

Lanthanide(III) Derivatives of β -Ketoamines

B S SANKHLA*, (Miss) SHAKUNTALA MATHUR & MEGH SINGH

Department of Chemistry, University of Jodhpur
Jodhpur 342 001

Received 12 July 1982; revised and accepted 5 October 1982

Bifunctional N,N' -butylene-bis (acetoacetanilideimine) reacts with lanthanide isopropoxide in (1:1, 1:2 and 2:3 molar ratios to yield products of the type $\text{Ln}(\text{OPr}^i)(\text{KA})$, $\text{Ln}(\text{KA})(\text{KAH})$ and $\text{Ln}_2(\text{KA})_3$, respectively (where KA^{2-} is the anion of the ligand). The complexes are yellow or cream coloured solids insoluble in benzene and common organic solvents. Their structures have been inferred from their elemental analyses, molecular weight determinations and IR spectral data.

A large number of β -ketoamine complexes of lanthanides have been reported. Presently we report the preparation and characterisation of the complexes of N,N' -butylene-bis(acetoacetanilideimine) with lanthanons. This ligand which is derived from acetoacetanilide and butylenediamine is capable of existing in the tautomeric forms and can act as a doubly negatively charged quadridentate ONNO donor.

Lanthanon isopropoxides were prepared by the sodium alkoxide method¹. N,N' -Butylene-bis(acetoacetanilideimine) was prepared by the condensation of acetoacetanilide (2 mol) with butylenediamine (1 mol) in ethanol.

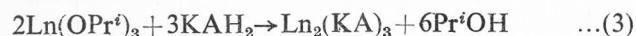
Lanthanide isopropoxide was dissolved in dry benzene (~60 ml) and to this was added a calculated amount of β -ketoamine and the reaction mixture

Table 1—Synthetic & Analytical Data of the N,N' -Butylene-bis (acetoacetanilideimine) Complexes of Lanthanon(III)

Alkoxide: Ligand	Reflux time (hr)	Product	Isopropyl alcohol found in azeotrope(g) (Calc)	Found (Calc.), %		m.p. °C
				Metal	N	
Pr(III) complexes						
1:1	18	$\text{Pr}(\text{OPr}^i)(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)$	0.3206 (0.3310)	23.85 (23.33)	9.12 (9.27)	215(d)
2:3	26	$\text{Pr}_2(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)_3$	0.4132 (0.4162)	18.49 (18.87)	11.11 (11.25)	228-30
1:2	28	$\text{Pr}(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)(\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}_4)$	0.2867 (0.2876)	14.67 (14.84)	11.63 (11.80)	180-82
Nd(III) complexes						
1:1	18	$\text{Nd}(\text{OPr}^i)(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)$	0.2039 (0.2051)	24.90 (24.81)	9.18 (9.22)	220(d)
2:3	26	$\text{Nd}_2(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)_3$	0.2378 (0.2328)	19.34 (19.23)	11.10 (11.19)	208-10
1:2	28	$\text{Nd}(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)(\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}_4)$	0.2787 (0.2798)	15.94 (15.13)	11.09 (11.75)	200
Sm(III) complexes						
1:1	18	$\text{Sm}(\text{OPr}^i)(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)$	0.2730 (0.2765)	24.49 (24.58)	8.93 (9.12)	210(d)
2:3	26	$\text{Sm}_2(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)_3$	0.2840 (0.2842)	20.00 (19.94)	11.09 (11.10)	178-80
1:2	28	$\text{Sm}(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)(\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}_4)$	0.2359 (0.2364)	15.55 (15.63)	11.04 (11.67)	176-78
Dy(III) complexes						
1:1	18	$\text{Dy}(\text{OPr}^i)(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)$	0.2033 (0.2043)	25.99 (25.94)	8.80 (8.93)	200(d)
2:3	26	$\text{Dy}_2(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)_3$	0.2487 (0.2492)	21.10 (21.14)	10.77 (10.92)	170
1:2	28	$\text{Dy}(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)(\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}_4)$	0.2582 (0.2581)	16.24 (16.73)	11.29 (11.51)	174-175
Ho(III) complexes						
1:1	18	$\text{Ho}(\text{OPr}^i)(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)$	0.2522 (0.2542)	26.16 (26.26)	9.04 (8.91)	200-02(d)
2:3	26	$\text{Ho}_2(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)_3$	0.3528 (0.3588)	21.39 (21.39)	10.90 (10.81)	172-74
1:2	28	$\text{Ho}_2(\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4)(\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}_4)$	0.2921 (0.2989)	16.83 (16.92)	11.23 (11.48)	168-70

refluxed over a fractionating column and the progress of the reaction ascertained by the estimation of isopropyl alcohol in the azeotrope with benzene. The products were rendered free from solvent under reduced pressure and finally dried at room temperature at 10^{-2} torr for $\sim 2-3$ hr. The details of the synthesis, analysis and physical properties of the products are reported in Table 1.

The reactions of lanthanide isopropoxides (Pr, Nd, Sm, Dy and Ho) with N,N'-butylene-bis (Acetoacetanilideimine) (BBAAH₂) in 1:1, 1:2 and 2:3 molar ratios in refluxing benzene can be represented by Eqs (1-3).



where KA^{2-} represents the anion of the β -ketoamine KAH_2 (BBAAH₂).

These reactions are endothermic and the resulting derivatives have been isolated in almost quantitative yield (90-95%). All the resulting compounds are cream coloured solids, except samarium (1:2 product) and holmium (1:1, 1:2 and 2:3 products) complexes are obtained as yellow powders. These complexes are insoluble in benzene and common organic solvents; however, all appeared to be soluble in DMF and DMSO. The insoluble nature of all these derivatives may be due to their polymeric nature. Attempts to sublime some of them even under reduced pressure were unsuccessful and resulted in their decomposition.

The molecular weight of monoisopropoxy lanthanide N,N'-butylene-bis(acetoacetanilideiminato) derivatives, determined by Rast's method, indicated these to be dimeric in which the lanthanides are hexacoordinated. The derivatives $\text{Ln}(\text{KA})(\text{KAH})$ and $\text{Ln}_2(\text{KA})_3$ respectively were found to be monomeric.

The infrared spectra of the ligand exhibits a strong band at $\sim 3300 \text{ cm}^{-1}$ assignable to $\nu\text{N-H}$ of the anilide moiety. This band does not undergo any appreciable shift on complex formation indicating that the N-H group of β -ketoanilide moiety does not take part in coordination. This is consistent with the observations of Dutt and De² for lanthanide com-

plexes of acetoacetanilides. The two medium to strong bands at $\sim 3250-3100 \text{ cm}^{-1}$ may be assigned to the νNH of diamine moiety. The shift of these bands to lower frequency region suggests that the two NH groups of the β -ketoamine are intramolecularly hydrogen bonded to the carbonyl groups with different strengths forming six-membered rings. The disappearance of these bands in the complexes signify that the β -ketoamine has lost both the hydrogen atoms by enolisation.

The appearance of νCO of the ligand at lower frequency (~ 1630 with a shoulder at $\sim 1600 \text{ cm}^{-1}$) suggests that the $\text{C}=\text{O}$ group is involved in intramolecular hydrogen bonding. This band disappears in the complexes of lanthanides indicating the coordination of metal ion to the carbonyl group via enolisation with the formation of a $\text{>C}-\text{O}-\text{M}$ bond^{3,4}.

This is substantiated by the appearance of new bands ~ 1580 and $\sim 1200 \text{ cm}^{-1}$ which are due to $\nu\text{C}=\text{N}$ (ref. 5) and $\nu\text{C}-\text{O}$ (ref. 6) respectively.

The monoisopropoxy lanthanide β -ketoamine complexes show characteristic frequencies of isopropoxy group⁷ at 1175, 1150 and 805 cm^{-1} .

The bands in the regions $700-400 \text{ cm}^{-1}$ and $300-250 \text{ cm}^{-1}$ in the infrared spectra of the complex may be assigned to $\nu(\text{M}-\text{O})$ (ref. 8) and $\nu(\text{M}-\text{N})$ (ref. 9) respectively.

The authors are thankful to the UGC, New Delhi for a financial support.

References

- Misra S N, Misra T N & Mehrotra R C, *Aust J Chem*, **21** (1968) 797.
- Dutt N K & De R, *Indian J Chem*, **12** (1974) 1320.
- Ueno K & Martell A E, *J phys Chem*, **59** (1955) 988; **61** (1957) 257.
- Srivastava T N, Chauhan A K S & Agarwal Manjula, *Transition met Chem*, **3** (1978) 378.
- Bellamy L J, *The infrared spectra of complex molecules* (Chapman and Hall, London) 1975.
- Rao C N R, *Chemical application of infrared spectroscopy* (Academic Press, New York) 1963.
- Lynch C T, Mazdiyasi K S, Smith J S & Crawford W J, *Analyt Chem*, **36** (1964) 2332.
- Liang C Y, Schimitschek E J & Trias J A, *J inorg nucl Chem*, **32** (1970) 811.
- Ferraro J R, Basile L J, & Kovcic D L, *Inorg Chem*, **5** (1966) 391.
- Bradley D C, Abad-El-Halim F M & Wardlow W, *J chem Soc*, (1950) 3450.