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Mono- and Homobinuclear Dioxouranium(VI) Complexes of Various Compartmental Ligands

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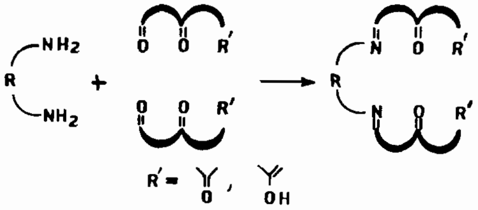
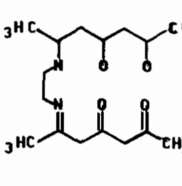
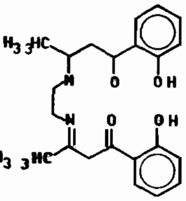
Compartmental ligands are defined as having two adjacent, dissimilar coordination sets for metal complexation [1]. The reaction of an α,ω-diamine with one terminal keto-function of a β-triketone, or β-ketophenol, leads to the formation of compartmental ligands in which one site contains an $-N_2O_2$ donor set, and the other site an $-O_2O_2$ donor set.

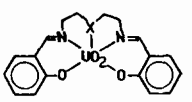


In a metal complexation reaction mononuclear positional isomers may result, but if mononuclear dioxouranium(VI) complexes are prepared only the outer $-O_2O_2$ set is occupied giving $L\cdot UO_{2(O_2O_2)}$, solvent complexes [1]. The solvent molecule occupies an equatorial site in order to maintain the preferred seven coordination of the uranium. A wide range of such complexes derived from ligands having 1,2-diaminoethane as the bridging unit have been reported [1, 2] and the crystal structure of (H_2-daaen)$UO_2\cdot$MeOH confirms the site occupancy as $-O_2O_2$ [3]. Binuclear complexes are formed from the mononuclear species by addition of a second metal. Several heterobinuclear complexes have been prepared in which the outer $-O_2O_2$ set is occupied by dioxouranium(VI) and the inner $-N_2O_2$ set is occupied by a transition metal such as copper(II) or nickel(II), [1]. The X-ray structures of $CuUO_2$(aapen)(dmso)$_2$ and $NiUO_2$(aapen), dmso have been reported [4, 5] and show that the uranium again achieves seven coordination by solvent addition.


H_4-daaen


H_4-aapen

Studies on the related Schiff bases UO_2(saloden) and UO_2(salsen) have shown that if the bridging unit is extended to incorporate a fifth donor atom then a seven-coordinated uranium complex results [6, 7]. This suggests 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 simultaneously achieve seven coordination.



X = O UO_2(saloden)
X = S UO_2(salsen)

A series of mononuclear complexes were first prepared. Stoicheiometric reaction of the keto-precursor, facultative ligand and dioxouranium(VI) acetate in ethanol–chloroform using metal template techniques was required to prepare complexes from (I) and (II), (Table I). The free Schiff bases were prepared from (III) and (IV) and then reacted with dioxouranium(VI) acetate in ethanol–chloroform. The free ligands were characterised by IR, m.s., and, where soluble, by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Table II) and were shown to exist in the keto-amine form. The mononuclear complexes were yellow to orange in colour and those derived from (I) showed no free carbonyl peaks in the IR. O_2O_2 occupancy was assigned to these complexes as this criterion has been used previously with success [1]. By analogy the mononuclear complexes of (II)–(IV) have also been assigned outer set occupancy, and this is seen as a reflection of the hard and soft nature of the available donor sites. The mononuclear complexes all retained one molecule of solvation, either ethanol or water depending on the reaction conditions, and this would assist in the achievement of seven coordination by the uranium in the outer four donor atom set.

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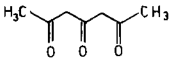
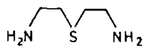
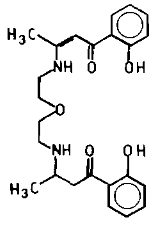
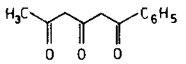
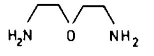
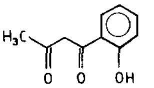
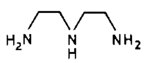
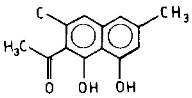
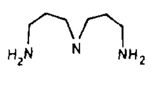
TABLE I. Schiff Base Derivatives.

	Keto-precursor	Facultative amine		Representative product
I			a	
II			b	
III			c	
IV			d	

Homobinuclear dioxouranium(VI) complexes have been prepared for the systems I(b–d), and II(b–d) by template procedures, and for the systems III(a–d) and IVb by addition of lithium hydroxide and dioxouranium(VI) acetate in methanol to a pyridine solution of the mononuclear precursor or from the free ligand by using a 2(metal):1(ligand) stoicheiometry in ethanol–chloroform. The orange to red complexes show retention of a molecule of solvent, as with the mononuclear precursors, and the O=U=O stretch moves to higher frequencies on incorporation of the second metal atom. Typical shifts are *e.g.*, IIb, 895 cm^{-1} (1:1) and 920 cm^{-1} (2:1), and IIIc, 890 cm^{-1} (1:1) and 920, 900 sh cm^{-1} (2:1). This movement is explained by a decreased tendency to transfer charge from the bridging oxygens to the uranium on coordination of the second metal ion [8]. The availability of the above homobinuclear complexes suggests the plausibility of using such multimetal systems in improving the efficiency of solvent extraction processes for metals such as uranium.

Acknowledgement

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TABLE II. NMR Spectra of Schiff Bases derived from (III).

a) ^1H NMR ($CDCl_3$: TMS standard).

IIIa	2.08 (s, 6H, CH_3); 3.55, 3.69 (m, 8H, CH_2); 5.65 (s, 2H, CH); 6.75(t), 6.88(d), 7.29(t), 7.56(d) (8H, aromatics); 11.1 (s, 2H, OH) and 13.6 (s, 2H, NH) ppm.
IIIb	2.15 (s, 6H, CH_3); 2.78(t), 3.51(q) (8H, CH_2); 5.65 (s, 2H, CH); 6.78(t), 6.89(d), 7.31(t), 7.58(d) (8H, aromatics); 10.95 (s, 2H, OH) and 13.42 (s, 2H, NH) ppm.
IIIc	2.15 (s, 6H, CH_3); 2.92(t), 3.51(q) (8H, CH_2); 5.66 (s, 2H, CH); 6.78(t), 6.90(d), 7.30(t), 7.58(d) (8H, aromatics); 11.05 (s, 2H, OH) and 13.60 (s, 2H, NH) ppm.*
IIId	1.77 (m, 4H, CH_2); 2.13 (s, 6H, CH_3); 2.69(m), 3.38(m) (8H, CH_2); 5.63 (s, 2H, CH); 6.75(t), 6.86(d), 7.27(t), 7.58(d) (8H, aromatics); 10.90 (s, 2H, OH) and 13.5 (broad, NH) ppm.*

*No signals for the NH proton in the facultative ligand were detected in these spectra.

b) $^{13}C\{^1H\}$ NMR ($CDCl_3$: TMS standard).

IIIa	19.96 (CH_3); 43.37 (CH_2–N); 70.31 (CH_2–O); 91.13 (CH); 118.06, 120.37, 127.53, 133.17, 162.11 (aromatics); 165.81 (C=N) and 190.19 (C=O) ppm.
IIIb	19.89(CH_3); 33.00 (CH_2–S); 43.37 (CH_2–N); 91.31 (CH); 118.06, 120.31, 127.53, 133.55, 162.11 (aromatics); 165.27 (C=N) and 190.32 (C=O) ppm.
IIIc	20.08 (CH_3); 43.62, 48.71 (CH_2–N); 90.94 (CH); 118.00, 120.43, 127.47, 133.11, 162.04 (aromatics); 165.75 (C=N) and 190.02 (C=O) ppm.
IIId	19.78 (CH_3); 30.21 (CH_2–C); 41.68, 47.14 (CH_2–N); 90.64 (CH); 118.06, 120.49, 127.34, 133.11, 162.11 (aromatics); 165.62 (C=N) and 189.83 (C=O) ppm.

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