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### COMPLEXES OF LANTHANIDE(III) SALTS WITH *N,N'* - BIS(2' - PYRIDINECARBOXAMIDE) - 1, 8 - NAPHTHALENE

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## NOTE

# COMPLEXES OF LANTHANIDE(III) SALTS WITH *N, N'* - BIS(2' - PYRIDINECARBOXAMIDE) - 1, 8 - NAPHTHALENE

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## INTRODUCTION

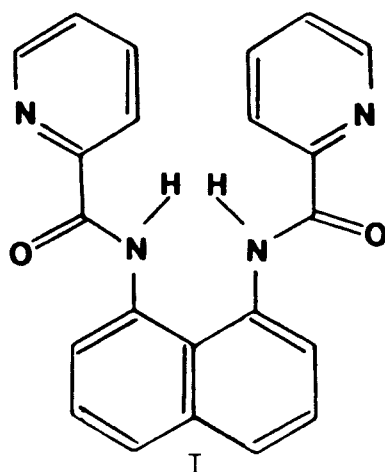
A survey of the literature on lanthanide (III) coordination compounds reveals that ligands involving secondary amide groups as donor sites have received little attention.<sup>1,2</sup> *N, N'*-bis(2'-pyridinecarboxamide)-1,8-naphthalene (LH<sub>2</sub>, I), a potentially tetradentate bis-amide ligand, has been shown to coordinate to transition metal ions in several modes.<sup>3-5</sup> As part of our systematic investigation of metal-amide interactions,<sup>3-6</sup> we have prepared and studied new complexes of lanthanide(III) bromides, nitrates, perchlorates and thiocyanates with LH<sub>2</sub>. Some preliminary results of this work, concerning rare earth chloride-LH<sub>2</sub> interactions, have been published elsewhere.<sup>7</sup>

## EXPERIMENTAL

LH<sub>2</sub> was synthesized as described earlier.<sup>3</sup> Physical measurements were carried out by published methods.<sup>6,8</sup> Complexes of the general formulae Ln(LH<sub>2</sub>)<sub>2</sub>Br<sub>3</sub> and Ln<sub>2</sub>(LH<sub>2</sub>)<sub>3</sub>Br<sub>6</sub>.nH<sub>2</sub>O were prepared by adding a solution of the hydrated metal bromide (2 mmol) in 96% ethanol (80 cm<sup>3</sup>) to a vigorously stirred warm solution of LH<sub>2</sub> (4.5 mmol) in ethanol (70 cm<sup>3</sup>). The complexes Ln(LH<sub>2</sub>)Br<sub>3</sub>.nH<sub>2</sub>O were prepared by mixing warm equimolar ethanolic solutions of the ligand and the lanthanide bromides. For the preparation of the nitrate compounds, to 1 mmol of the required hydrated lanthanide nitrate in 15 cm<sup>3</sup> of hot anhydrous ethanol was added 6 cm<sup>3</sup> of triethylorthoformate as dehydrating agent and the solution was refluxed for 45 min; to this solution 2.2 to 1.7 mmol of LH<sub>2</sub> in 25-35 cm<sup>3</sup> of hot anhydrous ethanol was added dropwise. Complexes of LH<sub>2</sub> with lanthanide(III) perchlorates were easily obtained by mixing and stirring 1 mmol of the cation in 25 cm<sup>3</sup> of anhydrous ethanol and 5 cm<sup>3</sup> of triethylorthoformate with 2.2 mmol of the ligand dissolved in the minimum required volume of hot anhydrous ethanol. For the preparation of the thiocyanate complexes an ethanolic solution of potassium thiocyanate (6 mmol, 15 cm<sup>3</sup>), warmed to ca 45°, was slowly added to an ethanolic solution of the appropriate lanthanide (III) chloride

hexahydrate (2 mmol, 10 cm<sup>3</sup>). The resulting mixture was stirred at 50° for 10 min and then allowed to cool to room temperature, whereupon the precipitated potassium chloride was removed by filtration. In the case of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Eu(III) the filtrate was added to a hot solution of the ligand (4.2 mmol) in anhydrous ethanol (60 cm<sup>3</sup>), while in the case of Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Yb(III) the filtrate was mixed with a boiling equimolar solution of LH<sub>2</sub> in anhydrous ethanol (30 cm<sup>3</sup>).

Solid product formation was usually instantaneous, although precipitation of some of the 1:2 bromide and perchlorate compounds occurred slowly over 2–3 hours. All precipitates were collected by filtration after several hours refluxing, washed with ethanol, acetone and ether and dried in vacuum over P<sub>4</sub>O<sub>10</sub>. Efforts to prepare complexes with other stoichiometries met with failure. Only La(III) and Ce(III) bromides gave two types of complexes (1:1, 1:2) with LH<sub>2</sub>.



## RESULTS AND DISCUSSION

All the prepared complexes (Table I) gave good analytical results. They are crystalline and stable in the atmosphere. X-ray powder diffraction patterns indicate that each compound represents a definite complex and not merely mixtures of simpler stoichiometric types or simple mixtures of the starting materials. The results also indicate the formation of three series of isomorphous compounds corresponding to the formulae Ln(LH<sub>2</sub>)<sub>2</sub>Br<sub>3</sub> (Ln = La, Ce, Nd, Sm, Eu), Ln(LH<sub>2</sub>)(NO<sub>3</sub>)<sub>3</sub> (Ln = La–Tb) and Ln(LH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub> (Ln = La–Ho). The small number of diffraction lines observed suggests dimeric or polynuclear arrangements. The complexes are insoluble in non-polar solvents, alcohols, acetone, CH<sub>3</sub>NO<sub>2</sub>, CH<sub>3</sub>CN, slightly soluble in water and donor organic solvents, while they are decomposed by mineral acids. Thermal (TGA) studies show that the water molecules present in the Ln(LH<sub>2</sub>)Br<sub>3</sub>.nH<sub>2</sub>O series are coordinated to the metal ions, while the water in the 2:3 complexes and in the Ln(LH<sub>2</sub>)(NCS)<sub>3</sub>.nH<sub>2</sub>O series is held in the lattice.

The room temperature magnetic moments of the prepared complexes show little deviation from Van Vleck values,<sup>9</sup> indicating thereby that the f-electrons do not participate much in bonding. The bonding parameters  $\beta$ ,  $\delta$ (%) and  $b^{1/2}$  of the Pr(III), Nd(III), Sm(III), Ho(III) and Er(III) complexes, calculated from the electronic diffuse reflectance f-f spectra, indicate that the interaction between the trivalent lanthanides and the ligands is essentially electrostatic and that there is a small participation of 4f orbitals in bonding.<sup>10–12</sup> By comparing the spectra of standard compounds<sup>13,14</sup> with

Table I  
The lanthanide (III) complexes prepared.<sup>a,b</sup>

| Compound   | Ln   |
|--|--|
| $\text{Ln}(\text{LH}_2)\text{Br}_3 \cdot n\text{H}_2\text{O}$        | La, Ce, Dy, Ho( $n = 1$ ) and Gd( $n = 2$ )    |
| $\text{Ln}(\text{LH}_2)_2\text{Br}_3$                                | La, Ce, Nd, Sm, Eu                             |
| $\text{Ln}_2(\text{LH}_2)_3\text{Br}_6 \cdot n\text{H}_2\text{O}$    | Er( $n = 1$ ) and Tm( $n = 2$ )                |
| $\text{Ln}_2(\text{LH}_2)_3\text{Br}_6$                              | Yb   |
| $\text{Ln}(\text{LH}_2)(\text{NO}_3)_3$                              | La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb |
| $\text{Ln}(\text{LH}_2)_2(\text{ClO}_4)_3$                           | La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb |
| $\text{Ln}_2(\text{LH}_2)_3(\text{NCS})_6$                           | La, Ce, Eu                                     |
| $\text{Ln}_2(\text{LH}_2)_3(\text{NCS})_6 \cdot n\text{H}_2\text{O}$ | Pr, Nd( $n = 2$ ) and Sm( $n = 1$ )            |
| $\text{Ln}(\text{LH}_2)(\text{NCS})_3 \cdot n\text{H}_2\text{O}$     | Gd, Tb, Ho( $n = 1$ ) and Dy( $n = 2$ )        |
| $\text{Ln}(\text{LH}_2)(\text{NCS})_3$                               | Er, Tm, Yb                                     |

<sup>a</sup>The yields ranged from 71 to 96%. <sup>b</sup>The La, Ce, Eu, Gd, Dy and Yb complexes are white or off-white, the Sm complexes are cream or pale yellow, the Tb complexes are white or white-pink, the Ho complexes are yellowish or pale orange, the Nd complexes are pale lilac or violet, the Er complexes are pink or peach and the Pr and Tm ones are green or pale green coloured.

those of our Nd(III) compounds in the region of the hypersensitive band  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$ ,  ${}^2\text{G}_{7/2}$  (at *ca* 17 kK), it is concluded that the complexes  $\text{Nd}(\text{LH}_2)_2\text{X}_3$  ( $\text{X} = \text{Br}, \text{ClO}_4$ ) and  $\text{Nd}_2(\text{LH}_2)_4(\text{NCS})_6 \cdot 2\text{H}_2\text{O}$  are either 8- or 9-coordinated. Analogous studies for the Ho(III) and Er(III) complexes, demonstrate that these compounds are 7- or 8-coordinated.<sup>13,14</sup>

The IR spectrum of  $\text{LH}_2$  exhibits the  $\nu(\text{N-H})$ , Amide I, II, III, in-plane and out-of-plane pyridine bands<sup>3-5</sup> at 3285, 1669, 1519, 1278, 622 and 410  $\text{cm}^{-1}$ , respectively. The Amide I band shifts *ca* 45  $\text{cm}^{-1}$  to a lower frequency, while the Amide II and III bands shift *ca* 25 and 30  $\text{cm}^{-1}$ , respectively, to higher frequencies in the spectra of the complexes. These shifts indicate amide-O coordination.<sup>15</sup> The observation of only one sharp absorption for each Amide I and II band in the spectra of all complexes indicates that all amide groups are coordinated.<sup>15</sup> The in-plane and out-of-plane deformation modes of the pyridine ring shift to higher frequencies and indicate coordination of the N-atoms.<sup>16</sup> The IR anion bands indicate the presence of ionic perchlorate<sup>17</sup> ( $T_d$  symmetry) and N-bonded thiocyanato<sup>18</sup> groups. In the spectra of the complexes  $\text{Ln}(\text{LH}_2)(\text{NO}_3)_3$  ( $\text{Ln} = \text{La-Dy}$ ) only bands associated with coordinated nitrate groups appear, while the spectra of the heaviest cations (Ho, Er, Tm, Yb) show the simultaneous presence of bands arising both from  $D_{3h}$  and  $C_{2v}$  symmetries.<sup>19</sup> The separation of the combination bands  $\nu_2 + \nu_3$  and  $\nu_2 + \nu_5$ , appearing around 1775 and 1740  $\text{cm}^{-1}$ , is about 35  $\text{cm}^{-1}$  and this fact indicates the presence of bidentate nitrate groups.<sup>19</sup>

From available data, a tentative coordination number of eight is assigned to all the  $\text{Ln}(\text{LH}_2)_2\text{Br}_3$  and  $\text{Ln}(\text{LH}_2)_2(\text{ClO}_4)_3$  complexes with each of  $\text{LH}_2$  molecules behaving in a bis-bidentate ONON bridging fashion.<sup>15,20</sup> For the  $\text{Ln}(\text{LH}_2)\text{Br}_3 \cdot n\text{H}_2\text{O}$  similar oligomeric or polymeric structures are proposed; these complexes contain 8(La, Ce, Dy, Ho)- and 9(Gd)-coordinated metal ions, if we assume all the bromides to be coordinated. The 2:3 complexes most probably exists in a dimeric form with each lanthanide ion exhibiting  $\text{N}_6\text{O}_3$  coordination in the case of isothiocyanate compounds. Synthetic and spectroscopic data suggest that the complexes  $\text{Ln}(\text{LH}_2)(\text{NO}_3)_3$  ( $\text{Ln} = \text{La-Dy}$ ) consist of the  $[\text{LnN}_2\text{O}_8]$  entity formed by three bidentate nitrate groups and one bis-bidentate  $\text{LH}_2$  molecule. Ten-coordination attained by three bidentate nitrate groups and organic ligands has been established.<sup>17,21</sup> Finally there is little doubt that the compounds  $\text{Ln}(\text{LH}_2)(\text{NO}_3)_3$  ( $\text{Ln} = \text{Ho-Yb}$ ) consist of the octacoordinated  $\text{LnN}_2\text{O}_6$  entity formed by two bidentate nitrate groups and one bis-bidentate bridging

ligand molecule. Work is in progress in our laboratories to obtain crystals for full X-ray analysis for some 2:3 complexes.

## REFERENCES

1. C. Airoidi, F.S. Dias, G.F. De Sá and J.G. Espinola, *J. Inorg. Nucl. Chem.*, **40**, 1537 (1978).
2. N. Rajasekar and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **43**, 977 (1981).
3. J.M. Tsangaris, S. Perlepes and A.G. Galinos, *Z. Naturforsch. Sect. B*, **34**, 456 (1979).
4. Th.F. Zafiroopoulos, S.P. Perlepes, P.V. Ioannou, J.M. Tsangaris and A.G. Galinos, *Z. Naturforsch. Sect. B*, **36**, 87 (1981).
5. S.P. Perlepes, Th.A. Kabanos and J.M. Tsangaris, *Bull. Soc. Chim. Belg.*, **92**, 859 (1983).
6. Th.A. Kabanos and J.M. Tsangaris, *J. Coord. Chem.*, **13**, 89 (1984).
7. S.P. Perlepes and A.G. Galinos, *J. Less-Common Met.*, **96**, 69 (1984).
8. Th.F. Zafiroopoulos, A.G. Galinos and S.P. Perlepes, *J. Coord. Chem.*, **13**, 197 (1984).
9. J.H. Van Vleck and A. Frank, *Phys. Rev.*, **34**, 1494, 1625 (1929).
10. C.K. Jorgensen, *Modern Aspects of Ligand Field Theory*, North Holland Publishing Co., Amsterdam, 1971, p. 293.
11. D.E. Henrie and G.R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968).
12. S.P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).
13. D.G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967).
14. D.G. Karraker, *Inorg. Chem.*, **7**, 473 (1968).
15. D.J. Barnes, R.L. Chapman, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **51**, 155 (1981).
16. R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, **4**, 350 (1965).
17. A. Seminara, A. Musumeci and A. Chisari, *Inorg. Chim. Acta*, **82**, 173 (1984).
18. A.G. Galinos, J.K. Kouinis, P.V. Ioannou, Th.F. Zafiroopoulos and S.P. Perlepes, *Z. Naturforsch. Sect. B*, **34**, 1101 (1979), and references therein.
19. V. Casellato, P.A. Vigato and M. Vidali, *Coord. Chem. Rev.*, **36**, 183 (1981).
20. R.L. Chapman, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **52**, 161 (1981).
21. A. Musumeci, R.P. Bonomo, V. Cucinotta and A. Seminara, *Inorg. Chim. Acta*, **59**, 133 (1982).