

$\text{Mo}_2\text{O}_8^{4+}$ species is quite common as explained by Cotton and Curtis¹¹. The feeble paramagnetism of complex $[\text{Mo}_2\text{O}_8(\text{PBzH})_2\text{Br}_4]$ can be attributed to bulky volume of the bonded ligand molecule. In

this case, the angle of twist of $\text{Mo}-\text{O}-\text{Mo}$ bond may be greater than $\pi/4$ due to bulky volume of the bromine which causes incomplete pairing of spins of $\text{Mo}_2\text{O}_8^{4+}$ species¹¹.

Both mono- and di-nuclear complexes display electronic reflectance bands at 13 330-14 300, 19 610-20 800 and 22 390-24 400 cm^{-1} attributable to ${}^2\text{B}_2 \rightarrow {}^2\text{E}(\text{I})$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{E}(\text{II}) + \text{C}-\text{T}$ transitions, respectively, similar to ligand field bands of octahedral molybdenum(V) complexes¹²⁻¹⁴.

Ir spectra: From the studies of ir spectra of PBzH and its complexes with metal ions, the coordination of the ligand has been suggested from tertiary pyridine nitrogen of benzimidazole part^{15,16}. The N-H stretching mode of PBzH (3 249 cm^{-1}) is shifted to lower frequency only by 5-30 cm^{-1} in complexes but raised to higher frequency in complex salt $(\text{PBzH})_2\text{H}_2[\text{MoOCl}_5]$ by 30 cm^{-1} suggesting that NH nitrogen is not involved in coordination. The $\nu_{\text{C-N}}$ of PBzH (1 638 cm^{-1}) is shifted to lower frequency in complexes suggesting the coordination of ligand through tertiary pyridine nitrogen of benzimidazole part¹⁶. The pyridine ring breathing mode of vibration of ligand (996 cm^{-1}) is raised to higher frequency (5-25 cm^{-1}) which has been taken to be diagnostic of the coordinated pyridine nitrogen^{15,16}.

The complexes $(\text{PBzH})_2\text{H}_2[\text{MoOX}_5]$ and $[\text{MoO}(\text{PBzH})\text{X}_2]$ ($\text{X}=\text{Cl}$ or Br) display strong and sharp $\nu_{\text{Mo=O}}$ stretch at 990-975 cm^{-1} while the dinuclear complexes $[\text{Mo}_2\text{O}_8(\text{PBzH})_2\text{X}_4]$ ($\text{X}=\text{Cl}$ or Br) exhibit $\nu_{\text{Mo=O}}$ as strong and broad band at ~ 965 cm^{-1} . The observed order of wave number and nature of $\nu_{\text{Mo=O}}$ vibration are in good agreement with $\nu_{\text{Mo=O}}$ occurring in oxomolybdenum(V) complexes containing MoO^{8+} and $\text{Mo}_2\text{O}_8^{4+}$ species^{17,18}. Due to a number of ligand vibrations

between 850 and 650 cm^{-1} the $\text{Mo}-\text{O}-\text{Mo}$ vibration could not be located definitely (the region 800-650 cm^{-1} is the range of vibration^{17,18}). In far-infrared region, the ligand and its complexes display a number of bands between 600 and 400 cm^{-1} . The new ir bands located at 370-300 cm^{-1} have been tentatively assigned to $\nu_{\text{Mo-N}}$ and $\nu_{\text{Mo-X}}$ in these complexes¹⁹.

References

1. S. P. GHOSH and L. K. MISHRA, *Inorg. Chim. Acta*, 1973, 7, 547.
2. S. P. GHOSH, P. BHATTACHARJEE and L. K. MISHRA, *J. Indian Chem. Soc.*, 1974, 51, 47.
3. S. P. GHOSH, P. BHATTACHARJEE, L. DUBBY and L. K. MISHRA, *J. Indian Chem. Soc.*, 1977, 54, 230.
4. S. P. GHOSH and K. M. PRASAD, *J. Indian Chem. Soc.*, 1979, 56, 660.

5. S. P. GHOSH and A. MISHRA, *J. Indian Chem. Soc.*, 1975, 52, 791.
6. R. L. DUTTA and T. RAY, *J. Indian Chem. Soc.*, 1981, 58, 709 and references therein.
7. T. A. GEORG and C. D. SELBOLD, *J. Am. Chem. Soc.*, 1972, 94, 6859.
8. P. O. H. MITCHELL, *Quart. Rev.*, 1966, 20, 103.
9. H. K. SAHA and M. O. HALDAR, *J. Inorg. Nucl. Chem.*, 1971, 33, 3719; 1972, 34, 3097.
10. A. KAY and P. O. H. MITCHELL, *J. Chem. Soc., Dalton Trans.*, 1973, 1388; 1970, 2411.
11. F. A. COTTON and N. F. CURTIS, *Inorg. Chem.*, 1965, 4, 241.
12. A. SAZATINI and J. BERTINI, *Inorg. Chem.*, 1966, 5, 204.
13. R. N. JOWITT and P. C. H. MITCHELL, *J. Chem. Soc.*, 1970, 1702.
14. C. R. HARR and H. B. GRAY, *Inorg. Chem.*, 1962, 1, 368.
15. T. J. LANE, I. NAKAGAWA, J. L. WALTER and A. J. KANDATHIL, *Inorg. Chem.*, 1962, 1, 267.
16. B. CHISWELL, F. LIONS and B. S. MORRIS, *Inorg. Chem.*, 1964, 3, 110.
17. R. M. WING and K. P. CALLAHAN, *Inorg. Chem.*, 1969, 8, 871.
18. C. M. FRENCH and J. H. GARSIDE, *J. Chem. Soc.*, 1962, 2006.
19. K. NAKAMOTO, "The Infrared Spectra of Inorganic and Coordination Compounds", Wiley Eastern, New Delhi, 1967.

Studies on Quaternary Complexes of some Rare Earth Metals

A. S. GAHLAUT, BEENA CHATURVEDI

and

R. C. SHARMA*

Department of Chemistry, Agra University, Agra-282 004

Manuscript received 23 September 1985, revised 25 March 1986, accepted 23 April 1986

OUR recent studies¹⁻³ on quaternary complex formation of lanthanide ions indicated that inspite of being high electropositive in nature, the lanthanides are capable of extending their coordination sphere to acquire an unusual coordination number, greater than six. The present paper includes our extended studies on 1:1:1:1 Ln^{III} -NTA/EDTA/CDTA-SUA-PDA quaternary systems which have not yet been studied potentiometrically.

Experimental

Solutions of all the chemicals (A. R., B. D. H / E. Merck) were prepared in double-distilled water. Standard solutions of lanthanide nitrates were prepared and standardised^{4,5}. Solutions of di- and tri-potassium salts of NTA and EDTA/CDTA, respectively, were prepared by dissolving their calculated amounts in the required volume of potassium hydroxide. The concentrations of these solutions were further checked potentiometrically against 0.1 M KOH solution. All other solutions were prepared by direct-weighing method.

A Toshniwal CL46 digital pH meter with electrodes assembly was used and standardised

against (0.05 M) potassium hydrogen phthalate solution at $15 \pm 1^\circ$. The ionic strength (μ 0.1 M KNO_3) of the solution was maintained constant. The pH values were plotted against m (mole of base added per mole of metal ion or ligand) Fig. 1.

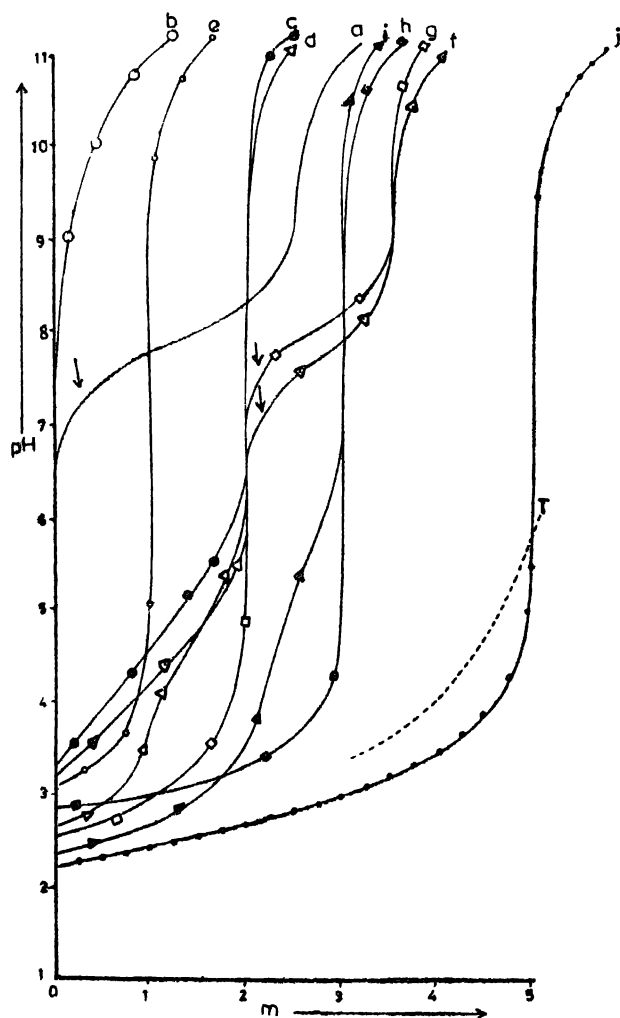


Fig. 1. System 1:1:1:1 La^{III} -CDTA-SUA-PDA: (a) $\text{La}(\text{NO}_3)_3$ (0.025 M), (b) K_2CDTA (0.025 M), (c) SUA (0.025 M), (d) PDA (0.025 M), (e) 1:1 La^{III} (0.02 M) + CDTA (0.025 M), (f) 1:1 La^{III} (0.025 M) + SUA (0.025 M), (g) 1:1 La^{III} (0.025 M) + PDA (0.025 M), (h) 1:1:1 La^{III} (0.025 M) + CDTA (0.025 M) + SUA (0.025 M), (i) 1:1:1 La^{III} (0.025 M) + CDTA (0.025 M) + PDA (0.025 M), (j) 1:1:1:1 La^{III} (0.025 M) + CDTA (0.025 M) + SUA (0.025 M) + PDA (0.025 M); initial volume = 50 ml, $\text{KOH} = 0.1$ M, T = theoretical composite curve, (\rightarrow) = appearance of precipitate.

The ionisation constants (Table 1) of ligands were calculated by the method of Chabereck and Martell⁶ and the formation constants (Table 1) of the resulting quaternary species by the method of Ramamoorthy and Santappa⁷.

Results and Discussion

A representative pH-titration curves for the 1:1, 1:1:1 and 1:1:1:1 mixtures of Ln^{III} , (NTA/

TABLE 1—PROTON-LIGAND CONSTANTS AND FORMATION CONSTANTS OF M^{III} -NTA/EDTA/CDTA-SUA-PDA QUATERNARY COMPLEXES (M = La, Pr, Nd)

Constant	SUA	PUA	K_2NTA	K_2EDTA	K_2CDTA
pK_1^{H}	3.96	2.40	9.86	9.81	10.13
pK_2^{H}	5.44	4.80	—	—	—
			La ^{III}	Pr ^{III}	Nd ^{III}
$\log K_{\text{M-NTA-SUA-PDA}}^{\text{M}}$			15.62	15.72	15.84
$\log K_{\text{M-EDTA-SUA-PDA}}^{\text{M}}$			15.95	16.02	16.09
$\log K_{\text{M-CTDA-SUA-PDA}}^{\text{M}}$			16.18	16.34	16.39

EDTA/CDTA), SUA, PDA is shown in Fig. 1. An initial lowering in the buffer region right from beginning as compared to that exhibited by the curves representing binary and ternary systems followed by an inflection at $m = 5$, may be correlated to the simultaneous attachment of all the three ligands to the metal ion, contributing one proton from $\text{K}_2\text{NTA}/\text{K}_2\text{EDTA}/\text{K}_2\text{CDTA}$ and two each from SUA and PDA forming 1:1:1:1, Ln^{III} -(NTA/EDTA/CDTA)-SUA-PDA quaternary species in solution.

The orders of the formation constant ($\log K_{\text{MLL}'\text{L}''}$) have been found to be $\text{La}^{\text{III}} < \text{Pr}^{\text{III}} < \text{Nd}^{\text{III}}$ for the lanthanide ions, and $\text{NTA} < \text{EDTA} < \text{CDTA}$ for the aminopolycarboxylic acids, arising out of decreasing size and increasing ionic potential (charge/radius ratio) of the lanthanide ions with the increase of atomic number. The increased stability of CDTA in comparison to EDTA complexes (as both the ligands being hexadentate), is probably due to the extra-stabilisation caused by the presence of an aryl ring in CDTA.

Acknowledgement

The authors feel grateful to Prof. K. N. Mehrotra, Agra University, and Prof. J. P. Tandon, Rajasthan University, Jaipur, for facilities and interest.

References

- P. O. DWIVEDI, S. P. TRIPATHI and R. O. SHARMA, *J. Indian Chem. Soc.*, 1984, **61**, 23.
- P. O. DWIVEDI, S. P. TRIPATHI and R. O. SHARMA, *Ann. Soc. Sci. Bruxelles*, 1983, **97**, 11.
- R. KUMAR, R. O. SHARMA and G. K. CHATURVEDI, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2503.
- S. P. TRIPATHI, G. K. CHATURVEDI and R. O. SHARMA, *Zh. Chem.*, 1978, **109**, 283.
- M. A. TISHCHENKO, I. I. ZHEITVAI and N. S. POLUREKTOV, *Zh. Neorg. Khim.*, 1974, **19**, 1793.
- S. CHABERCK and A. E. MARTELL, *J. Am. Chem. Soc.*, 1952, **74**, 5052.
- S. RAMAMOORTHY and M. SANTAPPA, *Indian J. Chem.*, 1971, **9**, 381.