Asian Journal of Chemistry Vol. 3, No. 3 (1991), 290–292

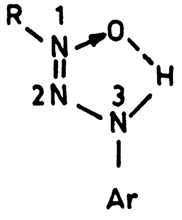
LANTHANIDE (III) COMPLEXES OF TRIAZENE-1- OXIDES†

RAMADHAR SHARMA* and A.K. THAKUR
P.G. Department of Chemistry
R.D. & D.J. College, Munger-811 201, India

Lanthanum(III), cerium(III), praseodymium (III), neodymium (III), samarium(III), gadolinium(III), terbium (III), dysprosium(III) and yttrium(III) complexes of substituted monobasic bidentate triazene-1-oxides (TH) have been synthesized and characterised. The complexes conform to the compositions $[LnT_3(H_2O)_n]$ (n = 1, 2). The characterisation of the eighteen newly synthesized complexes of the trivalent lanthanides has been made on the basis of elemental analyses, conductance measurements in dimethylformamide (DMF) at 0.001 M, magnetic moments, infra-red spectra and electronic absorption spectra.

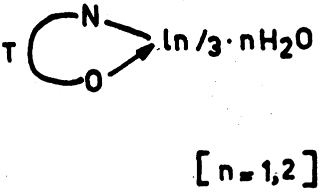
INTRODUCTION

Complexes of variedly substituted monobasic bidentate triazene-1-oxides with transition and non-transition metals have been reported[1]. The present study describes the complexes of these fascinating ligands with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Y(III). The ligands are represented by the general formula (I) and their lanthanide(III) chelates by the formula (II). The substituents in the aromatic ring are indicated by *-o*, *-m* and *-p* with respect to the N—C(Ar) bond.



I

R=alkyl, aryl or substituted aryl group



II

Ar=aryl or substituted aryl group

EXPERIMENTAL

The substituted monobasic bidentate triazene-1-oxides were synthesized by following the methods of M. Elkins and L. Hunter[2], *i.e.* by coupling substituted hydroxylamines with diazonium chloride solution at 0–5°C using sodium acetate to control pH. Purity of the ligands was ascertained by estimating the nitrogen content and melting point determination.

---

† Pesented at the 77th Session of the ISCA Annual Conference at Cochin (Feb. 4–9, 1990).

General Method of Preparing Complexes:

Lanthanon nitrate hydrate (0.001 mol.) was dissolved in warm ethanol (10 ml) and mixed with a solution of the triazene-1-oxides (0.0035 mol) in ethanol. The mixture was refluxed on a steam-bath for *ca* 1 hr. The pH of the solution was adjusted to *ca* 4–5 with dil. NH_4OH with stirring. On standing for *ca* 1/2 hr the complex separated, collected, washed with ethanol and dried over silica gel. In the cases of Sm(III), Gd(III), Tb(III) and Dy(III) complexes of monobasic bidentate triazene-1-oxides appeared during refluxing without any pH adjustment. Nd(III) complexes of triazene-1-oxides also appeared in crystalline form during refluxing.

RESULTS AND DISCUSSION

The analytical data indicate that the complexes contain three bidentate triazene-1-oxide ligands with the general composition $Ln\,T_3.nH_2O$ ($n = 1$ or 1.5). The water of crystallization associated with a few of these complexes are readily lost 110°C in an oven. Thermograms run for these hydrated samples also indicate ready loss of water in the temperature range 50–110°C indicating that water molecules are lattice held and not coordinated.

All these complexes behave as non-electrolytes in DMF ($\Lambda_M = 8.0$ to 22.7 $ohm^{-1}\ cm^2\ mol^{-1}$) as compared to 65–90 $ohm^{-1}\ cm^2\ mol^{-1}$ for 1 : 1 electrolytes in DMF[3]. The magnetic moment values are quite normal for the lanthanide complexes based on their J-values. Although the entire family of lanthanide could not be studied, it was however clear that the magnetic moments followed the trend of usual double humped curve[4].

Infrared Spectra and Bonding Sites:

The ligand 1,3-methyl-phenyl triazene-1-oxide and 1,3-diphenyl triazene-1-oxide exhibit characteristic sharp band at 3200 cm^{-1} which has been identified as internally hydrogen bonded $\overset{3}{N}$–H stretch. $\overset{1}{N} \rightarrow 0$ stretch is observed as a medium band[5] around 1300 cm^{-1} $\overset{1}{N} \rightarrow 0$ (bending vibration) has been found as split bands around 850 cm^{-1} and 830 cm^{-1}. $\overset{1}{N} \rightarrow 0$ band is considerably lowered (by about 60 cm^{-1}) due to electron drainage from the $\overset{1}{N} \rightarrow O \rightarrow M$ bond as a result of the oxygen-metal coordination. $\overset{1}{N} \rightarrow 0$ band (bending) is also lowered from 850 cm^{-1} to about 820 cm^{-1} giving a single and more intense band. The above i.r. spectra studies suggest the coordination of the $\overset{3}{N}$—nitrogen and $\overset{1}{N} \rightarrow O$, oxygen to the lanthanides.

Electronic Spectra

The electronic spectra for Nd^{3+} complexes of triazene-1-oxides, both in solid state (nujol) and in solutions of DMF and DMSO are almost similar, except for the broad shape of the mull spectra. This suggests that the complexes maintain the same stereochemistry in solid and solution phases. Compared to the spectra of the aquoneodymium (III) complex[6] the hypersensitive bands ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) in these complexes show significant red shift (Δv= 140–280 cm^{-1}). As to the other spectral bands ($^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}, {}^4I_{9/2} \rightarrow {}^4S_{3/2}, {}^4F_{7/21}, {}^4I_{9/2} \rightarrow {}^4G_{7/2}, {}^2G_{9/2}, {}^2K_{13/2}$) the extent of red shift compared to the aquocomplex is much less. The red shift of the hypersensitive bands have been utilised to calculate the nophelauxetic effect[7] β (β = the average value of $v_{complex}/v_{aquo}$) in these chelate complexes. From the β-values the covalency factor[8] $b^{1/2}$ ($b^{1/2} = [\frac{1}{2}(1 - \beta)]^{1/2}$] and the Sinha parameter[7] δ (metal-ligand covalency, per cent), δ (per cent) = $[(1 - \beta)/\beta] \times 100$ were also calculated. Compared to many other reported Nd^{3+} complexes[9, 10] the β-values in some of the cases are lower. Proportionate changes in $b^{1/2}$ and δ-values indicate some covalent character in the metal-ligand bonding. However, the small, positive values of $b^{1/2}$ indicate that the 4*f*-orbitals are only slightly involved in the bonding with the triazene-1-oxides.

Lanthanides have been found to exhibit higher coordination number[11]. In the present study a coordination number six could only be reached. The explanation lies in the fact that these ligands appear to neutralize the electron accepting property of the trivalent lanthanides better and is further substantiated by the similar electronic absorption bands for tris (β-diketonate) neodymium(III)[12].

REFERENCES

1. R.L. Dutta and R. Sharma, *J. Sci. and Ind. Res. (India)*, **40**, 715 (1981).
2. M. Elkins and L. Hunter, *J. Chem. Soc.*, 1346 (1938).
3. R.L. Dutta and B.R. Das, *Indian J. Chem.*, **22A**, 207 (1983).
4. L.G. Abakumova, G.A. Abakumova and D.A. Demarachav Dokal, *Akad. Nauk. SSSR*, **197**, 1315 (1971).
5. A. Vinciguerra, P.G. Simpson, Y. Kakiuti and J.V. Quagliano, *Inorg. Chem.*, **2**, 286 (1963).
6. G.R. Choppin, D.E. Henrie and K. Buija, *Inorg. Chem.*, **5**, 1743 (1966).
7. S.P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).
8. D.E. Henrie and G.R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968).
9. N. Rajasekhar and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **43**, 977 (1981).
10. G.K. Joshi, M.P. Bhutra and S.N. Mishra, *J. Inorg. Nucl. Chem.*, **43**, 525 (1981).
11. R. Jagannathan and S. Soundarajan, *Inorg. Nucl. Chem. Letters*, **17**, 65 (1981).
12. D.G. Karrakar, *Inorg. Chem.*, 1863 (1967).

(Received: 15 February 1990; Accepted: 20 June 1990) AJC–188