

Complexes of rare-earth perchlorates with di-*t*-butyl amides of di, tri and tetraglycolic acids*

C PREMLATHA and S SOUNDARARAJAN

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India

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Abstract. New complexes of lanthanide perchlorates with di-*t*-butyl amides of di, tri and tetraglycolic acids have been synthesised. The complexes have the general formula $\text{Ln}(\text{DiGA})_3(\text{ClO}_4)_3$; $\text{Ln}(\text{TriGA})_2(\text{ClO}_4)_3$ and $\text{Ln}(\text{TetGA})_2(\text{ClO}_4)_3$, where $\text{Ln} = \text{La}-\text{Yb}$ and Y and $\text{DiGA} = \text{N,N}'$, di-*t*-butyl diglycolamide, $\text{TriGA} = \text{N,N}'$, di-*t*-butyl triglycolamide and $\text{TetGA} = \text{N,N}'$ di-*t*-butyl tetraglycolamide, respectively. The complexes have been characterized by analysis, electrolytic conductance, infrared, ^1H and ^{13}C nuclear magnetic resonance and electronic spectral data.

Infrared spectra indicate the coordination of all the available ether oxygens and the amide carbonyls in each of the ligands, to the metal ions. IR and conductance data show that the perchlorate groups in all the complexes are ionic. ^1H and ^{13}C NMR data support the IR data regarding the mode of coordination of ligands to the metal ions. Electronic spectral shapes have been interpreted in terms of nine, eight and ten coordination in DiGA, TriGA and TetGA complexes respectively.

Keywords. Lanthanide perchlorate complexes ; infrared ; nuclear magnetic resonance ; di-*t*-butyl amides.

1. Introduction

As part of our studies on coordination compounds of lanthanides with multi-dentate oxygen donor ligands, we had reported the synthesis and characterization of complexes of lanthanide perchlorates with tertiary amides (tetramethyl, tetraethyl) of di, tri and tetraglycolic acids (Premlatha and Soundararajan 1980a, b, c). In continuation of the work, we present in this paper our reports on the complexes formed by lanthanide perchlorates with the corresponding secondary amides (di-*t*-butyl). Lanthanide complexes with primary and secondary amides are less known, compared to tertiary amide complexes.

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2. Experimental

2.1. Materials

The rare-earth oxides were obtained in 99.9% purity from Indian Rare Earths, Kerala.

The lanthanide perchlorates were prepared as described in an earlier report (Premlatha and Soundararajan 1980b). Solvents used were purified by the standard methods.

2.2. Preparation of the ligands

2.2a. *Synthesis of the di, tri and tetraglycolic acids*: The acids were prepared by the nitric acid oxidation of the corresponding diethylene glycol, triethylene glycol and the tetraethylene glycol.

2.2b. *Synthesis of the corresponding N,N'-di-t-butyl amides*: The acids (1 mol) when reacted with thionyl chloride (2.2 mol), in the presence of a few drops of dimethyl formamide acting as a catalyst, formed the respective acid chlorides. The excess thionyl chloride was removed azeotropically with benzene in a water aspirator. The crude acid chloride (1 mol) in each case was then taken in benzene and greater than 4 mol of tertiary butyl amine added. The reaction mixture was refluxed for 2-3 hr, and the amine hydrochloride filtered off. The filtrate was evaporated to yield the respective ligands. The purity of the products was confirmed by their ^1H and ^{13}C NMR spectra and the compounds were used as such for the preparation of the complexes.

2.3. Preparation of complexes

All the complexes were prepared in the same way. The metal perchlorate in ethyl acetate was added to a solution of the ligand (greater than the stoichiometric requirement) in ethyl acetate, with stirring. The precipitated (crystalline in the case of DiGA and oily in the case of TriGA and TetGA) complex was isolated as follows: (a) In the case of DiGA, the complex was filtered through a G-3 crucible, washed thoroughly with ethyl acetate, finally with ether and dried *in vacuo*. (b) Complexes of TriGA and TetGA separated as oily mass in ethyl acetate. The complexes were refluxed for 30 min with fresh ethyl acetate to ensure removal of unreacted ligand. The ethyl acetate was then decanted off, complexes washed with diethyl ether and dried *in vacuo* (1 mm Hg) with heating ($\sim 70^\circ\text{C}$).

2.4. Physical measurements

IR, ^1H and ^{13}C NMR, electronic spectra and conductance data were obtained by methods described earlier (Premlatha and Soundararajan 1980b).

2.5. Analysis

Methods for metal and perchlorate analysis have been given in our earlier paper (Premlatha and Soundararajan 1980b).

3. Results and discussion

Analytical and conductivity data for the complexes of DiGA, TriGA and TetGA are presented in tables 1, 2 and 3 respectively. The complexes conform to the formulae, $\text{Ln}(\text{DiGA})_3(\text{ClO}_4)_3$; $\text{Ln}(\text{TriGA})_2(\text{ClO}_4)_3$ and $\text{Ln}(\text{TetGA})_2(\text{ClO}_4)_3$, where Ln = La-Yb and Y. While the complexes of DiGA are air stable, those of TriGA and TetGA are extremely hygroscopic and were hence handled in closed vials. Complexes of all the three ligands are soluble in methanol, acetone, acetonitrile and dimethyl sulfoxide and insoluble in chloroform, carbontetrachloride and benzene. Molar conductivities measured in acetonitrile indicate a 1:3 electrolytic behaviour, showing the three perchlorate groups in each complex to be ionic in nature. Evidence for this in the solid state is provided by the presence of two unsplit bands at 625 cm^{-1} and 1100 cm^{-1} , assignable to the ν_4 and ν_3 modes of the T_d perchlorate (ionic) group, in all the complexes. IR data for the ligands and their complexes provide information regarding the mode of coordination of the ligands, to the metal ions. The probable donor sites are one, two and three ether oxygens in the DiGA, TriGA and TetGA respectively and two carbonyl

Table 1. Analytical and conductance data for complexes of general formula $\text{Ln}(\text{DiGA})_3(\text{ClO}_4)_3$.

Ln	% Metal		% ClO_4^-		Molar conductance in acetonitrile*
	Found	Calc.	Found	Calc.	
La	11.96	11.89	25.02	25.49	384.8
Nd	12.36	12.27	25.51	25.38	386.2
Tb	13.28	13.37	24.82	25.00	399.7
Ho	13.61	13.80	24.72	24.94	388.9
Er	13.88	13.96	24.66	24.89	382.4
Y	8.08	7.96	26.81	26.64	392.1

* Molar conductance values are in $\text{ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$.

Table 2. Analytical and conductivity data for the complexes $\text{Ln}(\text{TriGA})_2(\text{ClO}_4)_3$.

Ln	% Metal		% ClO_4^-		Molar conductance in CH_3CN , ($\text{ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$)
	Found	Calc.	Found	Calc.	
La	13.58	13.73	29.58	29.42	364.1
Nd	14.46	14.16	29.44	29.27	386.7
Ho	16.02	15.89	28.91	28.68	397.1
Er	15.84	16.06	28.04	28.62	401.9
Yb	16.38	16.55	28.21	28.46	402.6
Y	9.39	9.25	30.67	30.94	369.8

Table 3. Analytical and conductivity data for the complexes $\text{Ln}(\text{TetGA})_2(\text{ClO}_4)_3$.

Ln	% Metal		% ClO_4^-		Molar conductance in CH_3CN , ($\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$)
	Found	Calc.	Found	Calc.	
La	12.92	12.63	26.72	27.06	371.6
Nd	13.12	13.02	26.78	26.94	401.3
Ho	14.49	14.64	25.98	26.44	399.3
Er	14.91	14.79	25.81	26.39	362.6
Yb	15.13	15.24	26.61	26.25	403.0
Y	9.36	9.51	27.96	28.35	387.5

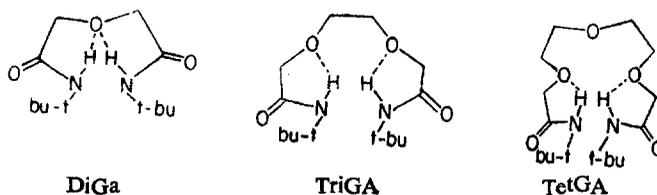
Table 4. ^1H and ^{13}C NMR data for the La^{3+} and Y^{3+} complexes of DiGA, TriGA and TetGA (δ with reference to TMS).

	Methylene protons	Methylene carbons	Carbonyl carbon
DiGA	3.73	71.767	168.676
La^{3+} -DiGA	4.53	71.829	172.272
Y^{3+} -DiGA	4.46	70.403	171.931
TriGA	3.73, 3.93	71.085, 70.961	169.296
La^{3+} -TriGA	4.60, 4.10	72.635, 70.217	172.706
Y^{3+} -TriGA	4.47, 4.03	72.945, 70.806	172.303
TetGA	3.6, 3.63, 3.8	70.806, 71.426, 71.519	169.699
La^{3+} -TetGA	3.63, 3.98, 4.5	71.364, 72.015, 73.658	173.636
Y^{3+} -TetGA	3.62, 4.06, 4.46	71.240, 71.953, 72.852	173.822

oxygen in each ligand. The evidence for the coordination of all the ether oxygens available in each case and the carbonyl oxygen is obtained from the shifts in the respective vibration bands. The shift to lower wave numbers of the carbonyl vibration band occurring around 1665 cm^{-1} in all the three ligands by about $25\text{--}40 \text{ cm}^{-1}$ in all their complexes, is a clear indication of the involvement of $\text{C}=\text{O}$ in coordination. The $\text{C}-\text{O}-\text{C}$ ether stretch in the ligands occurs at 1120 cm^{-1} in DiGA and 1115 cm^{-1} in TriGA and TetGA. In the spectra of the complexes, this band disappears and a broad band is observed around 1100 cm^{-1} region. Since the ν_3 mode of the T_d perchlorate group also appears at 1100 cm^{-1} , the shifted $\text{C}-\text{O}-\text{C}$ band is masked and what is observed is a single broad band for both the coordinated $\text{C}-\text{O}-\text{C}$ and the ν_3 of the ionic perchlorate group. Similar shifts have also been found in the tertiary amide complexes (Premlatha and Soundararajan 1980a, b, c). Thus in all the cases, IR data unambiguously prove ether oxygen and carbonyl oxygen coordination.

The ^1H and ^{13}C NMR data for the DiGA, TriGA and TetGA and their diamagnetic La^{3+} and Y^{3+} complexes are presented in table 4. The ^1H NMR data

reveal downfield shifts of all the methylene resonances, relative to the free ligand values, in each of the complexes. The downfield shifts are a consequence of bonding of ligands to the metal ions *via* ether oxygens. In the ^{13}C NMR spectra, of the complexes of the pentadentate TetGA, the expected downfield shifts are observed in the carbonyl carbon and the methylene carbon resonances, indicating bonding of ligand to metal ion through the carbonyl oxygens and the ether oxygens. The DiGA and TriGA complexes too exhibit downfield shifts of the carbonyl carbons in their ^{13}C NMR spectra. But the methylene carbon resonances behave in a slightly different manner. In DiGA, the methylene carbons resonate at a lower field in the La^{3+} complex compared to the free ligand, whereas, in the Y^{3+} complex there is a slight upfield shift. In TriGA, one set of methylene carbons is shifted downfield while the other exhibits upfield shift, in both the La^{3+} and Y^{3+} complexes, relative to the free ligand. The seemingly anomalous shifts have been tentatively attributed to the presence of intramolecular hydrogen bonding in the free ligands as shown below.



The shifts are probably dependent on whether the ether oxygen coordination is stronger than two H-bonds or vice versa. Since the methylene carbon is directly attached to the ether oxygen and also since the ^{13}C nuclei are inherently more sensitive to effects such as electron density changes, this apparent anomaly is observed in ^{13}C shifts only. The different behaviour of ^{13}C and ^1H shifts to electron density changes is due to contribution of σp term to ^{13}C shielding parameter (Jagannathan and Soundararajan 1980).

The electronic spectra, in the visible region for the Nd^{3+} , Ho^{3+} and Er^{3+} complexes of DiGA, TriGA and TetGA were taken both in nujol mull in solid state and in acetonitrile solution and they are both identical for each of the complexes. This indicates compatibility between the solid state IR data and solution NMR and conductance data. In all the complexes, a red shift of all the bands is observed compared to their aquo ion complexes. This nephelauxetic shift is related to the covalency in the metal-ligand bond (Jorgensen 1962; Sinha 1966). The shifts indicate complexation of ligands to metal ions with reasonable covalency in the Ln^{3+} -ligand bond.

The shapes of some of the electronic spectral bands called hypersensitive bands are governed by the coordination number around the central Ln^{3+} ion (Karraker 1967). The hypersensitive band shape analysis is best done by comparison with the band shapes of some model compound whose coordination number is clearly known from x-ray studies. In the case of DiGA complexes, comparisons were made with spectral shapes of Nd^{3+} , Ho^{3+} and Er^{3+} complexes of diglycolic acid, which are x-ray proven to be nine coordinate (Albertsson 1968). The significant similarity in the shapes demonstrates the similarity in coordination environment of the metal ion in the two cases. Thus, the DiGA complexes are probably

nine coordinate. For the TriGA complexes, similar comparisons could be made for the Nd^{3+} case only. Nd^{3+} ion in aqueous chloride solution (in HCl) spectrum in which NdCl_3 has been proved to be eight coordinate from x-ray diffraction study (Habenschuss and Spedding 1979) has been compared with Nd^{3+} -TriGA spectrum, and a marked resemblance found, suggesting a probable coordination number of eight in these complexes. Due to lack of suitable model compounds, the spectra of Nd^{3+} , Ho^{3+} and Er^{3+} -TetGA complexes could not be used to assign the coordination number. But, from the IR and ^1H and ^{13}C NMR data it is felt that the coordination number is ten in all the complexes of TetGA.

4. Conclusions

The analytical, conductivity, infrared, ^1H and ^{13}C NMR and electronic spectral data indicate that

- (i) each lanthanide ion in the complexes of DiGA is surrounded by three molecules of the ligand, each behaving in a tridentate '000' fashion;
- (ii) each of the lanthanide ion in the complexes of TriGA is surrounded by two molecules of the ligand, each one of them coordinating in a tetradentate '0000' manner;
- (iii) each of the lanthanide ion in the complexes of TetGA is surrounded by two molecules of the ligand, each of which is bound to the metal ion in a pentadentate fashion.

Hence tentative coordination numbers of nine, eight and ten can be assigned to the complexes of DiGA, TriGA and TetGA respectively, on the basis of data available.

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