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Template Synthesis and Characterization of 18-Membered Hexaaza Macrocyclic Complex of Lanthanum(III) Perchlorate

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We have previously described the preparation and characterization of magnesium(II), zinc(II) and scandium(III) complexes containing the 14-membered quadridentate hexaaza macrocyclic ligand [1]. The complexes have been synthesized from 2,6-diacetylpyridine and hydrazine using a metal ion as a template for the ring closure. The synthesis of the free macrocycle has also been achieved without the use of the coordination template effect, albeit with very low yield.

As a continuation of our studies on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of macrocyclic compounds we extended our investigations to the lanthanides, which have not so far been examined in this respect. A paper to be published later will deal with the template synthesis and characterization of 14-membered hexaaza quadridentate macrocyclic complexes of the heavier lanthanides. The lighter lanthanides have been found to be ineffective as templates for the synthesis of this macrocycle under similar conditions [2]. This finding appears to be in accord with general observation that the relationship between the complex formation and the ratio of metal ion diameter to ligand cavity size is of considerable importance for macrocyclic compounds [3–8]. It was therefore interesting to investigate the template action of lighter lanthanides in the synthesis of macrocyclic ligand with greater ring size. In this paper the synthesis and characterization of 18-membered hexaaza macrocylic complex of lanthanum(III) perchlorate is described.

The complex has been prepared as its perchlorate salt by the template reaction of 2,6-diacetylpyridine with ethylenediamine in the presence of $La(ClO_4)_3 \cdot 6H_2O$. A mixture of $La(ClO_4)_3 \cdot 6H_2O$ (2 mmol) (prepared from La_2O_3) in ethanol (20 ml) and 2,6-diacetylpyridine (4 mmol) in ethanol (30 ml) was heated with stirring at 80 °C under reflux. To this solution, ethylenediamine (4 mmol) in ethanol (20 ml) was added dropwise. The yellow-orange precipitate, which formed upon allowing the reaction mixture to reflux for 1 hour, was isolated by suction-filtration, washed with ether, and dried under vacuum over P_2O_5.

This isolated complex is formulated as $[La(C_{22}H_{26}N_6)(H_2O)_2] \cdot (ClO_4)_3$ on the basis of spectral data and thermogravimetric analysis. Elemental analysis figures are consistent with the above formula.

The infrared spectrum of the complex in KBr pellets taken in the region 4000–300 cm^{-1} confirms the formation of the macrocyclic compound by the absence of bands characteristic of carbonyl and amine groups of the starting materials. An important feature is the occurrence of a strong absorption at 1645 cm^{-1} attributable to C=N stretching modes [9, 10]. The spectrum exhibits the absorption bands at 1590 and 1460 cm^{-1} as expected for the two high energy pyridine vibrations [11, 12]. The low energy pyridine bands are observed at 625 and 420 cm^{-1} suggesting coordination of pyridine [13, 14]-.

The presence of non-coordinated perchlorate in the complex is inferred from the broad intense band centered at 1100 cm^{-1} and a very weak absorption at 930 cm^{-1}, and from the absence of splitting of the degenerate stretching and bending modes of ClO_4^- ion, which is indicative of coordinated species [15, 16].

A broad, diffuse band with the maximum at 3400 cm^{-1} may be assigned to the antisymmetric and symmetric O–H stretching modes [16]. Weak absorption bands found at 870, 855, and 560 cm^{-1} may suggest the presence of coordinated water in the complex [18, 19].

The electronic spectra of solutions of the complex in water and acetonitrile were recorded in the range 50000–14000 cm^{-1}. The spectrum of the complex in water exhibits three absorption bands at 46500, 41700, and 36000 cm^{-1}. Three bands are also observed in the spectrum of the complex in acetonitrile solution with the maxima at 480000, 42000, and 34000 cm^{-1}.

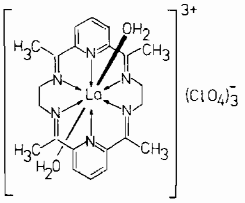
The diffuse reflectance spectrum of the solid complex taken in the range 40000–14000 cm^{-1} contains broad bands at *ca.* 41000 and 33000 cm^{-1}. These high energy absorption bands may be assigned to the $\pi \rightarrow \pi^*$ transitions of the coordinated macrocycle [10, 20].

The similarity of the spectra obtained in the solid state, in H_2O, and in CH_3CN solutions suggests, in agreement with other data, that the axial ligands are water molecules.

The thermogravimetric analysis indicates the loss of two molecules of water at 130–160 °C.

The nuclear magnetic resonance spectrum of the complex obtained in DMSO-d_6 solution with TMS as internal standard shows the pyridine protons at δ 8.2–8.6, the methylene protons at δ 3.6, and the methyl protons at δ 2.6 ppm. Integrated intensities of the above signals are in the ratio 3:4:6, respectively. This is consistent with the proposed formulation of the complex.

On the basis of spectral and analytical data it seems reasonable to assume that the perchlorate complex of lanthanum(III) ion has octa-coordinate hexagonal bipyramidal structure with the six nitrogen donor atoms of the 18-membered macrocyclic ligand occupying the equatorial plane and the axial positions being filled with water.



The formation of this macrocycle in reactions employing alkaline earth metal ions and lead(II) ion as templates has recently been reported [21].

The data presented here along with our earlier investigations involving the heavier lanthanides lead to the conclusion that the rare earth elements may act as templates on the synthesis of nitrogen donor macrocycles and that these macrocyclic ligands show selectivities towards the lanthanide ions as a function of ring size. The template process depends significantly on cation and ligand parameters, although other factors are undoubtedly important.

References

1 W. Radecka-Paryzek, *Inorg. Chim. Acta, 34,* 5 (1979); W. Radecka-Paryzek, *ibid., 35,* L349 (1979).

2 W. Radecka-Paryzek, in preparation.

3 J. J. Christensen, D. J. Eautough and R. M. Izatt, *Chem. Rev., 74,* 351 (1974).

4 Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait and D. H. Busch, *J. Am. Chem. Soc., 99,* 4029 (1977).

5 Y. Hung and D. H. Busch, *J. Am. Chem. Soc., 99,* 4977 (1977).

6 R. B. King and P. R. Heckley, *J. Am. Chem. Soc., 96,* 3118 (1974).

7 R. M. Izatt, J. D. Lamb, G. E. Maas, R. E. Asay, J. S. Bradshaw and J. J. Christensen, *J. Am. Chem. Soc., 99,* 2365 (1977).

8 R. M. Izatt, J. D. Lamb, R. E. Asay, G. E. Maas, J. S. Bradshaw, J. J. Christensen and S. S. Moore, *J. Am. Chem. Soc., 99,* 6134 (1977).

9 M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc. Dalton,* 438 (1977).

10 S.-M. Peng, G. C. Gordon and V. L. Goedken, *Inorg. Chem., 17,* 119 (1978).

11 S. C. Cummings and D. H. Busch, *J. Am. Chem. Soc., 92,* 1924 (1970).

12 J. D. Curry, M. Robinson and D. H. Busch, *Inorg. Chem., 6,* 1570 (1967).

13 N. S. Gill, R. H. Nuttall and D. E. Scaife, *J. Inorg. Nucl. Chem., 18,* 79 (1961).

14 C. Postums, *Inorg. Chem., 6,* 2030 (1976).

15 B. J. Hathaway and E. Underhill, *J. Chem. Soc.,* 3091 (1961).

16 A. E. Wickenden and R. A. Krause, *Inorg. Chem., 4,* 404 (1965).

17 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley-Interscience, New York (1970).

18 M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc. Dalton,* 1389 (1976).

19 M. S. Styka, R. C. Smierciak, E. L. Blinn, R. E. DeSimone and J V. Passariello, *Inorg. Chem., 17,* 82 (1978).

20 M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc. Dalton,* 1173 (1977).

21 J. de O. Cabral, M. F. Cabral, W. J. Cummins, M. G. B. Drew, A. Rodgers and S. M. Nelson, *Inorg. Chim. Acta, 30,* L313 (1978).