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Lanthanide Complexes of Compartmental Ligands*

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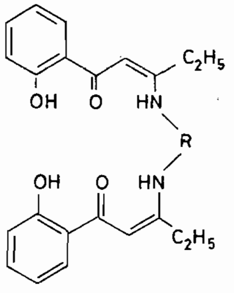
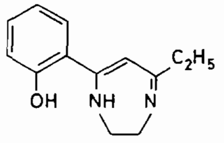
Schiff base ligands having available adjacent, dissimilar coordination sets have been collectively termed compartmental ligands [1]. Such ligands are capable of forming mononuclear positional isomers homobinuclear and heterobinuclear metal complexes and the application of such ligands to the area of 'd'-block transition metal chemistry has been recently reviewed [1]. We here describe some lanthanide complexes of compartmental ligands derived from the β-ketophenol, 2-propriono-acetylphenol [2].

The reaction of 2-proprionoacetylphenol (H_2–pap) with α,ω-alkanediamines leads to the Schiff bases I and II. The ligands are readily characterised by microanalysis, i.r., m.s., and ^1H n.m.r. spectroscopy [I: Found, C = 70.6, H = 6.7, N = 6.9%; $C_{24}H_{28}N_2O_4$ requires C = 70.6, H = 6.9, N = 6.9%. P^+ at m/e = 408, M = 408. I.r. 3425, 3200 (ν_{OH}, ν_{NH}), 1600, 1575, 1550, 1520 ($\nu_{C=O}$, $\nu_{C=N}$, $\nu_{C=C}$), 785 ($\nu_{C-H\,phenol}$) cm^{-1}. ^1H n.m.r. ($CDCl_3$), δ = 12.51(s, 2H, O$\underline{H}$), 10.30 (s, 2H, N$\underline{H}$), 6.80–7.65 (m, 8H, phenyl), 5.78 (s, 2H, –C$\underline{H}$=), 3.60(s, 4H, C$\underline{H}_2$), 2.38(q, 4H, C$\underline{H}_2$(ethyl)), 1.22 (t, 6H, C$\underline{H}_3$) ppm; II: Found, C = 69.9, H = 6.9, N = 6.6%; $C_{25}H_{30}N_2O_4 \cdot \frac{1}{2}H_2O$ requires C = 69.6, H = 7.2, N = 6.5%. P^+ at m/e = 422, M – $\frac{1}{2}H_2O$ = 422. I.r. 3495, 3195 (ν_{OH}, ν_{NH}), 1600, 1580, 1555, 1520 ($\nu_{C=O}$, $\nu_{C=N}$, $\nu_{C=C}$), 760 ($\nu_{C-H\,phenol}$) cm^{-1}. ^1H nmr ($CDCl_3$), δ = 13.40(s, 2H, O$\underline{H}$), 11.10 (s, 2H, N$\underline{H}$), 6.80–7.65(m, 8H, phenyl), 5.75 (s, 2H, –C$\underline{H}$=), 3.53(q, 4H, C$\underline{H}_2$ (term. bridge)), 2.40(q, C$\underline{H}_2$(ethyl)), 2.05(p, 2H, C$\underline{H}_2$ (centre bridge)), 1.25(t, 6H, C$\underline{H}_3$) ppm]. The reaction to form I was best carried out in toluene as if ethanol was used as the solvent then a 40% yield of the diazepin III accompanied the formation of I. Metal complexation reactions have been carried out using both the Schiff base ligands and the β-ketophenol precursors.



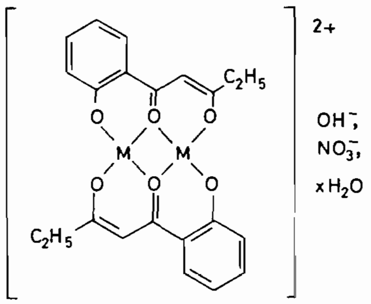


I R = $-CH_2CH_2-$
II R = $-CH_2CH_2CH_2-$

III

Complexes of the β-Ketophenol

The reaction of (H_2-pap) with $Ln(NO)_3 \cdot xH_2O$ (Ln = La, Pr. Eu) in methanol in the presence of LiOH gave fine powdery precipitates. The products analysed as $Ln_2(pap)_2(NO_3)OH \cdot nH_2O$ (n = 2 for La, 3 for Eu and 6 for Pr) and are assigned structure IV by analogy with transition metal analogues [3].



IV

The i.r. showed an absence of the carbonyl band at 1680 cm^{-1} in the free ligand and of the hydroxyl band at 3450 cm^{-1}. Only one strong broad band assignable to the $-NO_3$ was found *ca.* 1380 cm^{-1}, suggestive of an ionic nitrate. The compounds were too involatile for mass spectrometry.

Mononuclear Complexes of the Schiff Bases

The reaction of a chloroform solution of the Schiff base with a methanolic solution of $Ln(NO_3)_3 \cdot nH_2O$ gave fine powdery products. For I complexes were available for Ln = La–Eu and for II complexes were available for Ln = La–Sm and were of the form $Ln(H_2-L)NO_3 \cdot xH_2O$ (V). The absence of ν_{OH} for the phenolic

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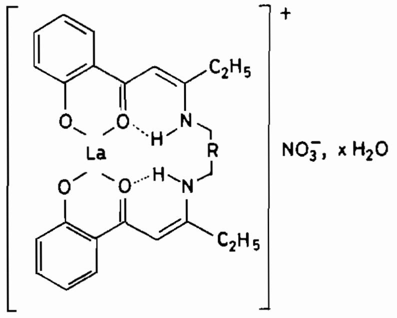
TABLE I. Microanalytical Data.

Complex	Required %			Found %		
	C	H	N	C	H	N
a) Mononuclear Schiff Base						
$La(H_2\text{-I})(NO_3)\cdot4H_2O$	42.4	5.0	6.2	42.5	4.9	6.1
$Ce(H_2\text{-I})(NO_3)\cdot2H_2O$	44.8	4.6	6.5	45.1	4.2	6.0
$Pr(H_2\text{-I})(NO_3)\cdot2H_2O$	44.6	4.6	6.5	44.4	4.4	6.6
$Nd(H_2\text{-I})(NO_3)\cdot2H_2O$	44.2	4.6	6.5	44.1	4.3	6.3
$Sm(H_2\text{-I})(NO_3)\cdot2H_2O$	44.0	4.5	6.4	43.4	4.2	6.2
$Eu(H_2\text{-I})(NO_3)\cdot3H_2O$	42.7	4.7	6.2	42.4	4.5	6.1
$La(H_2\text{-II})(NO_3)\cdot3H_2O$	44.4	5.0	6.4	44.4	4.6	6.7
$Ce(H_2\text{-II})(NO_3)\cdot3H_2O$	43.1	4.9	6.5	42.9	4.7	6.6
$Pr(H_2\text{-II})(NO_3)\cdot2H_2O$	44.9	4.9	6.5	44.6	4.6	6.7
$Nd(H_2\text{-II})(NO_3)\cdot2H_2O$	44.8	4.7	6.5	44.9	4.5	6.4
$Sm(H_2\text{-II})(NO_3)\cdot3H_2O$	43.0	4.9	6.2	44.4	4.8	6.5
b) Heterobinuclear Schiff Base						
$LaNi(\text{I})(NO_3)\cdot2H_2O$	41.1	4.0	6.0	41.0	3.7	5.9
$PrNi(\text{I})(NO_3)\cdot H_2O$	42.3	3.8	6.2	43.0	4.0	6.2
$EuNi(\text{I})(NO_3)\cdot3H_2O$	39.3	3.6	5.7	39.0	3.6	5.5
c) β-ketophenol						
$La_2(pap)_2(NO_3)\cdot2H_2O$	34.1	3.2	1.8	34.0	3.4	1.9
$Pr_2(pap)_2(NO_3)\cdot6H_2O$	31.1	3.8	1.6	30.9	3.4	1.9
$Eu_2(pap)_2(NO_3)\cdot3H_2O$	32.3	3.3	1.7	32.5	3.3	1.9

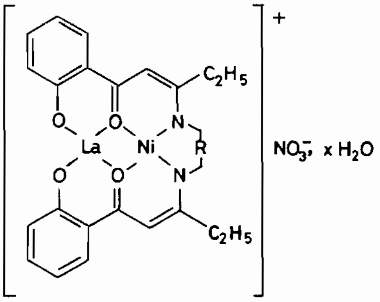
unit and the presence of ν_{NH} *ca.* 3150 cm^{-1} is indicative of the outer occupancy that would be predicted from a consideration of HSAB principles. The complexes were too involatile for mass spectrometry but it was possible to record the ^1H n.m.r. spectrum of the La derivatives in d_6-dmso, [$La(H_2\text{-I})NO_3$: δ = 1.19 (t, 6H, CH_3), 2.42 (q, 4H, CH_2), 3.62 (s, 4H, $-(CH_2)_2-$), 5.65 (s, 2H, –CH), 6.28–7.50(m, 8H, phenyl), 11.35(br, 2H, NH) ppm, and $La(H_2\text{-II})NO_3$: δ = 1.22(t, 6H, CH_3), 2.40(q, 4H, CH_2), 3.40 (m, 6H, $-(CH_2)_3-$), 5.58 (s, 2H, –CH), 6.20–7.45 (m, 8H, phenyl), 11.00 (br, 2H, NH) ppm].



V

Binuclear Complexes of the Schiff Bases

Attempts to obtain homobinuclear lanthanide complexes have so far been unsuccessful as have attempts to prepare heterobinuclear complexes by the reaction of the mononuclear lanthanum complexes with metal salts of VO(IV), Th(IV), and UO_2(VI). The reaction of the mononuclear complex $Ni(H_2\text{–I})$ in which the nickel(II) occupies the inner compartment [4], with $Ln(NO_3)\cdot nH_2O$ (Ln = La, Pr, Eu) in the presence of LiOH in methanol and in 1:1:2 mole ratio led to the precipitation of green heterobinuclear complexes for $LaNi(\text{I})NO_3\cdot2H_2O$ and $PrNi(\text{I})NO_3\cdot2H_2O$ and the brown heterobinuclear complex $EuNi(\text{I})NO_3\cdot3H_2O$, after stirring at reflux for three hours*. The i.r. show the absence of bands attributable to $\nu_{OHphenol}$ and ν_{NH}, and give three strong bands (*ca.* 1288, 1032 and 822 cm^{-1}) for the $-NO_3$ group. The nitrate groups in lanthanide complexes have generally been found to act as bidentate ligands [5, 6]. The hetero-binuclear complexes (VI) have insufficient volatility for mass spectral study.



VI

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*In all of these complexes the first-named metal occupies the O_2O_2 compartment and the second named metal occupies the N_2O_2 compartment.

Acknowledgement

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