

## Chemistry of Lanthanons: Part XLIII\*—Lanthanide Complexes of Acetoacet-*o*-chloroanilide & Acetoacet-*o*-toluidide

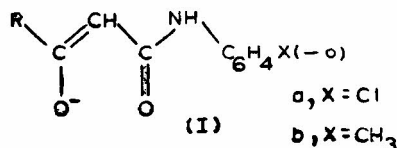
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Hydroxo bridged lanthanide complexes of the composition  $[\text{LnL}_2(\text{OH})_2]$ , [where Ln = Pr(III), Nd(III), Dy(III) or Ho(III) and L stands for the anion of acetoacet-*o*-chloroanilide or acetoacet-*o*-toluidide] have been isolated and characterized. The dimeric nature of the compounds has been established on the basis of molecular weight measurements. The IR spectra of the compounds indicate coordination through carboxyl oxygen atom and the presence of bridging hydroxyl groups. Thermal analysis of the compounds reveals the formation of LnOL as an intermediate decomposition product.

THE basic lanthanide acetates of the composition  $\text{Ln}_2\text{O}(\text{OAc})_4 \cdot 2\text{HOAc}$  have best been represented as binuclear hydroxobridged complexes, by Seaton *et al.*<sup>1</sup> Several other polymeric lanthanide complexes with oxygen donor ligands have been reported since then<sup>2,3</sup>. Newbery *et al.*<sup>4</sup> were able to isolate a product of the composition  $[\text{Ln}_2(\text{DBM})_2(\text{OH})_2]_n$  (where Ln = lanthanide ion and HDBM = dibenzoylmethane) with hydroxobridging groups similar to those present in basic acetate. Because of the structural similarity between  $\beta$ -ketoanilides and  $\beta$ -diketones, similar behaviour is expected with the lanthanide complexes of the former. This has been found to be true in the case of presently synthesized lanthanide complexes of  $\beta$ -ketoanilides, viz., acetoacet-*o*-chloroanilide (Ia) and acetoacet-*o*-toluidide (Ib). The complexes have been characterized on the basis of analytical, spectral and thermal data.



### Materials and Methods

Specpure lanthanide oxides (BARC, Bombay and Johnson Matthey reagents) were used. The organic solvents used were of reagent quality.

*Acetoacet-*o*-chloroanilide (HAACan)*—The procedure adopted is similar to that used for analogous compounds by Cashion<sup>5</sup>. Ethyl acetoacetate (35 g) and a little triethylene tetramine (1.5 g) were taken in monochlorobenzene (100 ml) and contents refluxed. A solution of freshly distilled *o*-chloroaniline (12 g) in monochlorobenzene (100 ml), preheated to 80-100°, was added in small portions with continuous stirring; the temperature of the system was maintained at 120-125°C during the

addition which was completed in 1 hr. After removing the condenser, the temperature was slowly raised to 135° when two-thirds of the solvent along with ethanol (a product of the reaction), distilled off. The residual portion was cooled to room temperature, slurried with water (200 ml) containing 2.5 ml of con. sulphuric acid and steam-distilled to remove associated solvent and unreacted reagents. The crude product was purified by recrystallizing from benzene; yield 70%, m.p. 103° (lit. m.p. 104°).

*Acetoacet-*o*-toluidide (HAAT)*—The above procedure was followed for condensation of ethyl acetoacetate with *o*-toluidine and the crude product recrystallized from benzene; yield 65%; m.p. 101° (lit. 102°).

*Lanthanide complexes*—A solution of the appropriate lanthanide nitrate (2 mmoles) in 10 ml of acetone-water (1:1, v/v) was added to the ligand solution (6 mmoles) in 30 ml of the same solvent. The pH of the resulting solution was slowly raised to 7-7.5 by dropwise addition of dilute ammonia with constant stirring. The solution was kept aside for 15 min when a sticky precipitate was obtained. It was rubbed down to powder form, filtered, washed several times with the mixed solvent and finally with a little ethanol. The residue was dried under suction, extracted with chloroform and filtered to remove any remaining metal hydroxide and ammonium nitrate. The filtrate was evaporated to dryness *in vacuo* over CaCl<sub>2</sub>.

*Physical measurements*—IR spectra (KBr) were recorded on a Perkin-Elmer spectrophotometer model 237. Molecular weights were obtained in chloroform using a Mechrolab vapour pressure osmometer. Thermal studies were carried out on a Metrimpex derivatograph type OD-102 (Hungary).

Lanthanides were estimated as their oxides by direct combustion of the compounds.

### Results and Discussion

On the basis of the analytical data (Table 1) the present lanthanides complexes with HAACan and HAAT may be assigned the empirical formula

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$[\text{LnL}_2(\text{OH})]_n$ . These compounds when freshly prepared are soluble in chloroform but, on storage over calcium chloride for a few days, revert to a sparingly soluble form. As a result studies were always made with the freshly prepared compounds.

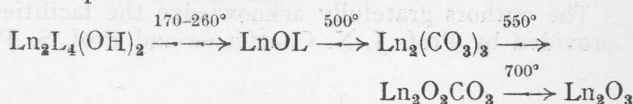
The observed molecular weights of the complexes (Table 2) indicate them to be the dimeric chelates of the type  $[\text{Ln}_2\text{L}_4(\text{OH})_2]$ . The observed molecular weights for the acetoacet-*o*-chloroanilide complexes are somewhat lower than expected for the dimeric species, but this discrepancy may be attributed to the relatively lesser solubility of these complexes and also probably to their lower stability in solution. Such deviations in molecular weight determination by vapor pressure method for similar reasons were reported by Newbery *et al.*<sup>4</sup>.

Though the IR spectra\* of the compounds are somewhat complicated sites of coordination can be inferred from the data in accordance with earlier assignments<sup>6</sup>. The sharp intense band due to  $\nu\text{C}=\text{O}$  located around  $1710\text{ cm}^{-1}$  in the ligands is shifted to a much lower frequency ( $\sim 1630\text{ cm}^{-1}$ ) in the complexes. The band around  $1670\text{ cm}^{-1}$  in the ligands, which is due to the amide-I vibration, also suffers a shift of about  $30\text{ cm}^{-1}$  to the lower frequency side on complexation. On the other hand, while the positions of the amide-II ( $\sim 1535\text{ cm}^{-1}$ ) and the amide-III ( $1310\text{ cm}^{-1}$ ) bands in the ligands remain undisturbed in the complexes, the amide-IV band ( $940\text{--}950\text{ cm}^{-1}$ ) shifted to the higher frequency side by  $15\text{--}25\text{ cm}^{-1}$  in the complexes. These observations suggest that bonding takes place through the oxygen atom and not through the nitrogen atom in the anilide part of the ligands.

The vibration due to NH stretching in the ligands (which are intermolecularly hydrogen bonded) observed in the range  $3260\text{--}3210\text{ cm}^{-1}$  are shifted to higher frequency ( $\sim 3420\text{ cm}^{-1}$ ) in the complexes, further indicating the non-involvement of the NH group in bond formation. The broad band of moderate intensity observed in the range  $3400\text{--}3200\text{ cm}^{-1}$  in complexes may be ascribed to the  $\nu\text{OH}$  frequencies.

In the compounds containing water molecules, the band due to  $\nu\text{OH}$  is usually observed in the range  $3600\text{--}3400\text{ cm}^{-1}$ . A new band appearing around  $840\text{ cm}^{-1}$  in the complexes which, is absent in ligands, has been assigned to OH deformation mode. The low value for  $\delta(\text{O-H})$  suggests that the hydroxyl group is involved in bridge formation<sup>4</sup>. This is in agreement with our dimeric formulation for the compounds. It may be mentioned that Newbery *et al.*<sup>4</sup> in their studies on the complexes of the type  $[\text{Ln}_2(\text{DBM})_5\text{OH}]_n$  could locate the band due to  $\nu\text{OH}$  after deuterating the lanthanum complexes. However the present complexes could not be deuterated.

The thermal behaviour of the lanthanide complexes of both the ligands is identical. The DTA and the DTG curves show no indication of decomposition of the complex below  $170^\circ$ , thus excluding any loss of water in the primary step. From a combination of the TG, DTA and DTG data, the following decomposition reactions have been inferred:



The formation of LnOL as the intermediate product has been observed in the lanthanide  $\beta$ -diketonates<sup>8</sup> also. The decomposition of  $\text{Ln}_2(\text{CO}_3)_3$  through the formation of dioxomonocarbonate,  $\text{Ln}_2\text{O}_2\text{CO}_3$ , is also reported in literature<sup>9,10</sup>.

TABLE 2 — MOLECULAR WEIGHT DATA OF THE COMPLEXES

Chelate	Mol. wt	
	Obs.	Calc.
$[\text{Pr}(\text{AACan})_2(\text{OH})_2]$	942	1156
$[\text{Nd}(\text{AACan})_2(\text{OH})_2]$	1085	1164
$[\text{Ho}(\text{AACan})_2(\text{OH})_2]$	1047	1204
$[\text{Pr}(\text{AAT})_2(\text{OH})_2]$	1126	1076
$[\text{Nd}(\text{AAT})_2(\text{OH})_2]$	1050	1082
$[\text{Ho}(\text{AAT})_2(\text{OH})_2]$	1110	1124

TABLE 1 — COLOUR, MELTING POINT AND ANALYTICAL DATA OF THE COMPLEXES

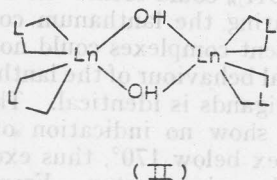
Chelate	Colour	Melting point* °C	M (%)		C (%)		H (%)		N (%)	
			Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$[\text{Pr}(\text{AACan})_2(\text{OH})_2]$	Green	183	24.35	24.34	41.52	41.46	3.24	3.28	4.82	4.84
$[\text{Nd}(\text{AACan})_2(\text{OH})_2]$	Pink	190	24.76	24.73	41.30	41.20	3.28	3.26	4.80	4.81
$[\text{Dy}(\text{AACan})_2(\text{OH})_2]$	Light-cream	170	27.15	27.07	40.10	39.96	3.12	3.16	4.64	4.66
$[\text{Ho}(\text{AACan})_2(\text{OH})_2]$	Light-yellow	165	27.30	27.35	39.85	39.83	3.14	3.15	4.67	4.64
$[\text{Pr}(\text{AAT})_2(\text{OH})_2]$	Green	170	26.22	26.19	49.00	49.07	4.45	4.46	5.25	5.20
$[\text{Nd}(\text{AAT})_2(\text{OH})_2]$	Dirty-pink	185	26.72	26.67	48.72	48.77	4.40	4.43	5.20	5.17
$[\text{Dy}(\text{AAT})_2(\text{OH})_2]$	Light-cream	150	29.03	29.07	47.28	47.22	4.30	4.29	5.01	5.00
$[\text{Ho}(\text{AAT})_2(\text{OH})_2]$	Light-yellow	155	29.40	29.32	46.88	46.97	4.25	4.27	5.00	4.98

\*Compounds melt with decomposition.

\*Detailed IR data can be procured from the authors on request.

Above experimental evidences clearly demonstrate that both acetoacet-*o*-chloroanilide (HAACan) and acetoacet-*o*-toluidide (HAAT) form binuclear hydroxobridged complexes with lanthanides. These complexes can be represented as (II).

Earlier, it has been reported that with acetoacetanilide<sup>6</sup> and benzoylacetanilide, the isolated lanthanide complexes possess hydroxoquo bis- and hydrated tris-composition respectively.



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The vibration due to NH stretching in the ligands suggest that bonding takes place through the oxygen atom and not through the nitrogen atom in the amide part of the ligands. The broad band of more intense intensity observed in the range 3400-3200 cm<sup>-1</sup> is complexed may be ascribed to the OH frequency. The broad band of more intense intensity observed in the range 3400-3200 cm<sup>-1</sup> is complexed may be ascribed to the OH frequency. The broad band of more intense intensity observed in the range 3400-3200 cm<sup>-1</sup> is complexed may be ascribed to the OH frequency.

TABLE I - MOLECULAR WEIGHT DATA OF THE COMPLEXES

Complex	Calc.	Obs.
[Ln(AACan) <sub>2</sub> (OH)] <sub>2</sub>	1134	1134
[Ln(AAT) <sub>2</sub> (OH)] <sub>2</sub>	1082	1082
[Ln(AAT)(OH)] <sub>3</sub>	1070	1070
[Ln(AAT) <sub>2</sub> (OH)] <sub>2</sub>	1047	1047
[Ln(AACan) <sub>2</sub> (OH)] <sub>2</sub>	1043	1043
[Ln(AACan)(OH)] <sub>3</sub>	943	943
[Ln(AACan) <sub>2</sub> (OH)] <sub>2</sub>	1134	1134

TABLE II - COLOUR, MELTING POINT AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	Melting point	N (%)		C (%)		H (%)	
			Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
[Ln(AACan) <sub>2</sub> (OH)] <sub>2</sub>	Green	183	24.33	24.34	41.23	41.46	3.24	3.28
[Ln(AACan)(OH)] <sub>3</sub>	Pink	190	24.78	24.73	41.30	41.30	3.28	3.26
[Ln(AACan)(OH)] <sub>2</sub>	Light green	170	27.12	27.07	40.10	39.96	3.12	3.16
[Ln(AACan)(OH)]	Light green	163	27.30	27.22	39.83	39.83	3.14	3.13
[Ln(AAT) <sub>2</sub> (OH)] <sub>2</sub>	Yellow	170	26.22	26.19	49.00	49.07	4.42	4.46
[Ln(AAT)(OH)] <sub>3</sub>	Green	182	26.72	26.67	48.72	48.77	4.40	4.43
[Ln(AAT)(OH)] <sub>2</sub>	Grey	182	26.72	26.67	48.72	48.77	4.40	4.43
[Ln(AAT)(OH)]	Grey	180	26.07	26.07	47.28	47.22	4.29	4.31
[Ln(AAT)(OH)] <sub>2</sub>	Light green	182	26.40	26.42	46.88	46.97	4.22	4.22

\* Compounds melt with decomposition

\* Reported IR data can be procured from the authors on request.