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Uranyl(VI), Copper(II) and Nickel(II) Complexes Derived from a New Compartmental Ligand

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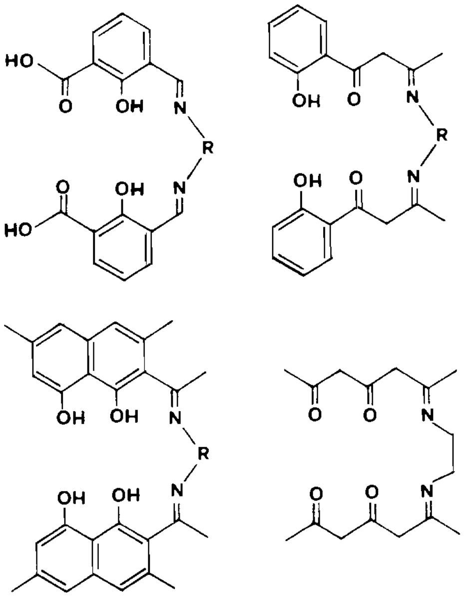
Abstract

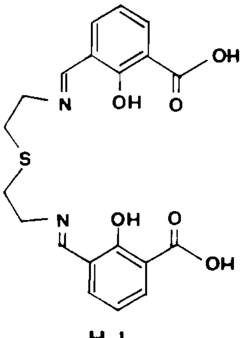
A new heptadentate compartmental ligand has been synthesized by condensation of 3-formylsalicylic acid and 1,5-diamino-3-thiapentane in methanol (H_4L_a). This Schiff base contains an inner N_2SO_2 and an outer O_2O_2 site and gives, by reaction with copper(II), nickel(II) and uranyl(VI) diacetate, mononuclear, homo- and heterobinuclear complexes. In the mononuclear copper and nickel complexes, the metal ion is in the inner N_2SO_2 site, while it is in the outer O_2O_2 for uranyl; a solvent molecule fills the fifth equatorial coordination position in this last complex. The physico-chemical properties of the compounds are discussed on the basis of infrared, electronic and magnetic data and by comparison with the analogous complexes with the ligand obtained by reaction of 3-formylsalicylic acid and diethylenetriamine (H_4L_b). The mononuclear copper and the heterodinuclear copper–uranyl complexes show anomalously low magnetic moments.

Introduction

In the past we have synthesized several hexadentate compartmental ligands in which the uranyl(VI) ion always occupied the external coordination site O_2O_2 [1–4] (Scheme1). More recently, a new series of heptadentate ligands have been prepared and their interaction with uranyl(VI), copper(II) and nickel(II) studied [5, 6]. The aim of these studies was to offer more flexible and versatile ligands for transition metal ions and a more appropriate inner site for large ions such as UO_2^{2+}.



Scheme 1.



H_4L_a

As an extension of this investigation, we have synthesized the heptadentate binucleating ligand H_4L_a, which shows the usual outer O_2O_2 chamber and an inner chamber, N_2SO_2, in which a 'soft' thioetheric donor has been added to the more familiar tetradentate N_2O_2 set. With this ligand it was feasible to investigate the influence of the 'soft' thioetheric sulfur on the prepared complexes and to correlate them with those obtained with the 'harder' aminic nitrogen, with the possibility to obtain binuclear uranyl(VI) complexes, with the consequent formation of a U–S thioetheric bond [7]. It must be noted that we have recently prepared and characterized, also by X-ray diffraction, the uranyl(VI) complex [8]

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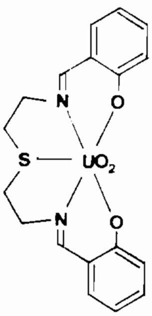


UO_2 salsen

UO_2(salsen) where the Schiff base represents the internal site of the heptadentate ligand reported in this work.

The present paper describes the preparation and the properties of H_4L_a, its interaction with uranyl(VI), copper(II) and nickel(II) and the physicochemical properties of the complexes.

Experimental

1,5-Diamino-3-thiapentane was a K & K product; the metal salts were C. Erba products and were used without further purification. 3-Formylsalicylic acid was prepared according to literature [9]. The Schiff base H_4L_b was obtained by condensation of 3-formylsalicylic acid and diethylenetriamine and the related mono and binuclear uranyl(VI), copper(II) and nickel(II) complexes were synthesized according to references [5] and [6].

Preparation of the Ligand H_4L_a

(a) The product was prepared by adding at room temperature 2 mmol of 3-formylsalicylic acid in methanol (20 ml) to 1 mmol of 1,5-diamino-3-thiapentane in 3 ml of methanol. The yellow compounds so formed was filtered, washed with methanol and dried *in vacuo. Anal.* Found: C, 57.23; H, 4.85; N, 6.78. Required for $C_{20}H_{20}N_2SO_6$: C, 57.83; H, 4.82; N, 6.75%. Yield 65%.

(b) The ligand was also prepared by mixing a methanolic dilute solution of 2 mmol of 3-formylsalicylic acid (60 ml) and 1 mmol of 1,5-diamino-3-thiapentane (40 ml) and refluxing the resulting solution for 6 h. *Anal.* Found: C, 58.01; H, 4.90; N, 6.63. Required for $C_{20}H_{20}N_2O_6S$: C, 57.83; H, 4.82; N, 6.75%. Yield 58%.

The product obtained by the procedures (a) and (b) show a different chemical behaviour as described in the Results and Discussion.

Preparation of Mononuclear Complexes (MH_2L_a)

$UO_2(H_2L_a)\cdot 3H_2O$ (1)

The complex was prepared by slow addition of a methanolic solution of $UO_2(CH_3COO)_2\cdot 2H_2O$ (1 mmol) suspended in the same solvent. The yellow solid obtained, after stirring under reflux for several hours, was filtered, washed three times with methanol and dried *in vacuo. Anal.* Found: C, 32.24; H, 2.85; N, 3.57. Required for $C_{20}H_{24}N_2O_{11}SU\cdot UO_2(H_2L_a)\cdot 3H_2O$: C, 32.52; H, 3.25; N, 3.79%.

$Cu(H_2L_a)\cdot 2H_2O$ (2) and $Ni(H_2L_a)\cdot 2H_2O$ (3)

The complexes were prepared by slow addition of a methanolic solution of the appropriate metal acetate (1 mmol) to a suspension of H_4L_a (1 mmol) in the same solvent. After stirring under reflux for 4–6 h, the green solid obtained was filtered, washed with methanol (three times for copper and with a small quantity for the nickel complex) and dried *in vacuo. Anal.* for **2**. Found: C, 47.05; H, 3.82; N, 5.48. Required for $C_{20}H_{22}O_8SCu$, $Cu(H_2L_a)\cdot 2H_2O$: C, 46.74; H, 4.28; N, 5.45%. *Anal.* for **3**. Found: C, 46.94; H, 4.14; N, 5.56. Required for $C_{20}H_{22}O_8SNi$, $Ni(H_2L_a)\cdot 2H_2O$: C, 47.18; H, 4.14; N, 5.51%.

Preparation of Homobinuclear Complexes (Me_2L_a)

$(UO_2)_2(L_a)\cdot CH_3OH\cdot H_2O$ (4)

A solution of the ligand was obtained for the addition of 4 mmol of LiOH to the stirred methanolic suspension of H_4L_a (1 mmol, 30 ml). To this solution $UO_2(CH_3COO)_2\cdot 2H_2O$, in a molar ratio 1:2, was added. The yellow product obtained was filtered, washed with methanol and dried *in vacuo. Anal.* Found: C, 25.11; H, 2.50; N, 2.60. Required for $C_{20}H_{22}N_2O_{12}SCl_2$, $(UO_2)(L_a)\cdot CH_3OH\cdot H_2O$: C, 25.15; H, 2.20; N, 2.79%.

$Cu_2(L_a)\cdot 2H_2O$ (5) and $Ni_2(L_a)\cdot 4H_2O$ (6)

To a methanolic suspension of H_4L_a (1 mmol, 30 ml), 4 mmol of LiOH were added. To the resulting solution the appropriate metal acetate (2 mmol) was added. The green product obtained was filtered, washed with methanol and dried *in vacuo. Anal.* for **5**. Found: C, 41.39; H, 3.39; N, 4.85. Required for $C_{20}H_{20}N_2O_8SCu_2$, $Cu_2(L_a)\cdot 2H_2O$: C, 41.73; H, 3.48; N, 4.87%. *Anal.* for **6**. Found: C, 39.27; H, 3.86; N, 4.42. Required for $C_{20}H_{24}N_2O_{10}SNi_2$, $Ni_2(L_a)\cdot 4H_2O$: C, 39.91; H, 3.99; N, 4.66%.

All these binuclear complexes were also obtained by refluxing a methanolic suspension of the mononuclear complex for several hours with LiOH and the appropriate metal diacetate in a molar ratio 1:2:1.

Preparation of Heterobinuclear Complexes (MUO_2L_a) (M = Cu, Ni)

7

(a) To a methanolic suspension of $M(H_2L_a)\cdot 2H_2O$ (1 mmol, 30 ml), 2 mmol of LiOH and 1 mmol of $UO_2(CH_3COO)_2\cdot 2H_2O$ were added. The suspension was refluxed for 6 h. The product obtained, (green for $CuUO_2(L_a)$ and yellow-green for $NiUO_2(L_a)$), was filtered, washed with methanol and dried *in vacuo.*

(b) The same $NiUO_2(L_a)\cdot 2H_2O$ or the analogous $CuUO_2(L_a)\cdot CH_3OH$ was obtained by refluxing, for several hours, a methanolic suspension of $UO_2(H_2L_a)\cdot 3H_2O$, LiOH and $M(CH_3COO)_2\cdot xH_2O$ in a molar ratio 1:2:1. The products obtained were filtered, washed in methanol and dried *in vacuo.*

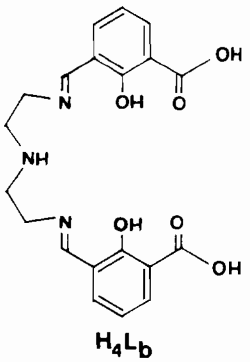
(c) To a methanolic suspension of Cu_2L_a (**5**) (1 mmol) a methanolic solution of $UO_2(CH_3COO)_2\cdot 2H_2O$ (1 mmol) was added. The green precipitate obtained, after a reflux of several hours, was washed several times with methanol and dried *in vacuo. Anal.* for the $CuUO_2(L_a)$ complex. Found: C, 31.06; H, 2.41; N, 3.67. Required for $C_{20}H_{18}N_2O_9SCuU$, $CuUO_2(L_a)\cdot H_2O$: C, 31.43; H, 2.62; N, 3.67%. *Anal.* for the $NiUO_2(L_a)$ complex. Found: C, 30.85; H, 2.70; N, 3.32. Required for $C_{20}H_{20}N_2O_{10}SNiU$, $NiUO_2(L_a)\cdot 2H_2O$: C, 30.90; H, 2.57; N, 3.60%. *Anal.* for the $CuUO_2(L_a)$ complex. Found: C, 32.89; H, 2.74; N, 3.76. Required for $C_{20}H_{20}N_2O_{10}SCuU$, $CuUO_2(L_a)\cdot CH_3OH$: C, 32.41; H, 2.57; N, 3.60%.

Results and Discussion

By reaction of 3-formylsalicylic acid and 1,5-diamino-3-thiapentane in methanol, the heptadentate Schiff base, H_4L_a, has been obtained in two different modifications (**A** and **B**). The first (**A**) has been obtained when the reaction is carried out at room temperature, while the second (**B**) was obtained in hot methanol. **A** turns into **B** by refluxing for several hours in methanol. Both species are yellow solids, which melt above 270 °C; they differ in IR, UV and reactivitiy towards metal ions. The reactivity of the modification **B** towards transition metal ions, becomes similar to that of **A**, only when a stoichiometric quantity of base (*i.e.* LiOH) ($LiOH/H_4L_a$ = 2/1) is added, before the reaction with metals takes place. An explanation for this different behaviour is difficult; and is exacerbated by the low solubility of the two samples in organic solvents which prevents a full physico-chemical identification.

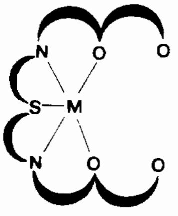
By reaction of H_4L_a with uranyl(VI), copper(II) and nickel(II), the reaction scheme (Scheme 2) has been obtained. The reaction scheme is similar to that obtained with the ligand H_4L_b [6] which has an aminic NH group instead of a thioetheric sulphur. It is thus possible to correlate the physico-chemical results of similar complexes with the two ligands. With both ligands, as can be seen from Scheme 2, mononuclear, homobinuclear and heterobinuclear complexes are obtained; the homobinuclear species can be obtained in a single stage whereas the heterobinuclear must be obtained step by step.

For the mononuclear complexes, the coordination chamber occupied by different metal ions has been detected by infrared evidences and by reactivity. The results, below reported, can be considered as indications of the site occupancy and not as a definitive proof.



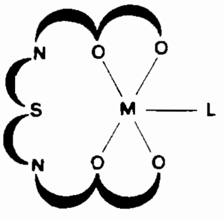
H_4L_b

For the mononuclear complexes, the two positional isomers can be proposed for copper(II) or nickel(II) (**A**) and uranyl(VI) (**B**), respectively. In this last complex the usual equatorial pentacoordination around the uranyl(VI) ion is reached by a solvent molecule.



A

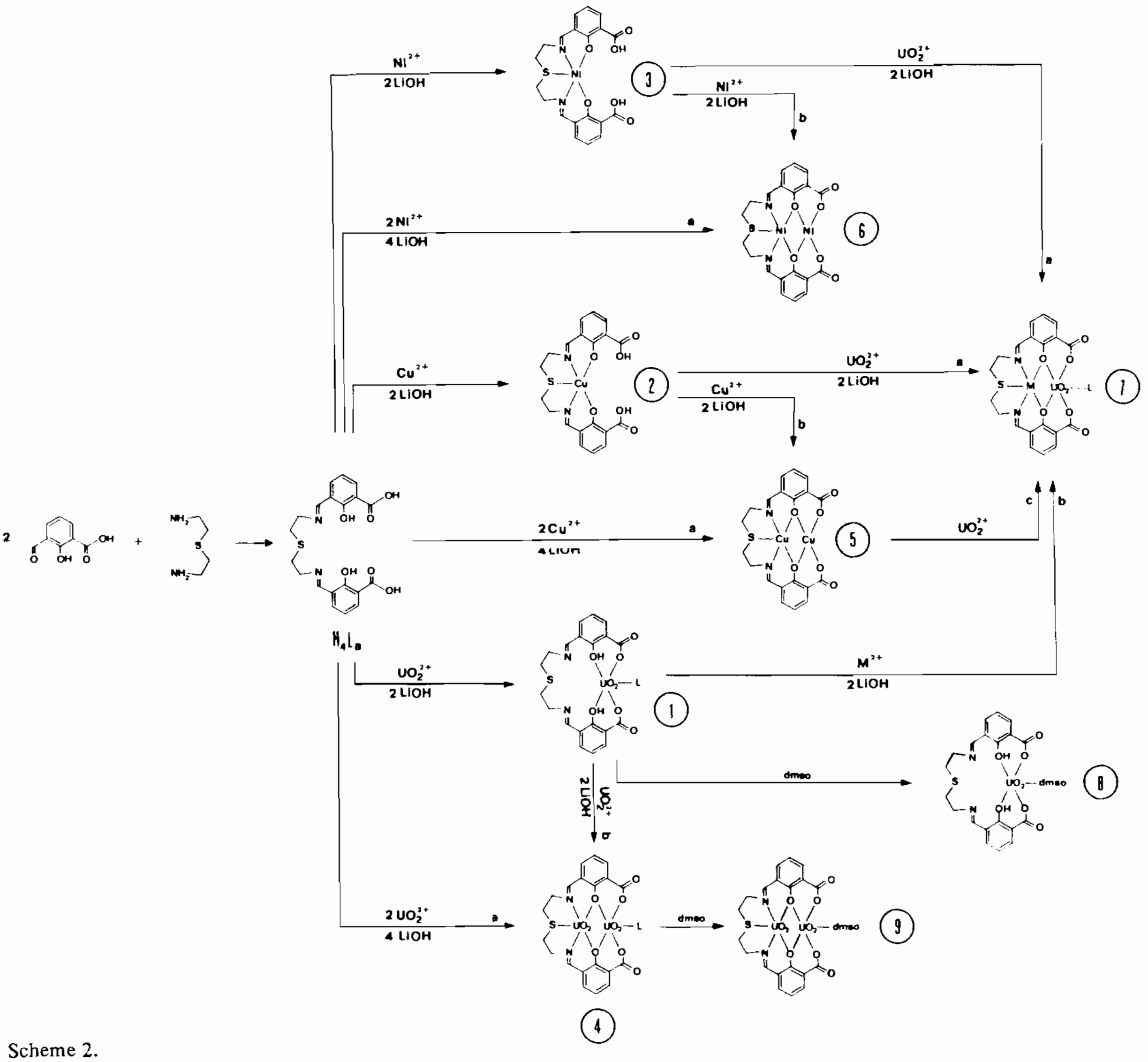
or



B

For $Cu(H_2L_a)$ and $Ni(H_2L_a)$ complexes the $\nu C{=}O$ of the carboxylic groups lies, respectively, at 1698–1690 cm^{-1}, completely comparable with that found for the free ligand (1700 cm^{-1}). It has been already found that nickel(II) strongly prefers the internal chamber, with hexa-[1, 10] and also heptadentate ligands [5, 6]. For copper(II) both isomers have been found to exist, depending on the solvent used [10]. For these complexes, however, a change from the outer to the inner coordination chamber seems to be obtained more easily than the converse. The similarity of the shape of IR spectra for nickel(II) and copper(II) mononuclear complexes strongly suggest that the central metal ion is in the same inner coordination environment. In the homodinuclear $Cu_2(L_a)$ and $Ni_2(L_a)$ complexes, where both coordination sites are occupied, there is a lowering in the $\nu C{=}O$ of $\cong 60$ cm^{-1}; it lies at 1635 cm^{-1} for the copper complex and 1610 cm^{-1} for the nickel complex.

For the uranyl(VI) mononuclear species $UO_2(H_2L_a)$ the IR spectrum shows a $\nu C{=}O$ at 1655 cm^{-1}, 45 cm^{-1} lower than in the free ligand, in accordance with the structure **B**. An analogous lowering in the $\nu C{=}O$ is observed in the homobinuclear uranyl(VI) complex $(UO_2)_2(L_a)$.



Scheme 2.

A further evidence of the coordination site occupied by UO_2^{2+} derives from the reaction of $UO_2(H_2L_a)(S)$ with neutral monodentate coordinating ligands, such as dimethylsulphoxide (dmso). If the complex has the structure (A) no reaction should occur, as the equatorial coordination is filled by the five donor atoms of the inner chamber. It was well established that the uranyl(VI) ion prefers an equatorial pentacoordination with chelating ligands forming five or six membered rings [11, 12]. If it has the structure (**B**) on the contrary, the reaction:

$$UO_2(H_2L_a)(S) + dmso \longrightarrow UO_2(H_2L_a)(dmso) + S$$

must occur; the solvent molecule directly bonded to the central metal ion (in the first case, a molecule of crystallization) forms the equatorial pentacoordination, and is replaced by dmso. The reaction does occur, suggesting the coordination of uranyl(VI) ion in the outher O_2O_2 chamber. A new band, due to the νS–O of the coordinate dimethylsulphoxide at 1025 cm^{-1} appears in the infrared spectrum. An analogous behaviour has been found for the outer uranyl(VI) ion in the homobinuclear complex $(UO_2)_2(L_a)(S)$ which, by reaction with dimethylsulphoxide produces $(UO_2)_2(L_a)(dmso)$. In this complex a new band, due to the νS–O appears at 1018 cm^{-1}.

As mentioned above the inner uranyl(VI) ion does not coordinate to an additional dmso molecule, being the equatorial coordination of the metal ion saturated by the five, N_2SO_2, donor set of the Schiff base.

It should be noted, however, that chamber change in solution cannot be ruled out, depending on the

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

Complex	IR frequencies in the range 1700–1500 cm^{-1} assignable to C–O, C–N and C–C	Other characteristic bands
H_4L_a (cold)	1698vs, 1660vs, 1600m, 1560m, 1530vs	760m, 740m
H_4L_a (hot)	1730vs, 1660vs, 1600m, 1560s, 1525s	
$UO_2(H_2L_a)\cdot 3H_2O$	1660vs, 1610vs, 1555vs	905vs (O–U–O)
$Cu(H_2L_a)\cdot 2H_2O$	1692s, 1640vs, 1601vs, 1572vs, 1539s	
$Ni(H_2L_a)\cdot 2H_2O$	1685s, 1640vs, 1595vs, 1558s	
$(UO_2)_2(L_a)\cdot CH_3OH\cdot H_2O$	1658vs, 1605vs, 1555vs, 1530s	920vs (O–U–O)
$Cu_2(L_a)\cdot 2H_2O$	1635vs, 1595vs, 1565vs, 1550s	
$Ni_2(L_a)\cdot 4H_2O$	1638vs, 1600vs, 1565vs, 1540s	
$NiUO_2(L_a)\cdot 2H_2O$	1645vs, 1600vs, 1555vs	910vs (O–U–O)
$CuUO_2(L_a)\cdot 1H_2O$	1655s, 1635vs, 1600vs, 1555vs	910vs (O–U–O)
H_4L_b	1685vs, 1652vs, 1605vs, 1558vs	3170m (NH)
$Cu(H_2L_b)\cdot 1H_2O$	1680vs, 1655vs, 1640m, 1590m, 1550s	3235m (NH)
$Ni(H_2L_b)\cdot 2H_2O$	1683vs, 1650vs, 1600m, 1560s	3235m (NH)
$UO_2(H_2L_b)\cdot 3H_2O$	1660vs, 1655vs, 1640m, 1590m, 1565s	3220m (NH), 927vs (O–U–O)
$Cu_2(L_b)\cdot 4H_2O$	1650vs, 1605m, 1570m, 1555s	3240m (NH)
$Ni_2(L_b)\cdot 2H_2O$	1647vs, 1621m, 1600m, 1565s	3240m (NH)
$(UO_2)_2(L_b)\cdot 3H_2O$	1670vs, 1655vs, 1630m, 1560s	3230m (NH), 903vs (O–U–O)
$NiUO_2(L_b)\cdot 1H_2O$	1655vs, 1635vs, 1600m, 1565s	3235m (NH), 900vs (O–U–O)
$CuUO_2(L_b)\cdot 2H_2O$	1600vs, 1565m, 1555s	3220m (NH), 900vs (O–U–O)
$CuNi(L_b)\cdot 2H_2O$	1640vs, 1600m, 1565s	

solvent used. An X-ray structural determination would be necessary; unfortunately we were not able to grow good crystals for such an investigation. The ν_3 O–U–O is shifted to higher frequencies on going from the mononuclear $UO_2(H_2L_a)\cdot CH_3OH$ (900 cm^{-1}) and $UO_2(H_2L_a)\cdot$dmso (900 cm^{-1}) to the binuclear $(UO_2)_2(L_a)\cdot CH_3OH$ (919 cm^{-1}) complexes; an opposite trend was observed for the uranyl(VI) complexes with H_4L_b (925 cm^{-1} for $UO_2(H_2L_b)$, 903 cm^{-1} for $Li_2UO_2(L_b)$ and 900 cm^{-1} for $(UO_2)_2(L_b)$; a lower value was found for $LiUO_2(L_b)$dmso 896 cm^{-1} and for $(UO_2)_2(L_b)$dmso 897 cm^{-1}). This different behaviour for apparently similar systems cannot yet be explained. As already reported [19, 20] the ν_3 O–U–O is probably due to vibrational and electronic interaction; consequently it is rather difficult to understand, on this basis, the influence of the uranium–monodentate ligand bond.

The homodinuclear copper and nickel complexes are easily prepared by reaction of the mononuclear precursor and the appropriate metal(II) acetate or of H_4L_a, metal(II) acetate and LiOH in molar ratio 1:2:4.

The heterodinuclear complexes can be prepared by the different pathways reported in Scheme 2. In addition to the step by step procedures ((a) and (b) of the Scheme) starting from the different mononuclear complexes, transmetallation reaction (c) can be used.

It must be noted, however, that in solution a migration reaction, particularly for the copper(II) and uranyl(VI) ions, cannot be ruled out from one site to the other, and a correlation between the properties of the complex in the solid state and in solution is not completely sure. The very low solubility of the complexes does not help in obtaining a correct knowledge of this eventual phenomenon . We are now trying to prepare more soluble complexes with similar ligands in order to understand completely the chemical behaviour of the species prepared in solution.

For the heterodinuclear $CuUO_2(L_a)$ and $NiUO_2(L_a)$ complexes, there is a lowering of the $\nu C{=}O$ of $\cong 45$ cm^{-1} in respect to the mononuclear complexes (1655 cm^{-1} and 1655 cm^{-1} respectively), comparable with the values obtained for the homodinuclear complexes. The presence of the uranyl(VI) ion is easily detected by a strong band at 900 cm^{-1} and 905 cm^{-1} for $CuUO_2(L_a)$ and $NiUO_2(L_a)$, respectively, due to ν_3 O–U–O.

A comparison of the magnetic data obtained for the H_4L_a and H_4L_b complexes offers interesting analogies and remarkable differences. The nickel(II) complexes with both of ligands show a comparable magnetic behaviour; the mononuclear $Ni(H_2L_a)$ has a μ_{eff} of 3.16 B.M.; the heterodinuclear $UO_2Ni(L_a)$ 3.22 B.M. (uranium(VI) is obviously diamagnetic); for the homodinuclear $Ni_2(L_a)$ μ_{eff} is 4.34 B.M. The values obtained for $Ni(H_2L_b)$, $UO_2Ni(L_b)$ and $Ni_2(L_b)$ are 2.83, 2.87, and 4.22 B.M., respectively. These values indicate that the magnetic interactions between the paramagnetic centres are rather weak.

The magnetic moments of $Cu(H_2L_b)$ (1.92 B.M.), $UO_2Cu(L_b)$ (1.99 B.M.) and $Cu_2(L_b)$ (1.96 B.M. or 1.39 B.M. per copper atom) indicate that there is an antiferromagnetic interaction between copper(II) ions in the binuclear species. The mononuclear and the heterobinuclear complexes show a normal magnetic behaviour, typical of a copper(II) ion. On the contrary, the copper(II) complexes of H_4L_a show an anomalous magnetic behaviour with respect to the analogous H_4L_b complexes and to the complex obtained by reaction of copper(II) acetate monohydrate and the preformed Schiff base (o-OH–C_6H_4–CH=N–CH_2–$CH_2)_2S$ (H_2salsen). This complex, which strongly resembles the internal site SN_2O_2 has a normal magnetic moment (μ_{eff} = 1.73 B.M.). $Cu(H_2L_a)$ shows a magnetic moment of 0.75 B.M., comparable to that obtained for the heterodinuclear $CuUO_2(L_a)$ (0.86 B.M.). The homodinuclear $Cu_2(L_a)$ has a μ_{eff} of 1.16 B.M.

The same results have been obtained for the copper complexes when the synthesis is carried out with anhydrous solvent and in an inert atmosphere.

It should also be noted that all the samples obtained by the different pathways show the same value of magnetic moment (within the experimental error). Even if complexes containing some copper(I) species can be supposed for the explanation of the magnetic data, the stability of the complexes, in the solid state and in solution, seems to be an indication of copper(II) ions strongly interacting with each other.

The EPR spectra, carried out at room temperature in the solid state, on $Cu(H_2L_a)$, $Cu_2(L_a)$ and Cu(salsen) well agree with the magnetic data. The strong signal at 3270 Gaus, typical of an isolated copper(II) ion, in Cu(salsen) strongly decreases for $Cu_2(L_a)$, with an indication of a copper(II)–copper(II) antiferromagnetic interaction. This signal decreases more for the mononuclear species. The values for the mononuclear copper complex is the most surprising and is difficult to explain.

Electronic spectra of the copper(II) and nickel(II) complexes, carried out in dimethylsulphoxide, are reported in Table II. The copper(II) complexes with H_4L_b, strongly indicate detectable bands in the 680–720 nm range while the analogous nickel(II) complexes have a band or a shoulder at 530–570 nm and additional bands at 850–1000 nm; the nickel(II) is in a non planar configuration, in accordance with the magnetic data.

TABLE II. Electronic (nm) Data of the Prepared Compounds.

Complex	Electronic data (nm)
$Cu(H_2L_a) \cdot 2H_2O$	625, 450, 393, 339
$Ni(H_2L_a) \cdot 2H_2O$	1600, 950, 615, 368
$UO_2(H_2L_a) \cdot 3H_2O$	393
$Cu_2(L_a) \cdot 2H_2O$	390, 340, 305
$Ni_2(L_a) \cdot 4H_2O$	308, 200
$(UO_2)_2(L_a) \cdot CH_3OH \cdot H_2O$	500, 470, 374
$NiUO_2(L_a) \cdot 2H_2O$	970, 600, 450, 399
$CuUO_2(L_a) \cdot 1H_2O$	700, 470, 450, 362
Cu(salsen)	600, 440, 367, 300
$UO_2(H_2L_b) \cdot 3H_2O$	560, 470, 380
$Ni(H_2L_b) \cdot 2H_2O$	930, 780, 550, 420, 365
$Cu(H_2L_b) \cdot 1H_2O$	575, 415, 350
$Ni_2(L_b) \cdot 2H_2O$	980, 770, 600, 550
$Cu_2(L_b) \cdot 4H_2O$	630, 435, 350
$(UO_2)_2(L_b) \cdot CH_3OH$	575, 485, 375
$CuNi(L_b) \cdot 2H_2O$	625, 355
$CuUO_2(L_b) \cdot 3H_2O$	600, 460, 365
$NiUO_2(L_b) \cdot 1H_2O$	870, 770, 600, 420, 375

The uranyl(VI) complexes show, in the 500–400 nm range, bands or shoulders due to a charge transfer L–UO_2 or to internal transitions in the O–U–O group. For the copper(II) complexes with H_4L_a, owing to their low solubility in dimethylsulphoxide, the d–d bands are not clearly identifiable while they are seen in the Cu(salsen) complex. Nickel(II) with H_4L_b complexes show d–d bands or shoulders due to the nickel(II) ion in a non planar coordination. By comparison of these results with the EPR and magnetic data, it magnifies the difficulty in correct evaluation of the oxidation state of the copper in these complexes. Nevertheless, the information obtained, clearly indicates that on moving from H_4L_b to H_4L_a (*i.e.* changing the fifth internal donor set from NH to S) there is a drastic variation on the physico-chemical properties of the copper complexes.

This different behaviour must be studied in more depth in the future, and by employing other similar ligands.

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