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Lanthanide Complexes of Compartmental Ligands

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Schiff base ligands having available adjacent, dissimilar coordination sets have been termed collectively compartmental ligands [1]. Such ligands may be prepared from the reaction of an α,ω-diamine with one terminal keto-function of a β-triketone or β-ketophenol (Fig. 1). The ligands are capable of forming mononuclear positional isomers, homobinuclear and heterobinuclear metal complexes (Fig. 2). 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-proprionoacetylphenol.

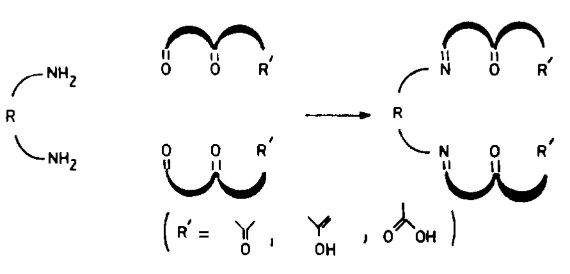
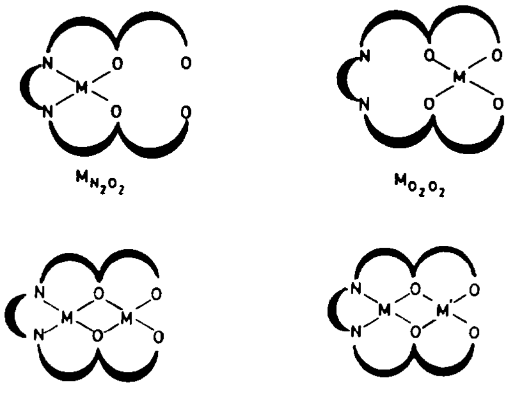


Fig. 1. Synthesis of compartmental ligands.



Homodinuclear complex

Heterodinuclear complex

Fig. 2. Mononuclear positional isomers.

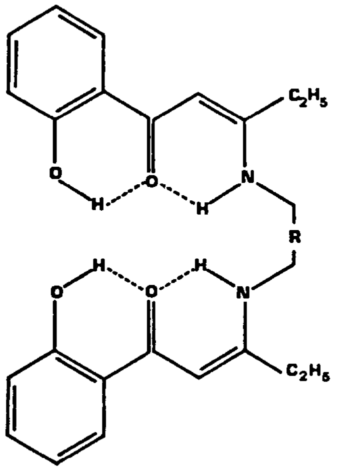


Fig. 3. I, R = $-CH_2-CH_2-$; II, R = $-CH_2-CH_2-CH_2-$.

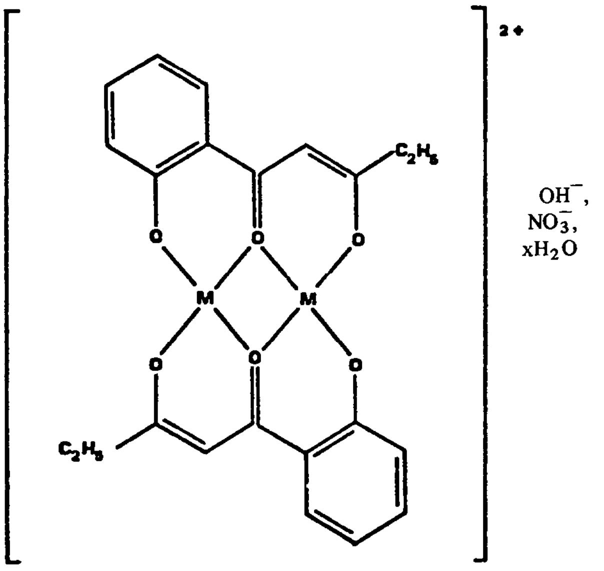


Fig. 4. Structure III.

The reaction of 2-proprionoacetylphenol, (H_2–pap), with α,ω-diamines leads to the Schiff bases I and II in Fig. 3. The ligands are readily characterised by i.r., m.s. and ^{1}H n.m.r. spectroscopy. Metal complexation reactions have been carried out using both the Schiff base ligands and the β-ketophenol precursor.

Complexes of the β-Ketophenol

The reaction of H_2–pap with $Ln(NO_3)_3 \cdot xH_2O$ (Ln = La, Pr, Eu) in methanol in the presence of

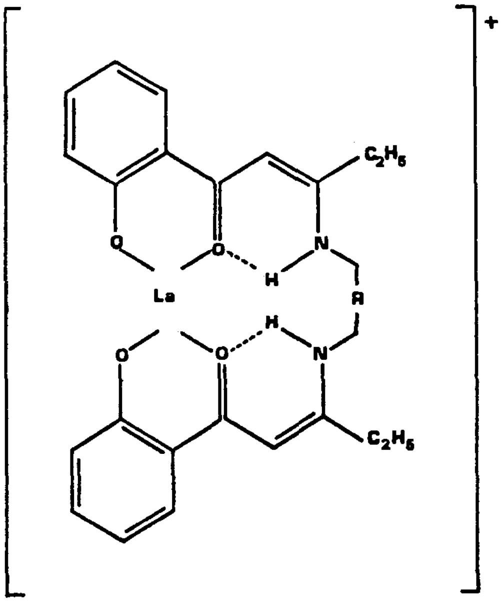


Fig. 5. NO_3^-, xH_2O.

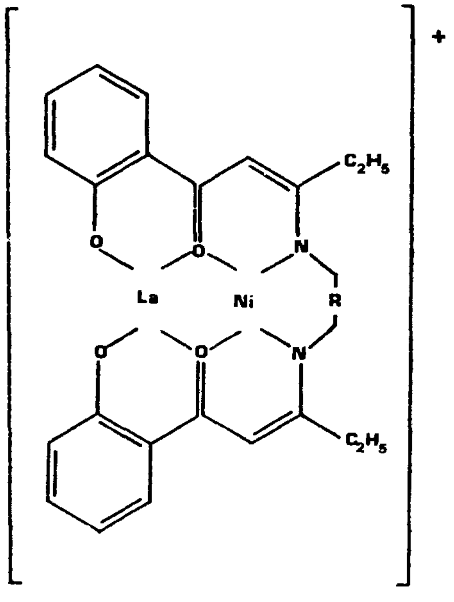


Fig 6. NO_3^-, xH_2O.

LiOH gave fine powdery products. The products analysed as $Ln_2(pap)_2(NO_3)(OH)$, nH_2O (n = 2 for La, 3 for Eu and 6 for Pr), and are assigned the *cis*-binuclear structure, III, by analogy with transition metal analogues [2].

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. The complexes were of the form $Ln(H_2{-}L)NO_3 \cdot xH_2O$ and are assigned structure IV. Outer compartment occupancy is indicated by the absence, in the i.r., of ν_{OH} for the phenol and the presence of ν_{NH}. ^{1}H n.m.r. spectra of the La derivatives also support this proposition. The preference of lanthanide ions for oxygen donor environments would also suggest such an occupancy.

Binuclear Complexes of the Schiff Bases

Attempts to obtain homobinuclear lanthanide complexes have so far been unsuccessful as have been attempts to prepare heterobinuclear complexes by the reaction of the mononuclear lanthanum complexes with metal salts such as VO(IV), Th(IV), $UO_2(VI)$ – all metals with strong $-O_2O_2$ preferences. The reaction of copper(II) ethanoate with IV gave the homobinuclear copper(II) derivative. The reaction of the mononuclear copper(II) complex of I having $-N_2O_2$ occupancy with $Ln(NO_3)_3$, nH_2O gave no heterobinuclear product but reaction of the corresponding nickel(II) complex with $Ln(NO_3)$, nH_2O did give heterobinuclear complexes of I (Ln = La, Pr, Eu).

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Complexes of Lanthanide Chlorides with Macrocyclic Polyethers

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Macrobicyclic polyether ligands I, II, III and IV have been shown [1] to form complexes with alkali salts having high formation constants even in water (10^5 l mol^{-1}).