Lanthanide(III) Complexes with a Schiff Base as a Binucleating Ligand

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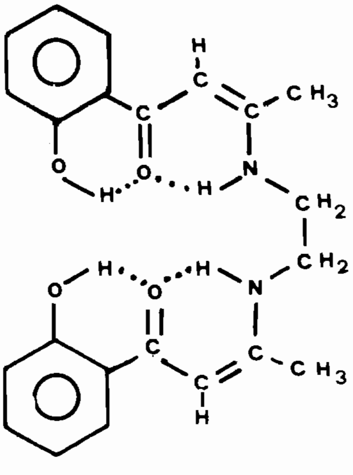
The field of polynuclear complexes has increased greatly, stimulated by the interest in areas such as metallo-enzymes, heterogeneous catalysis and real physico-chemical properties.

A comprehensive range of heterobinuclear complexes derived from compartmental ligands and d- and f- metal ions have been prepared by reaction of pure mononuclear chelates with the required metal salt [1]. To our knowledge, few papers concerning polynuclear compounds of binucleating ligands containing lanthanide(III) ions have been reported [2].

This work relates with the synthesis and characterization of binuclear complexes of lanthanide(III) ions with a binucleating ligand having two different sites of coordination (I).

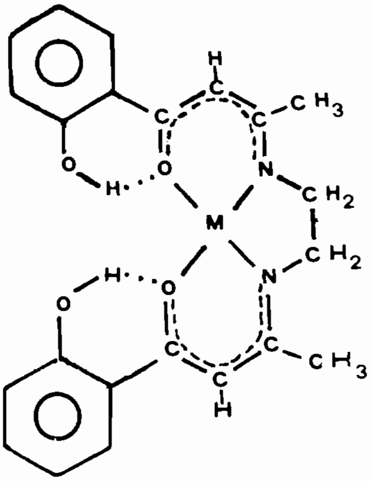


I (H_4aapen)

Experimental

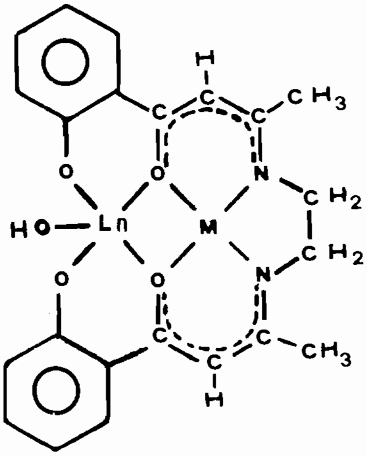
o-Acetoacetylphenol (H_2aap), the ligand I (H_4aapen) and the ligands Cu(H_2aapen) and Ni(H_2aapen) (II) were prepared following previous procedures [1, 3].

Preparation of Heterobinuclear Complexes of II



II (M(H_2aapen)) M = Cu, Ni

The mononuclear complex II (1.0 mmol) was dissolved in hot pyridine (80 ml) and mixed with an ethanol solution of LiOH (2.0 mmol). After 20 min the appropriate lanthanide(III) nitrate (1.0 mmol) in ethanol was added. The solution was heated under stirring for about 4 hr. Pyridine was removed under reduced pressure at 40 °C and the solid residue was treated with hot ethanol. By filtration a solid residue was obtained which was washed with ethanol and dried *in vacuo* at room temperature (III).



III (Ln(OH)M(aapen)) Ln = La–Lu; M = Cu, Ni

Measurements

IR spectra were obtained by a Perkin-Elmer 684 spectrophotometer on samples suspended in a KBr and CsBr matrix, or mulled with mineral oil. Electronic absorption spectra were recorded with a Perkin-Elmer 330 spectrophotometer on the solutions of the complexes in pyridine. The diffuse reflectance spectra were determined with the same instrument on solid compounds pasted with nujol and spread on a disk of filter paper. Magnetic susceptibilities were measured by the Gouy method using a Brucker-

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TABLE I. Analytical Data for Lanthanide(III) Complexes with $M(H_2aapen)$ (M = Cu, Ni). In parenthesis the calcd. values.

Compound	C%	H%	N%	Ln%	μ(B.M.)
$La(OH)Ni(aapen)\cdot 3H_2O$	41.37(40.96)	4.08(4.22)	4.50(4.34)	22.18(21.67)	diam.
$Nd(OH)Ni(aapen)\cdot 3H_2O$	41.73(40.62)	4.28(4.18)	4.20(4.31)	22.33(22.18)	3.8
$Eu(OH)Ni(aapen)\cdot 3H_2O$	39.96(40.15)	4.01(4.14)	4.12(4.26)	23.60(23.09)	3.5
$Ho(OH)Ni(aapen)\cdot 3H_2O$	40.51(39.37)	3.97(4.06)	3.94(4.17)	25.07(24.58)	10.7
$Yb(OH)Ni(aapen)\cdot 2H_2O$	40.78(39.96)	3.69(3.81)	4.33(4.24)	26.40(26.17)	4.5
$Lu(OH)Ni(aapen)\cdot 2H_2O$	40.25(39.84)	3.70(3.80)	4.06(4.22)	26.11(26.39)	diam.
$La(OH)Cu(aapen)\cdot 3H_2O$	41.67(40.66)	3.99(4.19)	4.12(4.31)	21.55(21.37)	1.7
$Nd(OH)Cu(aapen)\cdot 3H_2O$	41.82(40.32)	3.95(4.15)	4.31(4.28)	22.36(22.03)	5.5
$Eu(OH)Cu(aapen)\cdot 3H_2O$	41.06(39.85)	4.09(4.11)	4.25(4.23)	23.06(22.92)	5.1
$Ho(OH)Cu(aapen)\cdot 3H_2O$	40.82(39.09)	4.18(4.03)	4.38(4.14)	24.20(24.40)	12.2
$Yb(OH)Cu(aapen)\cdot 2H_2O$	39.55(39.67)	3.67(3.78)	4.14(4.21)	26.07(25.98)	6.1

Sartorius instrument. The apparatus was calibrated with $Ni(en)_3(ClO_4)_2$. The diamagnetic corrections were calculated from Pascal's constants. Other experimental procedures (molar conductivity and thermal analysis measurements) were the same as previously described [4].

Results and Discussion

The lanthanide(III) complexes with nickel ligand II are red-orange, while the complexes with copper ligand II are green. All complexes are sparingly soluble or insoluble in common solvents, except pyridine and similar materials.

Binuclear complexes of I with divalent metal ions have been previously prepared. This ligand has one site with two nitrogen and two oxygen atoms and a second site with four oxygen atoms, two of which are common in both sites. It has been established that in the mononuclear species $Cu(H_2aapen)$ and $Ni(H_2aapen)$ the metal ion occupies the N_2O_2 internal site thus leaving the external one further available for accommodating a second cation. If this is a trivalent cation, polymeric, hydroxo- or mixed species are expected to form. The analytical data of the complexes of II with lanthanide(III) cations agree with those expected from the hydroxo species. Thus, the prepared complexes can be represented by the general formula $Ln(L)OH\cdot nH_2O$ where Ln = La, Nd, Eu, Ho, Yb, Lu; L = Ni(aapen) or Cu(aapen); n = 3, 2 (Table I). The thermogravimetric and differential thermal analysis curves show an endothermic process of dehydration beginning at 105–120 °C and ending at 150–170 °C.

IR Spectra

Ligand II shows a very broad band between 3200 and 2700 cm^{-1}, assigned as the stretching mode of the intramolecular hydrogen-bonded OH. This absorption exhibits additional weak peaks arising from aromatic and aliphatic CH stretching modes. The bands at 1620 and 1598 cm^{-1} arise prevalently from phenolic ring modes while the strong and broad band at 1520 cm^{-1} can be associated mainly with mixed $C\overset{\cdots}{-}C$, $C\overset{\cdots}{-}N$ and $C\overset{\cdots}{-}O$ stretching vibrations of the internal $O\overset{\cdots}{-}C\overset{\cdots}{-}C\overset{\cdots}{-}C\overset{\cdots}{-}N$ chain. In the spectra of the heterobinuclear complexes with lanthanide(III) cations the broad band centered at 3050 cm^{-1} disappears totally, thus leaving only the CH absorptions. Two sharp bands appear at 3610 and 3500 cm^{-1}, which can be assigned as the stretching mode of the hydroxyl bound to the cation. The bands at 1620 and 1598 cm^{-1} appear essentially unchanged in the spectra of the lanthanide complexes while the composite band at 1520 cm^{-1} shifts globally 15–20 cm^{-1} to lower frequencies, as expected from further drainage of electron density from the oxygen atoms because of tridentation with lanthanide(III) cations.

The phenolic C–O stretching vibration that occurs at 1298 cm^{-1} in free ligand shifts unexpectedly to higher frequencies upon complexation with lanthanide(III) cations. A reasonable explanation is likely to be connected with an increased electron density on the oxygen atom as a result of increased ionicity of the lanthanide–oxygen bonding.

In the CsBr region ligand II shows absorptions arising from the various skeletal, M–O and M–N (M = Ni, Cu) stretching vibrations. In the spectra of the lanthanide complexes a new and asymmetric, though weak, band appears at 375–365 cm^{-1}. Although this band may arise from an activated vibration because of a lowering in symmetry, it is also reasonable to assign it as the Ln–O stretching mode.

Electronic Spectra

Apart from f–f bands, the reflectance spectra of ligand II and of the two series of complexes with lanthanide(III) cations are similar to one another and are not significantly different from their absorption spectra, even in pyridine solution, thus indicating that the structure of the solid remains unchanged in solution.

The ligand Ni(H_2aapen) shows, on the tail of a strong intra-ligand or charge-transfer band at 25000 cm^{-1}, a shoulder at 21276 cm^{-1} and a unique band, at 17857 cm^{-1}, in the region 20000–5000 cm^{-1}. This spectrum is similar to those usually observed for nickel(II) complexes in square-planar or nearly planar environments. In the spectra of the binuclear complexes with lanthanide(III) cations the last band undergoes a shift of 300–400 cm^{-1} to higher frequencies as a result of reinforcement of the ligand field. These results agree with magnetic susceptibility data which indicate that either free ligand and complexes with spin-paired lanthanide(III) cations are diamagnetic, while the complexes with spin-unpaired cations exhibit magnetic moments which are those due to the second metal ion.

The spectral trend of the ligand Cu(H_2aapen) and its complexes with lanthanide(III) cations is the same as that observed for the nickel systems. Free ligand has the copper(II) ion in the square-planar N_2O_2 internal site and a reflectance spectrum which consists, in the region 20000–5000 cm^{-1}, of a shoulder at 19230 cm^{-1} and a weaker band at 16806 cm^{-1}. Only small enhancements in the position (<200 cm^{-1}) and intensity (<10%) of the bands occur upon complexation with lanthanide(III) cations, as expected from essentially unchanged geometry. The magnetic moments of the complexes with spin-paired lanthanide(III) cations agree with the copper(II) ion in square-planar environment while the moments of the complexes with spin-unpaired cations are most probably the sum of the magnetic moments of the two cations.

These results show the internal divalent cation to be unaffected by the presence of the trivalent lanthanide cation in the adjacent O_2O_2 compartment.

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