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LANTHANIDE COMPLEXES—II*

COMPLEXES OF 1:10-PHENANTHROLINE WITH LANTHANIDE ACETATES AND NITRATES

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Abstract—Well-crystalline, thermally stable complexes of the types $M(CH_3COO)_3(phen)$ and $M(NO_3)_3(phen)_2$, where M = all the lanthanides except Pm and phen = 1:10-phenanthroline, have been isolated. Magnetic moments and infra-red spectra are reported and structures are discussed.

We have previously described[1,2] complexes of the types

$$MCl_3(phen)H_2O,$$
$$MCl_3(phen)C_2H_5OH,\ MCl_3(phen)_2,$$
$$MCl_3(phen)_2H_2O,\ MCl_3(phen)_2C_2H_5OH,$$
$$M(CNS)_3(phen)_2 \text{ and } M(CNS)_3(phen)_3,$$

where M is a lanthanide. It seemed of interest to investigate analogous complexes of lanthanide acetates and nitrates because these anions, often monodentate, might be bidentate in co-ordination with the lanthanides and in that case they would have less bulk per co-ordination place than do chloride or thiocyanate and so might furnish complexes having a high co-ordination number. Again, acetate has a much greater avidity for lanthanide ion than has chloride[3] and this might affect the number of co-ordination places taken up by phenanthroline molecules.

We wish to report the preparation and simple properties of the complexes

$$M(CH_3COO)_3(phen) \text{ and } M(NO_3)_3(phen)_2$$

where M = La–Nd and Sm–Lu. No complexes of lanthanide acetates have been described previously but the compounds $M(NO_3)_3(phen)_2$ where M = La, Ce, Pr, Nd and Sm have been prepared but not in any way investigated.[4]

The nitrato-complexes, $M(NO_3)_3(C_{12}H_8N_2)_2$

When a dilute solution of a lanthanide nitrate in ethanol was treated with a dilute alcoholic solution of two molecular proportions of 1:10-phenanthroline, a crystalline precipitate of the complex $M(NO_3)_3(C_{12}H_8N_2)_2$ was formed. The use of higher or lower molecular ratios of ligand did not lead to the isolation of any other complexes. This contrasts with the chloride and thiocyanate complexes,[2] where 2:1 or 1:1 and 3:1 or 2:1 ligand: metal ratios could be obtained respectively.

The colours of the complexes are closely similar to, but not always identical with,

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* *J. Inorg. Nucl. Chem.* **26**, 579 (1964) is to be considered Part I of this series.

[1] F. A. Hart and F. P. Laming, *Proc. Chem. Soc.* 107 (1963).

[2] F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.* **26**, 579 (1964).

[3] Special Publication No. 6, The Chemical Society, London (1957).

[4] N. I. Lobanov and V. A. Smirnova, *Zhur. Neorg. Khim.* **9**, 2206 (1963).

the colours of the corresponding hydrated lanthanide ions. This is also true of the acetate complexes described below and of the previously reported chloride and thiocyanate complexes. The nitrates show very fair thermal stability, decomposition points lying between 160° and 250° except for the La compound which surprisingly is more stable, being unchanged at 300°. The nitrates are insoluble in most common organic solvents but dissolve with dissociation in dimethylformamide and dimethylsulphoxide. They also dissolve in hot water with dissociation but crystallize out in a less pure form on cooling.

A typical infra-red spectrum of a nitrate is shown in Fig. 1. The bands due to 1 : 10-phenanthroline will not be discussed in detail but show several changes from the free ligand due to co-ordination. For example, the strong CH out-of-plane bending absorptions at 852 cm^{-1} and 738 cm^{-1} are lowered to 840–847 cm^{-1} and 720–730 cm^{-1}, the latter band becoming a doublet except in the cases of the Yb and Lu compounds.

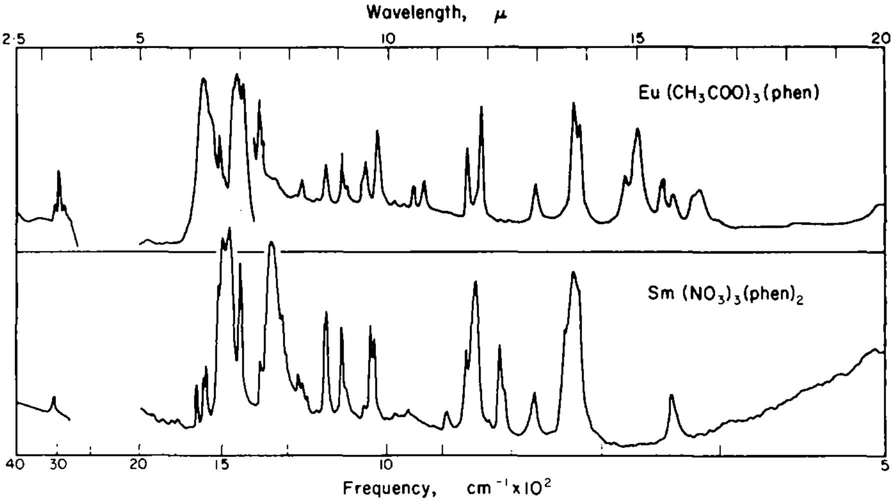

FIG. 1

The bands due to the nitrate ions have greater diagnostic value. The characteristic frequencies of the free nitrate ion alter on co-ordination and the generally accepted ranges are shown in Table 1 together with the ranges observed in the phenanthroline complex nitrates. Our assignments shown in Tables 1 and 2 are deduced by comparison of the spectra of all the acetate and nitrate complexes with the spectra of 1 : 10 phenanthroline and of its complex chlorides and thiocyanates. The symmetries of mono- and bidentate nitrato groups are each C_{2v}, so they each show the same number of bands and it is found experimentally that these occur at essentially the same frequencies. The two types of co-ordination cannot therefore be distinguished. The nitrate groups in these complexes are clearly all co-ordinated, whether in a bi- or monodentate manner, and the co-ordination number of the lanthanide ion must be at least seven or correspondingly higher if any nitrate groups are bidentate. Molecular models indicate however that there is unlikely to be enough room around the lanthanide ion for all three nitrate groups to be bidentate, but that co-ordination numbers of seven, eight or nine are possible.

TABLE 1.—NITRATE INFRA-RED FREQUENCIES

	$E(\nu_3)$		$A_1(\nu_1)$	$A_2(\nu_2)$	$E(\nu_4)$	
[a] Nitrate ion (D_{3h})	1390–1350		1060–1040	835–815	745–715	
	$B_1(\nu_4)$	$A_1(\nu_1)$	$A_1(\nu_2)$	$B_2(\nu_6)$	$B_1(\nu_5)$	$A_1(\nu_3)$
[b] Nitrato group (C_{2v})	1530–1480	1290–1250	1035–970	[e]820–780	...	...
[c] $[Co(NO_3)(NH_3)_5]\ PtCl_4$	1481	1269	1012	796	—	—
[d] $Rb[UO_2(NO_3)_3]$	1536	1276	1023	803	736	711
$[La(NO_3)_3(phen)_2]$	1490	1290	1027	814	—	
$[Lu(NO_3)_3(phen)_2]$	1490	1319	1039, 1032	814		—

[a] B. M. GATEHOUSE, S. E. LIVINGSTONE and R. S. NYHOLM, *J. Chem. Soc.* 4222 (1957). K. BUIJS and C. J. H. SCHUTTE, *Spectrochim. Acta* 307 (1962).

[b] B. M. GATEHOUSE *et al., loc. cit.*

[c] *Ibid.* (Monodentate nitrato-groups)

[d] B. M. GATEHOUSE and A. E. COMYNS, *J. Chem. Soc.* 3965 (1958) (Bidentate nitrato-groups)

[e] F. BANNISTER and F. A. COTTON, *J. Chem. Soc.* 2276 (1960).

TABLE 2.—SOME INFRA-RED ACETATE FREQUENCIES

	$NaCH_3COO$[a]	$Na[UO_2(CH_3COO)_3]$[b]	$[Eu(CH_3COO)_3(phen)]$
OCO unsym. str. (B_1)	1575	1537	1597
OCO sym. str. (A_1)	1422	1472	1441
OCO bend (A_1)	651	678	645, 666, 678
OCO rock (B_2)	620	612	617 broad

[a] J. K. WILMSHURST, *J. Chem. Phys.* **23**, 2463 (1955).

[b] L. H. JONES, *J. Chem. Phys.* **23**, 2105 (1955).

The acetato-complexes $M(CH_3COO)_3(C_{10}H_{12}N_2)$

These are prepared in a similar way to the nitrato-complexes, but using equal molecular proportions of lanthanide acetate and of phenanthroline. An excess or deficiency of ligand does not furnish any different complex. The acetates are thermally stable, decomposition points lying between 260° and 300°. They are soluble in hot water to the extent of about 10 per cent but crystallize from water only in a very impure form. Their behaviour with other solvents is similar to that of the nitrato-complexes and so meaningful molecular weight or conductivity determinations could not be carried out. It is noteworthy that the lanthanum compound of this series could not be obtained pure; the cerium compound was obtained in low yield only. This is probably due simply to the increased ionic size affecting the equilibrium in the alcoholic solution but the exact nature of the effect is unknown.

The fact that only one phenanthroline molecule would complex with the metal ion contrasts with the chlorides, nitrates and thiocyanates which could complex with two, two and three phenanthroline molecules respectively. This strongly suggests that in the acetate complexes all three acetate groups are co-ordinated and that probably all three are bidentate; this would then leave room for only one phenanthroline molecule and give a co-ordination number of eight. It is true that a lanthanum complex $[La(edta\ H)(H_2O)_4]$ having co-ordination number ten has been established by X-ray diffraction,(5) but this co-ordination number is unlikely to be possible when the bulky phenanthroline is present.

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(5) J. L. HOARD, *Int. Conf. Coordination Chemistry*, Vienna (1964).

TABLE 3.—MAGNETIC SUSCEPTIBILITIES AT 20°C ($\times 10^6$)

	$[M(NO_3)_3(phen)_2]$		$[Mphen_3](SCN)_3$		$[Mcpd_3]^c$			
	$\chi_M{}^a$	μ^b	$\chi_M{}^a$	μ^b	$\chi_M{}^d$	Δ	μ^e	μ(calc.)^f
La	−5	0	—	—	—	—	—	0
Ce	2559	2·46	—	—	2244	15	2·46	2·56
Pr	5142	3·48	5290	3·54	4728	37	3·61	3·62
Nd	5027	3·44	5316	3·54	4283	72	3·63	3·68
Sm	1142	1·64	1152	1·65	1081	—	1·65	1·55–1·65
Eu	4771	3·36	4662	3·32	—	—	—	3·40
Gd	26860	7·97	—	—	26983	0	7·98	7·94
Tb	40740	9·81	39716	9·69	—	—	—	9·7
Dy	47520	10·6	46893	10·5	40260	15	10·0	10·6
Ho	48240	10·7	—	—	—	—	—	10·6
Er	37910	9·46	—	—	35830	17	9·45	9·6
Tm	23880	7·51	—	—	—	—	—	7·6
Yb	8459	4·47	—	—	6199	21	4·00	4·5
Lu	23	0	—	—	—	—	—	0

[a] Corrected for molecular diamagnetism including that of lanthanide ion.
[b] From Curie equation.
[c] J. M. BIRMINGHAM and G. WILKINSON, *J. Amer. Chem. Soc.* 42 (1956).
[d] Corrected for molecular diamagnetism excluding that of lanthanide ion. Adjusted from 22° to 20°C by present authors.
[e] From Curie-Weiss equation.
[f] J. H. VAN VLECK and N. FRANK, *Phys. Rev.* **34**, 1494 (1929).

The infra-red spectra of the acetates show, besides bands due to phenanthroline, again modified from those of the free ligand due to chelation, bands due to acetate (Table 2) which, however, give little information as to the type of acetate group (ionic, monodentate or bidentate) present. The unambiguous and complete assignment of acetate bands presents some difficulty even in the simple case of sodium acetate and in the present instance the bands due to phenanthroline might cause additional confusion. We content ourselves with the assignments in Table 2. The complex structure in the 600–700 cm^{-1} region is not too surprising since although the three acetato groups may be similar in the gross features of their bonding they cannot, on grounds of symmetry, all be in equivalent positions in the molecule. The frequencies of the symmetrical and unsymmetrical OCO stretching modes are separated by 156 cm^{-1} but it is possible for these modes to be separated as far as this even when the group is bidentate.(6)

Fluorescence

Of these complexes, the europium and terbium acetates and nitrates fluoresce particularly strongly when irradiated with light of 350 mμ wavelength, the europium complexes fluorescing in the orange and the terbium in the yellow region. This is due to an intramolecular energy transfer from the organic ligand to the lanthanide ion of a type previously noted for other lanthanide complexes.(7)

Magnetic data

Very few complete series of lanthanide compounds exist whose magnetic susceptibilities are known. In Table 3 room temperature magnetic moments of lanthanide

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(6) K. NAKAMOTO, J. FUJITA, S. TANAKA and M. KOBAYASHI, *J. Amer. Chem. Soc.* 4904 (1957).
(7) S. P. SINHA, *Spectrochim. Acta* 879 (1964).

ions in cyclopentadienyls are compared with corresponding data for the nitrates $[M(NO_3)_3(phen)_2]$ and for some thiocyanates $[M(phen)_3](CNS)_3$. The phenanthroline compounds show little deviation from the Van Vleck values although the simple Curie equation has been used. This is to be expected as the crystal field splitting of the *f*-orbitals is of the order of 100 cm^{-1}; a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited states whose degenerate energy levels have been split by the crystal field. It was just possible that the splitting of the lowest excited states of Sm($^6H_{7/2}$) or Eu($^7F_1$; in a low symmetry field) might have given an altered value of the magnetic moment but this effect was not observed.

There is clearly a marked difference in the degree of magnetic dilution between the phenanthroline complexes and the cyclopentadienyls (the latter are taken as examples of well-defined compounds prepared from the pure lanthanides readily available to modern workers). Agreement of the χ values is good in the case of Gd, which is in an S state, but in other cases the cyclopentadienyl values decrease markedly due to interionic magnetic coupling.

EXPERIMENTAL SECTION

Decomposition points were measured by use of a hot-stage microscope; they are uncorrected. The lanthanides except for La and Ce were obtained as their oxides of 99·9% purity (Eu 98%) from Messrs. Johnson and Matthey, whose spectroscopic grade La, Ce and Eu were used for magnetic measurements.

Trinitratobis (1:10*-phenanthroline*) *lanthanum* (III)

A boiling solution of hydrated lanthanum nitrate (0·58 g; 1 mol.) in ethanol (100 ml) was added to a boiling solution of 1,10-phenanthroline (0·55 g; 2·1 mol) in ethanol (100 ml). The clear solution was allowed to stand for 24 hrs., after which time well-formed crystals of the complex were collected, washed with ethanol and dried over alumina at 20°/12 mm. Yield 90%.

Similarly prepared were the analogous compounds of cerium, praseodymium, neodymium, samarium, *europium*, *terbium*, *dysprosium*, *holmium*, *thulium*, *ytterbium* and *lutetium*. Yields varied from 90 to 100%. The remaining analytical figures are listed below; in each case the calculated values correspond to an empirical formula $C_{24}H_{16}O_9N_7M$.

	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)		Decomposition point (°C)*
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	
La	20·3	20·3	42·3	42·1	2·4	2·4	14·05	14·3	300
Ce	20·5	20·4	42·1	42·0	2·3	2·4	14·3	14·3	200
Pr	20·7	20·5	41·6	41·9	2·4	2·3	14·6	14·3	200
Nd	20·9	20·9	41·8	41·7	2·6	2·3	14·45	14·2	190
Sm	21·5	21·6	41·4	41·4	2·5	2·3	13·6	14·1	160
Eu	21·8	21·8	41·4	41·3	2·1	2·3	14·1	14·05	180
Gd	22·4	22·4	40·6	41·0	2·6	2·3	14·1	13·9	170
Tb	22·6	22·5	41·1	40·85	2·4	2·3	14·0	13·9	160
Dy	23·0	22·9	40·25	40·65	2·25	2·3	14·2	13·85	170
Ho	23·1	23·2	40·45	40·5	2·4	2·3	13·5	13·75	170
Er	23·5	23·5	40·1	40·4	2·3	2·3	13·6	13·7	170
Tm	23·7	23·6	40·2	40·3	2·5	2·3	13·7	13·7	160
Yb	24·2	24·05	39·7	40·1	2·4	2·25	12·9	13·6	170
Lu	24·55	24·3	39·8	40·0	2·7	2·25	13·5	13·6	200

* Diffuse and difficult to observe. Temperatures of incipient decomposition are shown.

*Triacetato-*1 : 10*-phenanthrolinecerium* (III)

A solution of cerium (III) nitrate heptahydrate (0·71 g; 1 mol.) in ethanol (20 ml) was treated with a solution of sodium acetate trihydrate (0·68 g; 3 mols.) in ethanol (30 ml). After filtration to remove the precipitated sodium nitrate the solution was added to a solution of 1,10-phenanthroline hydrate (0·31 g; 0·9 mol.) in ethanol (20 ml). The clear yellow solution was allowed to stand for 24 hrs., after which time the crystalline yellow complex was collected, washed with alcohol and dried at 10 mm over Drierite. Yield 20%.

Similarly prepared were the analogous compounds of *praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium* and *lutetium*. The yields varied from 80% for praseodymium to 40% for lutetium and the remaining analytical figures are listed below; in each case the calculated values correspond to an empirical formula $C_{18}H_{17}O_6N_2M$.

	Metal (%)		Acetate (%)		Decomposition point (°C)
	Found	Calculated	Found	Calculated	
Ce	28·2	28·2	35·2	35·6	270–272
Pr	28·1	28·2	35·0	35·5	270–300
Nd	28·6	28·8	34·95	35·3	300–310
Sm	29·7	29·6	34·3	34·9	286–290
Eu	30·0	29·8	34·5	34·75	268–272
Gd	30·4	30·6	34·0	34·4	265–268
Tb	30·5	30·8	33·8	34·3	270–275
Dy	31·2	31·3	33·65	34·05	270–274
Ho	31·6	31·6	33·6	33·9	261–263
Er	31·7	31·9	33·4	33·75	267–270
Tm	32·1	32·1	33·1	33·6	275–280
Yb	32·6	32·6	32·8	33·4	288–290
Lu	32·8	32·9	32·9	33·3	277–280

All attempts to prepare a corresponding lanthanum complex resulted in the formation of an impure product.

Magnetic susceptibilities

These were determined by the Gouy method using a permanent magnet of 5500 oersted field strength.

Infra-red spectra

These were obtained from Nujol or hexachlorobutadiene mulls using a Grubb-Parsons GS2A spectrometer.

Analyses

C,H and N were determined in the laboratory of A. Bernhardt at Mulheim. Lanthanide was determined using EDTA as described previously. Acetate was determined thus: about 0·2 g complex was decomposed by boiling water (10 ml), A. R. phosphoric acid (5 ml) was added and the mixture slowly distilled in a small all-glass apparatus, further water being added as necessary. A very slow stream of nitrogen was passed during the period of collection of distillate (1 hr). The acetic acid was then titrated against standard alkali. Blank experiments showed that no phosphoric acid was carried over.

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