

## Rare Earth Perchlorate Complexes of 4-(2',4'-Dihydroxyphenylazo)antipyrine

MARIAMMA ABRAHAM and P. K. RADHAKRISHNAN\*

School of Chemical Sciences, Mahatma Gandhi University, Ettumanoor, Kottayam-686 631

Manuscript received 2 March 1990 revised 6 August 1990, accepted 12 December 1990

In an earlier communication<sup>1</sup>, we reported the nitrates of rare earth complexes with the azodye derived from 4-aminoantipyrine, viz. 4-(2',4'-dihydroxyphenylazo)antipyrine (abbreviated as H-RAP) (Fig. 1) acting as a neutral bidentate ligand coordinating through the carbonyl oxygen, and one of the nitrogens of the azo group and the nitrate group is coordinated monodentately. In the present communication, we report the preparation and characterisation of rare earth perchlorate complexes of H-RAP. Compared to the nitrate group which is generally coordinated to the rare earth ion, the perchlorate group prefers to remain uncoordinated. Hence in such complexes, the donor sites are contributed fully by H-RAP and the possibility of phenolic (deprotonated)<sup>2</sup> oxygen coordination is enhanced to account for the steric effect.

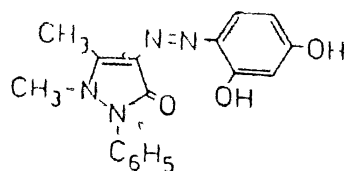


Fig. 1

### Experimental

The perchlorates of La, Pr, Nd, Sm, Gd, Dy and Y were prepared by dissolving the respective oxides (99.9% pure) in 60% perchloric acid and crystallising out the salts by evaporating the solution on a steam-bath. The ligand H-RAP was prepared as reported<sup>1</sup>.

**Preparation of complexes:** Rare earth perchlorate (2 mmol) was dissolved in acetone (15 ml). H-RAP (4 mmol) was suspended in acetone (150 ml), refluxed on a water-bath and the salt solution was then added dropwise to it. The resulting solution was further refluxed for 2 h, cooled to room temperature and filtered. The filtrate was concentrated to a viscous mass which was further stirred well with the addition of diethyl ether. The precipitated complex was recrystallised from acetone and dried under reduced pressure over phosphorus(v) oxide.

The metal content of the complexes was determined by the method of 'peaceful pyrolysis'<sup>2</sup> and the perchlorate ion was determined by the Kurz method<sup>3</sup>. The physical methods used in the present investigation were the same as reported earlier<sup>1</sup>. The molar conductance of the complexes in nitrobenzene, acetonitrile and methanol was determined at room temperature ( $28 \pm 2^\circ$ ) using a Toshniwal CL01.02A conductivity bridge with a dip-type

conductance cell (CL01/01) and platinised platinum electrodes (cell constant =  $0.81 \text{ cm}^{-1}$ ).

### Results and Discussion

The analytical data (Table 1) of the complexes indicate 1 : 2 (metal-ligand) stoichiometry. All the complexes are intensely coloured (brownish red) non-hygroscopic solids. They are soluble in polar solvents like acetone, acetonitrile, methanol, ethanol and nitrobenzene, and insoluble in solvents of low polarity like benzene, carbon tetrachloride and chloroform. The molar conductivities of the complexes in nitrobenzene (24–23), acetonitrile (121–142) and methanol (113–126  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) are in the ranges expected for 1 : 1 electrolytes<sup>4</sup>. Thus the complexes may be formulated as  $[\text{Ln}(\text{RAP})_2]\text{ClO}_4$  (where Ln = La, Pr, Nd, Sm, Gd, Dy and Y).

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compd.	M. p. °C	Analysis % : Found/(Calcd.)		$\mu_{\text{eff}}$ B M.
		Metal	$\text{ClO}_4$	
$[\text{La}(\text{RAP})_2]\text{ClO}_4$	200	15.60 (15.67)	11.33 (11.25)	0.00
$[\text{Pr}(\text{RAP})_2]\text{ClO}_4$	230	15.88 (15.90)	11.38 (11.22)	3.44
$[\text{Nd}(\text{RAP})_2]\text{ClO}_4$	235	16.33 (16.21)	11.20 (11.18)	3.51
$[\text{Sm}(\text{RAP})_2]\text{ClO}_4$	225	16.70 (16.75)	11.19 (11.08)	1.61
$[\text{Gd}(\text{RAP})_2]\text{ClO}_4$	200	17.42 (17.42)	11.07 (10.98)	7.79
$[\text{Dy}(\text{RAP})_2]\text{ClO}_4$	230	17.59 (17.72)	11.10 (10.98)	10.50
$[\text{Y}(\text{RAP})_2]\text{ClO}_4$	220	10.59 (10.65)	11.83 (11.92)	0.00

The ir spectra indicate that the medium broad band around  $3350 \text{ cm}^{-1}$  in the ligand assignable to the stretching vibration of free OH group (at position-4') is retained in the complexes showing that the phenolic group at position-4' is not coordinated. However, the broad band at  $2900 \text{ cm}^{-1}$  in H-RAP due to the H-bonded phenolic group (at position-2') is absent in the complexes indicating that the phenolic group at position-2' is deprotonated and the resulting  $\text{O}^-$  ion is coordinated to the rare earth ion<sup>5-7</sup>. The strong carbonyl stretching band at  $1660 \text{ cm}^{-1}$  in H-RAP is shifted to lower frequency (about  $1590 \text{ cm}^{-1}$ ) and coupled with the band due to ring vibrations of pyrazolone and phenyl rings, which is thereby broadened and hence the carbonyl oxygen is coordinated<sup>1</sup>. A strong band at  $1460 \text{ cm}^{-1}$  in H-RAP assignable to the stretching vibration of the azo group is shifted to higher frequency (about  $1480 \text{ cm}^{-1}$ ) with enhanced intensity. This shows that one of the nitrogens (the nitrogen bonded to the phenyl ring) is coordinated<sup>8,9</sup>. In the absence of facilities of crystal structure data, it is impossible to confirm which nitrogen is coordinated. However, out of the two nitrogens, the nitrogen bonded to the phenyl group is coordinated. This is because the

deprotonated phenolic oxygen is coordinated to the rare earth ion first (in preference to carbonyl oxygen) due to the strong ionic interaction towards the positively charged metal which is followed by the stable five-membered chelate formation with the nitrogen. The IR spectra of the complexes also show a strong unsplit band around  $1080\text{ cm}^{-1}$  and a medium unsplit band around  $620\text{ cm}^{-1}$ , assignable to the  $\nu_3$  and  $\nu_4$  vibrations, respectively, of ionic perchlorate. Therefore, the perchlorate is not coordinated<sup>10</sup> as confirmed by conductance studies. Hence a coordination number of six may be assigned to the rare earth ion in these complexes.

The magnetic moment of these complexes (Table 1) show little variation from Van Vleck values suggesting that the  $4f$ -electrons, well shielded by the  $5s^25p^6$  octet, play only a small role in bonding<sup>11</sup>.

The electronic spectra indicate that all the absorptions due to the  $f-f$  transition of the rare earth ions in the visible region are obscured in the present complexes by the strong absorption of the ligand and by the very broad charge transfer band spreading over the whole visible region. Hence the electronic spectra are not very helpful in the investigations of transitions involving the  $f$ -electrons of the rare earth ion<sup>1</sup>.

The present complexes are of industrial as well as physiological applications. It is interesting to note that the rare earth perchlorate complexes of H-RAP are soluble in common polar solvents whereas the corresponding nitrate complexes are insoluble. Thus the anion change will effect the dye application of these complexes on fibres. Also, these complexes can be recommended to study the change in the physiological action of H-RAP on complexation with the rare earth ions.

## References

- 1 P K RADHAKRISHNAN, *J Less-Common Met*, 1985, **107**, 45
- 2 M. R. G NAIR, M J KURIEN and C P PRABHAKARAN, *Talanta*, 1981, **28**, 395.
- 3 E KURZ, G KOBER and M BERL, *Anal Chem*, 1983, **30**, 1958
- 4 W T GRARY, *Coord Chem Rev*, 1971, **7**, 81
- 5 H. D COBLE and H F HOLTZCLAW, *J Inorg Nucl. Chem*, 1974, **36**, 1048
- 6 J E KOVACIC *Spectrochim Acta, Part A*, 1967, **23**, 183
- 7 L DORETTI, S SITRAN, F MADALOSSO, G BANDOLI and G. PAOLUCCI, *J. Inorg Nucl. Chem*, 1980, **42**, 1060
- 8 K J MORGAN, *J Chem Soc.*, 1961, 2151.
- 9 M R G NAIR and C P PRABHAKARAN, *J Inorg. Nucl Chem*, 1981, **43** 3390
- 10 B J HATHAWAY and A E UNDERHILL, *J Chem. Soc*, 1961, 3091
- 11 J. H VAN VLECK and N. FRANK, *Phys Rev.*, 1929, **34**, 1497

## Stability Constants of Mixed Ligand Chelates of Lanthanum(III), Praseodymium(III) and Neodymium(III) with NTA, HEDTA, CYDTA and DTPA as Primary Ligands and some Polymethylene Dicarboxylic Acids as Secondary Ligands

B. D. KALE and T. H. MHASKE

Department of Chemistry,  
Government Vidarbha Mahavidyalaya, Amravati-440 604  
Manuscript received 18 September 1989, revised 10 July 1990,  
accepted 22 August 1990

**L**ANTHANUM(III), praseodymium(III) and neodymium(III) with nitrilotriacetic acid (NTA), *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA), cyclohexanediaminetetraacetic acid (CYDTA) and diethylenetriaminepentaacetic acid (DTPA) as primary ligands and polymethylenedicarboxylic acids pimelic acid (PMA), suberic acid (SUA), azelic acid (AZA) and sebacic acid (SEA) as secondary ligands have been investigated at 25, 35 and 45° at fixed ionic strength  $0.2\text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ) by potentiometric method and the effects of these mixed ligand chelates on the germination, survival and seedling height of barley plants (*Jav* or *Hordeum vulgare*) was also studied.

## Experimental

Solutions of metal nitrates  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Indian Rare Earths Ltd.) were prepared in nitric acid. The metal contents were estimated by spectrophotometric<sup>2,3</sup> and gravimetric<sup>4</sup> methods. Solutions of primary ligands NTA,  $\text{Na}_2\text{CYDTA}$ , DTPA (B.D.H.), HEDTA (Sigma) and secondary ligands PMA, SUA, AZA, SEA were prepared in oxygen-free double-distilled water.

The experimental details for potentiometric measurement and computational methods were the same as described earlier<sup>5</sup>. The results are presented in Table 1.

## Results and Discussion

The values of first and second dissociation constants are found to be very close in case of all four polymethylenedicarboxylic acids and indicate that these dicarboxylic acids are moderately acidic in nature. The nature of complex formation equilibria whether stepwise or simultaneous was investigated according to the method suggested by Carry and Martell<sup>6</sup>. The primary ligands NTA, HEDTA, CYDTA and DTPA are considered to occupy four, six and eight coordination positions around lanthanide ions. The secondary ligands PMA, SUA, AZA and SEA are penta-, hexa-, hepta- and octamethylenedicarboxylic acids respectively and act as bifunctional oxygen donors and bidentate in mixed ligand chelate formations. The trends in stabilities of mixed ligand chelates with respect to