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# Complexes of Lanthanide Perchlorates with N,N,-N′,N′-tetramethyl-α-carboxamido-O-anisamide and N,N′-di-t-butyl-α-carboxamido-O-anisamide

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A survey of the literature on lanthanide coordination compounds reveals that ligands involving ether oxygens as donor atoms have received very little attention [1]. Only recently have the complexes of lanthanides with cyclic polyethers been characterized [1–3]. We report in this communication that interaction of rare-earth perchlorates with two new ligands namely N,N,N′,N′-tetramethyl-α-carboxamido-O-anisamide (TMCA) and N,N′-di-t-butyl-α-carboxamido-O-anisamide (DTBCA). The two ligands are potentially tridentate possessing two amide moieties and an ether linkage in between. The isolated complexes have been characterized by analysis, electrolytic conductance, infrared and electronic spectra. The $^1H$ and $^{13}C$ NMR spectra for the diamagnetic $La^{3+}$ and $Y^{3+}$ complexes are also discussed.

## Experimental

All chemicals were reagent grade. Hydrated lanthanide perchlorates were obtained by procedures described previously [4].

### *Preparation of the Ligands*

α-Carboxy-O-anisic acid was obtained by a reported procedure [5]. The dicarbonyl chloride of the acid was obtained by reaction of the acid with thionyl chloride in the presence of a few drops of dimethyl formamide as catalyst. The amides were prepared by reacting the crude acid chloride with greater than four fold excess of amine in chloroform. After the well known working up procedures, the amides were obtained in 60–70% yields. The tetramethyl amide was obtained as a viscous liquid and was used as such for the preparation of the complexes. The di-t-butyl amide was found to be a low melting solid which could be recrystallized from ethylacetate, m.p. 94 °C. The purity of the ligands was confirmed by the $^1H$ and $^{13}C$ NMR (see discussion).

### *Preparation of the Complexes*

Hydrated lanthanide perchlorate (1 mmol) was dissolved in acetone (10 ml) and mixed with the ligand (4 mmol) in acetone (20 ml). After refluxing the solution for an hour, acetone was removed by warming on a water bath. The residue was washed several times with chloroform to remove unreacted ligand and subsequently with diethylether. Finally, the residue was heated to dryness on a water bath. The powdery product was obtained in greater than 90% yield.

### *Analysis*

Metal and perchlorate analyses were performed by methods already reported [4]. C, H analyses of a representative set of complexes were obtained by combustion methods.

### *Physical Methods*

Conductance data, infrared, $^1H$ NMR and electronic spectra were obtained by procedures determined earlier [4]. $^{13}C$ NMR spectra were obtained on a Bruker WH-270 spectrometer operating at 67.89 MHz for $^{13}C$. The spectra were run in the FT mode with broad band proton decoupling. Nearly 200 mg of samples were dissolved in $CH_3CN$ (1 ml) and $CDCl_3$ (0.5 ml) was added to provide the deuterium lock. About 400 scans were accumulated with a time interval of 3 sec between each pulse.

## Results and Discussion

Analytical data for a representative set of complexes are presented in Table I. The complexes analyse for the formula $Ln(TMCA)_3(ClO_4)_3 \cdot 2H_2O$ and $Ln(DTBCA)_3(ClO_4)_3 \cdot 2H_2O$ where Ln = La, Pr, Nd, Sm, Tb, Ho, Er, Yb and Y. All the complexes are reasonably stable in the atmosphere but slowly absorb moisture over a period of 8–10 hours. All the complexes are soluble in polar solvents such as methanol, acetone, acetonitrile, dimethylformamide and dimethylsulfoxide and insoluble in chloroform, ethylacetate, ether and benzene.

Values of molar conductance in acetonitrile are in the range (380–390 $Ohm^{-1}$ $cm^2$ $mol^{-1}$) for 1:3 electrolytes suggesting that the perchlorates are ionic in all the complexes.

The broad absorptions in the 3400–3500 $cm^{-1}$ region and the absence of new bands in the 600–700 $cm^{-1}$ region in the infrared spectra of the complexes suggest that the water molecules are lattice held. The appearance of two strong unsplit bands at 1100 and 625 $cm^{-1}$ indicates the noncoordinated nature of the perchlorate groups.

In the ligand TMCA the carbonyl stretch pertaining to the two tertiary amide moieties appears at 1635 and 1665 $cm^{-1}$. In all the complexes these bands are shifted to lower frequencies by 30–35 $cm^{-1}$. This decrease in the C=O frequency suggests a lowering of

TABLE I. Analytical Data for a Representative Set of TMCA and DTBCA Complexes.[a, b]

| Complex | % Metal | % Anion | % Carbon | % Hydrogen |
|---|---|---|---|---|
| $Nd(TMCA)_3(ClO_4)_3\cdot2H_2O$ | 11.71<br>(11.72) | 24.13<br>(24.30) | 38.00<br>(38.10) | 4.69<br>(4.72) |
| $Ho(TMCA)_3(ClO_4)_3\cdot2H_2O$ | 13.18<br>(13.21) | 23.74<br>(23.89) | 37.54<br>(37.46) | 4.59<br>(4.64) |
| $Y(TMCA)_3(ClO_4)_3\cdot2H_2O$ | 7.49<br>(7.58) | 25.31<br>(25.44) | 39.73<br>(39.88) | 4.79<br>(4.94) |
| $Nd(DTBCA)_3(ClO_4)_3\cdot2H_2O$ | 10.26<br>(10.31) | 21.09<br>(21.37) | 43.69<br>(43.82) | 5.84<br>(5.87) |
| $Er(DTBCA)_3(ClO_4)_3\cdot2H_2O$ | 11.69<br>(11.78) | 20.83<br>(21.03) | 43.00<br>(43.11) | 5.63<br>(5.78) |
| $Y(DTBCA)_3(ClO_4)_3\cdot2H_2O$ | 6.54<br>(6.63) | 22.39<br>(22.25) | 45.48<br>(45.62) | 6.03<br>(6.11) |

[a] Calculated values in parentheses. [b] Complexes of all other metal ions gave satisfactory metal and anion analysis.

TABLE II. Important $^1H$ and $^{13}C$ NMR Data. All values are in $\delta$ ppm w.r.t. TMS.

| Compound | $OCH_2$ ($^1H$) | $OCH_2$ ($^{13}C$) | Aromatic ($^{13}C$) | Amide carbonyl ($^{13}C$) |
|---|---|---|---|---|
| TMCA | 4.80 | 67.303 | 154.385, 130.452, 128.189, 127.414, 121.803, 112.998 | 169.327, 167.684 |
| $La(TMCA)_3(ClO_4)_3\cdot2H_2O$ | 5.00 | 69.318 | 155.036, 132.994, 129.274, 123.787, 123.663, 117.245 | 170.567, 169.792 |
| $Y(TMCA)_3(ClO_4)_3\cdot2H_2O$ | 5.01 | 68.729 | 155.036, 133.800, 130.018, 123.818, 122.144, 117.090 | 171.001, 170.071 |
| DTBCA | 4.68 | 68.698 | 155.625, 131.754, 129.987, 126.174, 121.896, 113.494 | 166.909, 165.793 |
| $La(DTBCA)_3(ClO_4)_3\cdot2H_2O$ | 4.78 | 73.193 | 155.222, 134.937, 131.072, 125.430, 125.337, 118.423 | 171.621, 169.389 |
| $Y(DTBCA)_3(ClO_4)_3\cdot2H_2O$ | 4.87 | 71.581 | 154.509, 134.606, 130.421, 124.841, 123.725, 116.842 | 171.187, 168.955 |

the bond order resulting from the coordination of the two amide carbonyl oxygen atoms to the metal ions. In DTBCA, Amide I bands appearing at 1670 and 1650 $cm^{-1}$ is shifted to 1645 and 1610 $cm^{-1}$ on complexation. The amide II, III and IV bands in DTBCA are found at 1555 and 1535, 1310 and 1290 and 650 $cm^{-1}$ respectively. All these bands exhibit 15–40 $cm^{-1}$ shift to higher frequencies in the complexes. These facts suggest coordination of the two secondary amide groups of DTBCA through the oxygen atoms.

The $R-O-CH_2$ bands appearing at 1270 and 1245 $cm^{-1}$ in TMCA and at 1230 $cm^{-1}$ in DTBCA are found shifted to lower frequencies (10 $cm^{-1}$) on complexation to the $Ln^{3+}$ ions. The shifts clearly suggest ether oxygen coordination. Similar shifts have been found in Scandium polyether complexes [6].

Further evidence for the coordinating nature of the ligands is obtained from the $^1H$ and $^{13}C$ NMR spectra of the ligands and the diamagnetic $La^{3+}$ and $Y^{3+}$ complexes. The relevant data are presented in Table II. Deshielding of the methylene protons and the methylene carbon on complexation clearly demonstrates ether oxygen coordination. The low-field shift in the carbonyl carbon resonance in the complexes compared to the ligands shows the reduction of electron density in the C=O bond due to coordination of the carbonyl oxygen atoms to the metal ions.

The electronic spectra in the visible region for the $Nd^{3+}$, $Ho^{3+}$ and $Er^{3+}$ complexes were obtained. The sharp f–f bands exhibited redshifts compared to the aquo ion. The shifts were large enough to suggest some covalency in the $Ln^{3+}$–ligand bond. The shapes of some of the bands in the complexes of $Nd^{3+}$, $Ho^{3+}$ and $Er^{3+}$ have been related to coordination number around the $Ln^{3+}$ ion [7]. For effective comparison of shapes of the hypersensitive bands we have chosen a

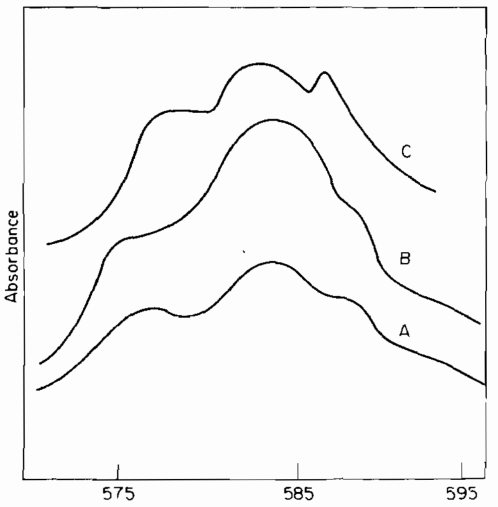

Fig. 1. Shapes of hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ band in Nd$^{3+}$ complexes of (A) TMCA, (B) DTBCA and (C) ODA.

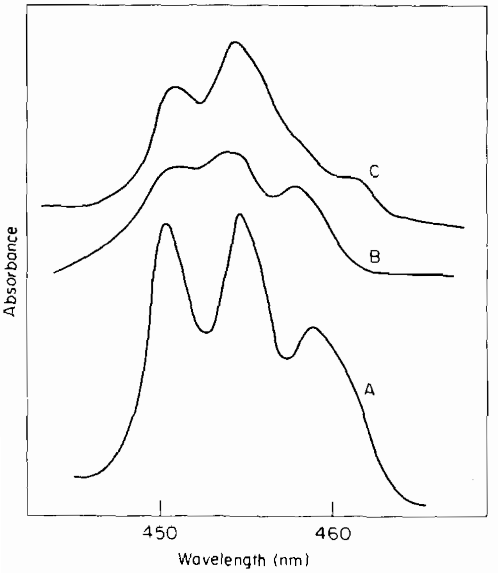

Fig. 2. Shapes of hypersensitive $^5G_6 \leftarrow {}^5I_8$ band in Ho$^{3+}$ complexes of (A) TMCA, (B) DTBCA and (C) ODA.

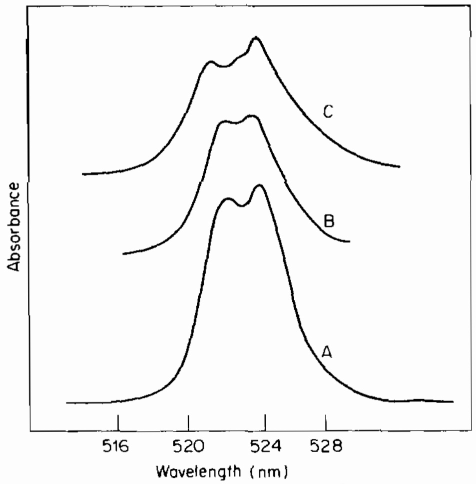

Fig. 3. Shapes of hypersensitive $^2H_{11/2} \leftarrow {}^4I_{15/2}$ band in Er$^{3+}$ complexes of (A) TMCA, (B) DTBCA and (C) ODA.

set of model compounds of known coordination number and geometry with a similar set of donor atoms as TMCA and DTBCA. It was found from the literature that oxydiacetic acid (ODAH$_2$) forms a series of lanthanide compounds of the type Na$_3$-[Ln(ODA)$_3$], where a coordination number of nine, with each ODA behaving in a tridentate fashion, has been proved by X-ray crystallography [8]. In Figs. 1, 2, and 3 are presented the shapes of hypersensitive bands in the complexes of TMCA, DTBCA and ODA with Nd$^{3+}$, Ho$^{3+}$ and Er$^{3+}$ respectively. It is found that the shapes of the bands in TMCA, DTBCA and ODA exhibit remarkable similarity and hence suggest that the coordination number around Ln$^{3+}$ ions in the TMCA and DTBCA complexes is also nine. Further it was found that the shapes of the bands in aqueous solutions of ODA complex and acetonitrile solutions of TMCA and DTBCA complexes were exactly similar to the shapes in the solid state. In the figures therefore the shapes obtained in solution are presented.

Thus from a study of all the physical properties it can be seen that each of the TMCA and DTBCA ligands behaves in a tridentate 'O, O, O' fashion resulting in a probable coordination number of nine around the Ln$^{3+}$ ions.

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