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Preparation and Properties of Mono, Homo- and Heterobinuclear Complexes with a New Heptadentate Schiff Base Ligand

U. CASELLATO, D. FREGONA, S. SITRAN, S. TAMBURINI, P. A. VIGATO
Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Padua, Italy

and P. ZANELLO
Dipartimento di Chimica dell'Università di Siena, Siena, Italy

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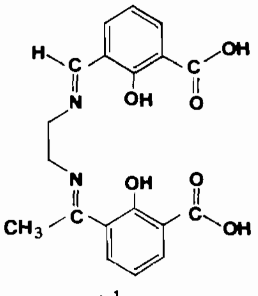
A new heptadentate Schiff base, containing an inner N_3O_2 and an outer O_2O_2 site, has been obtained by the reaction of 3-formylsalicylic acid and diethylenetriamine. By reaction of this ligand with copper(II), nickel(II) or uranyl(VI) salts, mononuclear and dinuclear complexes have been synthesized. The mononuclear complexes can act as ligands towards a second metal ion giving rise to homodinuclear or heterodinuclear complexes. The enlargement of the inner coordination chamber allows the synthesis of dinuclear uranyl(VI) species, impossible to obtain with the inner N_2O_2 site of the ligands previously employed. The equatorial pentacoordination of the UO_2^{2+} group in the outer O_2O_2 chamber is reached with the coordination of a solvent molecule to the central metal ion. The electrochemical behaviour of some complexes prepared is also reported.

Introduction

In the uranyl(VI) complexes the coordination polyhedra, which allow the *trans* O–U–O group to be linear, are the octahedron (a), the pentagonal (b) and the hexagonal bipyramid (c). The shape of the coordination polyhedron depends strongly on the ligands used. With the halides, owing to their different ionic radii, a pentagonal bipyramid has been obtained with $[UO_2F_5]^{3-}$ while an octahedral arrangement was found for $[UO_2X_4]^{2-}$ (X = Cl, Br) [1]. A hexagonal bipyramidal has been generally found with bidentate ligands with a short 'bite' (*i.e.* distance between the two donor atoms) [2, 3], as evidenced by the structural determination of $[UO_2(NO_3)_3]^-$, $[UO_2(NO_3)_4]^{2-}$, $[UO_2(CO_3)_3]^{4-}$, $UO_2(NO_3)_2(Ph_3PO)_2$ [2, 3].

Most uranyl(VI) complexes, however, show a pentagonal bipyramidal geometry, and even when the stoichiometry of the complex suggests a lower coordination number (as, for instance, the anhydrous $UO_2(\beta\text{-diketonate})_2$ complexes), X-ray determinations have shown a pentagonal bipyramidal structure [4]. Accordingly it is impossible to prepare homodinuclear uranyl(VI) complexes with hexadentate compartmental ligands of the type: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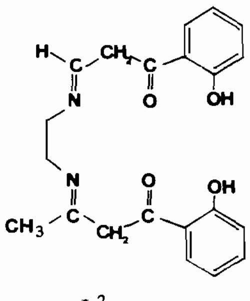
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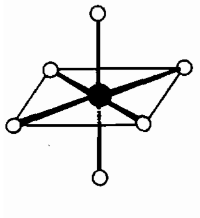
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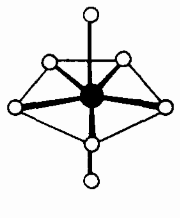
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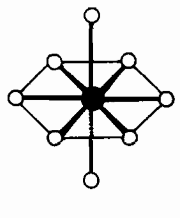
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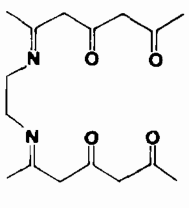

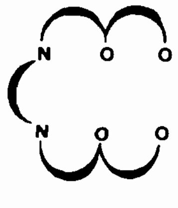
Schematic ligand

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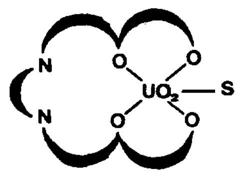
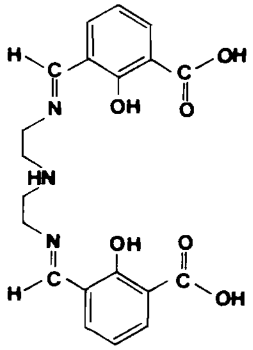
and only mononuclear complexes have been synthesized. The uranyl ion occupies the outer O_2O_2 site and its equatorial pentacoordination is reached with a solvent molecule giving rise to complexes of the type:



as confirmed by X-ray structural determinations [5, 6]. We have thus enlarged the inside chamber; synthesizing the ligand:



H_4L_a

which offers the interesting possibility to coordinate an uranyl(VI) ion also in the inner N_3O_2 site.

By reaction of this ligand with several metal ions, a series of mononuclear, homobinuclear and heterobinuclear complexes containing the uranyl(VI) group have been prepared. In previous papers [7–9] we studied the electrochemistry of complexes with the ligands L^1 and L^2, reported above. Here we study the electrochemical behaviour of the complexes derived from the ligand H_4L_a, with the aim to investigate to what extent a higher flexibility of the inner compartment together with its N_3O_2 five-coordination affects the redox parameters in comparison with the previously tested, more rigid, N_2O_2 four-coordination.

Experimental

3-formylsalicylic acid was prepared according to a literature procedure [10]. Diethylenetriamine, $UO_2(CH_3COO)_2 \cdot 2H_2O$, $Ni(CH_3COO)_2 \cdot H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ and the solvents were reagent grade and were used without further purification.

Preparation of the Ligand (H_4L_a)

To the methanolic solution of diethylenetriamine (10^{-2} mol) solid 3-formylsalicylic acid (2×10^{-2} mol) was added. The resulting solution was stirred for 2 h at room temperature; the solid formed was filtered, washed 2 times with a few millilitres of methanol and dried *in vacuo*. Yield: 75%. Found: C, 59.95; H, 5.25; N, 10.44; required for $C_{20}H_{21}N_3O_6$: C, 60.15; H, 5.26; N, 10.53.

Preparation of the Mononuclear Complexes

$Li_2[UO_2L_a] \cdot 3H_2O$ (1)

To H_4L_a (1 mmol) in methanol LiOH (4 mmol) was added; to the resulting filtered solution and after a period of time $UO_2(CH_3COO)_2 \cdot 2H_2O$ (1 mmol) was added. The resulting solution was stirred for 3 h and the yellow solid obtained was filtered, washed three times with methanol and dried *in vacuo*. Found: C, 32.96; H, 2.72; N, 5.61; required for $C_{20}H_{17}N_3O_8ULi_2 \cdot 3H_2O$: C, 32.74; H, 2.32; N, 5.73.

$UO_2[H_2L_a] \cdot 3H_2O$ (2)

1 mmol of H_4L_a was stirred and heated in a methanol/pyridine (4:1) solution. To this solution an equimolar quantity of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (1 mmol) was added; after stirring under reflux for 24 h the yellow/orange solid obtained was filtered, washed three times with methanol and dried *in vacuo*. Found: C, 33.44; H, 3.26; N, 5.24; required for $C_{20}H_{19}N_3O_8U \cdot 3H_2O$: C, 33.29; H, 3.47; N, 5.83.

$Cu[H_2L_a] \cdot H_2O$ (3)

a) 3-formylsalicylic acid (2 mmol) and diethylenetriamine (1 mmol) were heated in water (100 ml) at 80 °C. To the resulting yellow solution, LiOH (2 mmol) and copper(II) acetate (1 mmol) were added. The hot solution was stirred for 3 h; the green precipitate obtained was filtered, washed with water and dried *in vacuo*. Found: C, 50.03; H, 4.13; N, 8.90; required for $C_{20}H_{19}N_3O_6Cu \cdot H_2O$: C, 50.21; H, 4.39; N, 8.79.

b) To the methanolic suspension of H_4L_a (10^{-3} mol) a solution of copper(II) acetate (10^{-3} mol) was added. The dark green solution obtained was stirred for 3 h. The solvent was removed under reduced pressure and the resulting green solid was washed several times with water, filtered and dried *in vacuo*. Found: C, 49.93; H, 4.48; N, 8.67; required for $C_{20}H_{19}N_3O_6Cu \cdot H_2O$: C, 50.21; H, 4.39; N, 8.79.

Preparation of Homo-binuclear Complexes

$(UO_2)_2[L_a] \cdot CH_3OH$ (4)

a) To 1 mmol of H_4L_a in methanol, LiOH (4 mmol) was added; the resulting yellow solution was filtered and added to a stoichiometric quantity of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (2 mmol). The yellow solid obtained was stirred and refluxed for 4 h and then filtered, washed three times with metahnol and dried *in vacuo*. Found: C, 26.01; H, 2.46; N, 4.43; required for $C_{20}H_{17}N_3O_{10}U_2 \cdot CH_3OH$: C, 25.85; H, 2.17; N, 4.34.

b) To 1 mmol of $Li_2UO_2(L_a) \cdot 3H_2O$ in methanol/pyridine (1:1) an equimolar quantity of $UO_2(CH_3COO)_2 \cdot 2H_2O$ was added. The product was stirred for 2 h under reflux, then filtered, washed three times with methanol and dried *in vacuo*. Found: C, 25.97; H, 2.24; N, 4.21; required for $C_{20}H_{17}N_3O_{10}U_2 \cdot CH_3OH$: C, 25.85; H, 2.17; N, 4.34.

c) To a methanolic suspension of $UO_2(H_2L_a) \cdot 3H_2O$ (1 mmol), 2 mmol of LiOH and 1 mmol of $UO_2(CH_3COO) \cdot 2H_2O$ were added. The product obtained was stirred under reflux for 4–5 h, then filtered, washed with methanol and dried *in vacuo*. Found: C, 25.94; H, 2.42; N, 4.22; required for $C_{20}H_{17}N_3O_{10}U_2 \cdot CH_3OH$: C, 25.85; H, 2.17; N, 4.34.

$Cu_2[L_a] \cdot 4H_2O$ (5)

To H_4L_a (1 mmol) in methanol LiOH (4 mmol) was added; to the resulting yellow solution copper(II) acetate was added (2 mmol). The blue-green solution obtained was stirred and refluxed for 5 h. The blue-green precipitate obtained was filtered, washed three times with methanol and dried *in vacuo*. Found: C, 39.81; H, 4.01; N, 6.97; required for $C_{20}H_{17}N_3O_6Cu_2 \cdot 4H_2O$: C, 40.40; H, 4.21; N, 7.07.

Preparation of the Heterobinuclear Complex

$CuUO_2[L_a] \cdot 3H_2O$ (6)

This complex was obtained as follows:

a) To a methanolic solution of the mononuclear copper complex $Cu[H_2L_a] \cdot H_2O$ (1 mmol), LiOH (2 mmol) and the appropriate uranyl acetate (1 mmol) dissolved in methanol were added. The yellow-green precipitate was filtered, washed with methanol and dried *in vacuo*. Found: C, 30.82; H, 2.69; N, 5.45; required for $C_{20}H_{17}N_3O_8CuU \cdot 3H_2O$: C, 30.67; H, 2.94; N, 5.37.

b) 1 mmol of $Li_2[UO_2L_a] \cdot 3H_2O$ in a methanol solution was stirred at about 50 °C and an equimolar quantity of copper(II) acetate was added. The product was stirred and refluxed for 24 h, then filtered and the green-yellow product obtained was washed with methanol and dried *in vacuo*. Found: C, 30.58; H, 2.72; N, 5.31; required for $C_{20}H_{17}N_3O_8CuU \cdot 3H_2O$: C, 30.67; H, 2.94; N, 5.37.

c) To 1 mmol of $UO_2(H_2L_a) \cdot 3H_2O$ in a methanolic solution, LiOH (2 mmol) and copper(II) acetate (1 mmol) were added. The product obtained was stirred under reflux for 24 h, then filtered. The yellow-green compound obtained was washed with methanol and dried *in vacuo*. Found: C, 30.24; H, 2.54; N, 5.13; required for $C_{20}H_{17}N_3O_8CuU \cdot 3H_2O$: C, 30.67; H, 2.94; N, 5.37.

d) $Cu_2[L_a] \cdot 4H_2O$ (1 mmol) in methanol/pyridine (1:1) was stirred at about 50 °C and 1 mmol of $UO_2(CH_3COO)_2 \cdot 2H_2O$ in methanol was added. The product was stirred and refluxed for 24 h, then filtered and the green-yellow compound obtained was washed with methanol and dried *in vacuo*. Found: C, 30.65; H, 2.70; N, 5.35; required for $C_{20}H_{17}N_3O_8CuU \cdot 3H_2O$: C, 30.67; H, 2.94; N, 5.37.

The mononuclear and dinuclear nickel complexes were prepared by the same procedure employed for the analogous copper(II) complexes; the details of the preparation procedure have been reported elsewhere [25].

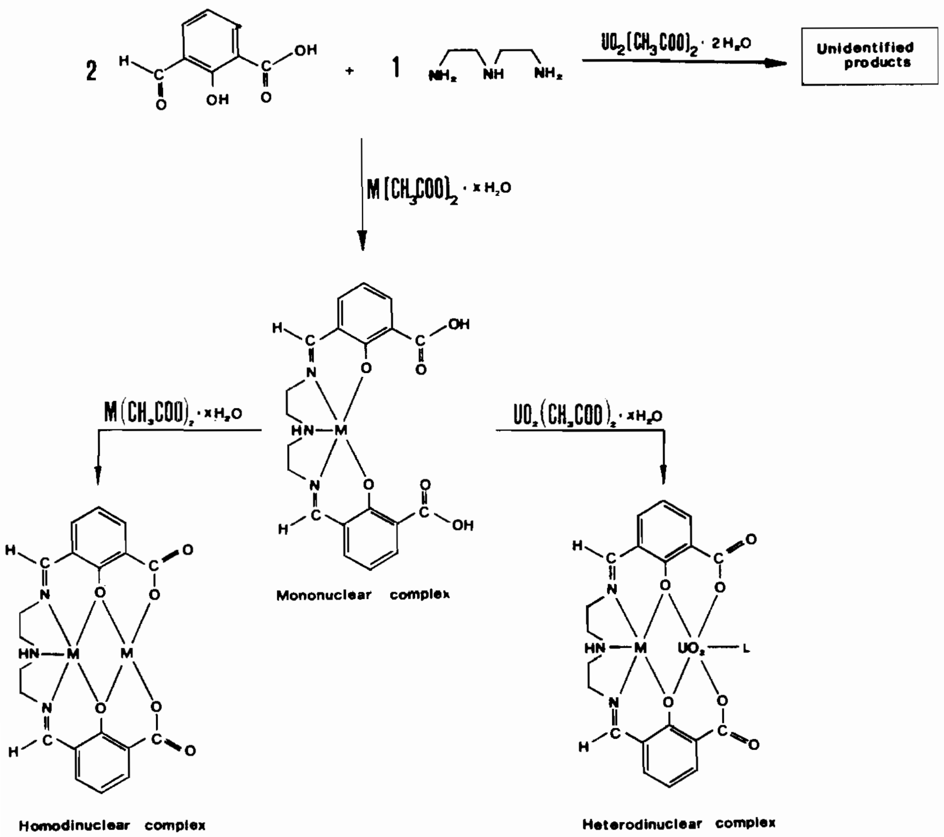
Materials and Apparatus

The materials and the apparatus for the electrochemical tests have been described elsewhere [11]. The potential values reported herein refer to the ferrocenium–ferrocene couple [12]. All experiments were performed at 20 ± 0.1 °C. The compounds reported in Table II were prepared according to the literature, compounds B and D according to ref. 13, compounds A and C according to ref. 14, compound E according to ref. 15 and compound F according to ref. 16. The electrode activity of the ligand was measured using $Mg_2L_b \cdot 4H_2O$ where H_4L_b is $[o\text{-}HO\text{–}C_6H_4\text{–}CH{=}N\text{–}(CH_2)_3]_2\text{–}P(C_6H_5)$. In dimethylsulphoxide solution containing tetraethylammonium perchlorate (0.1 mol dm^{-3}) it gives rise in cyclic voltammetry at a platinum microelectrode to a quasi-reversible response at $E_p = -1.59$ V ($E^{\circ\prime} = -1.45$ V); on the contrary at a mercury microelectrode an irreversible process is shown at −2.25 V, in addition to a few ill-defined signals at less negative potentials.

Results and Discussion

Preparation and Properties of the Complexes

We started preparing a series of mono- and heterobinuclear complexes by the reaction scheme 1 using a template synthesis, without a previous separation and purification of the heptadentate Schiff base H_4L_a. In the case of the heterobinuclear uranyl(VI) complexes a solvent molecule fills the fifth equatorial coordination position of the outer uranyl(VI) group. By this procedure we were completely unsuccessful in the preparation of mono and homobinuclear uranyl complexes; in any case complexes with an approximately 3:2 uranyl(VI):ligand ratio were



Scheme 1

obtained. It was however impossible to define the correct stoichiometry of these complexes.

Thus we made a successful attempt to isolate the potentially heptadentate ligand H_4L_a. This Schiff base was obtained as a yellow solid which melts above 270 °C. In the ir spectrum there is a broad band at 3170 cm^{-1} due to νN–H, at 1685 cm^{-1} due to νC=O and at 1652 and 1605 cm^{-1} due to the C=N and C=C modes.

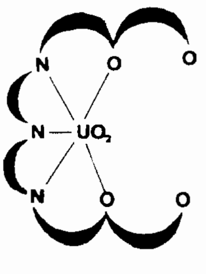
By reaction of this ligand, in alcoholic medium, with uranyl(VI) acetate dihydrate and/or copper(II) acetate, the reaction scheme 2 was obtained.

As can be seen, it is easy to obtain by this procedure mononuclear and homobinuclear uranyl(VI) complexes. It is also easy to obtain heterobinuclear complexes; in these complexes the uranyl(VI) ion occupies the outer O_2O_2 coordination chamber, while the copper(II) is in the inner N_3O_2 site. The homobinuclear copper(II) complex can undergo a transmetallation reaction with UO_2^{2+}, according to the reaction:

$$M_2L + UO_2^{2+} \longrightarrow MUO_2L + M^{2+}$$

in accordance with the higher tendency of the uranyl(VI) group to coordinate the external O_2O_2 site.

It was reported above that, with hexadentate compartmental ligands, the uranyl(VI) ion forms only mononuclear complexes, occupying the O_2O_2 site. The formation of homobinuclear species is prevented by the impossibility for the uranyl(VI) ion to reach the usual equatorial pentacoordination in the inner chamber. With the heptadentate ligand prepared, H_4L_a, it becomes feasible to obtain positional isomers of the type:



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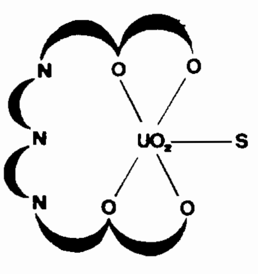
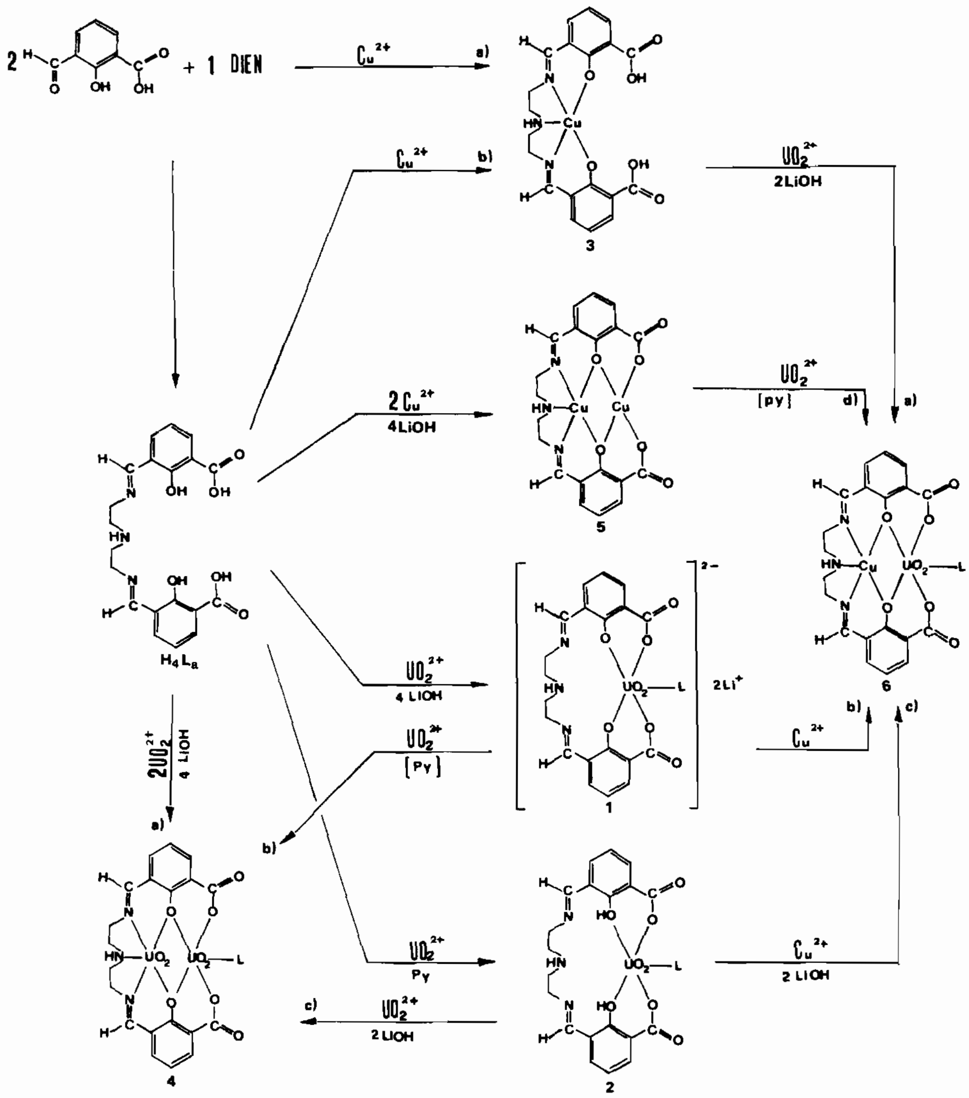


II

Previous studies demonstrated that it is easy to obtain uranyl(VI) complexes with pentadentate Schiff bases, which represent the inner chamber of the prepared ligand H_4L_a [17–24]. Physico-chemical



Scheme 2.

data and the reaction of the mononuclear species prepared with neutral monodentate ligands, such as dimethylsulphoxide, or with a second metal ion (as copper(II)), suggest the coordination of the uranyl ion in the outer O_2O_2 site as in **II** for the mononuclear complexes **1** and **2** of Scheme II. In the infrared spectra of **1** and **2** there is a lowering of the νC=O band of the carboxylic groups at about 25 cm^{-1} with regard to the ligand (1685 cm^{-1} in the free ligand and 1662 and 1660 cm^{-1} for the two complexes **1** and **2**). In the homobinuclear uranyl complex, **4**, there is an analogous lowering of the νC=O (1655 cm^{-1}). These infrared evidences support the involvement of the outer site in the coordination of UO_2^{2+} in the mononuclear species.

In the mononuclear copper(II) complex, **3**, where the central metal ion occupies the inner N_3O_2 site, the νC=O lies at 1680 cm^{-1}, a value comparable with that of the free ligand. In the homobinuclear copper(II) complex, **5**, the νC=O is shifted at 1650 cm^{-1}, the O_2O_2 site also being involved in the coordination. The ν_3 O–U–O lies at 905 cm^{-1} for **1** and at 925 cm^{-1} for **2**, showing that the equatorial coordination in the neutral and in the ionic complex is not exactly equal.

The low solubility of the mononuclear uranyl complexes even in coordinating solvents such as dimethylsulphoxide does not allow an unambiguous identification of the chemical shifts of the protons upon coordination.

The reaction with dimethylsulphoxide for the mononuclear and binuclear uranyl(VI) species is further evidence of the outer occupancy of the UO_2^{2+} ion in the mononuclear complexes. When **1** and **2**

TABLE I. Reduction Potentials (Volt) (*vs.* ferrocenium–ferrocene) for the Metallic Complexes of H_4L_a and (**2**) Ligands as a Function of the Coordination Compartment.

Metal (M) ion, or ions in the complex ML		Inner compartment			Outer compartment		
		$M_{N_3O_2}L/[M_{N_3O_2}L]^-$ (H_4L_a)		$M_{N_2O_2}L/(M_{N_2O_2}L)^-$ (L^2)	$M_{O_2O_2}L/(M_{O_2O_2}L)^-$ (H_4L_a)		$M_{O_2O_2}L/(M_{O_2O_2}L)^-$ (L^2)
		Pt	Hg		Pt	Hg	
Ni(II)		–2.43[b]	–2.27[b]	–1.59[a]			
Cu(II)		–1.06[b]	–0.87[a]	–0.92[a]			
UO_2(VI)					–1.77[b]	–1.57[b]	–1.14[a]
Ni(II)$_{inner}$	Ni(II)$_{outer}$	–2.45[b]	–	–1.80[a]	–2.13[b]	–	–2.05[a]
Cu(II)$_{inner}$	Cu(II)$_{outer}$	–1.18[b]	–	–1.10[a]	–2.29[a]	–	–1.67[b,c]
UO_2(VI)$_{inner}$	UO_2(VI)$_{outer}$	–1.52[b]	–1.51[b]	–	–1.52[b]	–1.51[b]	–
Cu(II)$_{inner}$	Ni(II)$_{outer}$	–1.75[b]	–1.65[b]	–1.42[a]	–2.44[b]	–	–2.17[a]
Ni(II)$_{inner}$	Cu(II)$_{outer}$	–2.02[b]	–	–2.05[a]	–1.09[b]		–1.05[a]
Cu(II)$_{inner}$	UO_2(VI)$_{outer}$	–1.05[b]	–0.99[a]	–1.22[a]	–1.97[a]	–2.05[b]	–1.22[a]
Ni(II)$_{inner}$	UO_2(VI)$_{outer}$	–2.57[b]	–	–1.69[a]	–1.50[a]	–1.50[a]	–1.44[a]

[a] Formal electrode potential. [b] Peak potential values at 0.2 V s^{-1}. [c] At a platinum electrode.

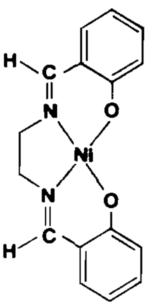
are dissolved in dimethylsulphoxide, the water of the methanol molecule is replaced by the more basic dmso, giving rise to $UO_2(H_2L_a)$(dmso) and $Li_2UO_2(L_a)$(dmso). In the infrared spectra of these two complexes a new band appears at 1025 cm^{-1} for $Li_2UO_2(L_a)$(dmso) and at 1020 cm^{-1} for $UO_2(H_2L_a)$(dmso), respectively. The coordination of the dmso to the uranyl(VI) ion is an indication that the equatorial pentacoordination of the UO_2^{2+} group is reached in the mononuclear species *via* the coordination of the O_2O_2 set and the oxygen of a solvent molecule, analogously to what was found for the outer uranyl(VI) coordination in the binuclear complex, where the reaction with dmso produces $(UO_2)_2(L_a)$(dmso), which has an infrared absorption at 1017 cm^{-1} due to the νS–O of the coordinated dmso. The uranyl(VI) ion in the inner N_3O_2 site does not coordinate an additional dmso, its equatorial coordination being saturated by the donor atoms of the Schiff base ligand.

An additional evidence of the outer occupancy in the mononuclear species comes from the different reactions, reported in Scheme 2, for the preparation of heterobinuclear copper(II)–uranyl(VI) complexes. The different routes give complex **6**, the infrared and the electronic spectra being the same for the samples obtained by the procedure **a**, **b**, **c** and **d**.

In the infrared spectra of these **6a**, **6b**, **6c** and **6d** there are four bands in the range 1680–1500 cm^{-1} at 1655, 1600, 1560 and 1525 cm^{-1} and the ν_3 of the O–U–O group lies at 900 cm^{-1}. The electronic spectra, measured in dimethylsulphoxide solution, show d–d bands at about 590 nm and another band at about 455 nm. It must be noted however that the complexes, coming from different reaction routes, show a different solubility in dmso. This different solubility, which does not follow any logical sequence, has been ascribed to the various molecules of solvent present in the complexes, rather than to the presence of positional heterobinuclear isomers.

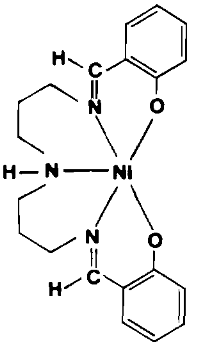
Ultimately, on the basis of the above reactions and/or physicochemical measurements, it seems reasonable to suggest that the uranyl(VI) ion is in the outer O_2O_2 site in the mononuclear complexes. With this assumption, however, the formation of homobinuclear uranyl(VI) complexes starting from the mononuclear species is not immediately understandable. These reactions proceed easily and in high yield. These results are not in line with the supposed difficulty for the uranyl(VI) group to coordinate in the inner chamber when the outer is filled. A migration of the uranyl ion might be invoked as the first step of the reaction, favoured by the experimental condition employed, followed by an easier coordination of the second uranyl(VI) ion to the outer O_2O_2 site, which has become available. If this is the reaction pathway, it means that it is possible for the uranyl ion to change the coordination set under particular conditions, which casts doubts on the conclusions suggested above on the basis of the physico-chemical and the reactions results. Additional studies, also on similar complexes, are thus necessary in order to better understand the chemical behaviour and the correct coordination of these mononuclear uranyl(IV) complexes and consequently of the related heterobinuclear species.

TABLE II. Formal Electrode Potentials (*vs.* ferrocenium–ferrocene) for the One-electron Reduction of Complexes showing both N_2O_2 and N_3O_2 Coordination of the Central Metal Ion.



Ⓐ

$E^{\circ\prime} = -2.05$ V



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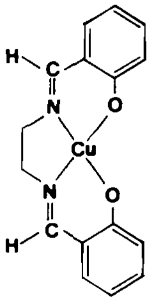
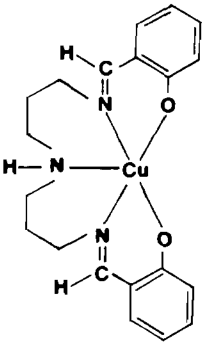
$E^{\circ\prime} = -2.12$ V



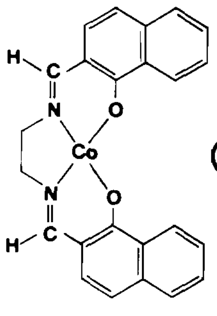
Ⓒ

$E^{\circ\prime} = -1.62$ V



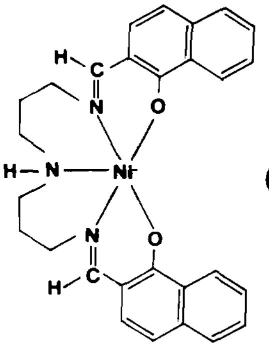
Ⓓ

$E^{\circ\prime} = -1.48$ V



Ⓔ

$E^{\circ\prime} = -1.66$ V



Ⓕ

$E^{\circ\prime} = -2.41$ V

Electrochemical Behaviour

As in the case of the derivatives of the hexadentate ligands L^1 and L^2 the electrochemistry of the complexes with H_4L_a has been studied in dimethylsulphoxide solution containing tetraethylammonium perchlorate as supporting electrolyte, both at platinum and mercury microelectrodes, by cyclic voltammetry and by controlled potential coulometry.

Unfortunately the cyclic voltammetric responses are often ill-defined because of the high degree of irreversibility of the involved charge transfers and because of the reduction of the ligand itself (see Experimental) in the potential ranges of interest; however, the electrode processes substantially parallel those from the corresponding metal complexes of L^1 and L^2, so that the potentials of the one-electron reduction of the central metal ion, or ions, can be evaluated. Table I reports the resulting electrode potentials (*vs.* ferrocenium–ferrocene couple), together with those relevant to the corresponding complexes of L^2.

The irreversibility of most charge transfers prevents the obtainment of reduction potentials significant from a thermodynamic viewpoint, *i.e.* formal electrode potentials: however on the basis of available formal electrode potentials and of the location of potentials of the irreversible processes, complexes of H_4L_a seem more reducible than those of L^2 as regards the inner compartment. The enlargement of the cavity size is expected to make the access to the one-electron reduced state of the central metal ion easier. On the contrary it is hard to foresee the effect of the variation of the donor atom set around the central metal ion from N_2O_2 to N_3O_2 if the geometries of these metal ions in both reduced and oxidized states and solvation energies are not known. In addition, considering that in the above described conditions, complexes such as A–B, C–D and E–F, reported in Table II (which sufficiently mimic the coordination spheres of the inner compartment of the complexes of H_4L_a and L^2, respectively) show the formal electrode potentials for the one-electron reduction reported in Table I, we cannot make any generalization on the effect of N_3O_2 coordination on the redox properties of the central metal ion with respect to N_2O_2 coordination. Notwithstanding this it seems likely that in the present case, even when the effect of five-coordination tends to stabilize the oxidized state of the metal ion, the effect of enlargement of the compartment dominates in stabilizing the reduced state of the metal ion.

As regards the outer compartment, the differences in reduction potentials, rarely significant, cannot be rationalized except in generic terms of collateral electronic effects.

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