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NOTES

Rare Earth Complexes with Benzil-α-Dioxime

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Simple complexes of Y(III), Ce(IV), La(III), Pr(III), ND(III), Sm(III), Gd(III) using benzil-α-dioxime (diphenyl-glyoxime) have synthesised. These complexes have been characterised by a study of elemental analysis, conductivity and infra-red spectra. Physical properties and analytical data of the complexes reveal that each metal ion is attached to one molecule of the ligand. The presence of coordinated water molecules in all the complexes may be confirmed by thermal study and from infra-red spectral studies of the complexes. The conductivity data obtained in the solvents ethanol and methanol indicate that all the complexes are 1 : 1 electrolytes. Hence one can assign the general formula $[LnLCl_2 2H_2O]Cl$ where Ln = Y, Ce, La, Pr, Nd, Sm, Gd and L is benzil-dioxime. It can be said that the coordination number in these complexes is six.

Rare earth complexes with nitrogen containing donors have been reported by Rao and Co-workers[1-5]. Recently Rao and co-workers[6] prepared complexes of rare earth with dimethylglyoxime. The same study is extended to the preparation and characterisation of complexes of Y, Ce, La, Pr, Nd, Sm and Gd with benzil-α-dioxime (diphenylglyoxime).

Benzil-α-dioxime, m.pt. 237°C, was of BDH(AR) quality. Pure rare earths oxide were obtained from Indian Rare Earths Ltd., Alwaye, Kerala. The infrared spectra were recorded on a Perkin-Elmer spectrophotometer using KBr phase in 4000 cm^{-1}–500 cm^{-1}. Conductance is measured on Toshniwal Conductivity Bridge in methanol and ethanol at a concentration of 10^{-3} M.

The complexes were prepared by refluxing a solution of ligand in ethanol (with a little dioxine) with corresponding metal salts (metal chlorides) dissolved in ethanol separately for 6 hrs. The reaction mixture was taken out and the pH was adjusted to about 5.5 by using alcoholic ammonia solution. Again it was refluxed for few minutes and the complex was separated by filtration when the mixture was hot and washed repeatedly with acetone, ether to remove excess of ligand. The complexes were dried over calcium chloride and analysed. The metal to ligand ratio was found to be 1 : 1. The chloride content of the complexes was estimated by gravimetric method as well as by volumetric method and the water molecules were determined by loss in weight of the compound at 100°. The conductivity data obtained in the solvents ethanol and methanol indicate that all the complexes are 1 : 1 electrolytes. Physical properties and elemental analysis of complexes are detailed in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF COMPLEXES

Complex	Colour	pH of precipi-taiton	Decomp. point.	Metal %		Cl %		Λ (Mhos) $(10^{-3}$ M)	
				Found	Requi.	Found	Requi.	Metha-nol	Etha-nol
$YLCl_3 2H_2O$	Yellowish white	5.5	260°C	18.50	18.16	22.23	22.58	126.21	66.90
$CeL(NO_3)_4$ $2H_2O$	Pale brown	5.5	260°C	21.08	22.12	—	—	—	—
$LaLCl_3 2H_2O$	Brown	5.5	260°C	26.44	26.65	21.64	20.42	130.00	64.21
$PrLCt_3 2H_2O$	Pale yellowish	5.5	260°C	26.95	26.92	19.53	20.34	101.60	53.50
$NdLCl_3 2H_2O$	Pale lilac	5.5	260°C	28.72	27.58	20.05	20.21	107.00	53.50
$SmLCl_3 2H_2O$	Pale pinkish	5.5	260°C	28.45	28.21	19.70	19.98	103.80	55.19
$GdCl_3 2H_2O$	Pale yellowish	5.5	260°C	29.06	29.13	19.70	19.72	114.00	64.90

L = Benzil α-Dioxime

Normal oximes[7-10] have bands at 3300 cm^{-1}–3150 cm^{-1} (OH Str), 1690 cm^{-1}–1620 cm^{-1} (C=N Str) and near 930 cm^{-1} (N–O Str). In the ligand a broad and strong band is observed at 3260 cm^{-1}–3240 cm^{-1} which may be attributed[11] to —OH stretching frequency. In all the rare earth complexes a band is located between 3100 cm^{-1} and 3550 cm^{-1}, which may be assigned to the —OH stretching frequency. In the ligand a medium band at 1668 cm^{-1} is observed which may be due to C=N stretch. In all the complexes the band is observed in between 1570 cm^{-1} and 1595 cm^{-1}. Similarly a strong band is observed in the ligand at 980 cm^{-1} due to N–O stretching. In all the complexes there is a strong band in between 938 cm^{-1} and 985 cm^{-1}. Coordinated water in general absorbs around 3550 cm^{-1} to 3200 cm^{-1} (asymmetric and symmetric OH stretching modes) and 1630 cm^{-1}–1600 cm^{-1} (H—O—H bending modes). The band between 1570 cm^{-1} and 1595 cm^{-1} in the metal complexes may either be due to coordinated water molecules or due to shift in the C=N stretching frequency. Table 2 details the bands observed in the spectra of ligand and the chelates.

TABLE 2

INFRA-RED DATA (cm^{-1}) OF RARE-EARTH COMPLEXES

Complex	O-H Stretch	C=N stretch	N-O Stretch
Benzil α-dioxime	3260–3240 (br & s)	1668 (m)	980 (s)
$YLCl_32H_2O$	3200–3120 (br & w)	1575 (s)	952 (vw)
$CeL(NO_3)_42H_2O$	3380–3300 (br)	1570 (s)	940 (m)
$LaLCl_32H_2O$	3300–3100 (br & w) 3550 (w), 3335 (vw)	1590–1580 (br & s)	980 (m) 938 (m)
$PrLCl_32H_2O$	3280–3225 (br) 3550 (s) 3530 (s)	1950 (m)	975 (s)
$NdLCl_32H_2O$	3250–3110 (br) 3550 (s), 3530 (s)	1595–1570 (br & s)	985 (s)
$SmLCl_32H_2O$	3300–3110 (br)	1580 (s)	980 (s)
$GdCl_32H_2O$	3145–3110 (br)	1590–1570 (s)	940 (m)

L = Benzil α-dioxime s = strong m = medium vw = very weak, br = broad.

Thus it can be tentatively concluded that each rare earth ion is attached to one molecule of the ligand through the two nitrogen of the N—OH groups. The complexes may be assigned a general formula $[MLCl_22H_2O]Cl$.

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REFERENCES

1. P. Radhakrishna Murthy and V. Ramchandra Rao, *Khimiya Geteroskilitsheskih Seodinenii*, 5, 729 (1966).

2. P. Radhakrishna Murthy and V. Ramchandra Rao, *Curr. Sci.*, (*India*), **36**, 233 (1967).
3. ———, *Indian J. Chem.*, **6**, 465 (1968).
4. B. K. Patil and V. Ramachandra Rao, *Curr. Si.* (*India*), **45**, 686 (1976).
5. ———, *Indian Medical Gazette*, **CXIII**, 375 (197)9.
6. V. H. Galgali, V. Ramachandra Rao and D. D. Khanolkar, *Indian J. Chem.*, **7**, 825 (1969).
7. J. Fabian, M. Legrand and P. Poirier, *Bull. Soc. Chim. France*, **23**, 1499 (1956).
8. J. F. Brown (Jr.), *J. Am, Chem. Soc.*, **77**, 6341 (1955).
9. A. Palm and H. Werbin, *Canad. J. Chem.*, **32**, 858 (1954).
10. D. Hadzi, *J. Chem. Soc.*, 2725 (1956).
11. K. Nakamoto, Infra-red Spectra of Inorganic and Coordination Compounds, John Wiley and Sons Inc., New York, p. 194 (1963).

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