelles May 1956.
51. JØRGENSEN, C. KLIXBÜLL and BJERRUM, J., *Nature* **175** (1955) 426.
52. KATZIN, L. I. and GEBERT, E., *J. Am. Chem. Soc.* **72** (1950) 4557.
53. KRÖYER, F. A. and BAKKER, J., *Physica* **8** (1941) 628.
54. LANG, R. J., *Can. J. Res.* **14 A** (1936) 127.
55. LIVELING, G. D., *Cambr. Phil. Soc. Trans.* **1899** 255, Collected Papers on Spectroscopy. Cambridge University 1915.
56. MAYER, M. GOEPPERT, *Phys. Rev.* **60** (1941) 184.
57. MAYER, S. W. and SCHWARZ, S. D., *J. Am. Chem. Soc.* **73** (1951) 222.
58. MERZ, A., *Ann. Physik* [5] **28** (1937) 569.
59. MOELLER, TH. and BRANTLEY, J. C., *J. Am. Chem. Soc.* **72** (1950) 5447.
60. MOELLER, TH. and BRANTLEY, J. C., *Anal. Chem.* **22** (1950) 433.
61. MOELLER, TH. and MOSS, F. A. J., *J. Am. Chem. Soc.* **73** (1951) 3149.
- 61a. MOELLER, TH. and ULRICH, W. F. J. *Inorg. Nucl. Chem.* **2** (1956) 164.
62. MUKHERJEE, P. C., *Z. Physik* **109** (1938) 573.
63. NEWTON, T. W. and ARCAND, G. M., *J. Am. Chem. Soc.* **75** (1953) 2449.
64. NUTTING, G. C. and SPEDDING, F. H., *J. Chem. Phys.* **5** (1937) 33.
65. ORGEL, L. E., *J. Chem. Phys.* **23** (1955) 1004 and 1824.
66. ORGEL, L. E., *J. Chem. Phys.* **23** (1955) 1958.
67. OWEN, J., *Proc. Roy. Soc. (London)* **A 227** (1955) 183.
68. PABST, A., *J. Chem. Phys.* **11** (1943) 145.
69. PRZIBRAM, K., *Z. Physik* **102** (1936) 331 and **107** (1937) 709.
70. PRZIBRAM, K., *Sitz. ber. Wien Akad. Mat. nat. Kl. II a* **147** (1938) 260.
71. QUILL, L. L., SELWOOD, P. W. and HOPKINS, B. S., *J. Am. Chem. Soc.* **50** (1928) 2929.
72. RACAH, G., *Phys. Rev.* **76** (1949) 1352.
73. RADOITCHITCH, M., *Ann. Chim.* [11] **13** (1940) 5.
74. ROBERTS, R. W., WALLACE, L. A. and PIERCE, I. T., *Phil. Mag.* **17** (1934) 934.
75. SATTEN, R. A., *J. Chem. Phys.* **21** (1953) 637.
76. SATTEN, R. A. and YOUNG, D. J., *J. Chem. Phys.* **23** (1955) 404.
77. SCHÄFFER, C. E., *Acta Chem. Scand.*
78. SCHÄFFER, H., *Phys. Z.* **7** (1906) 822.
79. SCHLÄFER, H. L., *Z. Physik. Chem.* **6** (1956) 201.
80. SCHUURMANS, PH., *Physica* **11** (1946) 475.
81. SEABORG, G. T. and KATZ, J. J., *The Actinide Elements. Nat. Nucl. Energy Ser. Vol. 14 A.* 1954.
82. SELWOOD, P. W., *J. Am. Chem. Soc.* **52** (1930) 3112 and 4308.
83. SHULL, C. G., STRAUSSER, W. A. and WOLLAN, E. O., *Phys. Rev.* **83** (1951) 333.

84. SPEDDING, F. H., PORTER, P. E. and WRIGHT, J. M., J. Am. Chem. Soc. **74** (1952) 2055.
  85. SPEDDING, F. H. and YAFFE, I. S., J. Am. Chem. Soc. **74** (1952) 4751.
  86. SPEDDING, F. H. and JAFFE, S., J. Am. Chem. Soc. **76** (1954) 882.
  87. STEWART, D. C., Light Absorption . . . I, AECD — 2389.
  88. TANABE, Y. and SUGANO, S., J. Phys. Soc. Japan **9** (1954) 753 and 766.
  - 88a. TINKHAM, M. Proc. Roy. Soc. (London) **A 236** (1956) 535 and 549.
  89. TOMASCHEK, R. and MEHNERT, E., Ann. Physik [5] **29** (1937) 306.
  90. TREFFTZ, E., Z. Physik. **130** (1951) 561.
  91. UZUMASA, Y. and OKUNO, H., Bull. Chem. Soc. Japan **6** (1931) 147
  92. UZUMASA, Y., Bull. Chem. Soc. Japan **7** (1932) 85.
  93. VAN VLECK, J. H., J. Chem. Phys. **3** (1935) 803 and 807.
  94. VICKERY, R. C., J. Chem. Soc. **1952** 421.
  95. VICKERY, R. C., J. Chem. Soc. **1955** 2360.
  96. WAEGNER, A., Z. anorg. Chem. **42** (1904) 118.
  97. Strukturbericht Band I (1931) 744 and Band II (1937) 38.
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# INDHOLD

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17. HUUS, TORBEN, BJERREGAARD, JØRGEN H., and ELBEK, BENT: Measurements of Conversion Electrons from Coulomb Excitation of the Elements in the Rare Earth Region. 1956 .....	1-72
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