

Complexes of rare earth perchlorates and nitrates with 3-methyl, 1-phenyl, pyrazol-5-one

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Abstract. Eighteen new complexes of lanthanide perchlorates and nitrates with 3-methyl 1-phenyl pyrazol-5-one (MPP) have been synthesized and characterized. The complexes have the general compositions $[\text{Ln}(\text{MPP})_3](\text{ClO}_4)_3$ and $[\text{Ln}(\text{MPP})_3(\text{NO}_3)_3]$ where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y. Conductance studies in nitrobenzene and acetonitrile indicate 1:3 electrolytic behaviour of perchlorate complexes and non-electrolytic behaviour of nitrate complexes. All the complexes show normal magnetic behaviour. The IR spectra show the monodenticity of the organic ligand and the presence of ionic perchlorate and coordinated nitrate. The electronic spectra indicate 6-coordination for perchlorate complexes and 9-coordination for nitrate complexes. Thermal studies (TG, DTG and DTA) indicate that the perchlorate complexes are thermally less stable than the nitrate complexes.

Keywords. Complexes ; rare earths ; pyrazolone.

1. Introduction

In earlier communications from these laboratories (Nair *et al* 1975, 1976), we have reported the synthesis and characterization of complexes of lanthanide perchlorates and nitrates with 4-amino antipyrine (i.e., 4-amino, 2,3 dimethyl, 1-phenyl, pyrazol-5-one, abbreviated as AAP). In this communication, we present the results of our studies of the synthesis, spectral and magnetic characteristics, and thermal decomposition behaviour of 18 new complexes of lanthanide perchlorates and nitrates with 3-methyl, 1-phenyl, pyrazol-5-one (abbreviated as MPP). The present ligand MPP differs from AAP in that the amino group in position 4 and methyl group in position 2 (on the N) are missing in MPP.

2. Experimental

2.1. Reagents

MPP was a BDH reagent of LR grade. The lanthanide perchlorates or nitrates were prepared from the oxides (99.9% pure) by the method reported earlier (Nair *et al* 1975, 1976). All the solvents were purified by standard methods (Weissberger *et al* 1956).

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2.2. Preparation of the complexes

A mixture of methanolic solutions of the lanthanide perchlorate (2 mmole) or the nitrate (2 mmole) and the ligand (12.5 mmole for the perchlorate and 6.5 mmole for the nitrate) was heated under reflux for 30 min. The yellow viscous mass obtained on concentration was washed several times with hot benzene to remove the excess ligand. The solid complex separated was dried over P_2O_5 in vacuum.

2.3. Physical methods and analyses

Conductance measurements were made at room temperature ($28 \pm 2^\circ C$) using ELICO type M82T conductivity bridge with dip type cell (type CC-03) and platinum electrodes (cell constant = 1 cm^{-1}). The magnetic susceptibilities were determined by Guoy method at ambient temperature ($28 \pm 2^\circ C$). The IR spectra were taken in KBr pellets on a Perking Elmer 237 IR spectrometer. The electronic spectra were recorded in methanol on Shimadzu double beam spectrophotometer. Thermogravimetric studies were carried out on Dupont thermobalance (heating rate $10^\circ/\text{minute}$; atmosphere: nitrogen).

The lanthanide content in the complexes was determined gravimetrically by the oxalate-oxide method (Kolthoff and Elving 1963) and the perchlorate content by Kurz's method (Kurz *et al* 1958). C, H and N microanalyses were carried out by the Australian Microanalytical Service, Melbourne, Australia (on payment).

3. Results and discussion

All complexes are non-hygroscopic solids. The complexes are soluble in methanol, ethanol, acetonitrile and acetone, but insoluble in benzene, chloroform and carbon tetrachloride. The analytical data (table 1) show that the perchlorate complexes can be represented by $\text{Ln}[(\text{MPP})_6](\text{ClO}_4)_3$ and the nitrate complexes by $\text{Ln}(\text{MPP})_3(\text{NO}_3)_3$.

3.1 Electrical conductance

Electrical conductivity data are presented in table 2. From a comparison of the conductance values of structurally similar complexes (Deacon *et al* 1965; Sathyanarayana and Patel 1967) it is inferred that the perchlorate complexes behave in the fashion of 1:3 electrolytes whereas the nitrate complexes behave more or less like non-electrolytes with partial dissociation due to interaction with the solvent. The perchlorate and nitrate complexes are therefore assigned the general formulæ given above.

3.2 Magnetic properties

The magnetic data are presented in table 2. La and Y complexes are diamagnetic, as is to be expected. It may be seen from table 2 that the observed magnetic moments are generally found to agree with the spin-orbit coupling model theoretical values, with the exception of Sm. It may also be seen that the experimental values agree in every case (including Sm) with the theoretical values calculated from the

Table 1. Analytical data.*

Complex	% Metal	% Anion	% Carbon	% Nitrogen	% Hydrogen
1. La (MPP) ₆ (ClO ₄) ₃	9.52 (9.38)	20.67 (20.15)			
2. Pr (MPP) ₆ (ClO ₄) ₃	9.55 (9.50)	20.40 (20.12)			
3. Nd (MPP) ₆ (ClO ₄) ₃	9.87 (9.72)	19.88 (20.07)			
4. Sm (MPP) ₆ (ClO ₄) ₃	10.23 (10.07)	19.62 (19.88)			
5. Gd (MPP) ₆ (ClO ₄) ₃	10.43 (10.48)	20.26 (19.89)			
6. Tb (MPP) ₆ (ClO ₄) ₃	10.35 (10.59)	19.22 (19.88)			
7. Dy (MPP) ₆ (ClO ₄) ₃	10.54 (10.80)	19.62 (19.83)			
8. Ho (MPP) ₆ (ClO ₄) ₃	10.78 (10.94)	19.80 (19.81)			
9. Y (MPP) ₆ (ClO ₄) ₃	6.34 (6.21)	21.16 (20.85)			
10. La (MPP) ₃ (NO ₃) ₃	16.62 (16.40)		42.46 (42.50)	13.97 (14.88)	3.40 (3.54)
11. Pr (MPP) ₃ (NO ₃) ₃	16.68 (16.59)		41.64 (42.44)	14.28 (14.85)	3.39 (3.53)
12. Nd (MPP) ₃ (NO ₃) ₃	16.96 (16.93)		41.04 (42.44)	14.50 (14.79)	3.49 (3.52)
13. Sm (MPP) ₃ (NO ₃) ₃	17.64 (17.52)		40.27 (41.94)	14.35 (14.68)	3.48 (3.49)
14. Gd (MPP) ₃ (NO ₃) ₃	18.07 (18.18)		41.12 (41.60)	14.36 (14.56)	3.42 (3.47)
15. Tb (MPP) ₃ (NO ₃) ₃	18.30 (18.33)		41.02 (41.53)	14.15 (14.53)	3.68 (3.44)
16. Dy (MPP) ₃ (NO ₃) ₃	18.51 (18.67)		41.17 (41.36)	14.38 (14.47)	3.23 (3.45)
17. Ho (MPP) ₃ (NO ₃) ₃	18.91 (18.89)		40.88 (41.24)	14.15 (14.43)	3.45 (3.44)
18. Y (MPP) ₃ (NO ₃) ₃	11.22 (11.15)		44.22 (45.17)	15.60 (15.81)	3.62 (3.76)

* Calculated values in parenthesis.

Table 2. Electrical conductance, magnetic and thermal data of the complexes.

Complex	Molar conductance*		Magnetic moment (B.M.)	Stability range in TG. (°C)
	Solvent acetonitrile	Solvent nitrobenzene		
1. La (MPP) ₆ (ClO ₄) ₃	350.3	Insoluble	Negligibly low	Ambient up to 140
2. Pr (MPP) ₆ (ClO ₄) ₃	352.2	Insoluble	3.78	Ambient up to 140
3. Nd (MPP) ₆ (ClO ₄) ₃	353.9	Insoluble	3.84	Ambient up to 140
4. Sm (MPP) ₆ (ClO ₄) ₃	358.1	Insoluble	1.83	Ambient up to 140
5. Gd (MPP) ₆ (ClO ₄) ₃	331.8	Insoluble	7.84	Ambient up to 140
6. Tb (MPP) ₆ (ClO ₄) ₃	338.4	Insoluble	9.51	Ambient up to 150
7. Dy (MPP) ₆ (ClO ₄) ₃	344.2	Insoluble	10.87	Ambient up to 150
8. Ho (MPP) ₆ (ClO ₄) ₃	330.9	Insoluble	10.50	Ambient up to 160
9. Y (MPP) ₆ (ClO ₄) ₃	353.5	Insoluble	Negligibly low	Ambient up to 110
10. La (MPP) ₃ (NO ₃) ₃	32.43	0.509	Negligibly low	Ambient up to 200
11. Pr (MPP) ₃ (NO ₃) ₃	29.02	0.401	3.54	Ambient up to 200
12. Nd (MPP) ₃ (NO ₃) ₃	25.55	0.395	3.50	Ambient up to 200
13. Sm (MPP) ₃ (NO ₃) ₃	25.55	0.485	1.72	Ambient up to 200
14. Gd (MPP) ₃ (NO ₃) ₃	26.40	0.602	7.72	Ambient up to 200
15. Tb (MPP) ₃ (NO ₃) ₃	26.04	0.691	9.77	Ambient up to 200
16. Dy (MPP) ₃ (NO ₃) ₃	24.75	0.802	10.31	Ambient up to 200
17. Ho (MPP) ₃ (NO ₃) ₃	21.90	0.672	10.52	Ambient up to 200
18. Y (MPP) ₃ (NO ₃) ₃	25.70	0.664	Negligibly low	Ambient up to 200

* Ohm⁻¹ cm² mole⁻¹: ~ 10⁻³ M solution used.

Van Vleck formula (Van Vleck and Frank 1929). The discrepancy in the case of Sm can be attributed to the fact that the first excited *J* state is sufficiently close to the ground state that this state is appreciably populated at ordinary temperature causing an increase in magnetic moment. This is the reason for the breakdown of the simple spin-orbit coupling model here.

3.3 IR spectra

The IR spectra show interesting differences when compared with those of complexes of AAP (Nair *et al* 1975, 1976). Unlike the ligand AAP, MPP does not show the normal carbonyl frequency in the free ligand. It shows a very strong band at 1610 cm⁻¹ which can be assigned to the carbonyl stretching vibration. This

discrepancy has been attributed (Katritzky and Maine 1964) to the inter-molecular H-bonding in MPP between the C=O and the N-H. The IR spectrum of MPP also shows very broad absorptions at 2640 cm^{-1} and 1840 cm^{-1} characteristic of H-bonding (Katritzky and Maine 1964). The disappearance of these bands and the appearance of new bands around 3000–3200 cm^{-1} (stretching vibration of free N-H) show that H-bonding disappeared on complexation. But there is no appreciable change in carbonyl stretching vibration on complexation. This shows that the H-bond in the free ligand in solid state is about as strong as the metal-ligand bond in the complexes. However, in acetonitrile solutions, the H-bond in the free ligand breaks showing a band at 1705 cm^{-1} , whereas the complexes retain the band at 1610 cm^{-1} . These values indicate a shift of $\sim 95 \text{ cm}^{-1}$ in the $\nu_{\text{C=O}}$ of the complexes. Thus the MPP shows monodenticity in the present complexes through carbonyl oxygen.

The IR spectra of the perchlorate complexes show a strong unsplit band in the range 1095–1115 cm^{-1} , a weak band in the range 935–940 cm^{-1} , and a medium unsplit band in the range 620–635 cm^{-1} , which are not present in the complexes. These bands are due to ν_3 , ν_1 and ν_4 vibrations, respectively, of the uncoordinated perchlorate ion (Hathaway and Underhill 1961).

The IR spectra of the nitrate complexes show strong bands in the range, 1475–1480 cm^{-1} and in the range 1285–1295 cm^{-1} which are not present in the spectrum of the ligand. These bands are attributed to the ν_4 and ν_1 vibrations, respectively, of the coordinated nitrate ion. The magnitude of $\nu_4 - \nu_1$ ranges from 180–195 cm^{-1} in these complexes, which might be in favour of the bidentate character of the C_{2v} nitrate (Curtis and Curtis 1965). Thus in the present complexes the nitrate groups may be bidentate.

3.4. Electronic spectra

The electronic spectra of the ligand and the complexes show a single strong band in the UV region. The band at 40984 cm^{-1} (244 nm) in the ligand is slightly red shifted to 40650 cm^{-1} (246 nm) in the perchlorate complexes and slightly blue-shifted to 41322 cm^{-1} (242 nm) in the nitrate complexes. The band at 26670 cm^{-1} present in the complexes can be assigned to charge transfer transitions.

Karraker observed (Karraker 1967, 1968) that the shape and intensity of hypersensitive bands vary with coordination number and symmetry of the lanthanide ion. From the shape of the hypersensitive ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ transition (around 17200 cm^{-1}) of Nd(III), a co-ordination number of 6 may be assigned to Nd(III) in the complex $[\text{Nd}(\text{MPP})_6](\text{ClO}_4)_3$ and a co-ordination number of 9 in the complex $[\text{Nd}(\text{MPP})_3(\text{NO}_3)_3]$. Similarly from the shape of the hypersensitive ${}^5I_8 \rightarrow {}^5G_6$, 5F_1 transition (around 22300 cm^{-1}) of Ho(III), a coordination number of 6 may be assigned to Ho(III) in the complex $[\text{Ho}(\text{MPP})_6](\text{ClO}_4)_3$ and a coordination number of 9 in the complex $[\text{Ho}(\text{MPP})_3(\text{NO}_3)_3]$. The hypersensitive transitions are sharper and more intense in the nitrate complexes than in the perchlorate complexes. This may be ascribed to the fact that the environment about the Ln(III) ion is less symmetric for nitrate complexes than for perchlorate complexes. Evidently the nitrate complexes have a higher coordination number than the perchlorate complexes.

3.5. Thermal behaviour

It may be seen from table 2 that the perchlorate complexes are thermally stable from ambient temperature to about 140°C. The Ho complex appears to be slightly stabler (up to 160°C) and Y complex appears to be less stable (only up to 110°C). The complexes undergo three decomposition stages. The DTG curves show three peaks, the sharp first peak at ~265°C, the broad second peak at ~360°C and the very broad third peak at ~460°C. These peaks are paralleled respectively by a weak exothermic peak at ~255°C, a strong exothermic peak at ~340°C and a weak broad exothermic peak at ~480°C in DTA. Also the complexes exhibit a weak DTG peak at ~190°C and a weak endothermic peak in DTA at ~190°C which may be due to phase changes accompanying melting and decomposition of the complexes.

The nitrate complexes are thermally stable from ambient temperature to about 200°C. In these complexes the main decomposition takes place in a single stage. The DTG curves show a strong and sharp peak at ~320°C. This peak corresponds to a strong and sharp peak in DTA at ~310°C which has a shoulder in the vicinity, about 30–50° higher than the peak temperature. Also in DTA there is a weak endothermic peak at ~190°C which has no parallel in DTG curves. This may be due to the phase change accompanying melting of the complexes.

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