$(depa)_4]^+$ $[UCl_5(depa)]^-$; depa = $EtCONEt_2$) also adopts pentagonal bipyramidal geometry with a Cl–U–Cl axis [14]. Subsequent work in my laboratory has provided evidence of a number of other complexes of the type MCl_4L_3 and it seems probable that 7-coordination will be found to be quite common in this area of the Periodic Table.

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A3

Acyclic and Macrocyclic Schiff Base Complexes of Lanthanides and Actinides

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The work reviewed here is the result of a collaborative project designed to explore the interaction of lanthanides and actinides with acyclic and macrocyclic Schiff base ligands. The ligands are penta- and hexa-dentate in character and have present arrays of donors drawn from oxygen, nitrogen and sulphur atoms. The acyclic ligands are capable of allowing binuclear incorporation to occur; this feature was included in the study as, in the area of selective metal extraction, a single ligand capable of removing two cations simultaneously would have cost benefit advantage over a ligand capable only of removing a single cation.

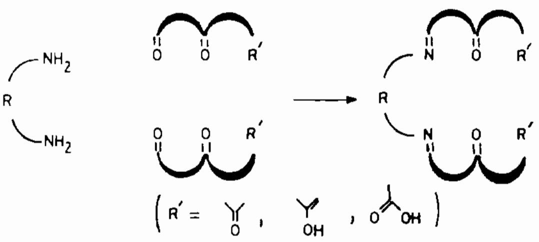
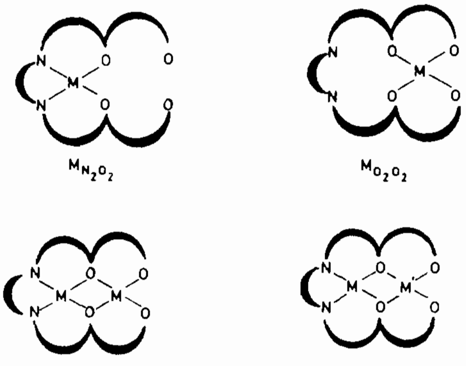


Fig. 1. Synthesis of compartmental ligands.



Homodinuclear complex　Heterodinuclear complex

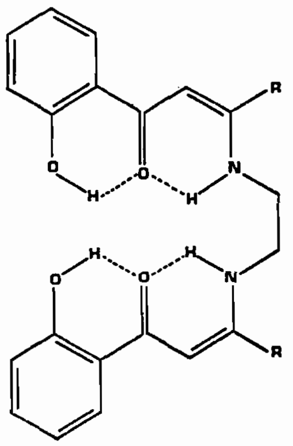
Fig. 2. Mononuclear positional isomers.

A. Complexes Derived from Acyclic Ligands

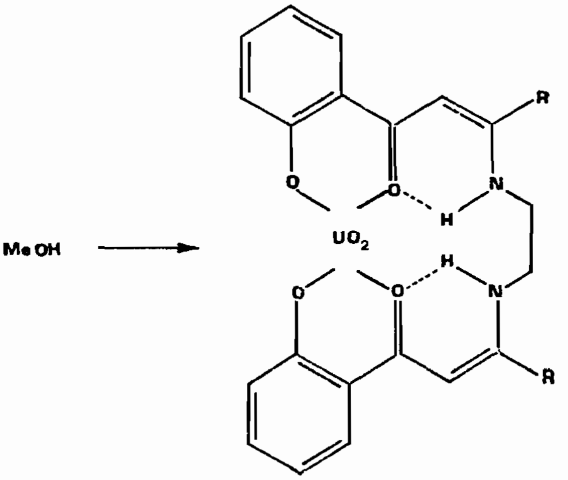
During the last few years we have developed a series of ligands capable of incorporating one, or two, metal cations derived from the reaction of α,ω-alkanediamines with β-triketones or β-ketophenols. These ligands have been collectively termed Compartmental Ligands [1] (Fig. 1). They provide adjacent, dissimilar donor sets capable of forming mononuclear positional isomers, homobinuclear and heterobinuclear complexes (Fig. 2). These ligands have been exploited in the formation of a wide range of transition metal complexes and we here describe the complexation properties of ligands, derived from β-ketophenols and α,ω-alkanediamines, towards dioxouranium(VI). The corresponding complexation of lanthanide cations will be presented in the poster session.

(i) Mononuclear Complexes

Mononuclear complexes of ligands I and II were prepared by stoicheiometric reaction of the ligand



R = CH$_3$, H$_4$–A; II, R = C$_2$H$_5$, H$_4$–B.

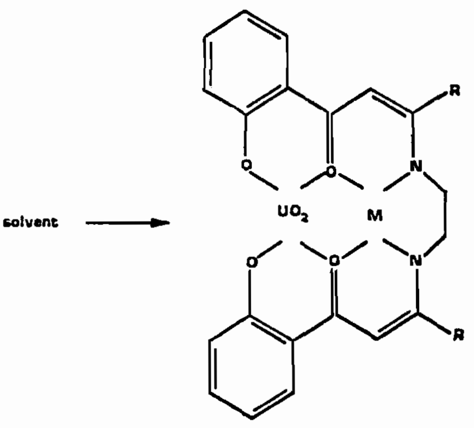


III

with dioxouranium(VI) ethanoate. The complexes were of the UO$_2$(H$_2$–L)$_{O_2O_2}$, H$_2$O and the site occupancy is indicated by i.r. and by analogy with the complex III in Fig. 4 for which an X-ray crystal structure is available [2]. The uranium(VI) is seven coordinate, this being achieved through interaction with the donor atoms of the outer set and a molecule of solvent.

(ii) Binuclear Complexes

Two types of binuclear complex are available, homobinuclear and heterobinuclear, and for the latter there is also the opportunity for positional isomerism to occur. However, the dioxouranium(VI) cation has been found to occupy only the outer donor set and so it is a relatively straightforward matter to prepare heterobinuclear complexes IV in Fig. 5, in which M = Cu or Ni. The complexes may be synthesised either by taking the mononuclear



IV

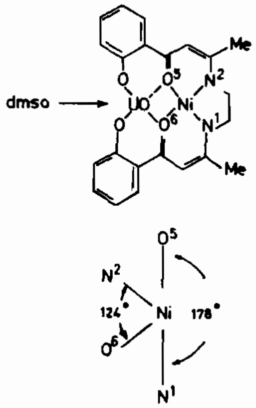


Fig. 3. The Ni environment in (5)-NiUO$_2$·dmso.

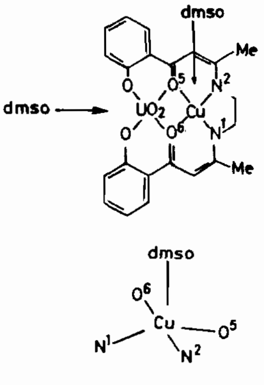


Fig. 4. The Cu environment in (5)-CuUO$_2$·dmso.

dioxouranium(VI) complex and reacting it with the appropriate metal ethanoate, or by taking the mononuclear transition metal complex (having –N$_2$O$_2$ donor occupancy) and reacting it with dioxouranium(VI) ethanoate. The X-ray crystal structures of the UO$_2$·Cu[3] and UO$_2$·Ni[4] complexes of I have been solved. The crystals were obtained from dmso and

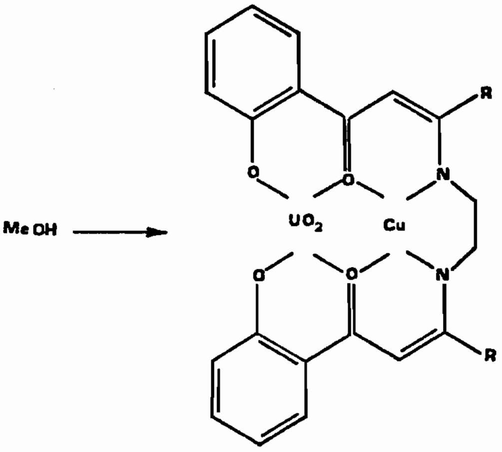
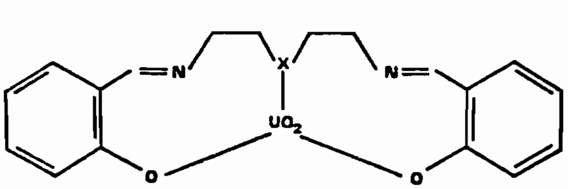


Fig. 5.



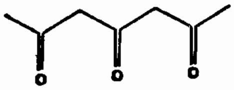
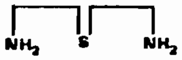
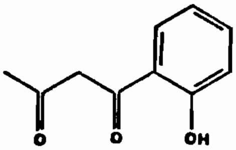
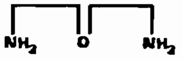
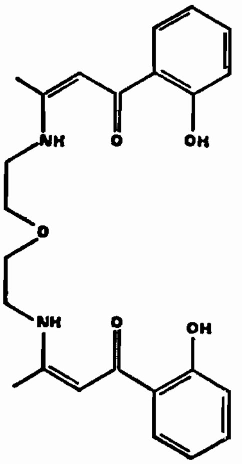
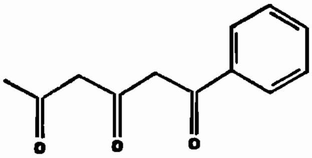
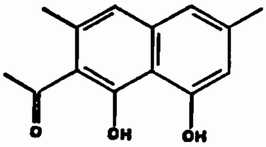
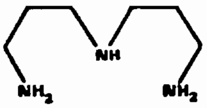
V (saloden) X = 0; (salsen) X = S.

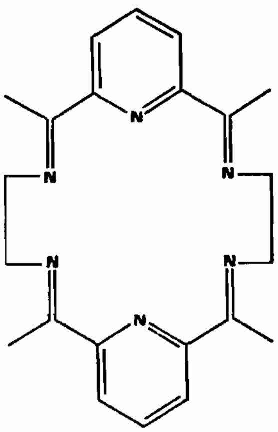
for each complex the dioxouranium(VI) moiety lies in the $-O_2O_2$ set and is further bound to a molecule of dmso. The transition metal environments are unusual; the nickel(II) atom is four-coordinated but severely distorted with a trigonal bipyramidal environment having an empty site (Fig. 6), and the copper(II) atom is pentacoordinated (having a dmso of solvation) and there is a slight deviation from a square pyramidal geometry (Fig. 7).

The origin of the distortions is unclear. Models indicate that it is impossible to accommodate the dioxouranium(VI) without severe ligand distortion so inhibiting the achievement of square planar geometries in the inner-sets: unfortunately a structure of $UO_2(H_2-A)_{O_2O_2}$, H_2O is not available. The structure of $Ni(H_2-A)_{N_2O_2}$ shows the nickel(II) to be square planar [5], and the structure of a related copper(II) complex [6], in which the bridging unit is cyclohexyl-, has a definite tetrahedral twist (14°). In contrast, the structure of the heterobinuclear complex V in (Fig. 8), in which there is an extra methylene group in the bridge allowing for an increased flexibility of the ligand has the copper(II) in a square planar environment [7].

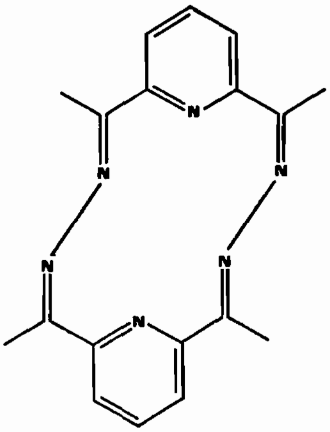
Studies on the related Schiff base complexes, UO_2(saloden) [8] and UO_2(salsen) [9] have shown that if the bridging unit is extended to include a

TABLE I. Schiff Base Derivatives.

Chetoprecursor	Facultative amine	Representation product
 VI	 a	
 VII	 b	
 VIII	 c	
 IX	 d	



X

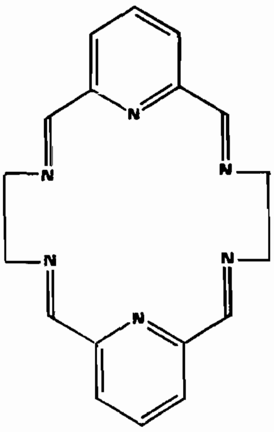


XI

further donor atom then a seven coordinated uranium complex results. This suggested that the incorporation of facultative bridges into compartmental ligands could yield homobinuclear complexes of uranium in which the dioxouranium(VI) could enter both compartments of the ligand and achieve seven coordination in each. No homobinuclear complexes of dioxouranium(VI) were prepared from ligands I and II, presumably because of the restricted size of the inner compartment.

A series of mononuclear complexes were prepared first via stoicheiometric reaction of the keto-precursor, facultative ligand and dioxouranium(VI) ethanoate using metal template techniques (Table I). The mononuclear complexes derived from VI showed no free carbonyl peaks in the i.r. and so were assigned $-O_2O_2$ occupancy as in Fig. 4. By analogy the mononuclear complexes of VII–IX were assigned outer occupancy and this is seen as a reflection of the relative hard and soft character of the available donor sites. The mononuclear complexes all retain one molecule of solvent, water or ethanol, depending upon the precise reaction conditions, and this would assist in the achievement of seven coordination by the uranium in the outer four donor atom set.

Homobinuclear dioxouranium(VI) complexes have been prepared from systems VI(b–d) and VII(b–d) by template procedures, and for systems VIII(a–d) and IXb by addition of LiOH and dioxouranium(VI) ethanoate either to the free ligand or to the mononuclear precursor. The complexes show retention of a mol of solvent as with the mononuclear precursors.

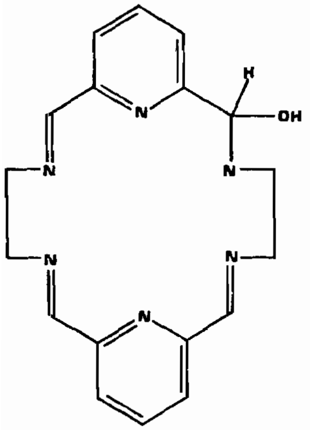


XII

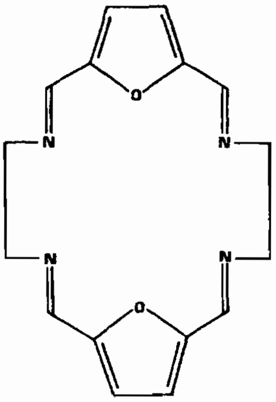
B. Complexes Derived from Macrocyclic Ligands

The facile generation of macrocyclic Schiff bases in the presence of alkaline earth metal cations [10] has led to an interest in the use of lanthanide cations as templating agents in similar circumstances. The comparable ion size suggests that such reactions should be successful. Complexes of the 18-membered hexaazamacrocycle X (Fig. 10) have been reported but were only obtained from $La(NO_3)_3$, $La(ClO_4)_3$ and $Ce(NO_3)_3$ [11, 12]. The heavier lanthanide cations were found to be effective as templating agents in the synthesis of the smaller 14-membered hexazamacrocycle XI (Fig. 11) [13]. The complexes obtained were of 1:1 stoicheiometry and had the general formula (m/c) $M(anions)_3$.

All of the lanthanide cations, except Pm, were found to be effective as templates in the synthesis of macrocyclic complexes from pyridine-2,6-dicarbaldehyde and 1,2-diaminoethane. It was anticipated that all of the complexes would be of the hexaazamacrocyclic ligand, XII, in Fig. 12, and would be of the general form (m/c)$M(anions)_3$. The i.r. spectra of the complexes of the heavier lanthanides (Nd → Lu, except Eu, Pm), however, were different from those for the complexes of the lighter lanthanides



XIII



XIV

(La → Pr, and Eu). The spectra exhibited a complete absence of bands due to carbonyl or primary amines in all cases, but for the former group a distinctive band was detected at *ca.* 3220 cm^{-1}, indicative of a secondary amine group. The addition of a water molecule across an imine group would lead to formation of the carbinolamine species, XIII, and the occurrence of such an addition was supported by ^{13}C and ^{1}H n.m.r. spectral data.

Attempts were made to obtain crystals for X-ray analysis and in the case of the samarium complex were successful. However the band present in the i.r. of the bulk sample at 3210 cm^{-1} had disappeared and a new band was present at 3560 cm^{-1}. This band can be assigned to a Sm–OH group, and the crystal structure shows that the complex analysed is (XII) $Sm(OH)(NO_3)_2 \cdot H_2O$.

For the lighter, and larger, lanthanide cations the preferred products are those involving the tetraimine (XII), (XII) $M(NO_3)_3$, whereas for the heavier and smaller lanthanide cations the modified ligand (XIII) in Fig. 13 is preferred. It is probable that in order to incorporate these latter ions the cavity size must be contracted to accompany the lanthanide contraction and this is done by making the ligand more flexible by addition of water, thus allowing it to bend round the cation. This effect has been noted in d-block transition metal chemistry.

The samarium complex is also hydrolysed on recrystallisation; it is not immediately obviously why this is required unless a reduction in samarium coordination number is accompanied by a radius contraction but this seemingly facile hydrolysis of lanthanium nitrate complexes has been observed by us in related systems which contain either compartmental, or macrocyclic ligands.

The reaction of furan-2,5-dialdehyde with lanthanium nitrates and 1,2-diaminoethane gave rise to 1:1 complexes of the macrocycle, XIV in Fig. 14, for the lighter lanthanides (La → Sm, except Pm) and are of the general form (m/c) $Ln(NO_3)_3$. For the heavier lanthanides the m.s. indicates that the macrocycle is present, but the best fit analyses indicate complexes having present three metal ions and two units of macrocycle, *e.g.* $Gd_3L_2(NO_3)_9 \cdot 4H_2O$. Recrystallisation of these complexes led to decomposition, in contrast to the pyridine-containing species, and the ^{1}H n.m.r. showed that the ring stayed intact in solution. This suggested that on redissolution the lanthanide is reached from the macrocycle which then, on attempted isolation, breaks down.

The complexes can be used in transmetallation reactions as can the alkaline earth metal analogues [14]. The reaction of $La(XIV)(NO_3)_3$ with $Cu(ClO_4)_2$ in ethanol gave a green precipitate of $Cu_2(XII)(ClO_4)_3(OH) \cdot 2H_2O$, a homobinuclear di-copper(II) species previously obtained from a barium source [15].

We thank the Department of Scientific Affairs, N.A.T.O. for an award.

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A4

Organometallic Compounds of the Lanthanides with Ylide Ligands

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$LuCl_3$ reacts with $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ yielding a 1:3 complex which shows dynamic behaviour in solution. The addition of $(C_5H_5)_2LuCl$ to $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ yields an 1:1 chelate complex with stable configuration.

$(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$ and $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ react with $CH_2{=}P(C_6H_5)_3$ and $Me_3SiCH{=}P(CH_3)_3$ in toluene with exchange of the THF ligand for the ylides and formation of new dicyclopentadienyl(alkyl)lutetinyl methylene triorganophosphoranes. New zwitterionic complexes of the type $(C_5H_5)_2Lu(R)(CHR'{=}PR''_3)$ have been isolated and characterized by their NMR spectra and by X-ray structural investigations.

Other ylide complexes of organolanthanides are unstable at room temperature. They decompose with evolution of hydrocarbons and formation of metallacycles or polymeric organolanthanide derivatives.

A5

New Aspects in the Chemistry of Uranocene

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A6

Lower Oxidation States of Lanthanides and Actinides

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A7

Recent Studies of Actinide Stereochemistry

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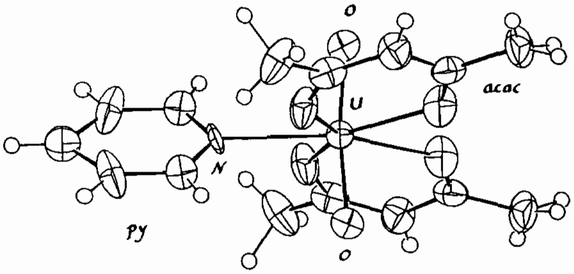
The result of recent work on co-ordination compounds will be described. Emphasis will be laid on the effects of changing the actinide element and on the detailed influence of the coordinating ligands. Among other examples, the structure of $UO_2(pyridine)(acac)_2$ will be discussed, which has been shown to contain a significantly bent O–U–O group (173.5(8)°); its crystals are orthorhombic, *Fdd2,* with $a = 29.702(4)$, $b = 11.433(2)$, $c = 10.593(2)$, R(final) = 0.032:



A8

Electron Spin Resonance Study of Uranium(V) Intermediate in Both Processes of Photo- and Electrolytic Reductions of Uranyl Complex in Organic Solution

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Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Suita, Osaka-565, Japan

Recently the appearance of pentavalent uranium was suggested indirectly by an analysis of photochemical- or electrolytic reduction processes of uranyl complexes in solution [1, 2] but we have first observed the electron spin resonance (ESR) spectra of uranium(V) and confirmed directly the existence of uranium(V) species on the way of both