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Synthesis of Homodinuclear Macrocyclic Complexes of Lanthanides and Phenolic Schiff Bases

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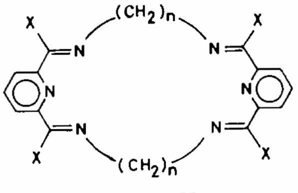
Abstract

Successful syntheses of the first examples of homodinuclear macrocyclic lanthanide complexes are reported. The complexes were obtained as compounds of the 2:2 Schiff base formed by condensing 2,6-diformyl-*p*-cresol and triethylenetetramine (L_7) by a template procedure using lanthanide nitrates and perchlorates. When reactant methanolic solutions were concentrated the complexes were deposited as yellow or orange microcrystalline precipitates, $Ln_2L_7(NO_3)_4 \cdot nH_2O$ or $Ln_2L_7(NO_3)_{4-x}(OH)_x$, $x =$ 1 or 2, whereas solutions diluted three times deposited complexes as flaky off-white crystalline precipitates of light lanthanides. The orange $Ln_2L_7(NO_3)_2(OH)_2$ complexes can be converted in quantitative yield to the off-white flaky form of $Ln_2L_7(NO_3)_4 \cdot nH_2O$ by refluxing them in methanolic solution containing triethylenetetramine and a three-fold excess of $Ln(NO_3)_3$. The complexes were characterized by elemental analysis, fast atom bombardment mass spectrometry, UV–Vis and infrared spectroscopy and thermogravimetry. Interesting and mostly new polyatomic oxo clusters, e.g. $Ln_2O_3^+$, $Ln_3O_4^+$, $Ln_4O_6^+$, $Ln_5O_7^+$ were dominant in the mass spectra but are treated in detail elsewhere.

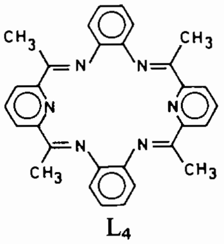
Introduction

Macrocyclic and macroacyclic ligands, mainly Schiff bases [1–3], cryptands [4] and crown ethers [5] have played a key role in our understanding of the nature of metal–metal ion interactions of the 3d-elements in systems of biological interest. While it appears widely acknowledged that homodinuclear complexes of macrocyclic or macroacyclic ligands and lanthanide cations (Ln^{3+}) could provide information regarding Ln^{3+}–Ln^{3+} interactions that is critical for our scientific understanding and technological applications of rare earths [4, 5, 7], no synthetic effort culminating in the formation of those compounds has been reported. Recently [8, 9] large open compartmental ligands have been used to trap lanthanide and 3d block cations resulting in heterodinuclear (3d–4f metal) complexes but no homodinuclear lanthanide compounds were obtained.

Efforts to encapsulate lanthanide cations in Schiff base macrocycles have so far yielded mononuclear complexes of the 2:2 ligands, L_1–L_4, derived from pyridine dicarbonyls and short chain primary diamines [10–12]. (Use of 2,5-furandialdehyde in place of 2,6-diacetylpyridine gave the corresponding 2:2 Schiff base complexes [13a]).



L_1: $n = 0; X = CH_3$
L_2: $n = 2; X = CH_3$
L_3: $n = 2,3; X = H$



L_4

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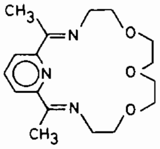
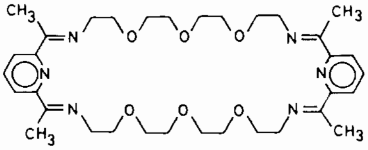
However, condensation of 2,6-diacetylpyridine with a long chain diamine $H_2N-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-NH_2$ in the presence of early lanthanide nitrates resulted in the formation of mononuclear complexes of the 1:1 ligand, L_5, rather than complexes of the 2:2 ligand, L_6 [7]. Attempts to condense 2,6-diacetylpyridine and tetraethylenepentamine also gave the corresponding 1:1 Schiff base complex [12a].

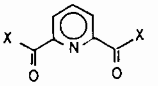


L_5

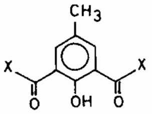


L_6

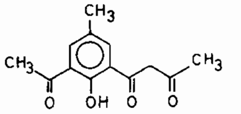
Our investigations have concentrated on deriving synthetic routes for the formation of homodinuclear macrocyclic Schiff base lanthanide complexes. In our experiments we have utilized the dicarbonyls (i)–(vii).



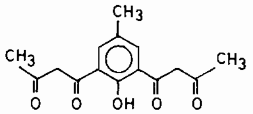
i, X = H
ii, X = CH_3



iii, X = H
iv, X = CH_3
v, X = CH_2CH_3

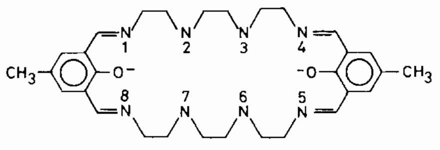


vi



vii

In the template condensation of 2,6-diformyl-*p*-cresol (**iii**) and triethylenetetramine we have successfully isolated the first (to our knowledge) homodinuclear macrocyclic complexes which are compounds of the 2:2 ligand L_7. The preparation and preliminary characterization of this new type of compounds are herein reported.



L_7

Experimental

Lanthanide nitrates and perchlorates used were obtained from a careful neutralization of the corresponding oxides of at least 99.9% purity and then used *in situ*. $Ln(NO_3)_3 \cdot 5H_2O$, Ln = Ce, Gd, Yb, were commercial products from Aldrich Chemical Co.

Triethylenetetramine was used as supplied by Fisher Laboratory Chemical without further purification.

2,6-diformyl-*p*-cresol (**iii**) was obtained from *p*-cresol by the procedure of Moore and Vigee [16], or by oxidation of 2,6-bis(hydroxymethyl)-*p*-cresol with MnO_2 [17]. ^1H NMR: 11.45 (OH) (1), 10.21 (CHO) (2) 7.77 (Ar–H) (2) and 2.39 (CH_3) (3), all singlets.

Preparation of Off-white Complexes of L_7

To 1 mmol of the lanthanide nitrate dissolved in 35 ml of methanol is added 0.164 g (1 mmol) of solid 2,6-diformyl-*p*-cresol and the solution is heated to reflux. Then 0.151 g (1 mmol) of 97% triethylenetetramine in 10 ml of methanol is added and the resulting orange solution is refluxed. Within 3–5 min a flaky off-white crystalline precipitate begins to form. Refluxing is continued for six h, followed by filtration (while hot) and washing with methanol and ether, followed by air drying. This procedure failed many times when Eu^{3+} was employed as a template cation, (even when the total volume of methanol was increased to 75 ml or 150 ml per mmol) but it worked well when the higher boiling n-butanol (boiling point (b.p.) 117 °C) was substituted for methanol. When methanol and ethanol were used, the exclusive product was the unhydrolyzed orange complex $Eu_2L_7(NO_3)_4 \cdot 2H_2O$; when n-propanol was used, a mixture of the off-white complexes and an unidentified yellow product were obtained. A small quantity of the off-white complex: $Gd_2L_7(NO_3)_4 \cdot 2H_2O$ was obtained with methanol as solvent once but subsequent attempts with solvents R–OH, (R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$ and $CH_3CH_2CH_2CH_2$) failed. Addition of acid or base in catalytic amounts did not influence the final product.

With Ce^{3+} it was necessary to bubble nitrogen through the reactants to prevent the formation of intractable dark brown solids. Yields are shown in Table I. When the mole ratio of La^{3+} to dialdehyde to triethylenetetramine (La^{3+}:iii:TETA) was changed to 1:1:2, the yield of the off-white complex increased to 95%, but when increased to 1:1:10 and Pr^{3+} substituted for La^{3+} the yield decreased to 67%.

Preparation of Yellow/Orange Complexes of L_7

To 1 mmol of the lanthanide nitrate or perchlorate dissolved in 10 ml of methanol is added 0.164 g (1 mmol) of solid 2,6-diformyl-*p*-cresol. The resulting orange or yellow solution is heated to reflux and then 0.151 g (1 mmol) of triethylenetetramine in 5 ml of methanol is added and refluxing is continued. Within 3–5 min a yellow or deep orange micro-

TABLE I. Analytical Results for Complexes of L_7

Compound (formula weigth)		% Yield	% Observed				% Calculated			
			C	H	N	Ash (TG)	C	H	N	Ash
Off-white										
$La_2L_7(NO_3)_4$	(1073)	28	33.65	3.90	15.04	29	33.6	3.9	15.7	30
$Ce_2L_7(NO_3)_4$	(1075)	34, 75[a]	33.97	4.12	15.06	32	33.5	3.9	15.6	32
$Pr_2L_7(NO_3)_4 \cdot 2H_2O$	(1113)	89	32.40	3.95	15.05	32	32.4	4.2	15.1	32
$Nd_2L_7(NO_3)_4 \cdot 2H_2O$	(1119)	66	32.38	3.97	14.96	32	32.2	4.1	15.0	30
$Sm_2L_7(NO_3)_4 \cdot 2H_2O$	(1132)	60	32.25	3.89	14.85	32	31.8	4.1	14.9	31
$Eu_2L_7(NO_3)_4 \cdot 2H_2O$	(1135)	74[b]	32.54	3.86	15.0	31	31.8	4.1	14.8	31
$Gd_2L_7(NO_3)_4 \cdot 2H_2O$	(1145)	4	31.88	3.80	14.88	31	31.5	4.0	14.7	32
Yellow – Orange										
$La_2L_7(NO_3)_4$	(1073)	45	33.01	4.18	14.88	32	33.6	4.0	15.7	30
$La_2L_7(NO_3)_2(OH)_2$	(983)	57	37.74	4.77	14.22		36.7	4.5	14.33	
$Ce_2L_7(NO_3)_4$	(1075)	35	33.84	4.14	15.06	30	33.5	3.9	15.6	32
$Pr_2L_7(NO_3)_4$	(1077)	82	33.58	4.05	15.14	29	33.5	3.9	15.6	32
$Nd_2L_7(NO_3)_4$	(1083)	74	33.29	4.06	14.91	28	33.3	3.9	15.5	31
$Nd_2L_7(NO_3)_2(OH)_2$	(993)	85	36.87	4.46	14.37		36.3	4.4	14.1	
$Eu_2L_7(NO_3)_4 \cdot 2H_2O$	(1135)	53	31.95	4.18	14.47	30	31.8	4.1	14.8	31
$Eu_2L_7(NO_3)_3(OH)$	(1054)	48	35.06	4.27	14.5		34.2	4.1	14.6	33
$Gd_2L_7(NO_3)_3(OH)$	(1064)	46	34.63	4.46	14.98	31	33.9	4.1	14.5	34
$Gd_2L_7(NO_3)_2(OH)_2$	(1019)	38	36.6	4.94	14.38		35.4	4.3	13.7	
$Tb_2L_7(NO_3)_3(OH)$	(1068)	13	32.95	4.24	14.56		33.8	4.1	14.4	34
$Dy_2L_7(NO_3)_3(OH)$	(1075)	33	34.15	4.29	14.77		33.5	4.0	14.3	35
$Ho_2L_7(NO_3)_3(OH)$	(1080)	39	33.62	4.33	14.84		33.4	4.0	14.3	35
$Ho_2L_7(NO_3)_4 \cdot 2H_2O$	(1160)		30.68	4.32	14.95		31.1	4.0	14.5	
$Er_2L_7(NO_3)_3(OH)$	(1084)	12	33.71	4.45	14.08		33.2	4.0	14.2	35
$Tm_2L_7(NO_3)_4 \cdot 2H_2O$	(1169)	57	31.48	4.04	14.03		30.8	4.0	14.4	
$Yb_2L_7(NO_3)_4 \cdot 2H_2O$	(1177)	22	29.54	4.01	14.35	32	30.6	3.9	14.3	33
$Lu_2L_7(NO_3)_4 \cdot 2H_2O$	(1181)	43	31.16	4.02	14.01		30.5	3.8	14.2	
$Y_2L_7(NO_3)(OH)$	(928)	35	38.73	4.75	16.25	21	38.8	4.7	16.6	24
$Nd_2L_7(ClO_4)_3(OH)$	(1151)	63	31.85	3.94	9.80		31.3	3.8	9.7	
$Sm_2L_7(ClO_4)_3(OH)$	(1163)	73	31.44	3.81	9.78		31.0	3.7	9.6	
$Gd_2L_7(ClO_4)_2(OH)_2$	(1094)	10	32.44	4.15	9.80		32.9	4.1	10.2	

[a] From an ethanolic (rather than methanolic) solution. [b] From n-butanol.

crystalline precipitate begins to deposit. Refluxing is continued for 6 h, followed by filtration and washing with methanol and ether and then air drying. The orange complex of L_7 with Sm^{3+} could not be made in this way if the counter anion is NO_3^- as the exclusive product was the off-white complex or a mixture of the off-white complex and some unidentified yellow product even in experiments where the total volume of methanol used was reduced to 12 ml per mmol of the dialdehyde. But when the counter anion was changed to ClO_4^- the compound $Sm_2L_8(ClO_4)_3(OH)$ was obtained.

When the mole ratio Ln^{3+}:iii:TETA is 1:2:1, the exclusive product is $Ln_2L_7(NO_3)_2(OH)_2$ (Ln = La, Nd, Gd).

The complex of Ce^{3+} needed to be prepared in a nitrogen atmosphere; otherwise intractable dark brown solids were obtained.

Complexes of Tm^{3+}, Yb^{3+} and Lu^{3+} prepared by the above procedure did not give good analyses so the procedure was modified to allow them to form at room temperature. Reactants were mixed at room temperature and sat for a week before filtration, washing and drying.

Conversion of the Orange Complexes $Ln_2L_7(NO_3)_2(OH)_2$ to the Off-white Complexes $Ln_2L_7(NO_3)_4 \cdot nH_2O$

To 0.1 mmol of $Ln_2L_7(NO_3)_2(OH)_2$ suspended in 6 ml of methanol is added 0.1 mmol of triethylenetetramine in 3 ml of methanol. Within a few min the orange compound dissolves entirely. Refluxing or allowing the mixture to sit at room temperature deposits the off-white complex $Ln_2L_7(NO_3)_4 \cdot nH_2O$ in typical flaky form and 37% yield. Elemental analysis data confirms this. *Anal.* Found for Ln = La and $n = 0$; C, 33.34; H, 4.41; N, 15.18. Calc. C, 33.6; H, 3.9; N, 15.7%. Found for Ln = Nd and $n = 2$; C, 32.45; H, 4.37; N, 15.11. Calc. C, 32.2; H, 4.1; N, 15.0%. When a three-fold excess (0.3 mmol) of $Ln(NO_3)_3$ is added prior to introducing triethylenetetramine and then the mixture refluxed the yield is quantitative.

Elemental analyses were performed by Micanal of Tucson, Arizona. The equipment used for thermogravimetry (TG) in air, infrared (IR) (KBr disk) and electronic absorption (Nujol mull) investigations have been described in a previous report [18]. NMR spectra were recorded on a Bruker WP-200 or an IBM NR/100 spectrometer operating at 300 K.

Fast Atom Bombardment Mass Spectrometry

A Kratos MS80RFA double focusing mass spectrometer equipped with a post-acceleration detector was used to analyze the samples. About 100 μg of each of the samples were suspended in 5 μl of glycerol, and placed on a direct sample probe, which was inserted into the ionization source for analysis. The mass spectrometer was operated in the positive ion mode, with accelerating voltage at 4 kV. Fast xenon atoms at 8 kV were used to bombard the samples. A mixture of cesium iodide and glycerol was used as a mass calibration standard. Xenon gas was supplied by Liquid Carbonic Corporation and had a quoted purity of 99.995%. For each sample studied at least 30 scans were accumulated. Data related to the ligand L_7 or species containing it were extracted from an average of the first 13 scans and only peaks appearing at least 5 times with a minimum intensity of 1% were included in the average spectrum. Peaks originating from the ligand or fragments containing it were dominant in the presence of glycerol, but as glycerol dried out less ligand information was available. Peaks of oxo species dominated spectra of drier samples.

Results and Discussion

Analytical data for the off-white and orange compounds are given in Table I. The off-white compounds obtained from dilute solutions are formulated as $Ln_2L_7(NO_3)_4 \cdot nH_2O$; $n = 0$, for Ln = La, Ce and 2 for Ln = Pr–Gd. The orange compounds fall into two major categories: (i) those which are not hydrolyzed, e.g., $Ln_2L_7(NO_3)_4 \cdot nH_2O$; $n = 0$ for Ln = La–Nd and $n = 2$ for Ln heavier than neodymium; and (ii) those which are hydrolyzed, e.g., $Ln_2L_7(NO_3)_x(OH)_{4-x}$; $x = 3$ for complexes of cations heavier than Nd^{3+} and obtained from refluxing solutions containing reactants in the mole ratio Ln^{3+}:**iii**:TETA = 1:1:1; and $x = 2$ for complexes obtained from refluxing solutions in which reactants are in the mole ratio Ln^{3+}:**iii**:TETA = 1:2:1. Orange complexes with the counter anion ClO_4^- were all hydrolyzed resulting in $Ln_2L_7(ClO_4)_3(OH)$ for Ln = Nd, Sm and $Gd_2L_7(ClO_4)_2(OH)_2$. The extent of hydrolysis is determined by the preparation procedure employed.

To find out whether or not the off-white and orange complexes were in fact compounds of the same Schiff base and if this Schiff base is a 1:1 or 2:2 condensation product of 2,6-diformyl-*p*-cresol and triethylenetetramine, the fast atom bombardment (FAB) mass spectra of lanthanum, cerium, neodymium, samarium, europium, gadolinium, dysprosium, ytterbium and yttrium samples were obtained. Samples run in the negative ion mode did not give stable spectra but the samples run in the positive ion mode gave interesting results. To a large extent, the complexes decomposed and the pseudomolecular ions were not observed. In samples of neodymium, europium, gadolinium, erbium and ytterbium complexes definite fragments of the original complexes and/or the protonated ligands (Figs. 1 and 2) were observed. In the spectra of the off-white sample $Eu_2L_7(NO_3)_4 \cdot 2H_2O$ (natural isotopes: $^{151}Eu = 47.82\%$, $^{153}Eu = 52.18\%$) a doublet was found at m/z 760, and 762, the expected positions for $[EuL_7NO_3 + H]^+$ (calc. $m/z = 760$ and 762). In the spectra of the off-white sample $Gd_2L_7(NO_3)_4 \cdot 2H_2O$ peak clusters with appropriate isotopic abundances for $[GdL_7(NO_3) + H]^+$ and GdL_7^+ were found as expected at m/z 763–769 and 700–706, respectively. The orange $Nd_2L_7(NO_3)_4$ sample gave a pattern due to $[NdL_7(NO_3) + H]^+$ at $m/z = 751$–759. In the spectra of the orange $Yb_2L_7(NO_3)_4 \cdot 2H_2O$ and $Er_2L_7(NO_3)_3OH$ sample, the peak at $m/z = 549$ makes a conspicuous showing and is attributed to the protonated ligand $H_3L_7^+$ (calculated $m/z = 549$). Two of the protons are phenolic and the third, unlocalized, provides the positive charge. The orange $Eu_2L_7(NO_3)_4 \cdot 2H_2O$ did not give a doublet

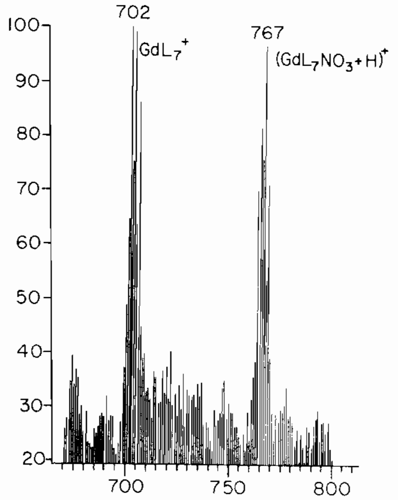


Fig. 1. Fast atom bombardment mass spectrum of the off-white $Gd_2L_7(NO_3)_4 \cdot 2H_2O$ sample.

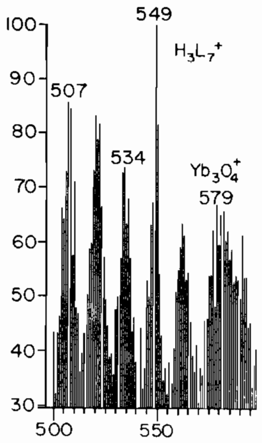


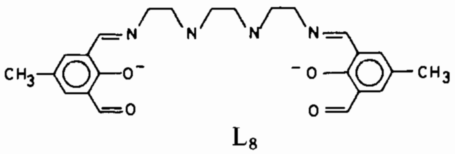
Fig. 2. Fast atom bombardment mass spectrum of the orange $Yb_2L_7(NO_3)_4 \cdot 2H_2O$ sample.

at $m/z = 760$, 762 but like the off-white $Eu_2L_7(NO_3)_4 \cdot 2H_2O$ it gave a cluster of peaks at $m/z =$ 545, 547 and 549 which did not match isotopic abundance patterns of Eu_2 clusters but can be attributed to the protonated ligand: $H_3L_7^+$, $m/z = 549$, and some species containing one europium cation.

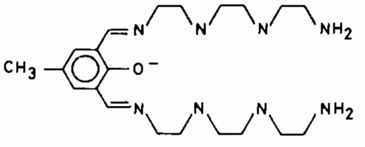
A prominent feature of the spectra obtained in the latter scans (glycerol evaporates thereby concentrating the sample in the matrix) is the occurrence of oxo clusters such as LnO^+, $Ln_2O_2^+$, $Ln_2O_3^+$, $Ln_3O_4^+$, $Ln_4O_6^+$ and $Ln_5O_7^+$. In the cases of Ln = La, Y, which are monoisotopic, higher oxocluster peak intensities were found at m/z corresponding to $Ln_6O_8^+$, $Ln_7O_{10}^+$, and $Ln_9O_{13}^+$. In those cases where the lanthanide cations are polyisotopic the calculated and observed isotopic patterns were identical and this subject is treated in detail in a separate communication [19].

The foregoing FAB mass spectroscopic evidence and the fact that the orange complexes $Ln_2L_7(NO_3)_2(OH)_2$ can be converted in quantitative yield to their off-white form by merely making their suspensions basic, lead us to the conclusion that the off-white and orange compounds are homodinuclear complexes of the same 2:2 Schiff base L_7. Differences in the colour shade are probably associated with differences in the detailed coordination mode of the lanthanide cations to the Schiff base macrocycle. We have not yet succeeded in growing crystals suitable for X-ray diffraction in order to establish conclusively the relative positions of the lanthanide cations and whether one or both cations are in or out of the macrocycle. Answers to these questions are important to Ln^{3+}–Ln^{3+} interactions and our crystal growing efforts are continuing.

Reactants in a mole ratio Ln^{3+}:iii:TETA = 1:2:1 failed to produce complexes of the open ligand L_8; and reactants in the mole ratios Ln^{3+}:iii:TETA = 1:1:2 and 1:1:10 failed to give complexes of the open ligand L_9 while in all three cases complexes of the completely cyclized ligand L_7 were obtained.



L_8



L_9

Complete cyclization is further elucidated by the presence of a very strong absorption peak at 1630–1640 cm^{-1}, typical of the $>C{=}N-$ stretching mode [3, 7, 8, 20–22] in related compounds, in the infrared spectra of both the off-white and orange complexes. No peaks attributable to unreacted $>C{=}O$ and $-NH_2$ were found in the infrared spectra of either the off-white or orange complexes. A strong peak found at 1545–1550 cm^{-1} is characteristic of the phenolic $>C{-}O$ acquiring partial double bond character through conjugation with the imine system in chelate rings [20]. The nitrato anion bands were found in the region 1200–1500 cm^{-1} in both off-white and orange complexes. The perchlorate compounds $Ln_2L_7(ClO_4)_x(OH)_{4-x}$ exhibit IR absorption features attributed to the ligand L_7 in the nitrate complexes. The bands at ~1100 and 630 cm^{-1}, due to ClO_4^-, are split suggesting the presence of coordinated ClO_4^- anions [7, 8, 10].

Electronic absorption data are dominated by 2 peaks: peak 1 occurs at ~23 000 cm^{-1} in the off-white complexes and at ~22–23 000 cm^{-1} for the yellow–orange complexes, and peak 2 occurs at ~27 000 cm^{-1} in all complexes. The weak lanthanide cation electronic absorptions are obscured by these intense and broad bands originating from the ligand. The latter also appear in the spectra of the closed shell lanthanum, lutetium and yttrium samples. Peak 1 is a shoulder in the spectra of all solid off-white complexes and whereas it is a shoulder at ~22 900 cm^{-1} in the solid yellow $La_2L_7(NO_3)_4$ complex, it increases in intensity in the corresponding cerium and praseodymium samples to become the prominent peak at lower energy (21–22 000 cm^{-1}) in the orange complexes of neodymium through lutetium and yttrium. The deep-orange compound $La_2L_7(NO_3)_2(OH)_2$ has the dominant peak 1 at 21 888 cm^{-1} compared to shoulders in this region in the off-white and yellow $La_2L_7(NO_3)_4$ compounds. When the complex $Nd_2L_7(NO_3)_4$ was reduced with $NaBH_4$, one peak was found at ~27 000 cm^{-1} in the UV–Vis spectrum of the solid sample in nujol. The peak at lower energy had disappeared

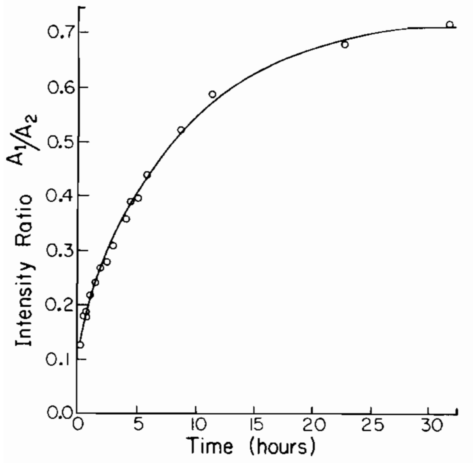


Fig. 3. Variations in the intensity ratio A_1/A_2 (A = absorbance at $\bar{\nu}_{max}$) of peaks 1 and 2 monitored at 24 096 and 26 667 cm^{-1}, respectively, for the $Sm_2L_7(NO_3)_4 \cdot 2H_2O$ sample in DMSO (11 μmol/l) at about 24 °C.

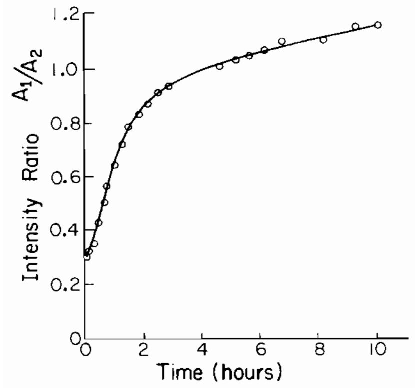


Fig. 4. Variations in the intensity ratio A_1/A_2 (A = absorbance at $\bar{\nu}_{max}$) of peaks 1 and 2 monitored at 24 390 and 27 027 cm^{-1}, respectively, with time for the $La_2L_7(NO_3)_4$ sample in DMSO (60.8 μmol/l) at about 24 °C.

and therefore it must be associated with the presence of the $>$C=N– chromophore, the tailing of which into the visible region gives rise to the orange colour.

The complexes are appreciably soluble in DMSO but only very dilute solutions were obtained with some complexes in DMF and methanol. In solution both the off-white and orange complexes $Ln_2L_7(NO_3)_4 \cdot nH_2O$, Ln = La–Pr, run immediately give electronic spectra similar to those of the solid samples run in Nujol mull. But the spectra of orange complexes of Ln = Nd–Lu, Y are radically different from the spectra of the corresponding solid samples, with the prominent peak in this case being centered at about 24 390–25 000 cm^{-1}, or 2650 cm^{-1} higher in energy from the solid state band found at ~21 740 cm^{-1}. In water all samples exhibit one prominent peak at about 24 390–25 000 cm^{-1}. Thus the compounds are transformed in solution to species not yet identified. In fact time-lapse traces of the solution spectra (DMSO) reveals intensity growth in peak 1 and decay in peak 2. Variations in the intensity ratio A_1/A_2 (A_1 = absorbance of peak 1 and A_2 = absorbance of peak 2 with A being absorbance at $\bar{\nu}_{max}$) with time are shown for off-white $Sm_2L_7(NO_3)_4 \cdot 2H_2O$ in Fig. 3 and for yellow $La_2L_7(NO_3)_4$ in Fig. 4. Comparison of Figs. 3 and 4 leads to the conclusion that the off-white form of the homodinuclear complexes we have reported is more stable in solution than the yellow–orange form. These results are in good agreement with the observation that the orange complexes $Ln_2L_7(NO_3)_2(OH)_2$ dissolved in methanol containing a little triethylenetetramine rapidly convert to the off-white $Ln_2L_7(NO_3)_4 \cdot nH_2O$ form in quantitative yield.

Because of the solution instability of the complexes reliable NMR spectra of solution samples could not be obtained. Similar NMR spectra complexity has been reported in some mononuclear lanthanide [13] and Ba^{2+} [23] Schiff base complexes.

One role of the lanthanide metal ion may thus be seen to serve to organize reactants towards an exclusive formation of the completely cyclized ligand and to stabilize the Schiff base once it is formed. This position is supported by our observation that condensation of 2,6-diformyl-*p*-cresol and triethylenetetramine in the presence of divalent cations Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} leads to intractable solids. Direct condensation in the absence of Ln^{3+} cations leads to intractable oils, although direct condensation of 2,6-diformyl-*p*-chlorophenol and short chain primary amines gives a variety of stable Schiff base ligands in good yields [22]. It seems therefore, at least in our hands that the lanthanide cations have the size and charge that are just right for the formation and stabilization of the Schiff base macrocycle L_7. It is also interesting to note that despite the extensive success in condensing 2,6-diacetyl-pyridine with diprimary amines to give 2:2 macrocyclic ligands, its condensation with triethylenetetramine in presence of Sr^{2+} or Ba^{2+} gave exclusively Schiff base ligands of the type L_8 which resisted cyclization [24]. Whereas open ligands of the type L_8 and L_9 are encountered frequently in condensations of dicarbonyls and diprimary amines [1, 10, 22, 24], in our experiments even under a two-fold excess of dialdehyde or ten-fold excess of triethylenetetramine the exclusive products are complexes of the completely cyclized ligand L_7.

The hydrated complexes have been found to lose water beginning at about 40 °C and all complexes start decomposing at about 250 °C in air. Water therefore appears to be loosely held in these lattices and is thus unlikely to be bound in the lanthanide coordination sphere [18]. The coordination scheme in which one Ln^{3+} bonds to one phenolic oxygen and nitrogen sites 1,2,7,8, while the other Ln^{3+} links to the second phenolic oxygen and nitrogen

TABLE II. Complexes of 2,6-dipropyl-*p*-cresol (L_{10}) and some Lanthanide Cations

Compound	% Observed			% Calculated		
	C	H	N	C	H	N
$La_2(L_{10})(NO_3)_3$ (1121.562)	40.92	4.28	3.78	41.8	4.0	3.7
$GdL_{10}(OH)_2$[a] (510.527)	38.01	3.99	1.36	38.0	4.2	0
$Lu_2(L_{10})_3(NO_3)(OH)_2$[b] (1103.69)	41.22	4.28	1.27	42.4	4.3	1.3
$Y_2(L_{10})_3(NO_3)(OH)_2$[b] (931.56)	49.96	4.88	1.52	50.3	5.0	1.5

[a] The material is probably more complex than formulated since repeated recrystallizations did not remove nitrogen entirely. The crystalline material was triclinic with the following crystal data: $a = 18.59(4)$, $b = 21.49(2)$, $c = 23.15(3)$ Å; $\alpha = 89.0(9)$, $\beta = 82.86(14)$, $\gamma = 87.66(13)$°. [b] The NMR spectrum of each of these compounds (in $CDCl_3$) exhibited three sets of triplets for the methyl groups on the alkyl side chains and three singlets for the aromatic protons, supporting these formulations for the listed compounds.

sites 3,4,5,6 of ligand L_7 is envisaged in the off-white complexes. This coordinating scheme requires that the Ln^{3+} cation be large enough to coordinate to the three adjacent N–O–N ligating sites. This is consistent with the observation that the off-white compounds become increasingly difficult to prepare as the radius of Ln^{3+} decreases. The coordination scheme in which one Ln^{3+} bonds to both phenolic oxygen sites and nitrogen sites 1,2,3,4, whereas the other Ln^{3+} is linked to both phenolic sites and nitrogen sites 5,6,7,8 in ligand L_7 is envisaged for the orange compounds and is expected to be favored by the small Ln^{3+} too. These differences in coordination may be responsible for the differences in the colors of the complexes. But detailed and firm structural conclusions cannot be made without X-ray structural information, so we cannot prove our postulated structures at this time.

Attempts to condense diketone (V) and dipropylenetriamine, triethylenetetramine or tetraethylenepentamine always resulted in the formation of ketophenolate complexes without condensation (Table II). Efforts to condense the other carbonyls listed earlier have not yet given us clearly defined products.

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