## Notes

## REFERENCES

- 1. J. T. Spence, Coord. Chem. Rev. 4, 475 (1969).
- 2. G. N. Schrauzer, Advan. Chem. Ser., No. 100, 1, (1971).
- R. C. Bray, P. F. Knowles, L. S. Meriwether, In *Magnetic Resonance in Biological Systems* (Edited by A. Ehrenberg, B. G. Malmström and T. Vänngård), p. 249. Pergamon Press, Oxford (1967).
- H. Beinert and W. H. Orme-Johnson, In Magnetic Resonance in Biological Systems, (Edited by A. Ehrenberg, B. G. Malmström and T. Vänngård) p. 221. Pergamon Press, Oxford (1967).
- A. Nason, In *The Enzymes* (Edited by P. D. Boyer, H. Lardy and K. Myrback), Vol. 7, p. 587. Academic Press, New York (1963).
- 6. K. B. Taylor, J. Biol. Chem. 244, 171 (1969).
- 7. A. Kay and P. C. H. Mitchell, Nature 219, 267 (1968).
- 8. A. Kay and P. C. H. Mitchell, J. Chem. Soc. (A), 2421 (1970).
- 9. L. R. Melby, Inorg. Chem. 8, 349 (1969).

- 10. J. R. Knox and C. K. Prout, Acta Crystallogr. B, 25, 1857 (1969).
- G. N. Schrauzer and P. A. Doemeny, J. Am. Chem. Soc. 93, 1608 (1971).
- 12. G. N. Schrauzer, P. A. Doemeny, G. W. Kiefer and R. H. Frazier, J. Am. Chem. Soc. 94, 3604, 7378 (1972).
- G. N. Schrauzer, P. A. Doemeny, G. W. Kiefer and H. Kisch, J. Am. Chem. Soc. 95, 5582 (1973).
- G. N. Schrauzer, G. W. Kiefer, K. Tano and P. A. Doemeny, J. Am. Chem. Soc. 96, 641 (1974).
- P. Souchay, M. Cadiot, M. Lamache-Duhameaux, Compt. Rend. Acad. Sci. Paris 262, 1524 (1966).
- 16. M. Lamache-Duhameaux, Rev. Chim. Miné. 5, 459 (1968).
- P. Souchay and B. Viossat, Bull. Soc. Chim. (France) 3, 892 (1970).
- M. Lamache-Duhameaux, J. Inorg. Nucl. Chem. 38, 1979 (1976).

J. inorg. nucl. Chem., 1977, Vol. 39, pp. 2083-2084. Pergamon Press. Printed in Great Britain

## Some lanthanide complexes of the conjugate base of 3-phenyl-5-methyl-1-hydroxypyrazole-2oxide

(Received 6 April 1977)

Previously we have reported the preparation and characterization of the transition metal ion complexes of the title liagand[1]. Of interest in that series was the inability of the trivalent metal ions (i.e. Cr(III) and Fe(III) to form the tris complexes with all ligands bound in a bidentate manner. The Cr(III) complex possessed one bidentate and two monodentate ligands with two water molecules completing its coordination sphere while the Fe(III) complex was considered to have two bidentate, one monodentate and one aquo ligand in its coordination sphere. For this reason it seemed worthwhile to see whether the larger trivalent lanthanide ions were capable of forming the completely chelated tris complexes and, furthermore, determining the maximum coordination number achieved by the metal ion with these sterically bulky ligands. We report here preparation and characterization of six representative compounds.

The lanthanide complexes were prepared and isolated as previously reported[1] except for the Er(III) complex. This complex appeared to interact with diethyl ether and was dried in a vacuum oven after washing with methanol. The partical elemental analyses of the isolated compounds as performed by Microanalytics. Wilmington, Delaware along with molar conductivities in DMF are presented in Table 1. The colors of the complexes (i.e. Eu, Er) are identical in shade and intensity to the colors of their respective perchlorate salts. As can be seen from Table 1 the first five complexes are isolated with one mole of water in addition to the three ligands, while the smaller erbium ion yielded an anhydrous solid with three ligands. DSC curves of the complexes containing a mole of water showed no evidence for the loss of the mole of water prior to decomposition or melting. It is interesting to note that  $ErL_3$  and  $TbL_3(H_2O)$  (m.p. 190 and 218°C, respectively) have m.ps while the earlier lanthanide compounds of this series gradually decompose. The FeL<sub>3</sub>(H<sub>2</sub>O), reported on previously[1], melted at 155°C indicating a more covalent nature with increasing hardness of the metal ion.

The molar conductivities measured in DMF are in the range attributed to 1:1 electrolytes[2]. This is likely due to partial decomposition in this solvent in that, with the exception of the erbium compound, the solids are only slightly soluble in other solvents generally used for conductivity determinations[2]. The erbium compound has molar conductivities of 180.3 (acetoni-trile), 125.5 (nitromethane) and 21.9 (nitrobenzene)  $\Omega^{-1}$  cm<sup>2</sup> mole<sup>-1</sup> which can be considered to be indicative of 1:1, 1:2 and 1:1 electrolytic behavior, respectively. Solvation and apparently, substitution, must be easier for what appears to be a 6-coordinate complex than for the rest of the solids which are probably 7-coordinate.

The IR spectral results shown in Table 2 yield further in-

Table 1. Partial elemental analyses and molar conductivities  $(\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1})$ for some lanthanide complexes of the conjugate base of 3-phenyl-5-methyl-1hydroxypyrazole 2-oxide (L)

	Calculated (%)			Found (%)			$\Lambda_{M}$	
	С	Н	Ν	С	Н	Ν	(DMF)	M.p.
LaL <sub>3</sub> (H <sub>2</sub> O)	49.73	4.03	11.60	50.11	4.22	11.64	81.3	7
$PrL_3(H_2O)$	49.60	4.02	11.57	50.18	4.02	11.53	107	÷
$SmL_3(H_2O)$	48.96	3.97	11.42	50.08	3.94	11.36	83.6	÷
$EuL_{3}(H_{2}O)$	48.85	3.96	11.39	49.39	4.01	11.45	76.6	Ť
$TbL_3(H_2O)$	48.40	3.93	11.29	48.92	3.81	11.46	108	218°
ErL <sub>3</sub>	49.04	3.70	11.44	49.51	4.00	11.28	73.3	190°

<sup>†</sup>Gradual decomposition.

Notes

 

 Table 2. Selected IR bands of some lanthanide complexes of the conjugate base of 3-phenyl 5-methyl-1-hydroxypyrazole 2-oxide (cm<sup>-1</sup>)

Compound	νNO	νN–N	νN-0	$\rho H_2O(wag)$	νM-OH <sub>2</sub>	νM-O(N)
KL	1261 s 10	1032 m 1020 m	850 s			
$LaL_3(H_2O)$	1277 s,b	1043 m 1025 m	853 s	482 m	435 m	370 m
PrL <sub>3</sub> (H <sub>2</sub> O)	1279 s,b	1042 m 1025 m	852 s	487 m	441 m	372 m
$SmL_3(H_2O)$	1280 s,b	1042 m 1027 m	857 s	488 m	449 m	373 m
$EuL_3(H_2O)$	1285 s,b	1048 m 1030 m	860 s	490 m	457 m	375 m
$TbL_3(H_2O)$	1281 s,b	1047 m 1028 m	858 s	498 m	457 m	380 m
ErL <sub>3</sub>	1281 s,b	1047 m	860 s			386 m

formation about the nature of the coordination sphere of these complexes. In particular, we are able to observe only one  $\nu NO$ , shifted to higher energy by about  $20 \text{ cm}^{-1}$  when compared to the potassium salt. This band is broad, which is probably indicative of the slight difference in the two N–O bands, although  $\delta NO$  is very narrow. The shift to higher energy is consistent with our results for the transition metal ion complexes; the shift for the lanthanides being slightly greater than that of the divalent metal ions, but less than the trivalent metal ions.

The  $\delta NO$  as stated previously is narrow and is shifted to somewhat higher energies which can be taken as an indication of bidentate bonding[1,3]. Two narrow bands in the  $1030 \,\mathrm{cm}^{-1}$ region have previously been assigned as having considerable  $\nu N-N$  character. These bands are shifted to somewhat higher energy, which is consistent with the shift of  $\nu NO$  upon coordination.

Because the region of the spectrum between 600 and 200 cm<sup>-1</sup> of the potassium salt is relatively free of bands, we have attempted to assign the more intense bands in this region to metal-ligand vibrations (i.e. a major contribution to the band). We are aided in our assignment by the anhydrous erbium complex in that we are able to distinguish between metal-aquo and metal-ligand vibrations. These bands are reported from spectra recorded as Nujol mulls between CsI plates since the absorbed water in KBr was evidently forced into the coordination sphere of the erbium complex in preparing KBr disks. The wagging mode of an aquo lignad coordinated to a lanthanide metal ion is assigned (Table 2) based on assignments of previous authors [4]. Similarly,  $\nu$ M–O(H<sub>2</sub>O) was assigned on the basis of the absence of a band in this region of the spectrum of the erbium complex and by analogy with previous assignments of other workers[4]. The band  $(370-385 \text{ cm}^{-1})$  is assigned to  $\nu$ M-O for the dioxide ligand since it appears at similar energy to the analogous band in dispositive transition metal ion complexes[1]. Another band at approximately 330 cm<sup>-1</sup>, which is somewhat weaker in intensity, may also have considerable contribution from  $\nu$ M-O. All of the metal-ligand vibrations assigned show, in general, an increase in energy with decrease in size of the lanthanide ion.

The electronic spectra recorded as Nujol mulls adhered to filter paper have two bands assignable to intraligand transitions. The higher energy band (i.e. ca. 42 kK) is broad and is most likely due to a  $\pi \rightarrow \pi^*$  transition. This band is not shifted, but it

is decreased in intensity, when the lanthanide complexes are compared to the potassium salt. It probably is a composite of  $\pi \rightarrow \pi^*$  transitions in both aromatic rings. The other band, which is of greater intensity for the lanthanides, appears at 33.3 kK for the potassium salt and is shifted to higher energy (i.e. 34.7 kK) in the lanthanide complexes. This region of the spectrum is usually assigned [5] to a  $n \rightarrow \pi^*$  transition which would be shifted to higher energy upon complexation. However, previous authors have indicated that this type of band should be unobservable in metal ion complexes of pyridine N-oxide[6]. A second  $\pi \rightarrow \pi^*$ band may be present at approx. 46.0 kK although we were not able to resolve this band completely. This would lend support to the assignment of the 33 kK band as a  $n \rightarrow \pi^*$  transition. Bands in the visible region of the spectrum are identical to those observed for related lanthanide complexes[7] with the charge transfer band for EuL<sub>3</sub>(H<sub>2</sub>O) observed at 29.0 kK.

We conclude that the complexes, with the exception of the erbium complex, are 7-coordinate and will slowly decompose in most solvents, and that  $ErL_3$  will add a seventh ligand rather easily.

Department of Chemistry	JOHN F. HANSEN
Illinois State University	SUSAN P. McCORMICK
Normal, IL 61671	DOUGLAS X. WEST
U.S.A.	

## REFERENCES

- J. F. Hansen, S. P. McCormick and D. X. West, J. Inorg. Nucl. Chem. 39, 1231 (1977).
- 2. W. J. Geary, Coord. Chem. Rev. 7, 81 (1971).
- C. A. Frank and D. X. West, J. Inorg. Nucl. Chem. 39, 793 (1977).
- J. R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, p. 70. Plenum Press, New York (1971).
- 5. N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, Coord. Chem. Rev. 11, 93 (1973).
- W. Byers, B. F. Chau, A. B. P. Lever and R. V. Parish, J. Am. Chem. Soc. 91, 1329 (1969).
- S. A. Boyd, R. E. Kohrman and D. X. West, *Inorg. Nucl. Chem. Lett.* 12, 603 (1976).