

CCA-1773

YU ISSN 0011-1643

UDC 546.654

Note

Magneto-Chemical and Spectral Investigations of Lanthanide(III) Perrhenato Complexes of Mono *N*-Oxides of 1,10-Phenanthroline and 2,2'-Bipyridine

R. K. Agarwal

Department of Chemistry, Lajpat Rai (Post-Graduate) College, Sahibabad-201 005 (Ghaziabad) India.

Received November 11, 1986

Lanthanide(III) perrhenato complexes of mono *N*-oxides of 1,10-phenanthroline (PhenNO) and 2,2'-bipyridine (BipyNO) with the general composition $\text{Ln}(\text{ReO}_4)_3 \cdot 2\text{L}$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho}$ or Yb and $\text{L} = \text{PhenNO}$ or BipyNO) have been synthesized and characterized by elemental analyses, molar conductance, magnetic susceptibility, DTA and infrared spectra. The probable coordination number of eight has been assigned to Ln^{3+} ion in these complexes.

INTRODUCTION

It is well known that coordination numbers greater than six are favoured in lanthanide systems.¹ The variation in coordination number (six to twelve) observed in lanthanide complexes may be attributed to steric factors and electrostatic forces of attraction and repulsion, rather than bond orientation by the well shielded 4f-orbitals of the metal ion. Thus, the relatively large size of the lanthanide ions generally allows accommodation of more than six donor atoms in the coordination sphere. In view of the variations in stoichiometry from ligand to ligand,² observed for the various lanthanide(III) complexes, it was considered worthwhile to study the complexes of lanthanide(III) perrhenates with mono *N*-oxides of 1,10-phenanthroline (PhenNO) and 2,2'-bipyridine (BipyNO).

EXPERIMENTAL

The hydrated lanthanide perrhenates were obtained by the reaction of dilute perrhenic acid and lanthanide basic carbonate.³ Ligands PhenNO and BipyNO were prepared by methods of the Corey *et al.*⁴ and Muzase.⁵ 2,2'-Dimethoxypropane (Aldrich) and other reagent grade organic solvents were used throughout.

All the complexes were synthesized by dissolving 2 mmol of the hydrated lanthanide(III) perrhenate in absolute ethanol and a dehydrating agent (2,2'-dimethoxypropane) and the mixture was warmed on a water bath with constant stirring. A warm ethanolic solution of respective ligand (2.25 mmol) was added dropwise. Allowing the reaction mixture to cool, a crystalline precipitate was gradually obtained. The new complex was filtered, washed with small portion of ethanol and then with ether and dried in vacuo over P_4O_{10} . All the physico-chemical analyses were made as reported earlier.⁶⁻⁷

RESULTS AND DISCUSSION

The analytical data (Table I) show that lanthanide(III) perrhenates form 1 : 2 adducts with PhenNO and BipyNO. The present complexes possess high melting points at which they decompose. All the complexes are moisture sensitive and are quite stable and can be stored for long periods without any apparent change. The complexes are generally soluble in common organic solvents. The molar conductance values in nitromethane show them to be 1 : 1 electrolytes; hence the perrhenate ions behave as ionic as well as covalent.

La(III) complexes are diamagnetic as may be expected from their closed shell electronic configuration and absence of unpaired electrons. All other complexes are paramagnetic in nature at room temperature. It is due to the presence of 4f-electrons which are effectively shielded by 5s²5p⁶ electrons. Experimental data show that the magnetic moment of the metals remain unchanged upon coordination with these ligands, indicating thereby that 4f-electrons do not participate in bond formation.^{6,7} The magnetic moments of these complexes are within the range predicted and observed in the compounds of paramagnetic ions as reported earlier.^{8,9}

Infrared spectra: The free ligands exhibit a rich spectrum in the 1620—200 cm⁻¹ region.^{10,11} The important IR data are given in Table II. All the spectra are similar in major details and show no significant dependence on the central metal ions. The (N—O) stretching frequencies, observed in the 1270—1230 cm⁻¹ region in the free ligands are shifted towards lower frequencies in the complexes due to coordination of oxygen to the metal ion.² The N—O bending in free ligands, observed in the 850—800 cm⁻¹ region exhibits small shifts in the spectra of the complexes as expected. Coordination through the heterocyclic nitrogen atom is suggested by frequency shifts and splittings of several IR bands associated with vibration of the heterocyclic ring.^{12,13} A positive shift has been observed in the vibrations associated with C—H out-of-plane deformation due to tightening of the aromatic ring on complexation. In far IR region ν (Ln—O) and ν (Ln—N) have been identified.^{6,7,14} The overall IR spectral evidence suggests that these ligands act as bidentate O,N-chelating agents forming six-membered chelate rings with Ln³⁺.

The occurrence of strong band at ca. 900 cm⁻¹ (ν_3) indicates at least one perrhenate group present outside the coordination sphere. This view is supported by the conductance measurement. In addition to this band, four other bands in 980—850 cm⁻¹ region also appeared suggesting the coordinated perrhenate groups in the adducts and coordinated in the bidentate manner.

Thus, it is inferred that the Ln³⁺ ion is surrounded by six oxygen atoms and two nitrogen atoms (four oxygens of bidentate perrhenate ions, two oxygens and two nitrogens from two bidentate ligands) in these complexes and, hence, a probable coordination number eight has been assigned to Ln³⁺ ion.

DTA. studies: A small endothermic peak at ca. 80 °C is due to the hygroscopic nature of these complexes. In the region 280—320 °C, the only exo peak is due to decomposition of the complexes. The peak at about 480 °C is due to oxidation of carbon formed during the decomposition. The endo peak around 580 °C is due to sublimation of Re₂O₇. Finally, an exotherm at ca. 820 °C is due to the formation of Ln₂O₃.

TABLE I
Analytical, Conductivity and Magnetic Data of Lanthanide(III) Perrhenates Adducts of PhenNO and BipynO

Complex	Found (Calcd.) %				H	N	Ω M* ohm ⁻¹ cm ² mol ⁻¹	Relative mol. weight	$\mu_{\text{eff.}}$ B. M.
	M	C							
La(ReO ₄) ₃ ·2PhenNO	10.72(10.85)	22.29(22.48)	1.20(1.24)	4.30(4.37)	83.4	1281	Diamag.		
Ce(ReO ₄) ₃ ·2PhenNO	10.80(10.92)	22.27(22.46)	1.20(1.24)	4.30(4.36)	84.9	1282	2.61		
Pr(ReO ₄) ₃ ·2PhenNO	10.85(10.98)	22.26(22.44)	1.20(1.24)	4.29(4.36)	96.3	1283	3.63		
Nd(ReO ₄) ₃ ·2PhenNO	11.05(11.19)	22.22(22.39)	1.19(1.24)	4.29(4.35)	99.2	1286	3.59		
Sm(ReO ₄) ₃ ·2PhenNO	11.44(11.60)	22.14(22.29)	1.19(1.23)	4.27(4.33)	101.1	1292	1.60		
Gd(ReO ₄) ₃ ·2PhenNO	11.92(12.08)	22.01(22.17)	1.19(1.23)	4.25(4.31)	85.9	1299	7.90		
Tb(ReO ₄) ₃ ·2PhenNO	12.06(12.22)	21.98(22.13)	1.18(1.22)	4.24(4.30)	93.2	1301	9.30		
Dy(ReO ₄) ₃ ·2PhenNO	12.30(12.45)	21.90(22.07)	1.18(1.22)	4.23(4.29)	90.9	1304.5	10.51		
Ho(ReO ₄) ₃ ·2PhenNO	12.46(12.62)	21.86(22.03)	1.17(1.22)	4.22(4.28)	91.3	1307	10.43		
Yb(ReO ₄) ₃ ·2PhenNO	13.01(13.15)	21.76(21.90)	1.17(1.21)	4.20(4.25)	92.7	1315	4.27		
La(ReO ₄) ₃ ·2BipynO	11.10(11.27)	19.32(19.46)	1.24(1.29)	4.49(4.54)	98.3	1233	Diamag.		
Ce(ReO ₄) ₃ ·2BipynO	11.16(11.34)	19.30(19.44)	1.24(1.20)	4.48(4.53)	86.9	1234	2.63		
Pr(ReO ₄) ₃ ·2BipynO	11.24(11.41)	19.29(19.43)	1.24(1.29)	4.48(4.53)	89.3	1235	3.60		
Nd(ReO ₄) ₃ ·2BipynO	11.45(11.63)	19.25(19.38)	1.24(1.29)	4.47(4.52)	91.4	1238	3.57		
Sm(ReO ₄) ₃ ·2BipynO	12.87(12.05)	19.14(19.29)	1.23(1.28)	4.45(4.50)	93.6	1244	1.62		
Gd(ReO ₄) ₃ ·2BipynO	12.38(12.54)	19.05(19.18)	1.23(1.27)	4.42(4.47)	94.9	1251	7.92		
Tb(ReO ₄) ₃ ·2BipynO	12.50(12.68)	19.01(19.15)	1.22(1.27)	4.41(4.46)	95.7	1253	9.32		
Dy(ReO ₄) ₃ ·2BipynO	12.75(12.93)	18.96(19.10)	1.22(1.27)	4.40(4.45)	96.7	1256.5	10.49		
Ho(ReO ₄) ₃ ·2BipynO	12.92(13.10)	18.92(19.06)	1.22(1.27)	4.39(4.44)	89.3	1259	10.41		
Yb(ReO ₄) ₃ ·2BipynO	13.51(13.65)	18.80(18.94)	1.21(1.26)	4.35(4.41)	91.2	1267	4.26		

* in nitromethane

TABLE II
Partial IR Bands (cm⁻¹) of Lanthanide(III) Perrhenates Adducts of PhenNO and BipynO

Compound ^a	(NO)	(NO)	(NO)	(Ln—O)	(Ln—N)	(ReO ₄)
PhenNO	1270s, 1250s	810s	—	—	—	—
La(ReO ₄) ₃ ·2PhenNO	1235s, 1230s	802m	410m	320m	980m, 940m, 900s, 880m, 860w	
Ce(ReO ₄) ₃ ·2PhenNO	1230s, 1225m	805m	405m	310m	978m, 942m, 905s, 882m, 865w	
Pr(ReO ₄) ₃ ·2PhenNO	1240s, 1220s	800m	395m	305m	982m, 945m, 902s, 880m, 862w	
Nd(ReO ₄) ₃ ·2PhenNO	1230s, 1220m	805m	395m	322m	980m, 942m, 905s, 882m, 860w	
Sm(ReO ₄) ₃ ·2PhenNO	1235s, 1225m	803m	390m	315m	980m, 940m, 900s, 882m, 862w	
Gd(ReO ₄) ₃ ·2PhenNO	1240s, 1225m	805m	400m	320m	980m, 942m, 902s, 880m, 852w	
Tb(ReO ₄) ₃ ·2PhenNO	1235s, 1220m	802m	410m	325m	978m, 940m, 902s, 882m, 860w	
Dy(ReO ₄) ₃ ·2PhenNO	1235s, 1225m	800m	405m	320m	980m, 937m, 900s, 880m, 850w	
Ho(ReO ₄) ₃ ·2PhenNO	1232s, 1220m	802m	408m	322m	975m, 935m, 900s, 875m, 855w	
Yb(ReO ₄) ₃ ·2PhenNO	1235s, 1220m	805m	400m	315m	980m, 940m, 950s, 870m, 850w	
BipynO	1250s, 1230s	855s	—	—	980m, 940m, 905s, 870m, 850w	
La(ReO ₄) ₃ ·2BipynO	1220s, 1210m	845m	410m	315m	982m, 940m, 902s, 870m, 860w	
Ce(ReO ₄) ₃ ·2BipynO	1222s, 1215m	842m	405m	305m	980m, 942m, 900s, 872m, 865w	
Pr(ReO ₄) ₃ ·2BipynO	1230m	840m	395m	300m	982m, 945m, 905s, 870m, 860w	
Nd(ReO ₄) ₃ ·2BipynO	1220s, 1210m	850m	415m	310m	980m, 940m, 900s, 872m, 858w	
Sm(ReO ₄) ₃ ·2BipynO	1218s, 1210m	847m	410m	312m	982m, 938m, 905s, 870m, 855w	
Gd(ReO ₄) ₃ ·2BipynO	1215s, 1205m	845m	405m	305m	980m, 940m, 900s, 875m, 860w	
Tb(ReO ₄) ₃ ·2BipynO	1215s, 1205m	840m	400m	305m	—	
Dy(ReO ₄) ₃ ·2BipynO	1212s, 1205m	845m	410m	310m	982m, 942m, 902s, 880m, 865w	
Ho(ReO ₄) ₃ ·2BipynO	1215s, 1205m	842m	415m	315m	985m, 940m, 905s, 880m, 860w	
Yb(ReO ₄) ₃ ·2BipynO	1215s, 1205m	845m	420m	320m	982m, 940m, 900s, 880m, 860w	

REFERENCES

1. D. G. Karraker, *J. Chem. Educ.* **47** (1970) 424.
2. D. K. Koppikar, P. V. Sivapullaiah, L. Ramakrishnan, and Soundararajan, *Struct. Bonding* **34** (1978) 135.
3. G. Vicentini, M. Perrier, and J. C. Prado, *J. Inorg. Nucl. Chem.* **31** (1969) 825.
4. E. J. Corey, A. L. Borrer, and T. Foglia, *J. Org. Chem.* **30** (1965) 288.
5. I. Muzase, *Nippon Kagaku Zasshi* **77** (1956) 682; *C. A.* **52** (1958) 9100a.
6. R. K. Agarwal and S. K. Gupta, *Thermochim. Acta* **98** (1986) 313; **99** (1986) 357.
7. R. K. Agarwal and S. Gupta, *Indian J. Chem.* **25A** (1986) 597.
8. N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski, and M. M. Labes, *J. Less Common Met.* **20** (1970) 29.
9. R. K. Agarwal, M. B. L. Sharma, and A. K. Srivastava, *Acta Chim. (Hungarica)* **122** (1986) 277.
10. R. K. Agarwal, P. C. Jain, V. Kapur, S. Sharma, and A. K. Srivastava, *Transition Met. Chem.* **5** (1980) 237.
11. A. K. Srivastava, S. Sharma, and R. K. Agarwal, *Inorg. Chim. Acta* **61** (1982) 235.
12. R. G. Inskeep, *J. Inorg. Nucl. Chem.* **24** (1962) 763.
13. S. P. Sinha, *Spectrochim. Acta* **20** (1964) 879.
14. R. K. Agarwal and S. K. Gupta, *Thermochim. Acta* **95** (1985) 99.

SAŽETAK

Magnetokemijsko i spektralno ispitivanje kompleksnih spojeva mono-N-oksida 1,10-fenantrolina i 2,2'-bipiridina s lantanid(III) perenatima

R. K. Agarwal

Pripremljeni su u naslovu nabrojani spojevi opće formule $\text{Ln}(\text{ReO}_4)_3 \cdot 2\text{L}$ ($\text{Ln}=\text{La}$, Ce , Pr , Nd , Sm , Gd , Tb , Dy , Ho , Yb i $\text{L}=\text{PhenNO}$, BipyNO) te im je određena molarna vodljivost, magnetska susceptibilnost, DTA i IR-spektri.

Ln^{3+} -ion u opisanim kompleksima ima vjerojatno koordinacijski broj osam.