coordination. For these complexes a coordination number seven, in an approximately pentagonal bipyramidal coordination geometry, can be reasonably attributed to the uranium atom.

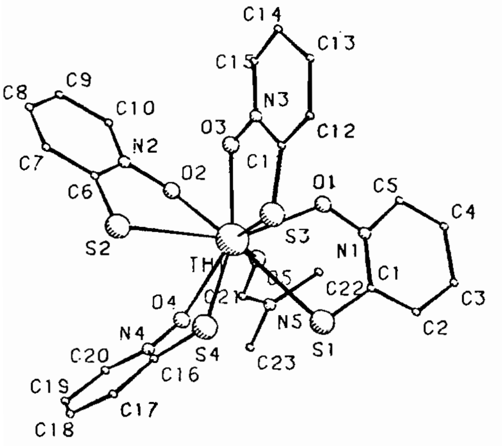
Thorium(IV) complexes of the type $[ThL_4S]\cdot xS$ were obtained with the potentially five-membered chelate ligands HpyOO and HpyOS, whereas complexes of the type $[Th(Quin)_4]\cdot xS$ were obtained with the six-membered chelate ligand HQuin. The coordinated solvent molecule in the first two complexes can be replaced by Ph_3PO, dmso, dma, dmf, as supported by the elemental analysis and by the i.r. spectra.

It must be noted that $[Th(Quin)_4]\cdot xS$ is, for instance, insoluble in dmso and remains uncharged. This behaviour seems to be ascribed to the observed tendency of thorium(IV) towards higher coordination number in complexes with five-membered chelate ligands, while it preferably maintains a coordination number eight, when forming complexes with six-membered chelate ligands.

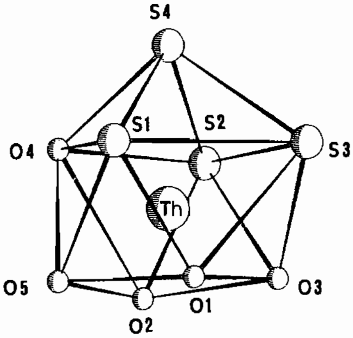
On the contrary $Th(pyOO)_4\cdot 2H_2O$ or $Th(PhOO)_2\cdot MeOH$, well as $Th(pyOS)_4\cdot H_2O$ rapidly dissolve in dmso, giving rise to complexes formulable as $ThL_4\cdot 2dmso$. These complexes can be formulated, from infrared evidences, as $[ThL_4(dmso)]$ dmso with the central metal ion nine-coordinated: a band at about 1000 cm^{-1} was assigned to the νS–O stretching frequency of the coordinated molecule, whereas a second band at about 1025 cm^{-1} can be probably ascribed to the uncoordinated dmso.

For a correct knowledge of the coordination geometry of the prepared complexes, crystals of $Th(pyOS)_4(dmf)$, suitable for an X-ray structural analysis, were grown from a dimethylformamide/diethylether solution.

$Th(pyOS)_4dmf$ is a nine-coordinate chelate with eight donor atoms contributed by the four monoanionic bidentate ligands and the ninth by the solvent molecule.



The coordination polyhedron is a distorted monocapped square antiprism with S(4) as cap. The thorium atom lies 1.38 Å above the base of the polyhedron O(1), O(2), O(3), O(5) and 1.08 Å below the base of the pyramidal cap S(1), S(2), S(3), O(4). The mean planes for the atoms comprising the two 'square' bases are approximately parallel with 2.4° between their normals.



The lanthanum(III) complexes are of the type LnL_3xH_2O or $Li[LnL_4]xH_2O$, the coordination number seems to be most likely eight, even if the stoicheiometry of $Ln(pyOO)_3H_2O$ and $Ln(Quin)_3$ supports coordination number seven and six respectively.

In these complexes however a partial oligomerization cannot be ruled out.

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The Electrochemistry of Mononuclear and Dinuclear Complexes of Transition and Inner Transition Metal Ions with Compartmental Ligands

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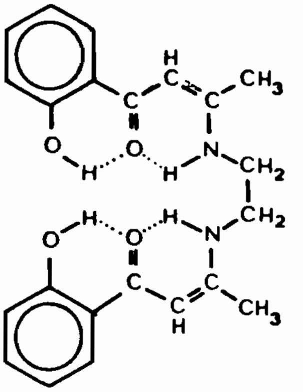
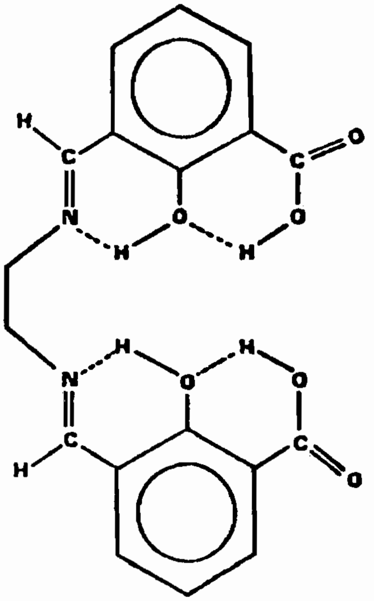
Electrochemical studies on binuclear complexes can serve to get light on the function of metalloenzymes incorporating two metal ions in close proximity at the active site. In this connection, compartmental ligands offer the opportunity to synthetize metal complexes with adjacent coordination sites differing in the donor set [1].

In previous papers [2, 3] we reported the electrochemical behaviour of mononuclear and dinuclear complexes of copper(II), nickel(II) and dioxouranium(VI) with the Schiff base ligand H_4aapen, derived from o-acetoacetylphenol and 1,2-diaminoethane.



H_4aapen

We report now the electrochemical properties of copper(II), nickel(II) and dioxouranium(VI) complexes of the Schiff base ligand H_4fsalacen, derived from 3-formylsalicylic acid and 1,2-diaminoethane [4].



H_4fsalacen

Mononuclear Complexes

The following mononuclear complexes have been taken into consideration *(See next column).*

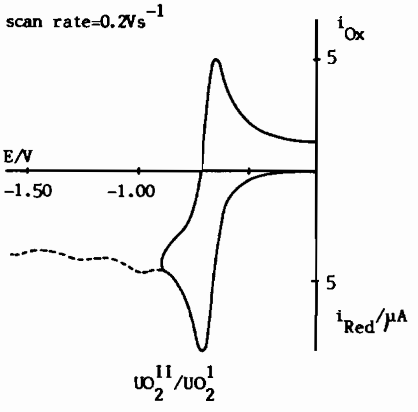
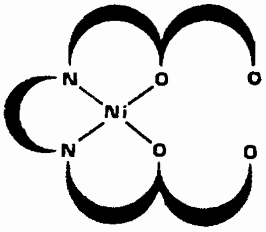
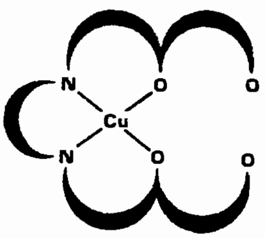
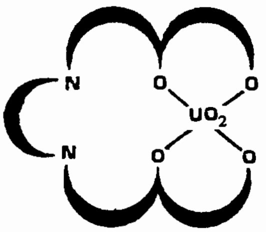


Fig. 1. Cyclic voltammogram of a DMSO solution containing H_2fsalacenUO_2 (8.9×10^{-4} mol dm^{-5}) and TEAP (0.1 mol dm^{-3}); Mercury working microelectrode.







The cyclic voltammetric behaviour of all the complexes, both at platinum and mercury microelectrodes in DMSO solution, shows the occurrence of a cathodic process which involves a quasireversible one electron charge transfer, uncomplicated in the case of the nickel(II) and the dioxouranium(VI) complexes, while followed by a subsequent chemical reaction (the decomposition of the anion) in the case of the copper(II) complex.

In any case the use of appropriate scan rates allows us the computation of the formal potentials for the reduction of the central metal ions (Table I).

As an example in Fig. 1 the cyclic voltammetric response of H_2fsalacenUO_2 is reported.

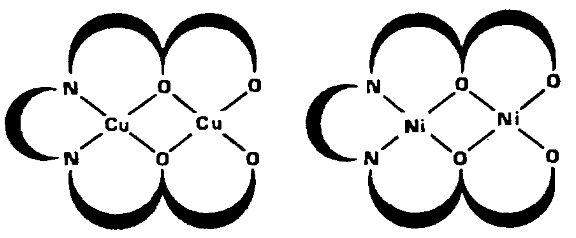
Dinuclear Complexes

Both homodinuclear and heterodinuclear complexes have been studied. *(See next page)*

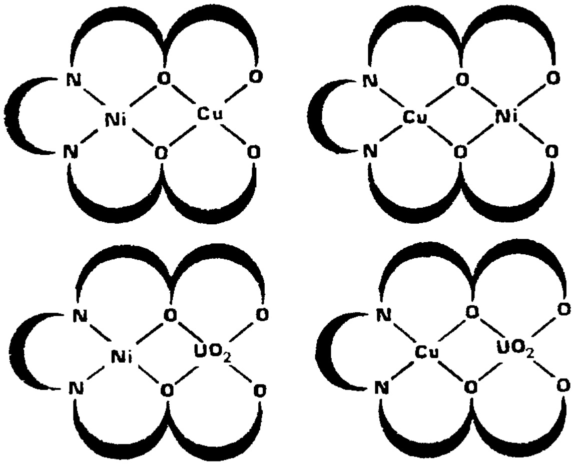
TABLE I. Formal Reduction Potentials (V *vs.* ferrocenium/ferrocene) of fsalacen Complexes as a Function of the Coordination Site.

Metal (M) or Metal ions in the fsalacen complex	$[M_{(N_2O_2)}\mathrm{fsalacen}]/[M_{(N_2O_2)}\mathrm{fsalacen}]^-$	$[M_{(O_2O_2)}\mathrm{fsalacen}]/[M_{(O_2O_2)}\mathrm{fsalacen}]^-$
Ni(II)	−1.59	
UO_2(VI)		−1.14
Cu(II)	−0.92	
$\mathrm{Ni(II)}_{N_2O_2}$ $\mathrm{Ni(II)}_{O_2O_2}$	−1.80	−2.05
$\mathrm{Cu(II)}_{N_2O_2}$ $\mathrm{Cu(II)}_{O_2O_2}$	−1.10	−1.67*
$\mathrm{Cu(II)}_{N_2O_2}$ $\mathrm{Ni(II)}_{O_2O_2}$	−1.42	−2.17
$\mathrm{Ni(II)}_{N_2O_2}$ $\mathrm{Cu(II)}_{O_2O_2}$	−2.05	−1.05
$\mathrm{Cu(II)}_{N_2O_2}$ $\mathrm{UO_2(VI)}_{O_2O_2}$	–	−1.22
$\mathrm{Ni(II)}_{N_2O_2}$ $\mathrm{UO_2(VI)}_{O_2O_2}$	−1.69	−1.44

*Peak potential value at $v = 0.2\ \mathrm{V\ s^{-1}}$.



Homodinuclear Complexes



Heterodinuclear Complexes

The electrochemical behaviour of dinuclear complexes essentially parallels that of the corresponding mononuclear species as to the electrode mechanism; on the contrary shifts of reduction potentials occur, due to the metal-metal interaction [5].

In Fig. 2 the cyclic voltammetric behaviour of $\mathrm{fsalacenNi}_{N_2O_2}\mathrm{UO_2}_{O_2O_2}$ is reported as a typical example.

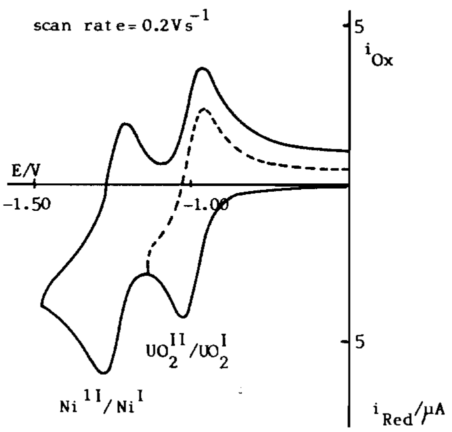


Fig. 2. Cyclic voltammetric behaviour of a DMSO solution containing $\mathrm{fsalacenNiUO_2}$ (5.0×10^{-4} mol dm^{-3}) and TEAP (0.1 mol dm^{-3}); working mercury microelectrode.

Table I summarizes the reduction potentials of all the complexes studied.

A comparison with reduction potentials of the corresponding aapen complexes indicates that fsalacen compounds are generally more easily reducible.

The easiest addition of electrons to fsalacen complexes to respect with aapen complexes can be explained in terms of electronic effects; in fact electron-withdrawing groups, $\rangle C{=}O$, are present in the side chains of the molecule of fsalacen ligand, whereas electro-donating groups, $-CH_3$ are present in the molecule of aapen ligand.

1 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev.*, *8*, 199 (1979).

2 P. Zanello, P. A. Vigato and G. A. Mazzocchin, *Transition Metal Chem., 7,* 291 (1982).
3 P. Zanello, P. A. Vigato, U. Casellato, S. Tamburini and G. A. Mazzocchin, *Transition Metal Chem.,* in press.
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5 R. R. Gagnè, C. L. Spiro, T. J. Smith, C. A. Hamman, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc., 103,* 4073 (1981).

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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.

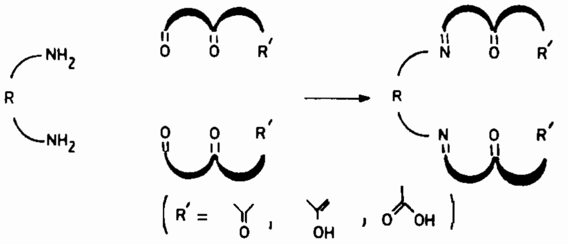
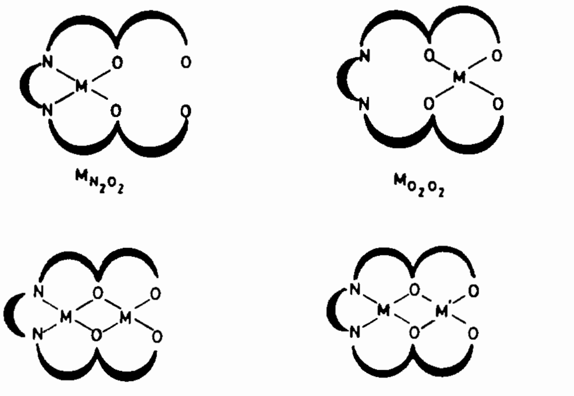


Fig. 1. Synthesis of compartmental ligands.



Homodinuclear complex

Heterodinuclear complex

Fig. 2. Mononuclear positional isomers.

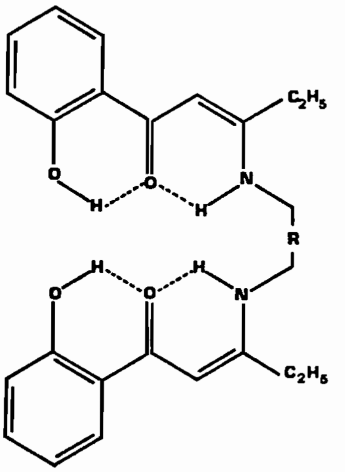


Fig. 3. I, R = $-CH_2-CH_2-$; II, R = $-CH_2-CH_2-CH_2-$.

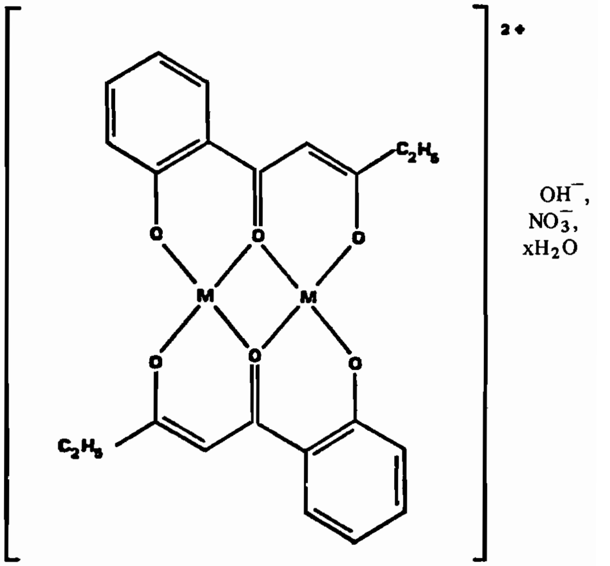


Fig. 4. Structure III.

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