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Mononuclear and Dinuclear Complexes Derived from New Potentially Heptadentate Acyclic Schiff Bases

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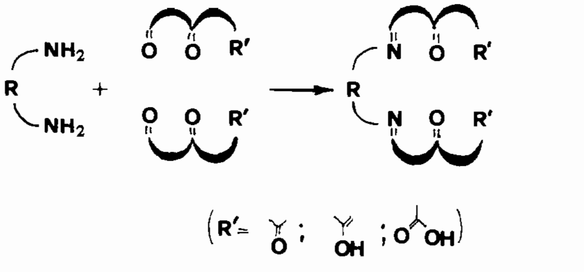
New potentially heptadentate compartmental ligands have been prepared by reaction of o-acetoacetylphenol or 3-formylsalycilic acid with diethylenetriamine or bis-3-aminopropyl-phenylphosphine.

These Schiff bases contain an inner O_2N_2X *(X = N, P) and an outer* O_2O_2 *coordination site which can bond, in close proximity, two similar or dissimilar metal ions.*

With some metal salts (nickel(II), copper(II) and uranyl(VI) acetates) mononuclear, homo- and heterodinuclear complexes have been synthesized. The spectroscopic, magnetic and electrochemical properties of these complexes have been studied. The catalytic activity of a binuclear copper(II) complex towards the oxidation of 3,5-di-t-butylcatechol to the corresponding quinone was also investigated.

Introduction

Many papers have been published in the last few years dealing with the synthesis and physico-chemical properties of binucleating ligands obtained by condensation of $\rangle$C=O carbonyl groups with amines according to the general scheme [1–3]:



Scheme 1. Synthesis of compartmental ligands.

These ligands have two adjacent sites; the inner containing the N_2O_2 coordination set and the second, outer, containing the O_2O_2 set. These ligands can thus coordinate two similar or dissimilar metal ions in close proximity giving rise to an interaction between the two metal centres [1–3].

A particular interest in these studies comes from biochemistry; it has been noted that many proteins can develop their activity in the presence of two or more metal ions [4–6].

Some enzymes contain heterodinuclear or homodinuclear complexes. Binuclear copper(II) complexes, formed by the ligands of the above scheme, can offer a good mimicry of the role of such ions in the emocyanine, where one of the active sites for the oxygen activation is a dinuclear copper complex [4–6].

With the present work we have tried to enlarge the internal site of the binucleating ligands with an additional donor atom.

It is well known that UO_2^{2+} prefers an equatorial pentagonal coordination [7, 8]; when the chelating ability of the ligands does not allow this coordination number to be reached, the free sites are filled by solvent (*i.e.* methanol, water *etc.*) or by oligomerization [7, 8].

Accordingly, the internal N_2O_2 site of the binucleating ligands so far prepared cannot coordinate an uranyl(VI) ion. Thus the enlargement of this site by means of a hydrocarbon chain containing a fifth donor atom can offer a very appropriate coordination geometry for UO_2^{2+} with the consequent formation of binuclear species [9].

By reaction of 3-formylsalicylic acid or *o*-acetoacetylphenol with triamines of the type: NH_2–$(CH_2)_n$–X–$(CH_2)_n$–NH_2 (n = 2; X = NH; n = 3, X = P), potentially heptadentate ligands, containing an inner N_2XO_2 and an outer O_2O_2 coordination site have been synthesized. These ligands can be used for the preparation of mononuclear and/or dinuclear complexes.

The internal chamber of these ligands is a potentially pentadentate Schiff base; thus the compounds derived from salicylaldehyde or *o*-hydroxyacetophenone and the triamines above described have also been prepared.

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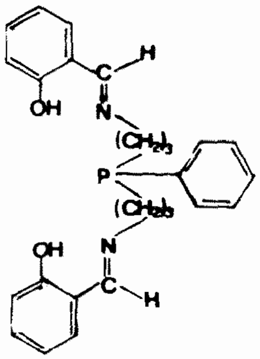
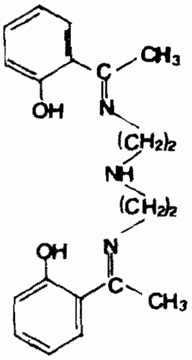
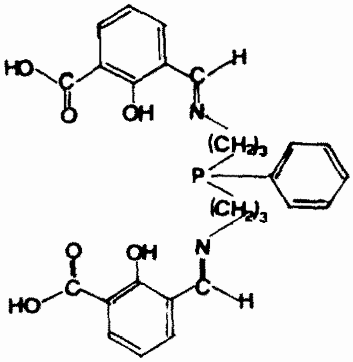
Therefore the present paper reports the preparation of the Schiff bases:



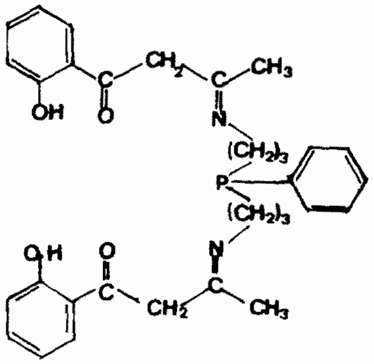
H_2L_a



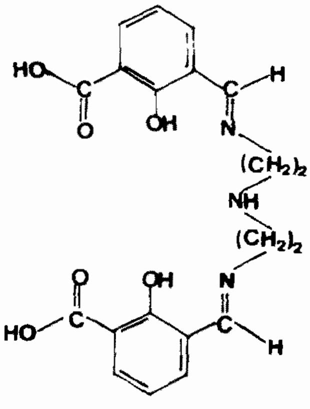
H_2L_b



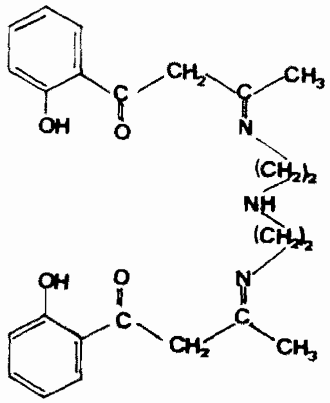
H_4L_c



H_4L_d



H_4L_e



H_4L_f

and their interaction with copper(II), nickel(II) and uranyl(VI) together with the physico-chemical properties of these complexes, particularly their magnetic and electrochemical behaviour and the catalytic activity of a copper(II) complex in the oxidation reaction.

Experimental

Materials

3-Formylsalicylic acid [10] and *o*-acetoacetylphenol [11], were obtained according to literature methods.

Salicylaldehyde, *o*-hydroxyacetophenone and diethylenetriamine are reagent grade products.

Bis(3-aminopropyl)phenylphosphine is a Strem Chemicals air sensitive product; consequently all the manipulations were carried out in dry boxes. The solvents employed for the manipulation in dry boxes were purified according to literature procedures [12].

Preparation of the Ligands

Preparation of H_2L_a

To a methanolic solution (25 ml) of bis(3-aminopropyl)phenylphosphine (4 mmol), a methanolic solution (25 ml) of salicylaldehyde (8 mmol) was added dropwise.

The resulting yellow solution was stirred at room temperature for 2 h. The yellow oil, obtained by evaporation of the solvent, was washed two times with methanol, dissolved in diethylether and dried over Na_2SO_4.

The solution, maintained overnight at room temperature, was filtered; by removing the solvent, a yellow oil was obtained which was dried *in vacuo.*

Preparation of H_4L_c

To a methanolic solution (25 ml) of 3-aminopropylphenylphosphine (1 mmol), a methanolic solution of 3-formylsalicylic acid (2 mmol) was added. The resulting solution was stirred for 3–4 h at room temperature; by evaporation of the solvent, a yellow solid was obtained.

This solid was dissolved with methanol, dried overnight over Na_2SO_4, precipitated with diethylether, filtered and dried *in vacuo.*

Preparation of H_4L_d

The same procedure as for the preparation of H_4L_c was employed for H_4L_d. This ligand was obtained as a yellow oil by reaction of *o*-acetoacetylphenol (2 mmol) and 3-aminopropylphenylphosphine.

Preparation of H_4L_f

Diethylenetriamine (3 mmol) in 25 ml of methanol was added to *o*-acetoacetylphenol (6 mmol) in methanol.

The resulting yellow solution was refluxed for 4 h, then cooled. The yellow solid, obtained by reducing the volume, was filtered, washed with methanol and dried *in vacuo.*

An additional amount of the ligand can be obtained by concentration of the mother liquor.

The compound can be crystallized by $CHCl_3$.

Preparation of H_2L_b

o-Hydroxyacetophenone (2 mmol) and diethylenetriamine (1 mmol) were stirred in methanol (50 ml) at room temperature for 3 h. By evaporation of the solution previously clarified by treatment with activated charcoal, a yellow compound was obtained.

This compound was purified by crystallization from methanol.

Preparation of H_4L_e

To a methanolic solution (30 ml) of diethylenetriamine (1 mmol), 3-formylsalicylic acid (2 mmol) was added. The yellow precipitate obtained was stirred for 2 h, filtered, washed two times with methanol and dried *in vacuo.*

Preparation of the Complexes

Preparation of $UO_2(L_a)\cdot H_2L$

A methanolic solution of $UO_2(CH_3COO)_2\cdot 2H_2O$ (1.06 mmol) and H_2L_a (1 mmol) were mixed together at room temperature. The orange precipitate, immediately obtained, was stirred for 2 h, filtered, washed with methanol and dried *in vacuo.*

Preparation of $Ni(L_a)\cdot CH_3OH$

To $Ni(CH_3COO)_2\cdot 4H_2O$ (264 mg, 1.06 mmol) in 25 ml of methanol, H_2L_a was added in a molar ratio 1:1. The resulting solution was refluxed for 3 h, then evaporated to dryness under vacuum. The solid was dissolved with ethanol and precipitated with n-hexane. The pale-green precipitate was filtered and dried *in vacuo.*

Preparation of $Cu(L_a)\cdot 2H_2O$

To a methanolic solution of $Cu(CH_3COO)_2\cdot H_2O$ (212 mg, 1.06 mmol), H_2L_a was added in a molar ratio 1:1. The solution, which turns from yellow to green, was refluxed for 3 h, then evaporated to dryness. The solid was dissolved in chloroform and precipitated with n-hexane. The green precipitate obtained was filtered and dried *in vacuo.*

Preparation of $UO_2(L_b)$

The complex was prepared by the same procedure employed for $UO_2(L_a)\cdot H_2O$.

Preparation of $M(H_2L_c)nS$

Only the complex $Ni(H_2L_c)\cdot H_2O$ was obtained by employing the following procedure:

$Ni(CH_3COO)_2\cdot 4H_2O$ (264 mg, 1.06 mmol) and H_4L_c (molar ratio 1:1) were stirred in methanol for 3 h. The solid obtained by removal from the solvent, was dissolved in ethanol and precipitated with n-hexane. The pale yellow product was washed with a ethanol/n-hexane mixture and dried *in vacuo.*

The preparation of the analogous uranyl(VI) and copper(II) complexes failed. In any case the binuclear species were obtained.

Preparation of $(UO_2)_2(L_c)\cdot CH_3OH$

$UO_2(CH_3COO)_2\cdot 2H_2O$ (2.12 mmol) and H_4L_c (1.06 mmol) were mixed at room temperature in methanol.

The yellow precipitate was stirred for 3 h, filtered, washed with methanol and dried *in vacuo.*

Preparation of $Ni_2(L_c)\cdot H_2O$

528 mg (2.12 mmol) of $Ni(CH_3COO)_2\cdot 4H_2O$ and 1.06 mmol of H_4L_c were refluxed in methanol (50 ml) for 4 h. The green precipitate, obtained on cooling the solution, was collected by filtration, washed with methanol and dried *in vacuo.*

Preparation of $Cu_2(L_c)\cdot H_2O$

The same procedure and the same molar ratio employed in the preparation of $Ni_2(L_c)\cdot H_2O$ were used.

Preparation of $MUO_2(L_c)\cdot 2H_2O$

A methanolic solution of a stoichiometric quantity (1:1) of $Ni(CH_3COO)_2\cdot 4H_2O$ or $Cu(CH_3COO)_2\cdot H_2O$, and H_4L_c were mixed together and stirred at room temperature for 3 h. To the resulting solution (violet for copper(II) and red for nickel(II)), $UO_2(CH_3COO)_2\cdot 2H_2O$ in a 1:1:1 $UO_2/M/H_4L_c$ ratio was added. The brown-green (for copper) or orange (for nickel) precipitate obtained was stirred for 2 h, washed in methanol and dried *in vacuo.*

Preparation of $NiCu(L_c)\cdot 2H_2O$

To the violet solution, obtained with the above procedure and containing $Cu(CH_3COO)_2\cdot H_2O$ and H_4L_c in a 1:1 molar ratio, a methanolic solution of $Ni(CH_3COO)_2\cdot 4H_2O$ in a 1:1 molar ratio was added. The green solution was reduced in volume; by addition of water a green solid was obtained, which was filtered, washed with diethylether and dried *in vacuo.*

Preparation of $Ni(H_2L_d)\cdot H_2O$

To 246 mg of $Ni(CH_3COO)_2\cdot 4H_2O$ in methanol, a stoichiometric quantity of H_4L_d (1 mmol) was added. The red solution was stirred for 3 h and reduced in volume. The yellow compound, obtained by addition of water, was filtered, and dried *in vacuo.*

The preparation of $UO_2(H_2L_d)\cdot S$, $Cu_2(H_2L_d)\cdot S$ (S = solvent) failed; in any case the binuclear species was obtained.

Preparation of $Ni_2(L_d)$

497 mg (2 mmol) of $Ni(CH_3COO)_2\cdot 4H_2O$ and H_4L_d (1 mmol) in 50 ml of methanol were stirred for 2 h. The precipitate obtained by reaction of the water with the red–yellow solution was filtered, washed with diethylether and dried *in vacuo.*

Preparation of $(UO_2)_2(L_d)\cdot CH_3OH$

$UO_2(CH_3COO)_2\cdot 2H_2O$ (848 mg, 2.00 mmol) and H_4L_d (1 mmol) were mixed together in 50 ml of methanol. The yellow precipitate obtained was stirred for 2 h at room temperature, filtered, washed with diethylether and dried *in vacuo.*

Preparation of $Cu_2(L_d)\cdot 2H_2O$

To a methanolic solution of H_4L_d (1 mmol), 333 mg (2 mmol) of $Cu(CH_3COO)_2\cdot H_2O$ were added. The dark green solution obtained was stirred for about 3 h until a green precipitate appeared. This compound was filtered, washed with diethylether and dried.

Preparation of complexes of the type $M(H_2L_e)\cdot H_2O$ $(M = Cu^{2+}, n = 1; M = Ni^{2+}, n = 2; M = UO_2^{2+}, n = 3)$

H_4L_e, LiOH and the appropriate metal acetate in the molar ratio 1:2:1 were stirred in 50 ml of methanol until a precipitate was formed. This precipitate (yellow for nickel(II) and green for copper(II)) was filtered, washed with methanol and dried *in vacuo.*

Preparation of complexes of the type $M_2(L_e)\cdot nS$ $(M = Ni^{2+}, nS = 2H_2O; M = Cu^{2+}, nS = 2CH_3OH; M = UO_2^{2+}, nS = CH_3OH)$

To a methanolic solution of H_4L_e (1 mmol) and LiOH (4 mmol) the corresponding metal acetates (2 mmol) were added. The solution, gently warmed, was stirred for 3 h.

The precipitate obtained was filtered, washed with methanol and dried *in vacuo.*

The copper(II) complex was also obtained by refluxing a methanolic solution of $Cu(CH_3COO)_2\cdot H_2O$ and the ligand (2:1 molar ratio) for 5 h, followed by evaporation of the solvent. The crude product was dissolved in CH_2Cl_2; by evaporation of the solvent the binuclear complex was obtained.

Preparation of complexes of the type $MM'(L_e)\cdot nS$ $(M = Cu^{2+}, M' = Ni^{2+}, n = 2; M = Cu^{2+}, M' = UO_2^{2+}, n = 2; M = Ni^{2+}, M' = UO_2^{2+}, n = 1; S = H_2O)$

These complexes were obtained by addition of a methanolic solution of the appropriate metal salt to an equimolar solution of the mononuclear complex with the metal in the O_2O_2 site. The products obtained were filtered, washed with methanol and dried *in vacuo.*

The preparation of the mono and binuclear complexes with the ligand H_4L_f is similar to that of the complexes of H_4L_e.

The materials and the apparatus for the electrochemical tests have been described elsewhere [13]. The potential values here reported refer to the ferrocenium–ferrocene couple [14]. All the experiments were performed at 20 ± 0.1 °C. The electrode activity of the ligand was measured using $Mg_2L_c \cdot 4H_2O$. 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

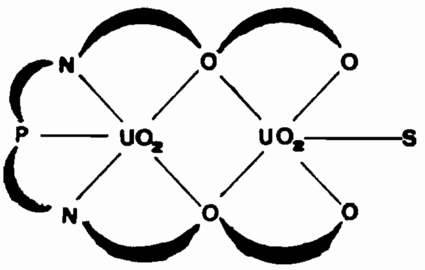
By reaction of $UO_2(CH_3COO)_2 \cdot 2H_2O$ with the ligand H_4L_c a binuclear complex of the type $(UO_2)_2(L_c) \cdot CH_3OH$ was obtained. If this binuclear structure is correct, one uranyl(VI) ion must be coordinated in the inner PN_2O_2 site, with the phosphinic donor atom directly bonded to the central metal ion; the other uranyl(VI) group lies in the outer O_2O_2 site; a solvent molecule fills the fifth equatorial coordination position, in order to give rise to the common pentagonal bipyramidal geometry around the uranium atom. The infrared spectrum shows very strong bands at 1664, 1611 and 1564 cm^{-1}, due to the stretching frequencies of the C=O and C=N groups. A single band due to the ν_3 of the uranyl(VI) group has been found at 922 cm^{-1}.

The solvent molecule can be replaced by basic monodentate ligands. By reaction with dimethylsulphoxide, $(UO_2)_2(L_c)(dmso)$ was obtained; in this complex a new band at 1020 cm^{-1} due to νS–O was observed.

In the $(UO_2)_2(L_c)(S)$ complexes νP–O bands have not been identified.

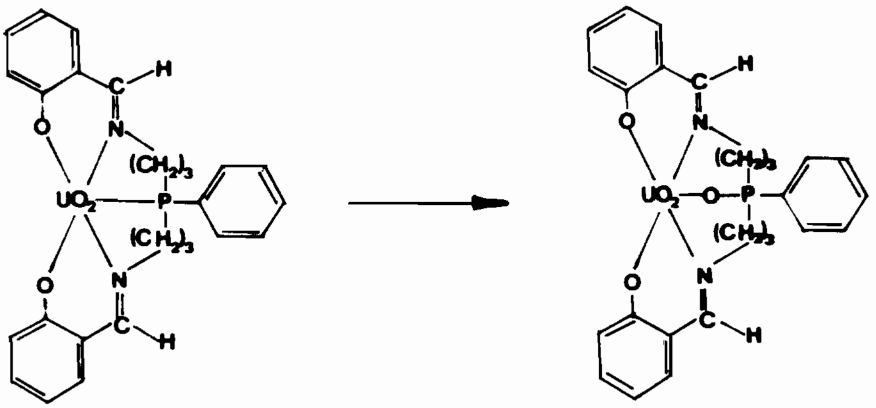
Similarly with the ligand H_4L_d the binuclear $(UO_2)_2(L_d) \cdot S$ complex was obtained. In this complex, the infrared bands at 1625, 1596, 1550 and 1535 cm^{-1} have been attributed to the absorptions of the C=O, C=N and C=C groups.

For all these complexes a binuclear structure of the type:



can be suggested; consequently a uranyl(VI)–phosphine bond should be proposed.

The same type of chemical bond has been recently proposed for the uranyl(VI), A even if the X-ray investigation has shown the presence of a phosphineoxide group bonded to UO_2^{2+} in the equatorial plane B. It was suggested, according to the physicochemical data, that the R_3P group is oxidized to R_3PO during the long period required for growing good crystals.

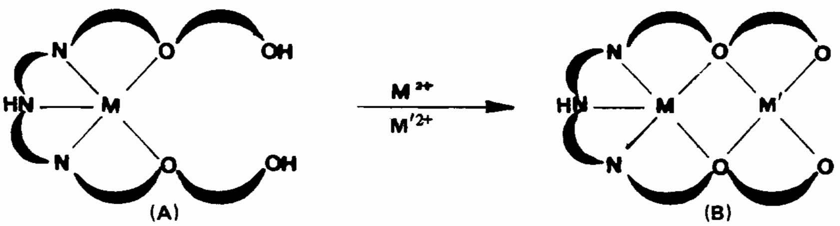


A B

For the binuclear uranyl(VI) complexes a similar behaviour towards oxidation of the phosphinic group can be supposed.

It must be noted that we were not able to isolate the mononuclear uranyl(VI) complexes with the binucleating ligands H_4L_c and H_4L_d employing different experimental conditions, *i.e.* a different uranyl(VI)/ligand ratio; in any case the homobinuclear complex was obtained.

Mononuclear complexes have been obtained instead by reaction of H_4L_e and H_4L_f with copper(II) and nickel(II) acetate, where the metal ion coordinates the inner N_3O_2 (A).

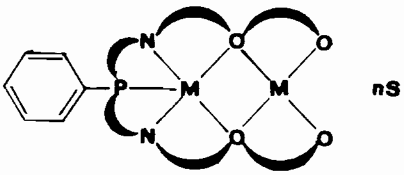


These complexes act as ligands towards a second metal ion giving rise to the homo and etherodinuclear complexes (**B**).

If the formation of etherobinuclear complexes is carried out directly, without the previous isolation and purification of the mononuclear compounds, products of unidentified stoichiometry or mixtures of products are obtained. The comparison of the spectra of the mononuclear and dinuclear complexes can add useful information about the coordination site occupied by the metal ions, especially with H_4L_e. In the mononuclear complexes $M(H_2L_e)$ (M = Cu, Ni) the coordination of the metal ion to the N_3O_2 site does not cause any shift on the stretching frequency of the C=O acidic group; in these complexes the νC=O lies at higher frequency than in the corresponding binuclear complexes, where the coordination of the second metal in the outer O_2O_2 site causes a lowering of the bond order in the C=O group, owing to a donation of electron density towards the metal ion. In the infrared spectra of the mononuclear copper(II) and the nickel(II) complexes $Cu(H_2L_e)$ and $Ni(H_2L_e)$ the νC=O lies at 1680 cm^{-1} and 1683 cm^{-1} respectively, while in the corresponding homodinuclear complexes it has been shifted to 1650 cm^{-1} and 1647 cm^{-1}. In addition the νN–H stretching at about 3240 cm^{-1} in the mononuclear complexes does not change after the coordination of a second metal ion; this confirms that the copper(II) and nickel(II) ions coordinate in the inner N_3O_2 site in the mononuclear complexes.

A different coordination behaviour has been found with the ligand H_4L_c, where an inner N_2PO_2 set is present. By reaction in alcoholic media of this ligand with copper(II) and nickel(II) acetate dihydrate, violet or brick-red solutions respectively are obtained also employing different metal/ligand molar ratios.

These solutions change their colour to green under reflux with formation of a green precipitate formulable as

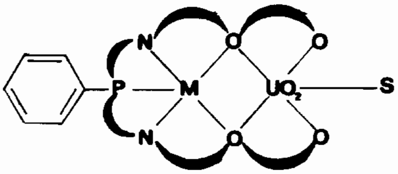


This binuclear structure has been confirmed by spectra; in addition to the various fragmentations, where the ratio of the peak is characteristic of the presence of two atoms of copper and nickel respectively, there is the parent peak at M^+ 643 m/z for $Cu_2(L_c)$ and at M^+ 632 m/z for $Ni_2(L_c)$. The same binuclear complexes have been obtained when the reaction is carried out at room temperature.

The same binuclear complexes have been obtained also employing milder conditions. At room temperature when the volume of the reaction solution is reduced, green binuclear precipitates have been recovered. However employing particular experimental conditions we were able to isolate a mononuclear nickel(II) complex, for which a structure with the metal ion in the inner N_2PO_2 site can be proposed also by analogy with the other mononuclear complexes prepared.

It must be supposed that the violet and brick-red solutions reported above for the preparation respectively of copper(II) and nickel(II) complexes with the ligand H_4L_c contain the mononuclear species with the metal ion in the inner N_2PO_2 compartment. This is supported also by the reaction of these solutions with uranyl salts; by addition of these solutions of the stoichiometric quantity of $UO_2(CH_3\text{-}COO)_2 \cdot 2H_2O$ a green-brown (for copper(II)) and a yellow-orange (for nickel(II)) precipitate were obtained almost immediately.

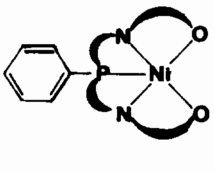
In these complexes formulable as



the presence of the uranyl(VI) group can be easily detected by the appearance of a very strong band in the infrared spectra at 925 cm^{-1} (for $NiUO_2$) and at 920 cm^{-1} (for $CuUO_2$) due to the ν_3 O–U–O. The infrared stretching frequencies of the νC—O and νC—N groups have been found at 1575, 1605 and 1639 cm^{-1} for $NiUO_2$ and at 1580, 1608 and 1642 cm^{-1} for $CuUO_2$.

Magnetic Data

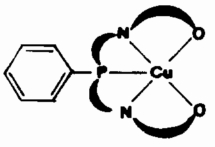
Only the nickel(II) mononuclear complex has been prepared with the ligand H_4L_c; it has a magnetic moment at room temperature of 2.66 B.M., very close to the value (2.64 B.M.) found for the complex $Ni(L_a)$.



These values again indicate that the nickel ion occupies the inner compartment N_2PO_2. The homodinuclear $Ni_2(L_c)$ has a μ_{eff} = 2.48 B.M. per nickel atom (3.15 B.M., for two metal ions). This lowering of the magnetic moment may be due to an antiferromagnetic coupling between the two ionic centres; this interaction is, however, weaker than that found in other similar species.

As reported above, we did not succed in the preparation of the mononuclear $Cu(H_2L_c)$ complex, consequently no comparison can be made between the magnetic values of the mononuclear and binuclear $Cu_2(L_c)$ complexes.

For this second compound a μ_{eff} of 1.15 B.M. (0.81 B.M. per copper atom) was obtained. This value is indicative of a strong antiferromagnetic interaction especially in comparison with the value (1.87 B.M.) found for the complex $Cu(L_a)$:



which can be easily correlated to the mononuclear complex. The heterodinuclear complex $CuNi(L_c)$ shows a μ_{eff} = 2.19 B.M. which again indicates a significant magnetic coupling between the two paramagnetic centres.

The values of μ_{eff} = 1.93 and 1.21 B.M. found for $NiUO_2(L_c)$ and $CuUO_2(L_c)$ respectively cannot be explained at this moment. Similarly the μ_{eff} of 1.53 B.M. for $Ni(H_2L_c)$ and 2.95 B.M. (2.08 per Ni atom) for $Ni_2(L_c)$ are unusual.

The magnetic moment of the complexes derived from the ligands H_4L_e and H_4L_f where an inner N_3-O_2 compartment is present, is easier to explain. The mononuclear nickel(II) complexes $Ni(H_2L_e)$ and $Ni(H_2L_f)$ have μ_{eff} = 2.83 and 2.95 B.M., very close to that (2.87 B.M.) found for the binuclear $NiUO_2(L_f)$ where the uranyl(VI) is diamagnetic.

For the corresponding homobinuclear complexes $Ni_2(L_e)$ and $Ni_2(L_f)$ a value of 4.22 and 4.08 has been found; the values per nickel atom are 2.98 B.M. and 2.88 B.M., very similar to those found for the corresponding mononuclear complexes.

The mononuclear copper(II) complexes $Cu(H_2L_e)$ (1.92 B.M.) and $Cu(H_2L_f)$ (1.94 B.M.) and the heterobinuclear $CuUO_2(L_e)$ (1.99 B.M.) have a normal magnetic moment. The homobinuclear $Cu_2(L_e)$ has a μ_{eff} = 1.96 B.M.; the value of 1.39 B.M. per copper(II) atom indicates that an antiferromagnetic coupling is operating in this complex. However by comparison of this value with that found for $Cu_2(L_c)$ (0.81 B.M. per copper atom) it can be easily observed that the interaction is weaker in the complex $Cu_2(L_c)$.

Electronic Spectra

The electronic spectra of the copper(II) and nickel(II) complexes, carried out in dimethylsulphoxide solution, show the characteristic d–d bands, the copper(II) complexes in the region 680–720 nm, while the nickel(II) are at 530–570 nm (a band or a shoulder) and at 800–1000 nm. These data exclude the fact that the nickel(II) has a square planar coordination. It must be noted that, owing to the low solubility of the prepared complexes in non-coordinating solvents, it was impossible to carry out the electronic spectra in other media in order to ascertain the correct coordination geometry of the central metal ion. The uranyl(VI) complexes show in the region 500–390 nm bands of shoulders due to charge transfers UO_2–L and to internal transition of the O–U–O group.

Oxidation Tests

We have tested the catalytic activity of the copper(II) homodinuclear complex $Cu_2(L_c)$ in the oxidation of 3,5-di-*t*-butylcatechol (3,5-DTBC) to 3,5-di-*t*-butylquinone (3,5-DTBQ). The activity of this complex was followed by optical spectrometry and by thin layer chromatography. The complex has little activity under a dinitrogen atmosphere while it acts as catalyst in both dioxygen and air with a small increase in activity on going from air to pure dioxygen atmosphere.

It has been noted that the catechol is almost completely oxidized while in other copper(II) complexes derived from triketones or *o*-acetoacetylphenol [15] the competition between reduced (3,5-DTBC) and oxidized (3,5-DTBQ) species in the coordination to the central metal ions does not allow such an oxidation to be complete. A possible mechanism for the oxidation reaction, which needs much more investigation, is that the electronic transfer from catechol to the copper(II) complex begins after the formation of an intermediate complex of the type $Cu_2(L_c)$-(DTBC). In a subsequent step the copper(II) ions are oxidized by dioxygen.

Electrochemical Behaviour

We have examined the electrochemical behaviour of metal complexes derived from the ligand H_4L_c, also by comparison with the redox properties of the corresponding metal complexes of H_4L_e and of the ligand: (see bottom page 288)

TABLE I. Elemental Analyses and Physical Properties of the Prepared Complexes.

	Calcd.			Found			Colour
	C%	H%	N%	C%	H%	N%	
$UO_2(L_a)\cdot H_2O$	44.57	3.86	4.00	44.04	3.53	4.15	orange
$Ni(L_a)\cdot CH_3OH$	62.22	5.85	5.38	62.25	5.58	5.49	yellow/green
$Cu(L_a)\cdot 2H_2O$	58.92	5.85	5.29	58.74	5.43	4.98	green
$UO_2(L_b)$	39.54	3.79	6.92	39.48	3.76	6.86	orange
$Ni(H_2L_c)\cdot H_2O$	56.49	4.87	4.71	55.93	4.97	4.80	pale green
$(UO_2)_2(L_c)\cdot CH_3OH$	31.99	2.66	2.57	31.99	2.75	2.13	yellow
$Ni_2(L_c)\cdot H_2O$	51.58	4.14	4.29	51.20	4.66	4.30	green
$Cu_2(L_c)\cdot 2H_2O$	49.48	4.27	4.12	49.97	4.36	4.35	green
$NiUO_2(L_c)\cdot 2H_2O$	38.15	2.29	3.18	37.69	3.50	2.96	orange
$CuUO_2(L_c)\cdot 2H_2O$	37.94	3.27	3.16	37.42	3.33	2.95	brown/green
$NiCu(L_c)\cdot 2H_2O$	49.83	4.30	4.15	49.23	4.12	3.91	green
$Ni(H_2L_d)\cdot H_2O$	62.04	5.98	4.52	62.46	3.32	4.86	yellow/green
$Ni_2(L_d)$	58.41	5.02	4.26	58.59	5.45	4.46	green
$(UO_2)_2(L_d)\cdot CH_3OH$	35.61	3.33	2.52	36.13	3.89	2.94	yellow
$Cu_2(L_d)\cdot 2H_2O$	54.62	5.26	3.98	53.92	4.93	3.86	dark green
$Cu(H_2L_e)\cdot H_2O$	50.15	4.38	8.77	49.92	4.37	8.80	green
$Ni(H_2L_e)\cdot 2H_2O$	48.78	4.67	8.53	48.25	4.23	8.72	yellow
$UO_2(H_2L_e)\cdot 3H_3O$	33.29	3.47	5.83	33.44	3.26	5.73	orange
$Ni_2(L_e)\cdot 2H_2O$	43.76	3.83	7.66	43.26	4.04	8.02	yellow/green
$Cu_2(L_e)\cdot 2H_2O$	43.01	3.76	7.53	42.76	3.25	7.05	green
$(UO_2)_2(L_e)\cdot CH_3OH$	25.85	2.17	4.34	25.94	2.42	4.22	yellow
$CuNi(L_e)\cdot 2H_2O$	45.61	3.99	7.98	45.33	4.03	7.78	pale yellow
$CuUO_2(L_e)\cdot 2H_2O$	31.39	2.75	5.49	31.42	2.98	5.60	yellow/brown
$NiUO_2(L_e)\cdot H_2O$	32.35	2.56	5.66	32.85	2.59	5.35	pale yellow
$Ni(H_2L_f)\cdot H_2O$	57.87	5.83	8.44	57.32	5.93	8.14	yellow
$Cu(H_2L_f)\cdot H_2O$	57.31	5.77	8.36	56.93	5.35	8.70	green
$UO_2(H_2L_f)\cdot CH_3OH$	41.49	4.29	5.81	41.09	3.89	5.74	yellow
$Ni_2(L_f)\cdot 2H_2O$	50.31	5.07	7.34	49.85	5.47	6.93	green
$Cu_2(L_f)\cdot 2CH_3OH$	51.15	5.41	6.89	51.84	5.64	6.66	dark green
$(UO_2)_2(L_f)\cdot CH_3OH$	30.27	2.93	4.24	29.99	3.01	4.15	yellow

TABLE II. Infrared Data (cm^{-1}) for the Prepared Complexes.

Complex	I.r. frequencies in the range 1700–1500 cm^{-1} assignable to νC–O, νC–N and νC–C	Other characteristic bands
$UO_2(L_a)\cdot H_2O$	1657, 1624, 1610, 1548	905(O–U–O)
$UO_2(L_a)\cdot H_2O$ cryst.	1660, 1630, 1600, 1558	888(O–U–O)
$Ni(L_a)\cdot CH_3OH$	1621, 1600, 1540	
$Cu(L_a)\cdot 2H_2O$	1625, 1602, 1542	
$UO_2(L_b)$	1605, 1580	3290(N–H) 898(O–U–O)
$Ni(H_2L_c)\cdot H_2O$	1688, 1628, 1600, 1558	
$(UO_2)_2(L_c)\cdot CH_3OH$	1664, 1611, 1564	922(O–U–O)
$Ni_2(L_c)\cdot H_2O$	1640, 1597, 1560	

(continued on facing page)

TABLE II. *(continued)*

Complex	I.r. frequencies in the range 1700–1500 cm^{-1} assignable to νC–O, νC–N and νC–C	Other characteristic bands
$Cu_2(L_c)\cdot 2H_2O$	1640, 1608, 1597	
$NiUO_2(L_c)\cdot 2H_2O$	1639, 1605, 1575, 1563	925(O–U–O)
$CuUO_2(L_c)\cdot 2H_2O$	1642, 1608, 1580, 1568, 1550	920(O–U–O)
$NiCu(L_c)\cdot 2H_2O$	1670, 1640, 1604, 1572	
$Ni(H_2L_d)\cdot H_2O$	1642, 1610, 1585, 1561, 1530	
$Ni_2(L_d)$	1650, 1605, 1579, 1556, 1528	
$(UO_2)_2(L_d)\cdot CH_3OH$	1625, 1596, 1550, 1535, 1490	899(O–U–O)
$Cu_2(L_d)\cdot 2H_2O$	1640, 1598, 1575, 1550, 1512	
$Cu(H_2L_e)\cdot H_2O$	1680, 1655, 1640, 1590, 1550	3235(N–H)
$Ni(H_2L_e)\cdot 2H_2O$	1683, 1650, 1600, 1560	3235(N–H)
$UO_2(H_2L_e)\cdot 3H_2O$	1655, 1630, 1605, 1565, 1520	3220(N–H) 900(O–U–O)
$Ni_2(L_e)\cdot 2H_2O$	1647, 1621, 1600, 1565	3240(N–H)
$Cu_2(L_e)\cdot 2H_2O$	1650, 1605, 1570, 1555	4230(N–H)
$(UO_2)_2(L_e)\cdot CH_3OH$	1670, 1598, 1560, 1518	3230(N–H) 906(O–U–O)
$CuNi(L_e)\cdot 2H_2O$	1640, 1600, 1565	3220(N–H)
$CuUO_2(L_e)\cdot 2H_2O$	1600, 1565, 1556	3220(N–H) 900(O–U–O)
$NiUO_2(L_e)\cdot H_2O$	1655, 1635, 1600, 1565	3235(N–H) 900(O–U–O)
$Ni(H_2L_f)\cdot H_2O$	1604, 1580, 1550, 1521	3250(N–H)
$Cu(H_2L_f)\cdot H_2O$	1602, 1579, 1552, 1510	3250(N–H)
$UO_2(H_2L_f)\cdot CH_3OH$	1598, 1563, 1540, 1502	3350(N–H) 904(O–U–O)
$Ni_2(L_f)\cdot 2H_2O$	1601, 1550, 1520	3240(N–H)
$Cu_2(L_f)\cdot 2CH_3OH$	1648, 1604, 1579, 1560	3240(N–H)
$(UO_2)_2(L_f)\cdot CH_3OH$	1613, 1590, 1534, 1508	3235(N–H) 902(O–U–O)

TABLE III. Electronic (nm) and Magnetic (B.M.) Data of the Prepared Complexes.

Complex	Electronic data (nm)	Magnetic moment (B.M.)	
		μ_{eff}	μ_{compl}
$UO_2(L_a)\cdot H_2O$	460, 385		[a]
$Ni(L_a)\cdot CH_3OH$	1050, 620, 560, 385	2.64	
$Cu(L_a)\cdot 2H_2O$	700, 620, 500, 480, 450, 370	1.87	
$UO_2(L_b)$	610, 450, 390, 360		[a]
$Ni(H_2L_c)\cdot H_2O$	850, 790, 550, 400, 380	2.66	
$(UO_2)_2(L_c)\cdot CH_3OH$	520, 470, 400		[a]
$Ni_2(L_c)\cdot H_2O$	970, 770, 560, 460, 410, 370	2.48	3.51
$Cu_2(L_c)\cdot 2H_2O$	700, 620, 490, 400, 340	0.81	1.15
$NiUO_2(L_c)\cdot 2H_2O$	970, 800, 550, 470, 400, 370	1.93	
$CuUO_2(L_c)\cdot 2H_2O$	650, 460, 400, 360	1.21	
$NiCu(L_c)\cdot 2H_2O$	980, 780, 700, 470, 380, 350		2.19
$Ni(H_2L_d)\cdot H_2O$	960, 550, 390, 360	1.53	
$Ni_2(L_d)$	950, 700, 570, 390, 360	2.08	2.95
$(UO_2)_2(L_d)\cdot CH_3OH$	610, 460, 390, 370		[a]

(continued overleaf)

TABLE III. *(continued)*

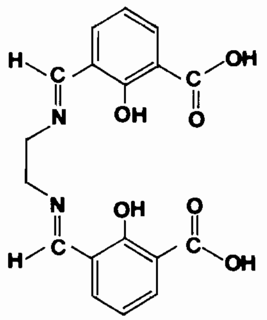
Complex	Electronic data (nm)	Magnetic moment (B.M.)	
		μ_{eff}	μ_{compl}
$Cu_2(L_d)\cdot 2H_2O$	770, 700, 500, 380, 360	–	–
$Cu(H_2L_e)\cdot H_2O$	575, 415, 350	1.92	
$Ni(H_2L_e)\cdot 2H_2O$	930, 780, 550, 420, 365	2.83	
$UO_2(H_2L_e)\cdot 3H_2O$	560, 470, 380		[a]
$Ni_2(L_e)\cdot 2H_2O$	980, 755, 365	2.98	4.22
$Cu_2(L_e)\cdot 2H_2O$	575, 415, 350	1.39	1.96
$(UO_2)_2(L_e)\cdot CH_3OH$	575, 485, 375		[a]
$CuNi(L_e)\cdot 2H_2O$	625, 355		3.33
$CuUO_2(L_e)\cdot 2H_2O$	600, 460, 365	1.99	
$NiUO_2(L_e)\cdot H_2O$	870, 770, 420, 375	2.87	
$Ni(H_2L_f)\cdot H_2O$	970, 770, 550, 400, 380, 350	2.95	
$Cu(H_2L_f)\cdot H_2O$	700, 620, 570, 450, 425	1.94	
$UO_2(H_2L_f)\cdot CH_3OH$	620, 440, 380, 360		[a]
$Ni_2(L_f)\cdot 2H_2O$	970, 770, 550, 400, 380, 350	2.88	4.08
$Cu_2(L_f)\cdot 2CH_3OH$	750, 600, 460, 360	–	–
$(UO_2)_2(L_f)\cdot CH_3OH$	540, 480, 390		[a]

[a] Diamagnetic complex.

TABLE IV. Reduction Potentials (volt) (*vs.* ferrocenium–ferrocene) for the Metallic Complexes of H_4L_c and H_4L_e as a Function of the Coordination Compartment.

Metal (M) ion, or ions in the complex ML		Inner compartment				Outer compartment			
		$M_{N_2PO_2}L/[M_{N_2PO_2}L]^-$ (H_4L_c)		$M_{N_3O_2}L/[M_{N_3O_2}L]^-$ (H_4L_e)		$M_{O_2O_2}L/[M_{O_2O_2}L]^-$ (H_4L_c)		$M_{O_2O_2}L/[M_{O_2O_2}L]^-$ (H_4L_e)	
		Pt	Hg	Pt	Hg	Pt	Hg	Pt	Hg
$Ni(II)_{inner}$	$Ni(II)_{outer}$	-2.40^a	-2.40^a	-2.45^b		-1.70^b	-1.87^b	-2.13^b	
$Cu(II)_{inner}$	$Cu(II)_{outer}$	-1.68^b		-1.18^b		-2.38^b		-2.29^a	
$UO_2(VI)_{inner}$	$UO_2(VI)_{outer}$	-1.75^b		-1.42^b	-1.51^b	-1.75^b		-1.52^b	-1.51^b
$Ni(II)_{inner}$	$Cu(II)_{outer}$	-2.38^a	-2.38^a	-2.02^b		-1.17^b	-1.10^a	-1.09^b	
$Cu(II)_{inner}$	$UO_2(VI)_{outer}$	-1.50^b		-1.05^b	-0.99^a	-2.38^a		-1.97^a	-2.05^b
$Ni(II)_{inner}$	$UO_2(VI)_{outer}$	-2.41^a	-2.41^a	-2.57^b		-1.38^b	-1.30^a	-1.50^a	-1.50^a

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



The complexes have been studied by cyclic voltammetry and controlled potential coulometry in dimethylsulphoxide solution both at platinum and mercury electrodes. The complexes examined give rise to electrochemical responses characterized by a low degree of reversibility with respect to those obtained from compartmental ligands having four-coordinate central metal ions [16–18], the electrode process being almost the same.

Table IV reports the potentials (*vs.* ferrocenium–ferrocene couple) relevant to the one-electron reduction of the central metal ions of the complexes of

H_4L_c, together with those from the corresponding complexes of the ligand H_4L_e. As can be seen, the N_2PO_2 five coordination makes the reduction of the metal ion more difficult with respect to the N_3O_2 coordination, in accordance with the higher electron-donor ability of the phenylphosphine group with respect to the amine nitrogen atom. The relative enlargement of the inner compartment in the case of the phosphinic complexes (H_4L_c) with respect to the aminic complexes (H_4L_e) seems to play no important role in the redox parameters.

No rational attempt is made to account for the differences, partly unimportant in the reduction ability of the outer compartments in the two classes of complexes.

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References

1 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev., 8,* 199 (1979).
2 D. E. Fenton, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta, 62,* 57 (1982).
3 D. E. Fenton, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta, 95,* 187 (1984).
4 D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc., 100,* 6367 (1978) and references therein.
5 R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc., 103,* 4073 (1981) and references therein.
6 F. L. Urbach, 'Metal Ions in Biological Systems', H. Siegel (Ed.), M. Dekker, New York and Basel, Vol. 13, p. 73 and references therein.
7 U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta, 18,* 77 (1976).
8 U. Casellato, M. Vidali and P. A. Vigato, *Coord. Chem. Rev., 28,* 231 (1979).
9 R. C. Coombes, D. E. Fenton, P. A. Vigato, U. Casellato and M. Vidali, *Inorg. Chim. Acta, 54,* L155 (1981).
10 J. C. Duff and E. J. Bills, *J. Chem. Soc.,* 1987 (1932).
11 G. Wittig, *Ann. Chem., 446,* 173 (1926).
12 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', 2nd Edition, Pergamon Press (1980).
13 P. Zanello, R. Cini, A. Cinquantini and P. L. Orioli, *J. Chem. Soc., Dalton Trans.,* 2157 (1983).
14 R. R. Gagné, C. A. Kowal and G. C. Lisensky, *Inorg. Chem., 19,* 2854 (1980).
15 U. Casellato, S. Tamburini, P. A. Vigato, A. De Stefani, M. Vidali and D. E. Fenton, *Inorg. Chim. Acta, 69,* 45 (1983).
16 P. Zanello, P. A. Vigato and G. A. Mazzocchin, *Transition Metal Chem., 7,* 291 (1982).
17 P. Zanello, P. A. Vigato, U. Casellato, S. Tamburini and G. A. Mazzocchin, *Transition Metal Chem.,* in press.
18 P. Zanello, S. Tamburini, P. A. Vigato and G. A. Mazzocchin, *Transition Metal Chem.,* in press.