

Complexes of lanthanide(III) nitrates with 10-(2-dimethylamino-1-methyl) phenothiazine

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Abstract. A new series of lanthanide(III) nitrate complexes with 10-(2-dimethylamino-1-methyl) phenothiazine (isopromethazine) having the general formula $[\text{Ln}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and IP = isopromethazine have been prepared and characterized by elemental analysis, molar conductance, electronic, infrared, proton NMR spectra, magnetic moments and thermogravimetric studies. Isopromethazine acts as a bidentate ligand, coordinating through heterocyclic nitrogen and tertiary alkyl side chain nitrogen atoms. Two of the nitrate groups are coordinated in a bidentate fashion to the metal ion, while another nitrate ion remains uncoordinated. A coordination number of eight may be assigned to the metal ion in these complexes. The electronic spectra reveal the weak covalent character of the metal-ligand bond.

Keywords. Complexes; lanthanides; isopromethazine; synthesis; characterization.

1. Introduction

The importance of toxicity in the compounds containing nitrogen and sulphur atoms have been well established in many fungicides¹. N-alkyl phenothiazines possessing both sulphur and nitrogen as coordinating atoms are widely used as tranquilizers in psychiatry and chemotherapy². They exhibit low ionization potentials and are found to be excellent electron donors³. The study of metal phenothiazine complexes has gained much importance in recent years due to their potential pharmacological activities⁴. In continuation of our earlier investigations on the complexes of transition metals with N-alkylphenothiazines^{5–8}, we report here the synthesis and characterization of a new series containing fourteen complexes of lanthanide(III) nitrates with 10-(2-dimethylamino-1-methyl) phenothiazine (figure 1).

2. Experimental

2.1 Materials

The nitrates of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy were received from Indian Rare Earths Ltd., Trivandrum and of Ho, Er, Tm, Yb and Lu were obtained from Aldrich Chemical Company, Inc., USA. Isopromethazine hydrochloride was received from Rhone-Poulenc, Vitry, France. All other chemicals used were of Analytical Grade.

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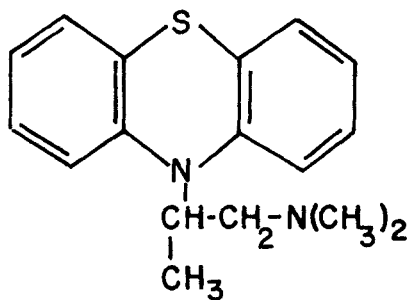


Figure 1. 10-(2-Dimethylamino-1-methyl)phenothiazine.

2.2 Preparation of the complexes

An aqueous solution of lanthanide(III) nitrate (2.5 mmol) was added slowly with stirring to an aqueous solution of isopromethazine hydrochloride (6.5 mmol). The solid complexes separated were filtered, washed several times with water followed by ethanol and dried *in vacuo* over fused calcium chloride.

2.3 Measurements

The microanalysis for C, H and N were performed on Carlo-Erba 1106 elemental analyser. The metal content of the complexes was determined by complexometric EDTA titration using xylenol orange as an indicator⁹ and ionic nitrate was estimated gravimetrically using nitron reagent¹⁰. The magnetic moment of the complexes were determined by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. The molar conductance of the complexes were measured using an ELICO-model conductivity bridge type CM-82T attached to a dip type conductivity cell with platinum electrode (cell constant: 0.8534). The infrared spectra of isopromethazine hydrochloride and its complexes were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ on a Shimadzu FT-IR 470 spectrophotometer. The electronic spectra of the ligand and the complexes were recorded in 10^{-3} M DMF solutions on a JASCO-UVIDEC-610 double beam spectrophotometer. The ^1H NMR spectra of the ligand and its complexes with lanthanum(III) and lutetium(III) were recorded on FT-NMR R-600 HITACHI spectrophotometer using DMSO-d_6 as the solvent.

3. Results and discussion

All the complexes are light bluish non-hygroscopic solids. They are soluble in DMF and DMSO, sparingly soluble in chloroform and acetonitrile but insoluble in water and other common organic solvents. The complexes are stable and do not possess sharp melting points. The analytical data (table 1) of the complexes show that all fourteen complexes have the general formula $[\text{Ln}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and IP = isopromethazine.

3.1 Electrical conductance

The observed conductance values of the complexes (table 1) in 10^{-3} M DMF are in agreement with the values corresponding to 1:1 electrolytes¹¹. Thus, all

Table 1. Analytical, molar, conductance and magnetic data of lanthanide(III) nitrate complexes of isopromethazine.

Complex	%Metal	%Carbon	%Hydrogen	%Nitrogen	μ_{eff} in BM	Mol. cond. $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	NO_3^- (ionic) ^a
[La(IP) ₂ (NO ₃) ₂] ₂ NO ₃	15.50 (15.54)	45.52 (45.69)	4.49 (4.51)	10.92 (10.97)	Dia	90	0.0693 (0.0694)
[Ce(IP) ₂ (NO ₃) ₂] ₂ NO ₃	15.58 (15.65)	45.56 (45.63)	4.48 (4.50)	10.91 (10.95)	2.60	94	0.0690 (0.0692)
[Pr(IP) ₂ (NO ₃) ₂] ₂ NO ₃	15.68 (15.73)	45.48 (45.59)	4.49 (4.50)	10.87 (10.94)	3.69	96	0.0690 (0.0692)
[Nd(IP) ₂ (NO ₃) ₂] ₂ NO ₃	15.95 (16.04)	45.30 (45.42)	4.47 (4.48)	10.80 (10.90)	3.75	92	0.0687 (0.0688)
[Sm(IP) ₂ (NO ₃) ₂] ₂ NO ₃	16.52 (16.64)	45.02 (45.11)	4.54 (4.45)	10.78 (10.83)	1.80	87	0.0682 (0.0684)
[Eu(IP) ₂ (NO ₃) ₂] ₂ NO ₃	16.73 (16.75)	44.88 (45.03)	4.42 (4.44)	10.75 (10.81)	3.40	94	0.0681 (0.0682)
[Gd(IP) ₂ (NO ₃) ₂] ₂ NO ₃	16.20 (16.24)	44.65 (44.77)	4.40 (4.42)	10.64 (10.74)	6.90	89	0.0678 (0.0680)
[Tb(IP) ₂ (NO ₃) ₂] ₂ NO ₃	17.35 (17.39)	44.56 (44.69)	4.40 (4.41)	10.63 (10.72)	9.45	86	0.0675 (0.0678)
[Dy(IP) ₂ (NO ₃) ₂] ₂ NO ₃	17.65 (17.71)	44.48 (44.56)	4.37 (4.39)	10.58 (10.68)	9.95	93	0.0671 (0.0674)
[Ho(IP) ₂ (NO ₃) ₂] ₂ NO ₃	17.88 (17.93)	44.34 (44.39)	4.36 (4.38)	10.52 (10.65)	10.26	84	0.0674 (0.0674)
[Er(IP) ₂ (NO ₃) ₂] ₂ NO ₃	18.08 (18.13)	44.12 (44.28)	4.35 (4.37)	10.50 (10.63)	9.68	86	0.0670 (0.0672)
[Tm(IP) ₂ (NO ₃) ₂] ₂ NO ₃	18.26 (18.28)	44.10 (44.20)	4.34 (4.36)	10.52 (10.61)	6.95	90	0.0670 (0.0670)
[Yb(IP) ₂ (NO ₃) ₂] ₂ NO ₃	18.58 (18.64)	43.92 (44.01)	4.33 (4.34)	10.48 (10.56)	4.95	88	0.0667 (0.0668)
[Lu(IP) ₂ (NO ₃) ₂] ₂ NO ₃	18.70 (18.81)	43.84 (43.91)	4.32 (4.33)	10.46 (10.55)	Dia	84	0.0665 (0.0666)

Calculated values in parentheses

^aSample taken for ionic nitrate determination = 1.0 g

the nitrate complexes of lanthanides with isopromethazine may be represented as $[\text{Ln}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$ which is in good agreement with the molecular formula suggested on the basis of analytical data.

3.2 Magnetic moments

The magnetic moment values (table 1) indicate that lanthanum(III) and lutetium(III) complexes are diamagnetic while all other tripositive lanthanide complexes are paramagnetic as expected for lanthanide(III) ions. The measured magnetic moment values show a little deviation from Van Vleck values¹² thereby indicating that the 4f-electrons do not participate in bond formation in these complexes. The data also suggest that there are no metal-metal interactions or spin-spin coupling.

3.3 Infrared spectra

The selected infrared spectral frequencies of the complexes are given in table 2. The sharp bands observed at 3030 cm^{-1} and 1275 cm^{-1} in the spectrum of the free ligand are attributed to the stretching vibrations of carbon-hydrogen and carbon-nitrogen respectively. The characteristic benzene ring vibration is located at 1445 cm^{-1} . It was reported¹³ that the ion R_3NH^+ combined with Cl^- present in N-alkylphenothiazines give rise to a broad band in the $2500\text{--}2300\text{ cm}^{-1}$ region. A broad band observed in the $2560\text{--}2430\text{ cm}^{-1}$ region in the spectrum of the ligand corresponds to the $-\text{CH}(\text{CH}_3)\text{CH}_2\text{NR}_2\text{H}^+$ combined with Cl^- ion. In the spectra of the corresponding lanthanide(III) complexes, this band has either disappeared or reduced to a small hump

Table 2. Selected infrared spectral bands(cm^{-1}) of the lanthanide(III) nitrate complexes.

Compound	$\nu_{\text{Ln-N}}$	NO_3 (coordinated)				NO_3^-
		ν_4	ν_1	ν_2	ν_5	(ionic) ν_3
$[\text{La}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	445	1460	1279	1035	821	1375
$[\text{Ce}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	443	1476	1278	1036	824	1378
$[\text{Pr}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	444	1460	1280	1035	826	1380
$[\text{Nd}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	445	1480	1280	1034	825	1378
$[\text{Sm}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	443	1460	1285	1036	826	1380
$[\text{Eu}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	444	1486	1285	1036	826	1370
$[\text{Gd}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	445	1480	1285	1035	823	1380
$[\text{Tb}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	443	1476	1285	1034	823	1370
$[\text{Dy}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	444	1460	1280	1035	825	1376
$[\text{Ho}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	445	1465	1280	1033	821	1378
$[\text{Er}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	444	1470	1285	1034	823	1378
$[\text{Tm}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	443	1475	1278	1036	823	1380
$[\text{Yb}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	445	1460	1280	1035	824	1375
$[\text{Lu}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$	444	1480	1279	1034	826	1375

showing that tertiary nitrogen atom of the side chain is a site of coordination. The sharp band observed at 2850 cm^{-1} region in the spectrum of the ligand is attributed to the heterocyclic nitrogen atom carrying an alkyl group. In the spectra of the corresponding lanthanide(III) complexes, this band has disappeared completely suggesting the coordination of heterocyclic nitrogen atom. This shows that isopromethazine acts as bidentate ligand with heterocyclic and tertiary nitrogen atoms as two coordination sites.

The sharp band at 750 cm^{-1} observed in the spectrum of the ligand assignable to $\nu(\text{CSC})$ stretching frequency¹⁴ remains unaffected in the spectra of the corresponding lanthanide(III) complexes suggesting the non-coordination of heterocyclic sulphur atom. The complexes also exhibit characteristic vibration frequencies of both ionic and coordinated nitrate groups. A very strong band observed around 1378 cm^{-1} indicates the presence of ionic nitrate group and it is due to ν_3 vibration of the nitrate group of D_{3h} symmetry. The complexes exhibit four bands at $1480\text{--}1460$, $1285\text{--}1278$, $1036\text{--}1033$ and $826\text{--}821\text{ cm}^{-1}$ which can be assigned to the vibrational modes of coordinated nitrate groups of C_{2v} symmetry¹⁴. The magnitude of splitting of the bands at higher energies ($\nu_4\text{--}\nu_1$) of the C_{2v} nitrate is about $195\text{--}182\text{ cm}^{-1}$ suggesting that the nitrate groups are attached to the metal atom in bidentate fashion¹⁵. The new bands observed in the region $445\text{--}443\text{ cm}^{-1}$ may be assigned to $\nu(\text{Ln-N})$ modes¹⁶.

3.4 Proton NMR spectra

The ^1H NMR spectrum of isopromethazine hydrochloride shows the resonance signal corresponding to the $-\text{C}-\text{CH}_3$, $-\text{N}-\text{CH}_3$ and the aromatic protons of the benzene ring in the region δ 1.80–1.95 ppm (doublet), δ 2.75 ppm (singlet) and δ 6.85–7.25 ppm (multiplet) respectively with respect to TMS. In the corresponding lanthanum and lutetium complexes, the signal corresponding to $-\text{N}-\text{CH}_3$ protons are found to be shifted to lower frequency region ($\delta = 2.85$ and 2.90 ppm respectively) indicating that nitrogen atoms are coordinated to the metal ion¹⁷. The other signals for the complexes are found to be in the regions δ 1.70–1.85 ppm as a doublet and δ 7.12–7.25 ppm as a multiplet with respect to TMS corresponding to $-\text{C}-\text{CH}_3$ and aromatic protons of benzene ring. A downfield shift in the absorption peaks of the complexes with respect to $-\text{N}-\text{CH}_3$ proton compared to their positions in the free isopromethazine ligand may be attributed to the corresponding effect of the alkyl side chain nitrogen atom, which results in deshielding of protons attached to it.

3.5 Electronic spectra

In the ultraviolet spectrum of isopromethazine hydrochloride the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are observed at 30303 cm^{-1} and 38759 cm^{-1} respectively. In the corresponding complexes the $n \rightarrow \pi^*$ band is blue-shifted to $33003\text{--}32362\text{ cm}^{-1}$ and $\pi \rightarrow \pi^*$ band is red-shifted to $37878\text{--}37174\text{ cm}^{-1}$. The electronic spectra of f-f transitions for Pr, Nd and Er complexes in the visible region and their tentative assignments^{18,19} in DMF solutions are given in table 3. These bands show appreciable red-shifts with respect to the corresponding aquo ions. Various bonding parameters have been calculated using appropriate equations^{18,20}. It is found that the values of the nephelauxetic ratio are less than unity. The bonding parameters also indicate a weak covalency for the metal-ligand bond²¹. The shapes of hypersensitive transition closely resemble the eight coordinated complexes reported by Karrakar¹⁹. Since Pr, Nd and

Table 3. The f-f transitions of the nitrate complexes of praseodymium(III), neodymium(III) and erbium(III) with isopromethazine.

$\lambda_{\max}(\text{cm}^{-1})$		Tentative assignment	β	$b^{1/2}$	$\delta\%$	η
Ln^{3+}	Complex					
$\text{Pr}^{\text{III}}(\text{NO}_3)_3$ $[\text{Pr}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$						
22222	22120	${}^3H_4 \rightarrow {}^3P_2$	0.9954	0.0679	0.4621	0.0023
21276	21140	$\rightarrow {}^3P_1$	0.9936	0.0565	0.6441	0.0032
20408	20250	$\rightarrow {}^3P_0$	0.9922	0.0624	0.7861	0.0039
16949	16845	$\rightarrow {}^1D_2$	0.9938	0.0556	0.6238	0.0031
$\text{Nd}^{\text{III}}(\text{NO}_3)_3$ $[\text{Nd}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$						
19607	19510	${}^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.9950	0.0708	0.5025	0.0025
17241	17125	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.9932	0.0583	0.6841	0.0034
13513	13405	$\rightarrow {}^2G_{3/2}, {}^4F_{7/2}$	0.9920	0.0632	0.8064	0.0040
12500	12425	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.9940	0.0547	0.6036	0.0030
$\text{Er}^{\text{III}}(\text{NO}_3)_3$ $[\text{Er}(\text{IP})_2(\text{NO}_3)_2]\text{NO}_3$						
20408	20300	${}^4I_{15/2} \rightarrow {}^2H_{11/2}$	0.9947	0.0514	0.5328	0.0026
18867	18735	$\rightarrow {}^4S_{3/2}$	0.9930	0.0591	0.7049	0.0035
15380	15285	$\rightarrow {}^4F_{9/2}$	0.9938	0.0556	0.6238	0.0031

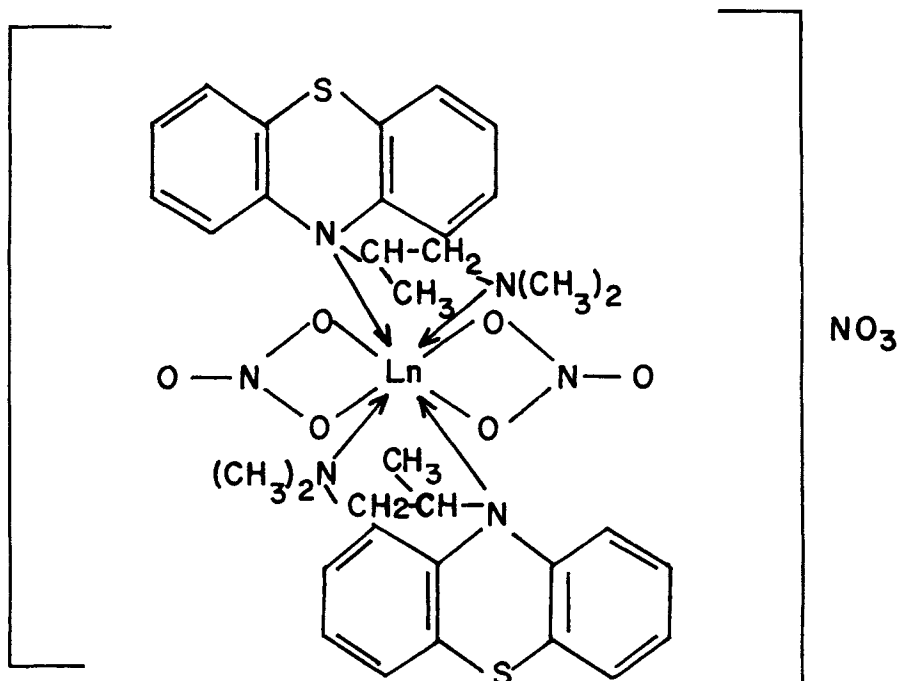
Er nitrate complexes of isopromethazine are isomorphous with the remaining nitrate complexes, the same coordination number may be assigned to other metal ions also in these complexes.

3.6 Thermogravimetric studies

The thermogravimetric studies show that all lanthanide(III) nitrate-isopromethazine complexes are stable up to 230°C which shows that there are no coordinated water and solvent molecules. The decomposition pattern consists of two steps. The first step consists of the loss of organic moiety at 250–320°C and the second step involves the decomposition of the nitrate followed by the formation of lanthanide(III) oxides at 340–730°C. The residue becomes constant at 750°C. The DTA studies show that the loss of organic moiety and formation of lanthanide(III) oxides are accompanied by an exothermic process.

4. Conclusion

On the basis of spectral studies, molar conductance values and thermal studies it is concluded that two neutral molecules of isopromethazine and two nitrate groups are bound to lanthanide ions in a bidentate manner and another nitrate group is present outside the coordination sphere exhibiting a coordination number of eight. None of the complexes gave single crystals of sufficient quality to conduct X-ray crystallographic analysis. The tentative structure of the complexes is given in figure 2.



Where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu.

Figure 2. Tentative structure of the complexes.

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References

1. Goldworthy W C 1942 *Phytopathology* **32** 498
2. Satoskar R S and Bhandarkar S D 1976 *Pharmacology and Pharmacotherapeutics* (Bombay: Popular press)
3. Dwivedi P C, Rao K G, Bhat S N and Rao C N R 1975 *Spectrochim. Acta* **A31** 129
4. Gasalvez M, Blance M F, Vivero C and Valles F 1978 *Eur. J. Chem.* **14** 1185
5. Keshvan B and Seetharamappa J 1987 *Inorg. Chim. Acta* **138** 135
6. Keshavan B and Seetharamappa J 1987 *Polyhedron* **6** 465
7. Keshavan B and Janardhan R 1986 *Indian J. Chem.* **A25** 1954
8. Keshavan B and Janardhan R 1985 *Trans. Met. Chem.* **10** 106
9. Welecher E J 1965 *The analytical use of EDTA* vol 4 (New York: Van Nostrand) pp 181
10. Vogel A I 1975 *A text book of quantitative inorganic analysis* 3rd edn. (London: ELBS) pp 583
11. Geary W J 1971 *Coord. Chem. Rev.* **7** 81
12. Van Vleck J H and Frank N 1929 *Phys. Rev.* **34** 1494
13. A R Kartrizky and A J Boulton (eds) 1976 *Advances in heterocyclic chemistry* (New York: Academic press) pp 338
14. Bellamy L J 1964 *The infrared spectra of complex molecules* (London: Methuen) pp 335
15. Nakamoto K 1986 *Infrared and Raman spectra of inorganic and coordination compounds* 4th edn. (New York: John Wiley) pp 256

16. Keshavan B and Ramalingaiah H 1998 *Synth. React. Met. - Org. Chem.* **28** 1
17. Keshavan B and Ramalingaiah 1997 *Trans. Met. Chem.* **22** 1
18. Sinha S P 1966 *Spectrochim. Acta* **22** 57
19. Karrakar D G 1967 *Inorg. Chem.* **10** 1863
20. Henrie D E and Choppin G C 1968 *J. Chem. Phys.* **49** 477
21. Mohan J, Tandon J P and Gupta N S 1986 *Inorg. Chim. Acta* **111** 187