

## STUDIES ON LANTHANIDE MIXED COMPLEXES

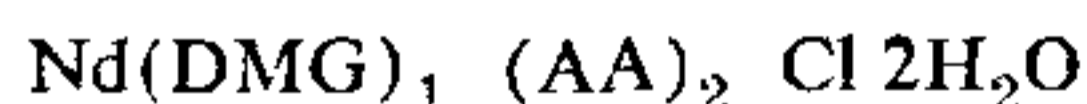
J. N. NANDAPURKAR\* AND V. RAMACHANDRA RAO\*\*

Department of Chemistry, Visvesvaraya Regional College of Engineering, Nagpur 440 011

**M**IXED chelates of lanthanide ions are comparatively of recent origin. Several lanthanide diketone mixed complexes were reported<sup>1</sup>. The ligands used were either picolinic acid, quinaldinic acid or dipyriddy. Hart and Laming<sup>2</sup> prepared mixed samarium complex with 1, 10 phenanthroline and acetylacetone. Rohatgi and Sen Gupta<sup>3</sup> have extended these studies further and prepared several lanthanide mixed complexes of the type Ln (Phen)<sub>2</sub> (Sal)<sub>3</sub>, where Phen = 1, 10, phenanthroline and Sal — salicylate.

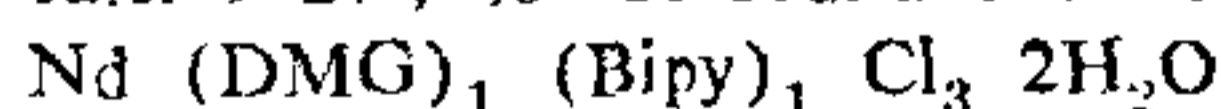
This communication details the preparation and spectral studies of Y, La, Pr, Nd, Sm, Gd, Dy mixed chelates using dimethylglyoxime as primary ligand and bipyridyl and anthranilic acid as secondary ligands. The thermal analysis of neodymium simple and mixed complexes is also reported.

The simple lanthanide dimethylglyoximates were prepared by adopting the procedure of Rao *et al.*<sup>4</sup>. The mixed complexes were prepared adopting the procedure of Vasireddi<sup>5</sup>. In all the mixed complexes the excess ligand was washed with ether. The complexes were vacuum dried for 48 hours and analysed for metal, nitrogen and anion. The analytical data indicated that each lanthanide ion is attached to one mole of dimethylglyoxime and two moles of anthranilic acid and in bipyridyl mixed complexes each lanthanide ion is attached to one mole of dimethylglyoxime and one mole of bipyridyl. Analysis of one lanthanide complex in each case is given below :



% M found 23.67 calc. 23.89 ; % N. found 9.15

calc. 9.27 ; % Cl found 5.74 calc. 5.88



% M found 26.25 calc. 26.67 ; % N. found 10.12  
calc. 10.35 ; % Cl found 19.20 calc. 19.69

Where DMG = dimethylglyoxime ; AA = anthranilic acid ion and BiPy = 2, 2' BiPyridyl.

### RESULTS AND DISCUSSION

Observations in the ultraviolet region are normally subject to two limitations : (i) the sparingly soluble nature of complexes in solvents transparent at this

region, (ii) and the high absorption of the ligands compared to the metal ions. Hence one can look for band shifts and intensity alterations of the ligand alone. In some cases the total disappearance of the ligand bands is also observed. In this investigation in the several mixed complexes only two band maxima are located. The 250 nm band of anthranilic acid is not located in the mixed complexes. In the dimethylglyoxime bipyridyl mixed complexes the characteristic band of dimethylglyoxime was not located. However, there is a reasonable intensification of absorption in all the complexes. The log  $\epsilon$  values at different absorption maxima of several lanthanide mixed complexes investigated are in the range 3.90–4.95.

A study of the visible spectra of Pr, Nd, Sm complexes indicates that the characteristic bands of Pr<sup>3+</sup> ion are located with intensification of absorption in its dimethyl glyoxime-anthranilate. It is also observed that the 485 nm band is split into two inflections and located at 475 nm (log  $\epsilon$  = 1.03) and 485 nm (log  $\epsilon$  = 0.94). In the dimethylglyoxime bipyridyl mixed complex only two bands are located at 450 nm (log  $\epsilon$  = 1.50) and 487 nm (log  $\epsilon$  = 1.74). In neodymium dimethylglyoxime-anthranilate only two bands are located at 527 nm (log  $\epsilon$  = 0.93) and 487 nm (log  $\epsilon$  = 1.07) whereas in its bipyridyl mixed complex only one band is located at 585 nm (log  $\epsilon$  = 1.24). The characteristic Sm<sup>3+</sup> ion band is located only in the dimethylglyoxime bipyridyl mixed complex at 405 nm (log  $\epsilon$  = 1.02).

In a study of the infrared spectra of dimethylglyoxime anthranilates and bipyridyl mixed complexes shifts in the O–H stretch region and N–H stretch region have been observed. The shift of N–H str. is normally to a lower frequency and it indicates an N→M dative bond. Such a lowering was observed by Rao *et al.*<sup>6</sup> in simple lanthanide anthranilates. Three bands in the region 1510–1625 cm<sup>-1</sup> were observed in the anthranilic acid mixed complexes and the two higher frequency peaks could be attributed to C=C and the third to the asymmetric COO stretching vibration<sup>7</sup>.

The characteristic bipyridyl bands around 760 and 745 cm<sup>-1</sup> which are due to the out of plane bending of the identical groups of four hydrogens are either split into two inflections or shifted in their position

\* Lecturer in Chemistry, Institute of Science, Nagpur.

\*\* Correspondence with this author.

in the mixed complexes. The spectral data of Pr and Nd mixed complexes is detailed in Table I. and visible spectra and to the Department of Chemistry, Osmania University, Hyderabad, for the infrared

TABLE I

*Infrared absorption bands (cm<sup>-1</sup>) of Praseodymium and Neodymium mixed complexes*

| DMG     | AA                                       | Pr (III)<br>complex                      | Nd (III)<br>complex                      | Assignment   |
|---------|--|--|--|--|
|         | 3700 sl                                  |  |  |  |
| 3400 b  | 3550 bl                                  | 3650 sh<br>3350 bl                       | 3300 } bs<br>3200 }                      | OH str<br>N—H str of anthranilic<br>acid                             |
| 1620 bl | 1675 sm<br>1625 sh<br>1600 sm<br>1580 sh | 1610 sm<br>1575 sl<br>1550 sl<br>985 sm  | 1610 ss<br>1575 sm<br>1510 ss<br>980 sm  | C=O str.<br>C=N str.<br>Asymmetric CCO <sup>-</sup> str.<br>N—O str. |
| 978 ss  |  |  |  |  |
| DMG     | Bipy                                     | Pr (III)<br>complex                      | Nd (III)<br>complex                      | Assignment   |
| 3400 b  | 3050 low                                 | 3300 br                                  | 3300 bs                                  | O—H str.   |
| 1620 bl | 1600 ss<br>1580 ss                       | 1625 sh<br>1600 ss<br>1580 br<br>1500 sm | 1625 sh<br>1600 ss<br>1590 sm<br>1500 sm | C=N str.<br>BiPyridyl bands  |
|         | 1470 ss                                  | 1480 sm                                  | 1480 ss                                  | BiPyridyl bands  |
|         | 1260 ss                                  | 1440 ss<br>1245 sm                       | 1445 ss<br>1250 sl                       | Orthosubstituted Pyridine<br>ring                                    |
| 978 ss  | 1000 sm<br>760 bs<br>745 sm              | 985 sm<br>765 ss<br>740 ss<br>715 l      | 990 sm<br>770 ss<br>740 ss<br>715 sl     | N—O str.<br>Out of plane bending of<br>ring hydrogens                |

DMG=Dimethylglyoxime.

AA=Anthranilic acid ion.

BiPy=2, 2' BiPyridyl.

The thermal analysis of simple neodymium, dimethylglyoximate and the mixed complexes indicated dehydration around 160° C. The organic part is eliminated in the mixed complexes in stages. Both in the simple and mixed complexes there is an intermediate halide formation and this can be postulated from weight loss calculations. Such a halide formation was also postulated in a study of thermal analysis of transitional metal pyridine complexes<sup>8</sup> and also in the dysprosium dimethyl glyoximate<sup>9</sup>. The sesquioxide is formed between 600–900° C in all the complexes.

#### ACKNOWLEDGMENT

One of the authors (J. N. N.) is grateful to Dr. V. M. Dokras, for the facilities and to Drs. A. Gopalakrishna and V. V. Deshpande, for their keen interest. He is also grateful to the Director, J.B. Research Institute, Wardha, for the ultraviolet

spectra. He is grateful to Prof. M. N. Sastry, Andhra University, for the thermal analysis.

1. Dutt, N. K. and Upadhaya, S., *J. Inorg. Nucl. Chem.*, 1967, 29, 1368.
2. Hart, J. A. and Laming, F. P., *Ibid.*, 1964, 26, 519.
3. Rohatgi, K. K. and Sen Gupta, S. K., *Ibid.*, 1970, 32, 2247.
4. Galgali, V. H., Ramachandra Rao, V. and Khanolkar, D. D., *Ind. J. Chem.*, 1969, 7, 825.
5. Vasireddi, S. P., "Studies on rare earth complexes," *Ph.D. Thesis*, Nagpur University, 1974, p. 103.
6. Deshpande, Y. H. and Ramachandra Rao, V., *Ind. J. Chem.*, 1969, 7, 1051.
7. Hill, A. G. and Curran, C., *J. Phys. Chem.*, 1966, 64, 1519.
8. Brown, H., *Proc. Soc. Analyst. Chem.*, 1971, 8 (8), 169.
9. Vasireddi, S. P., *Ph.D. Thesis*, Nagpur University, 1974, p. 375.