

## Raman and Infrared Study of Hexamethylphosphoramide Complexes of Lanthanide Perchlorates

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The syntheses of  $[M(\text{HMPA})_6](\text{ClO}_4)_3$  (HMPA = hexamethylphosphoramide;  $M = \text{Ln, Sc, Y}$ ) from acetonitrile and of  $M(\text{HMPA})_4(\text{ClO}_4)_3$  from ethanol are described. Combined Raman and infrared spectroscopy show that the first series contains non-coordinated perchlorate only. In the second series, the amount of ionic perchlorate diminishes from the lighter to the heavier lanthanides, while bidentate perchlorate coordination is progressively replaced by monodentate perchlorate coordination.

### Introduction

A characteristic of complexes of lanthanide ions with monodentate, neutral ligands is that the number of ligands bonded to the lanthanide ion generally varies across the series. This is mainly due to the increasing repulsion between ligands in the coordination sphere, as the size of the ion decreases. One notable exception are the complexes with hexamethylphosphoramide (HMPA), whose unusually high basicity enables it to form stable complexes even with alkaline earth metal ions. Two papers appeared in 1969<sup>1,2</sup> reporting the synthesis from ethanolic media of complexes of the general formulation  $M(\text{ClO}_4)_3 \cdot 6\text{HMPA}$  ( $M = \text{Ln, Sc, Y}$ ). Following the synthetic procedures outlined in these two articles, however, Durney<sup>3</sup> failed to obtain products that agreed with the reported stoichiometry. Instead, he obtained perchlorate-bonded lanthanide complexes of the type  $M(\text{ClO}_4)_3 \cdot 4\text{HMPA}$ . His attempts to prepare complexes free of coordinated anions were unsuccessful<sup>4</sup>, even when  $\text{ClO}_4^-$  was replaced by other large anions with less coordinating ability, e.g.  $\text{B}(\text{C}_6\text{H}_5)_4^-$ . However, by using acetonitrile ( $\epsilon = 38$ ) instead of ethanol ( $\epsilon = 24$ ) as the reaction medium, we were able to isolate unambiguously the anion free complexes with 6 HMPA ligands. Recrystallisation of these complexes from ethanol always yields the 4-HMPA compounds, regardless of the relative amount of HMPA present in solution. We report here the synthesis and the results of the vibrational studies of both series of complexes.

### Experimental

#### Materials

Chemicals were obtained from the following sources: rare earth oxides > 99.9% (Fluka and Rare Earth Products Ltd.); acetonitrile *puriss.*, ethanol *puriss.*, triethylorthoformate *purum* and hexamethylphosphoramide *pract.* (Fluka). Hexamethylphosphoramide was distilled prior to use.

#### Physical Measurements

Infrared spectra in the 4000–200  $\text{cm}^{-1}$  region were recorded on a Perkin–Elmer 577 grating IR spectrophotometer. The solid samples were milled in nujol and placed between CsBr plates. Calibration was effected with polystyrene film. For the liquid HMPA spectrum a KBr cell was used. Raman data in the 3200–50  $\text{cm}^{-1}$  region were obtained with a Spex 1403 Compact spectrophotometer using the 5145 Å line of an argon ion laser (Spectra Physics 164) as the exciting source. Solid samples and liquid HMPA were placed in ordinary capillary tubes.

#### Preparation of $[M(\text{HMPA})_6](\text{ClO}_4)_3$ and $M(\text{HMPA})_4(\text{ClO}_4)_3$

The dry rare earth perchlorates were obtained by dissolution of the corresponding oxides  $\text{M}_2\text{O}_3$  in a stoichiometric amount of 30% perchloric acid, followed by evaporation to dryness at reduced pressure ( $10^{-3}$  to  $10^{-4}$  mm Hg). Two procedures were followed to obtain the HMPA complexes:

I. The dry perchlorate was dissolved under stirring in acetonitrile in the presence of excess triethylorthoformate (TEOF) as dehydrating agent. Upon addition of HMPA in a mole ratio  $\text{HMPA}/\text{M} = 8/1$  a precipitate formed immediately. The solution was allowed to settle for approximately two hours. The precipitate was then filtered off, recrystallised from acetonitrile and dried *in vacuo* for 24 hours. The crystals were analysed as  $[M(\text{HMPA})_6](\text{ClO}_4)_3$  (Table I). High yields (80–90%) were obtained for the large rare earths and somewhat lower ones (60–70%) for the small ones. Recrystallisation from absolute ethanol in the presence of

TABLE I. Analytical Data.<sup>a</sup>

Compound	M <sup>b</sup>	C	H	N	Cl
[La(HMPA) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	9.16 (9.18)	28.80 (28.59)	7.04 (7.20)	16.62 (16.67)	7.84 (7.03)
[Nd(HMPA) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	9.49 (9.50)	28.40 (28.49)	7.26 (7.17)	16.62 (16.61)	
[Gd(HMPA) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	10.26 (10.27)	28.10 (28.25)	7.05 (7.11)	16.32 (16.48)	
[Ho(HMPA) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	10.70 (10.72)	28.27 (28.10)	7.08 (7.08)	16.40 (16.39)	7.20 (6.91)
[Yb(HMPA) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	11.17 (11.19)	28.28 (27.96)	7.21 (7.04)	16.43 (16.30)	7.08 (6.88)
La(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>	11.97 (12.04)	24.99 (25.09)	6.23 (6.27)	14.60 (14.63)	9.31 (9.15)
Nd(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>	12.39 (12.44)	24.89 (24.86)	6.32 (6.26)	14.44 (14.50)	
Gd(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>	13.36 (13.41)	24.74 (24.59)	6.26 (6.19)	14.35 (14.34)	
Ho(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>	13.99 (13.98)	24.39 (24.42)	6.10 (6.16)	14.31 (14.25)	9.16 (9.01)
Yb(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>	14.53 (14.56)	24.36 (24.26)	6.04 (6.12)	14.21 (14.15)	8.93 (8.95)

<sup>a</sup> Found (calculated). <sup>b</sup> M = metal. Complexes not reported in Table I were only analysed for their metal content:

(i) For the 6-HMPA series: Sc 3.17 (3.17), Y 6.07 (6.08), Ce 9.25 (9.26), Pr 9.33 (9.30), Sm 9.84 (9.87), Eu 9.97 (9.96), Tb 10.40 (10.37), Dy 10.60 (10.58), Er 10.84 (10.86), Tm 10.95 (10.95), Lu 11.34 (11.30); (ii) For the 4-HMPA series: Sc 4.25 (4.24), Y 8.08 (8.05), Ce 12.18 (12.13), Pr 12.22 (12.19), Sm 12.88 (12.90), Eu 13.00 (13.02), Tb 13.50 (13.54), Dy 13.76 (13.80), Er 14.08 (14.15), Tm 14.28 (14.27), Lu 14.69 (14.70).

1% TEOF yielded crystals whose analyses agreed with the formulation  $M(HMPA)_4(ClO_4)_3$  (Table I).

II. The dry perchlorate was dissolved in ethanol in the presence of excess TEOF. The 4-HMPA compound precipitated readily on addition of HMPA in a mole ratio HMPA/M = 4/1. The product was recrystallised from ethanol (+1% TEOF) and dried *in vacuo* under heating for 24 hours prior to analysis. Yields were comparable to those of the 6-HMPA species obtained from acetonitrile. Recrystallisation of the 4-HMPA compound from acetonitrile (+1% TEOF) after addition of HMPA (HMPA/M = 8/1) gives the 6-HMPA compound.

#### Analytical Measurements

The metal content of the complex was assessed by complexometric titration with  $10^{-2}M$  (NH<sub>4</sub>)<sub>3</sub>H(EDTA) in the presence of urotropine as buffer and xylene orange as indicator<sup>5</sup>. Microanalytical determinations of C, H, N and Cl were performed by W. Manser Mikrolabor, ETH Zurich.

#### Results and Discussion

ClO<sub>4</sub><sup>-</sup> may be present in complexes in purely ionic form (T<sub>d</sub> symmetry) or acting as a monodentate (C<sub>3v</sub>) or bidentate (C<sub>2v</sub>) ligand. Vibrational spectra should allow a differentiation between the three species, as indicated by the correlation diagram for the vibrational modes of the corresponding point groups (Table II)<sup>6</sup>. In this table we have listed in brackets the approximate regions of the spectrum where perchlorate vibrations have to be expected. The values have been compiled from a number of publications on complexes of rare earth<sup>7-11</sup> as well as transition metal perchlorates<sup>12-16</sup>.

Both  $\nu_1$  and  $\nu_2$  of ionic (T<sub>d</sub>) perchlorate are theoretically forbidden in the infrared, but  $\nu_1$  occurs usually in solids as a very weak absorption due to distortion of the ion in the crystal field. It is obvious from Table II that a straight differentiation between the 3 perchlorate species is difficult because of the mutual overlapping of absorption regions. From infrared spectra alone, for instance, it is practically impossible to distinguish between purely bidentate perchlorate (C<sub>2v</sub>) and a mixture of ionic and monodentate species, because we would observe the same number of bands in both cases<sup>3,17</sup>. Furthermore, HMPA frequencies occur in all 4 spectral regions, but fortunately with different relative intensities in IR and Raman.

Despite these complications we may accept two guidelines for identification: (i) If the 930 cm<sup>-1</sup> band is absent or very weak in the infrared spectrum, coordinated perchlorate groups may be ruled out. (ii) If the Raman spectrum shows an extra band in the 400 cm<sup>-1</sup> region, which is, like  $\nu_2$ [T<sub>d</sub>], infrared inactive, we may assume it to be the  $\nu_5$  mode of the C<sub>2v</sub> bidentate perchlorate group.

#### [M(HMPA)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>

In Table III are listed the infrared and Raman data of solid [M(HMPA)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> in the 300–1200 cm<sup>-1</sup> region\*. The tentative assignments of the HMPA frequencies are those made by De Bolster and Groeneveld<sup>18</sup>. We attribute the band at 367 cm<sup>-1</sup> (IR)/362 cm<sup>-1</sup> (R) to the M–OP stretch\*\*.

Throughout the lanthanide series, infrared and Raman spectra of these complexes remain virtually unchanged

\* Outside the tabulated region only the already known<sup>18</sup> ligand vibrations can be observed.

\*\* The M–O (anion) stretching mode should appear below 300 cm<sup>-1</sup><sup>18</sup> and was not assigned.

TABLE II. Assignment of the IR and Raman Perchlorate Frequencies (cm<sup>-1</sup>) Observed in Rare Earth HMPA Complexes.

Species	Point Group	Modes <sup>a</sup>
-O*-ClO <sub>3</sub> Monodentate	C <sub>3v</sub>	$\nu_2$ (A <sub>1</sub> ) ClO stretch (914-940) IR : 930 R : 929 $\nu_1$ (A <sub>1</sub> ) sym.bend (928-936) IR : inactive (935) R : 926 $\nu_6$ (E) rocking (460-480) IR : <sup>c</sup> R : 455 $\nu_2$ (E) sym.bend (458-476) IR : inactive R : 455 $\nu_4$ (A <sub>1</sub> ) Cl-O <sub>2</sub> * sym.stretch (928-945) IR : 913 R : 911 $\nu_5$ (A <sub>2</sub> ) torsion ( <sup>d</sup> ) IR : inactive R : 436 $\nu_4$ (A <sub>1</sub> ) ClO <sub>2</sub> * sym.bend (453-474) IR : <sup>c</sup> R : 485 $\nu_1$ (A <sub>1</sub> ) ClO <sub>2</sub> sym.stretch (1025-1038) IR : 1018 R : <sup>e</sup> $\nu_2$ (A <sub>1</sub> ) ClO <sub>2</sub> sym.stretch (1025-1040) IR : 1024 R : 1027 $\nu_3$ (F <sub>2</sub> ) as.stretch (1070-1100) IR : 1080-1100 R : 1082-1102 $\nu_4$ (E) as.bend (1120-1160) IR : 1160 R : 1160 $\nu_6$ (B <sub>1</sub> ) ClO <sub>2</sub> as.stretch (1125-1138) IR : <sup>f</sup> R : 1110 $\nu_7$ (B <sub>1</sub> ) ClO <sub>2</sub> as.stretch (1170-1215) IR : 1175 R : 1181 $\nu_3$ (A <sub>1</sub> ) ClO <sub>2</sub> sym.bend (635-666) IR : 642 R : <sup>c</sup> $\nu_4$ (F <sub>2</sub> ) as.bend (618-632) IR : 623 R : 623 $\nu_5$ (E) as.bend (616-620) IR : 623 R : 620 $\nu_8$ (B <sub>2</sub> ) ClO <sub>2</sub> * as.stretch (1170-1215) IR : 1175 R : 1181 $\nu_9$ (B <sub>2</sub> ) rocking (611-617) IR : 612 R : 612 $\nu_7$ (B <sub>1</sub> ) rocking (623-635) IR : 622 R : 620 $\nu_3$ (A <sub>1</sub> ) ClO <sub>2</sub> sym.bend (635-666) IR : 642 R : <sup>c</sup> $\nu_5$ (E) as.bend (616-620) IR : 623 R : 620 
		Ionic
-O* Bidentate	C <sub>2v</sub>	$\nu_1$ (A <sub>1</sub> ) ClO stretch (914-940) IR : 930 R : 929 $\nu_2$ (A <sub>1</sub> ) sym.bend (928-936) IR : inactive (935) R : 926 $\nu_3$ (F <sub>2</sub> ) as.stretch (1070-1100) IR : 1080-1100 R : 1082-1102 $\nu_4$ (E) as.bend (1120-1160) IR : 1160 R : 1160 $\nu_5$ (A <sub>2</sub> ) torsion ( <sup>d</sup> ) IR : inactive R : 436 $\nu_6$ (B <sub>1</sub> ) ClO <sub>2</sub> as.stretch (1125-1138) IR : <sup>f</sup> R : 1110 $\nu_7$ (B <sub>1</sub> ) ClO <sub>2</sub> as.stretch (1170-1215) IR : 1175 R : 1181 $\nu_8$ (B <sub>2</sub> ) ClO <sub>2</sub> * as.stretch (1170-1215) IR : 1175 R : 1181 $\nu_9$ (B <sub>2</sub> ) rocking (611-617) IR : 612 R : 612 $\nu_3$ (A <sub>1</sub> ) ClO <sub>2</sub> sym.bend (635-666) IR : 642 R : <sup>c</sup> $\nu_4$ (F <sub>2</sub> ) as.bend (618-632) IR : 623 R : 623 $\nu_5$ (E) as.bend (616-620) IR : 623 R : 620 

<sup>a</sup>The values in brackets are literature data<sup>7-16</sup>. <sup>b</sup>Not observed;  $\nu_3$  is presumed to be masked by the ligand NPN bending at these wavelengths. <sup>c</sup>Not observed; presumed to be masked by the very strong HMPA band in this region (see text and Table III). <sup>d</sup>No value reported. <sup>e</sup>Not observed; activity presumed to be too weak. <sup>f</sup>Masked by the broad  $\nu_3$  (F<sub>2</sub>) absorption of the ionic species.

TABLE III. Infrared and Raman bands ( $\text{cm}^{-1}$ ) of Solid  $[\text{M}(\text{HMPA})_6](\text{ClO}_4)_3$  ( $\text{M} = \text{La}, \text{Nd}, \text{Gd}, \text{Ho}, \text{Yb}$ ).

$[\text{M}(\text{HMPA})_6](\text{ClO}_4)_3^a$		Assignments	
IR <sup>b</sup>	Raman <sup>c</sup>	HMPA <sup>d</sup>	Perchlorate
1190 vs, m	1192 (2)	P–O stretching	
1177 shs	1168 (3)	C–N stretching	
1145 shm	1162 (7)	CH <sub>3</sub> rocking	
masked by anion vibration	1103 (7)	CH <sub>3</sub> rocking	
~1083 vs, vb	1090 (17)		$\nu_3(\text{F}_2)[\text{T}_d]$
1055 shm	1068 (8)	C–N stretching	
	1008 (5)	CH <sub>3</sub> rocking	
992 vs, b	995 (6)	P–N stretching	
935 vw	926 (100)		$\nu_1(\text{A}_1)[\text{T}_d]$
	912 (3)		
	904 (13)		
759 vs, m	755 (6)	P–N stretching	
744 s	745 (3)		
644 m, sp	645 (78)	NPN bending	
623 s, sp	623 (9)		$\nu_4(\text{F}_2)[\text{T}_d]$
502 shm	499 (10)	P–O bending	
480 s, m	477 (5)	CNP bending	
	453 (9)		$\nu_2(\text{E})[\text{T}_d]$
378 shm	377 (7)	CNC bending	
367 s	362 (13)	M–OP stretching	
354 shm	347 (14)	CNP bending	

<sup>a</sup> Frequencies are given as average values of the data observed for the five complexes ( $\pm 2 \text{ cm}^{-1}$ ). <sup>b</sup> Abbreviations for band characteristics:

1st symbol (band intensity): vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.  
2nd symbol (band width): sp = sharp; m = medium; b = broad; vb = very broad.

<sup>c</sup> Raman band intensities are given as percentages of the main peak. <sup>d</sup> cf. ref. 18.

from La to Yb. The absence of a strong IR absorption in the  $920 \text{ cm}^{-1}$  region is in favour of ionic perchlorate as the only species. In the Raman spectrum the very strong band at  $926 \text{ cm}^{-1}$  is obviously the  $\nu_1$  [ $\text{T}_d$ ] vibration; this band is accompanied by two small bands at  $904$  and  $912 \text{ cm}^{-1}$ , which might suggest the presence of other perchlorate species. Considering the absence of any other evidence, we may however assume that these small peaks are due to crystal field effects. The assumption that ionic perchlorate is the only species, is supported by the presence of only one strong and characteristically broad band ( $\nu_3$  [ $\text{T}_d$ ]) in the  $1100 \text{ cm}^{-1}$  region, both in IR and Raman spectra. With the help of the combination band ( $\nu_3 + \nu_1$ ) at  $2018 \text{ cm}^{-1}$  it is possible to locate the maximum of the broad  $\nu_3$  IR band at approximately  $1083 \text{ cm}^{-1}$  for all the lanthanides.

The splitting of the  $750 \text{ cm}^{-1}$  PN stretching band of HMPA does not necessarily imply the presence of two sets of equivalent HMPA molecules (although this

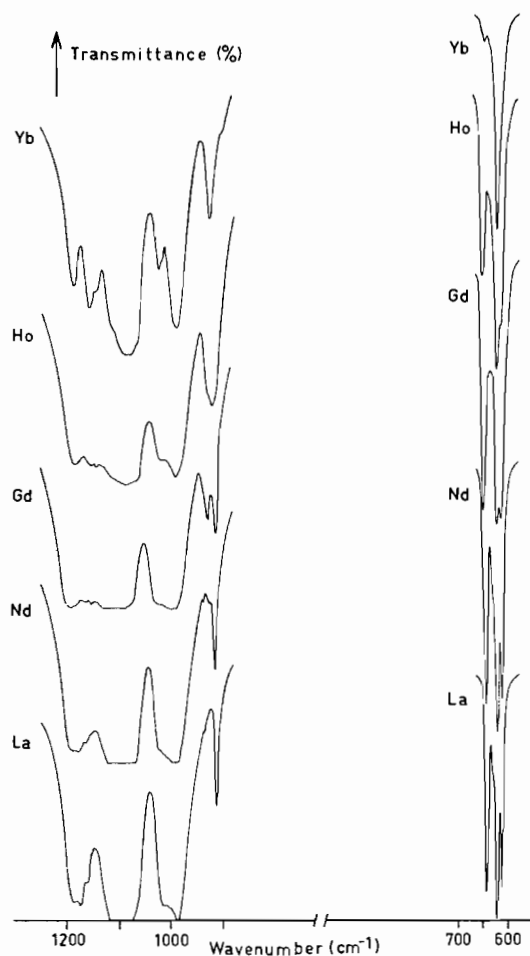


Figure 1. Infrared spectra ( $1250\text{--}850 \text{ cm}^{-1}$ ;  $670\text{--}600 \text{ cm}^{-1}$ ) of  $\text{M}(\text{HMPA})_4(\text{ClO}_4)_3$ .

would seem possible with the steric crowding created by 6 bulky ligands around the lanthanide ion) nor the non-equivalence of single amide groups in the HMPA molecule. De Bolster<sup>18</sup> attributes the splitting to crystal packing forces. Infrared and Raman data suggest the formulation of the 6-HMPA complexes as 1:3 salts with a lanthanide coordination number of 6:  $[\text{M}(\text{HMPA})_6](\text{ClO}_4)_3$ .

The powder diffraction patterns of these complexes are similar along the lanthanide series with only a small systematic shift in the line positions.

#### $\text{M}(\text{HMPA})_4(\text{ClO}_4)_3$

In Table IV the infrared and Raman data of La  $(\text{HMPA})_4(\text{ClO}_4)_3$  and Yb  $(\text{HMPA})_4(\text{ClO}_4)_3$  are compared in the  $300\text{--}1200 \text{ cm}^{-1}$  region. Outside this region the spectra of the 6-HMPA and the 4-HMPA series are virtually the same. For the latter series our IR data agree fairly well with those published, but

TABLE IV. Infrared and Raman Bands ( $\text{cm}^{-1}$ ) of Solid  $\text{La}(\text{HMPA})_4(\text{ClO}_4)_3$  and  $\text{Yb}(\text{HMPA})_4(\text{ClO}_4)_3$ .<sup>a</sup>

$\text{La}(\text{HMPA})_4(\text{ClO}_4)_3$		Perchlorate assignments	$\text{Yb}(\text{HMPA})_4(\text{ClO}_4)_3$	
IR	Raman		IR	Raman
1189 vs*	1187 (5)*	$\nu_8(\text{B}_2)$ [ $\text{C}_{2v}$ ]	1187 s*	1190 (5)*
1175 vs	1181 (6)			1175 (8)
1162 vs*	1167 (10)*	$\nu_4(\text{E})$ [ $\text{C}_{3v}$ ]	1158 vs	1159 (6)
			1145 s*	1144 (5)*
~1097 vs,vb	1110 (18)	$\nu_6(\text{B}_1)$ [ $\text{C}_{2v}$ ]	~1086 vs,vb	1116 (11)
	1101 (22)	$\nu_3(\text{F}_2)$ [ $\text{T}_d$ ]		1100 (8)
	1070 (11)*			1070 (11)*
		$\nu_1(\text{A}_1)$ [ $\text{C}_{3v}$ ]	1024 vs	1027 (19)
1018 vs		$\nu_1(\text{A}_1)$ [ $\text{C}_{2v}$ ]		
	1003 (7)*			1007 (13)*
988 vs,b*	990 (10)*		990 s,b*	994 (11)*
936 vw	926 (71)	$\nu_1(\text{A}_1)$ [ $\text{T}_d$ ]	936 vw	
		$\nu_2(\text{A}_1)$ [ $\text{C}_{3v}$ ]	925 s	929 (100)
913 s,sp	911 (72)	$\nu_2(\text{A}_1)$ [ $\text{C}_{2v}$ ]		907 (11)
755 vs,sp*	753 (8)*		758 s*	760 (11)*
642 s	645 (100)*	$\nu_3(\text{A}_1)$ [ $\text{C}_{2v}$ ]; ( $\nu_3(\text{A}_1)$ [ $\text{C}_{3v}$ ] ?)	649 vw*	653 (96)*
622 vs	620 (11)	$\nu_7(\text{B}_1)$ [ $\text{C}_{2v}$ ]; $\nu_5(\text{E})$ [ $\text{C}_{3v}$ ]; $\nu_4(\text{F}_2)$ [ $\text{T}_d$ ]	623 s	620 (9)
612 s	612 (14)	$\nu_9(\text{B}_2)$ [ $\text{C}_{2v}$ ]		
500 shm*	497 (12)*		506 vw*	507 (16)*
	485 (15)	$\nu_4(\text{A}_1)$ [ $\text{C}_{2v}$ ]		
481 s*			480 s*	480 (7)*
	455 (6)	$\nu_2(\text{E})$ [ $\text{T}_d$ ]; $\nu_6(\text{E})$ [ $\text{C}_{3v}$ ]		456 (15)
	436 (15)	$\nu_5(\text{A}_2)$ [ $\text{C}_{2v}$ ]		
375 shm*			376 shw*	
367 m	362 (10)	M-OP stretch	365 m	365 (11)
350 m*	343 (18)*		352 m*	350 (21)*

<sup>a</sup> Vibrations above  $1200 \text{ cm}^{-1}$  are not reported, as this part of the spectrum is essentially identical to the one observed for  $[\text{M}(\text{HMPA})_6](\text{ClO}_4)_3$ . All (\*) marked vibrations are HMPA bands.

unassigned by Durney and Marianelli<sup>3</sup>. Apart from the  $\text{T}_d$  perchlorate frequencies already observed in the 6-HMPA series, the spectra of  $\text{La}(\text{HMPA})_4(\text{ClO}_4)_3$  show a number of additional anion vibrations. Among these the  $436 \text{ cm}^{-1}$  Raman band has no counterpart in the infrared; therefore we assign it to the IR forbidden  $\nu_5$  mode of bidentate perchlorate. The other bands are then assigned accordingly as  $\text{C}_{2v}$  vibrations. However, as the number of new bands does not reach the number required theoretically for this site symmetry, we assume that the band at  $622 \text{ cm}^{-1}$  (IR)/ $620 \text{ cm}^{-1}$  (R) contains both  $\nu_4$  [ $\text{T}_d$ ] and  $\nu_7$  [ $\text{C}_{2v}$ ], while  $\nu_3$  [ $\text{C}_{2v}$ ] falls together with the NPN bending frequency of HMPA at  $642 \text{ cm}^{-1}$  (IR)/ $645 \text{ cm}^{-1}$  (R).

Significant changes in the regions of the anion vibrations occur in the spectra of the 4-HMPA complexes as we proceed from La to Yb (IR: Figure 1; Raman: Figure 2). The most conspicuous feature is the slow disappearance of the  $436 \text{ cm}^{-1}$  band in the Raman spectrum. As the ionic radius of the lanthanide ion shrinks, bidentate coordination by perchlorate groups becomes less and less possible. Accordingly, the absorptions at  $485$ ,  $912$  and  $1110 \text{ cm}^{-1}$  decline. In the

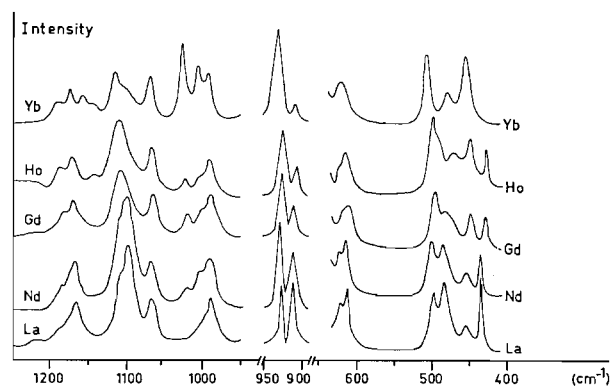


Figure 2. Raman spectra ( $1250\text{--}950 \text{ cm}^{-1}$ ;  $950\text{--}890 \text{ cm}^{-1}$  (reduced scale 1:5);  $640\text{--}410 \text{ cm}^{-1}$ ) of  $\text{M}(\text{HMPA})_4(\text{ClO}_4)_3$ .

meantime, new bands appear at  $1023$  and  $1160 \text{ cm}^{-1}$ , which we assign respectively to the  $\nu_1$  and  $\nu_4$  vibrations of the monodentate  $\text{C}_{3v}$  perchlorato group. While the  $\nu_3$  absorption of ionic perchlorate at  $1100 \text{ cm}^{-1}$  diminishes, its  $\nu_2$  band at  $455 \text{ cm}^{-1}$  grows. This can only be understood, if we assume that the  $\nu_6$  mode of

the  $C_{3v}$  species is located at about the same frequency as  $\nu_2$  [ $T_d$ ]. In the *infrared* spectrum the  $1175\text{ cm}^{-1}$  peak of the bidentate perchlorate is gradually absorbed by the HMPA band, while the peak at  $\sim 1160\text{ cm}^{-1}$  becomes more important. The  $1018\text{ cm}^{-1}$  band shifts to higher frequencies and separates totally from the neighbouring HMPA absorption; its position in the Yb 4-HMPA complex ( $1024\text{ cm}^{-1}$ ) can be considered as the frequency of the  $\nu_1$  [ $C_{3v}$ ] mode. In the  $900\text{ cm}^{-1}$  region a new peak rises at  $930\text{ cm}^{-1}$ , while the  $913\text{ cm}^{-1}$   $C_{2v}$  band diminishes ultimately to a shoulder in the Yb complex. We assign this new band to the  $\nu_2$  mode of monodentate perchlorate. In the  $600\text{ cm}^{-1}$  region the  $612\text{ cm}^{-1}$   $C_{2v}$  band gradually disappears. In the Yb 4-HMPA complex the strong peak at  $623\text{ cm}^{-1}$  combines  $\nu_4$  [ $T_d$ ] and probably  $\nu_5$  [ $C_{3v}$ ]. The symmetrical bending  $\nu_3$  of the monodentate perchlorate is presumed to be masked by the ligand NPN bending.

Our assignments and observed frequencies for the three types of perchlorates agree well with those of Pavkovic and Meek<sup>16</sup> for a series of Ni(II) coordinated perchlorate complexes.

### Conclusion

We have shown that  $[M(\text{HMPA})_6](\text{ClO}_4)_3$  contains only ionic perchlorate, while in  $M(\text{HMPA})_4(\text{ClO}_4)_3$  also coordinated perchlorato groups occur. In the latter series the amount of ionic perchlorate diminishes from La to Yb, while bidentate anion coordination is progressively replaced by monodentate coordination. Therefore the coordination number of the lanthanide ion in this series must lie between six and eight. An investigation of the structure and the dynamics of these complexes in solution by NMR spectroscopy is in progress.

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### References

- 1 J. T. Donoghue, E. Fernandez, J. A. Mc Millan and D. A. Peters, *J. Inorg. Nucl. Chem.*, **31**, 1431 (1969).
- 2 E. Giesbrecht and L. B. Zinner, *Inorg. Nucl. Chem. Letters*, **5**, 575 (1969).
- 3 M. R. Durney and R. S. Marianelli, *Inorg. Nucl. Chem. Letters*, **6**, 895 (1970).
- 4 M. T. Durney, "The Coordination and Organometallic Chemistry of the Lanthanides", *Ph. D. Thesis*, The University of Nebraska, 1972.
- 5 J. Körbl, R. Pribil and N. A. Emr, *Z. anal. Chem.*, **156**, 292 (1957); G. Brunisholz and M. Randin, *Helv. Chim. Acta*, **42**, 1932 (1959).
- 6 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.* **1961**, 3091.
- 7 N. P. Crawford and G. A. Nelson, *J. Chem. Soc. (A)*, **1970**, 141.
- 8 G. Vicentini and L. B. Zinner, *Inorg. Nucl. Chem. Letters*, **10**, 629 (1974).
- 9 V. N. Krishnamurty and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **29**, 517 (1967).
- 10 D. M. Mehs and S. K. Madan, *J. Inorg. Nucl. Chem.*, **30**, 3017 (1968).
- 11 R. C. Grandey and Th. Moeller, *J. Inorg. Nucl. Chem.*, **32**, 333 (1970).
- 12 N. M. Karayannis, E. E. Bradshaw, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, **32**, 1079 (1970).
- 13 N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, **9**, 582 (1970).
- 14 N. M. Karayannis, C. Owens, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, **31**, 2767 (1969).
- 15 B. J. Hathaway, D. G. Holah and M. Hudson, *J. Chem. Soc.*, **1963**, 4586.
- 16 S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).
- 17 A. N. Specá and L. L. Pytlewski, *Inorg. Nucl. Chem. Letters*, **9**, 365 (1973).
- 18 M. W. G. De Bolster and W. L. Groeneveld, *Recueil Trav. chim.*, **90**, 477 (1971).