

Dioxouranium(VI) Schiff Base Complexes as Ligands towards Cu(II) and Ni(II) Ions

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Received 11 November 1998
Accepted for publication 21 December 1999

Two mononuclear $\text{UO}_2(\text{VI})$ complexes of the general formula $[(\text{HL})\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$, where L is a pentadentate N_2O_3 asymmetric Schiff base ligand, were synthesized and used as ligands for further coordination of either Cu(II) or Ni(II) ions. The $\text{UO}_2(\text{VI})$ ion occupies the outer O_2O sites of the ligands, thus leaving the inner N_2O_2 sites of the ligands vacant for further coordination. Different types of products were obtained according to the type of the counter anion of the transition metal cations and using LiOH as a deprotonating agent. Metal acetates always yield heterotrimeric complexes of the type $[(\text{ML})_2\text{UO}_2(\text{OH}_2)]$, $\text{M} = \text{Cu}(\text{II})$ or $\text{Ni}(\text{II})$, in the presence or absence of LiOH. In these complexes, two transition metal cations are coordinated to the inner N_2O_2 sites of two parent molecules, losing one of their uranyl cations and the remaining one shifts its coordination to the outer O—O sites of these molecules. On the other hand, metal perchlorates yield different products depending on the presence or absence of LiOH. In the presence of LiOH the following complexes were obtained: $\{[\text{UO}_2\text{L}^1(\text{OH}_2)_2]_2\text{M}\} \cdot 4.5\text{H}_2\text{O}$, $\text{M} = \text{Cu}(\text{II})$ or $\text{Ni}(\text{II})$, and $[(\text{CuL}^2)_2\text{UO}_2(\text{OH}_2)] \cdot 4\text{H}_2\text{O}$. In the former case a transition metal cation was linked to the rear of two parent uranyl molecules, through their N_2N_2 coordinating sites. In the absence of LiOH, either a cationic complex ion is formed, similar to those obtained in the case of metal acetates but without deprotonating the inner imine groups, or transmetallation occurs where a transition metal cation replaces the uranyl ion, $[(\text{NiHL}^1)_2\text{UO}_2(\text{OH}_2)](\text{ClO}_4)_2$ and $[\text{HL}^2\text{M}]$, respectively. These latter products thus differ according to the type of ligand in the parent uranyl compound. The structures of the complexes were elucidated by elemental analyses, IR, UV VIS, and ^1H NMR spectroscopy, magnetic moments, and conductivity measurements.

Di- and polynuclear complexes incorporating similar or different metal ions are of special importance in the field of biochemistry. Many proteins can develop their activity in the presence of two or more metal ions [1—3]. Some enzymes such as emocyanine contain a dinuclear copper(II) complex which acts as one of the active sites for oxygen activation [1—3]. Uranyl complexes are usually prepared using compartmental ligands which offer enough room to accommodate the uranyl ion preferably with equatorial pentagonal coordination sites. Thus penta- and heptadentate ligands with N_3O_2 , N_3O_4 coordinating sites* proved to be the most suitable ones for coordinating transition metal cations and/or uranyl ions. However, hexadentate ligands with N_2O_4 coordinating sites having large outer cavities to accommodate the uranyl ion, which is further coordinated to a solvent molecule to complete its preferred heptacoordination sphere, are also known

* In spite of the resemblance to the chemical formulas, the abbreviations N_3O_2 , N_3O_4 , O_2O , etc. of the multiple ligands are commonly used in publications on coordination chemistry.

[4—11]. Examples of heterobinuclear metal complexes containing a uranyl ion and transition metal cation are shown in Fig. 1g and h. The preparations of these heterobinuclear metal complexes are usually preceded by the preparation of the mononuclear Cu(II) or Ni(II) complexes then reacting them with the uranyl salt [6, 7].

In our previous publications [12, 13] we have reported the preparation of the mononuclear Cu(II), Ni(II) or $\text{UO}_2(\text{VI})$ complexes of five pentadentate N_2O_3 ligands. Both Cu(II) and Ni(II) ions were coordinated to the inner N_2O_2 compartment, while the $\text{UO}_2(\text{VI})$ ion was coordinated to the outer O_2O compartment and completed its equatorial pentagonal coordination by coordinating two water molecules. Further reactions of the mononuclear Cu(II) or Ni(II) complexes with transition metal cations or uranyl ions yielded di- or trinuclear metal complexes of the type $[\text{LMM}'\text{Cl}]$, $[\text{LMM}'_2\text{Cl}_3]$, and $[(\text{LM})_2\text{UO}_2(\text{OH}_2)]$ (M' or $\text{M} = \text{Cu}$ or Ni) (Fig. 1a—f).

In the present study the mononuclear $\text{UO}_2(\text{VI})$ complexes of two asymmetric pentadentate N_2O_3 Schiff base ligands (Fig. 2) were used as ligands in or-

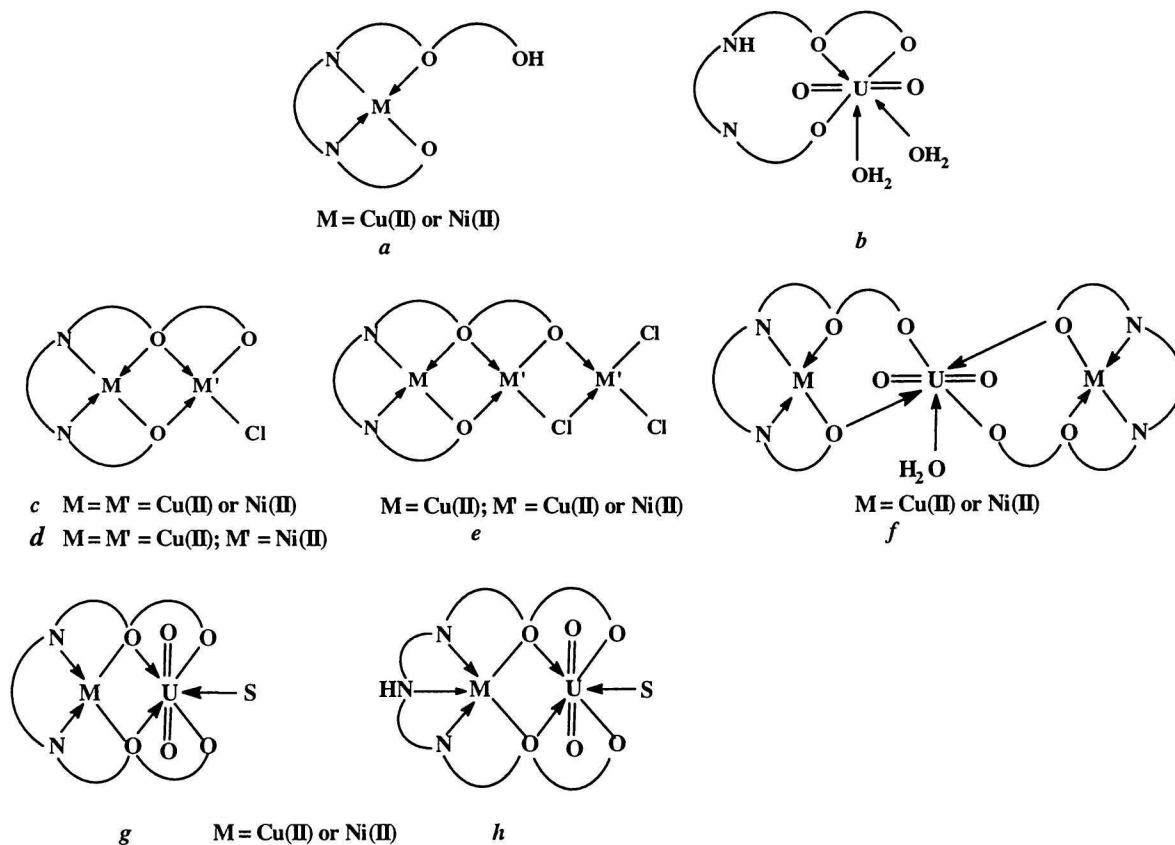


Fig. 1. Metal complexes: *a*, *b*) mononuclear; *c*) homodinuclear; *d*) heterodinuclear; *e*, *f*) heterotrimeric of pentadentate ligands; *g*) heterodinuclear of hexadentate ligands; *h*) heterodinuclear of heptadentate ligands.

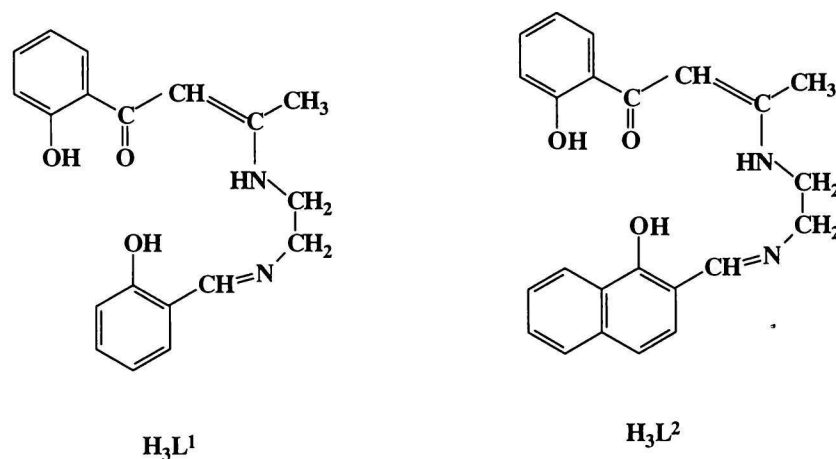


Fig. 2. Structures of the two asymmetric pentadentate Schiff bases, H_3L^1 and H_3L^2 .

der to study their chelating behaviour towards Cu(II) and Ni(II) salts in the presence and absence of a deprotonating agent, LiOH.

EXPERIMENTAL

All chemicals used were of Merck (Germany) or BDH (U.K.) grade. The two asymmetric pentadentate Schiff base ligands H_3L^1 and H_3L^2 (Fig. 3) and

their mononuclear $\text{UO}_2(\text{VI})$ complexes (Fig. 1) were prepared as previously described [13].

IR spectra were recorded with a Perkin—Elmer IR 598 spectrometer ($200\text{--}4000\text{ cm}^{-1}$) using KBr discs and polystyrene as a calibrant. Electronic spectra of the solutions of the metal complexes in DMF were recorded on a Perkin—Elmer 555 spectrophotometer. ^1H NMR of the Schiff base ligand, H_3L^2 , and its diamagnetic uranyl complex in DMSO were recorded on

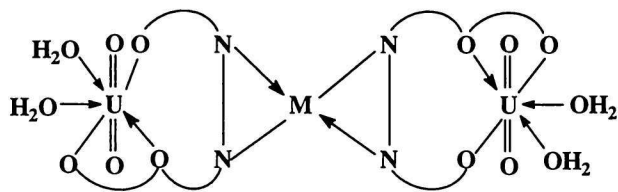


Fig. 3. Heterotrimeric metal complexes of ligand H_2L^1 , $M = Cu$ or Ni .

a Bruker WP 200 SY spectrometer at room temperature using tetramethylsilane (TMS) as an internal standard. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa Products, Model No. MKI magnetic susceptibility balance (U.K.). The effective magnetic moments were calculated from the expression $\mu_{\text{eff}} = 2.828 (\chi_M \cdot T)^{1/2}$ B.M., where χ_M is the molar susceptibility. Diamagnetic corrections were calculated from Pascal's constants for all atoms in the compounds. Conductivity measurements of solutions of the metal complexes in DMF (10^{-3} M) were carried out using a conductivity meter Model LBR 40A (Germany). The thermal data were obtained using TG, DTG, and DTA techniques. The measurements were carried out using an OD-102 Paulik—Erdey derivatograph (MOM, Budapest, Hungary) with a sensitivity 100 mg for TG measurements. The samples were heated in platinum crucibles within a *static air* atmosphere at a heating rate 5 K min^{-1} and up to 600°C , using Al_2O_3 as a reference compound.

Microanalyses of carbon, hydrogen, and nitrogen were carried out at the Microanalysis Centre, Cairo University, Giza, Egypt. Analyses of the copper and nickel in the mononuclear complexes followed the dissolution of the solid complex in hot concentrated HCl with subsequent diluting with water and filtering to remove the precipitated ligand. The solution was neutralized with ammonia solution and the metal ions were then titrated with EDTA standard solution [14].

Heterotrimeric Metal Complexes

$[(ML)_2UO_2(OH_2)]$, $M = Cu$ or Ni ; $L = L^1$ or L^2

Cu(II) or Ni(II) acetate (0.1 mmol) was dissolved in 40 cm^3 of methanol and added gradually to a hot methanolic suspension of the mononuclear uranyl complex $[(HL)UO_2(OH_2)_2] \cdot 0.5H_2O$ ($L = L^1$ or L^2 ; 0.1 mmol) in 40 cm^3 of methanol. The resulting solution was refluxed for 8–10 h on a water bath. Brick red and reddish orange precipitates, respectively, were obtained after cooling and were filtered off, washed several times with methanol, ether and finally air-dried. The solid complexes were preserved in a desiccator over anhydrous $CaCl_2$. The above reactions carried out in the presence of LiOH yielded the same products.

Heterotrimeric Metal Complexes

$[(L^1UO_2(OH_2))_2]_2M$, $M = Cu$ or Ni

A methanolic solution of LiOH (0.1 mmol in 10 cm^3 of methanol) was added slowly to a stirred suspension of the mononuclear $UO_2(VI)$ complex of ligand H_3L^1 , $[(HL^1)UO_2(OH_2)_2] \cdot 0.5H_2O$ (0.1 mmol in 30 cm^3 of methanol). Cu(II) or Ni(II) perchlorate hexahydrate (0.1 mmol) was dissolved in 20 cm^3 of methanol and added to the previous solution. The resulting mixture was refluxed for 10 h on a water bath. The colour of the solution changed from orange to brick red in the case of Cu(II) and to brown in the case of Ni(II). The solid complexes were precipitated after cooling and obtained by filtration, washed several times with water, methanol, then ether and finally air-dried.

Heterotrimeric Metal Complex

$[(HL^1Ni)_2UO_2(OH_2)](ClO_4)_2$

Nickel(II) perchlorate hexahydrate (0.1 mmol) was dissolved in 20 cm^3 of methanol and added gradually to a suspension of $[(HL^1)UO_2(OH_2)_2] \cdot 0.5H_2O$ complex (0.1 mmol) in 30 cm^3 of methanol. The resulting solution was refluxed for 10 h on a water bath. The colour changed from orange to brown. The product was obtained by filtration, washed several times with water, methanol, ether and then air-dried.

Mononuclear Cu(II) and Ni(II) Complexes, $[HL_2M]$ by Transmetalation

Copper(II) or nickel(II) perchlorate hexahydrate (0.1 mmol) was dissolved in 20 cm^3 of methanol and added gradually to a suspension of the mononuclear $UO_2(VI)$ complex $[HL^2UO_2(OH_2)_2] \cdot 0.5H_2O$ (0.1 mmol) in 30 cm^3 of methanol. The colour of the solution changed from orange to green in the case of the Cu(II) complex and to brownish yellow in the case of Ni(II) complex. The products were obtained by filtration, washed several times with water, methanol, ether and then air-dried.

RESULTS AND DISCUSSION

The structures of the two parent uranyl complexes were elucidated by chemical analyses (Table 1), UV VIS (Table 2), and IR spectra (Table 3). IR spectra showed that the absorptions of the azomethine groups in these complexes were the same as those in their corresponding ligands, *i.e.* 1635 cm^{-1} and 1630 cm^{-1} for H_3L^1 and H_3L^2 , respectively, which indicated that these groups did not participate in coordinating the uranyl cations. Besides, a characteristic absorption band appeared at $\tilde{\nu} = 900 \text{ cm}^{-1}$ and was assigned to the asymmetric stretching vibration of the linear $O=U=O$ moiety. Also, a broad absorption band appeared at around 3400 cm^{-1} and it was

Table 1. Characterization of the Metal Complexes

	Reactants	Complexes (Formulas)	Elemental analyses ^a				Yield %	$\theta/^\circ\text{C}$ (decomp.)	Colour
			C	H	N	M			
1	$\text{H}_3\text{L}^1 + \text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	$[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$ ($\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_7.5\text{U}$)	36.0 (35.8)	3.5 (3.6)	4.4 (4.4)		77.0	220	Orange
2	$[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + 2\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	$[(\text{NiL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 10\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{56}\text{N}_4\text{O}_{19}\text{Ni}_2\text{U}$)	37.2 (37.2)	4.5 (4.5)	4.5 (4.6)		56.0	> 270	Reddish brown
3	$\text{HL}^1\text{UO}_2(\text{OH}_2)_2 \cdot 0.5\text{H}_2\text{O} + 2\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O} + \text{LiOH}$	$[(\text{NiL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 10\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{56}\text{N}_4\text{O}_{19}\text{Ni}_2\text{U}$)	37.3 (37.2)	4.5 (4.5)	4.5 (4.6)		50.0	> 270	Reddish brown
4	$[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + 2\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$[(\text{NiHL}^1)_2\text{UO}_2(\text{OH}_2)](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{44}\text{N}_4\text{O}_{20}\text{Cl}_2\text{Ni}_2\text{U}$)	35.0 (35.0)	3.4 (3.4)	4.2 (4.3)		40.0	— ^c	Pale brown
5	$2[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + \text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} + \text{LiOH}$	$\{[\text{UO}_2\text{L}^1(\text{OH}_2)_2]_2\text{Ni}\} \cdot 6.5\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{55}\text{N}_4\text{O}_{20.5}\text{NiU}_2$)	31.8 (31.9)	3.7 (3.9)	3.8 (3.9)		40.0	> 270	Brown
6	$[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + 2\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	$[(\text{CuL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 9\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{54}\text{N}_4\text{O}_{18}\text{Cu}_2\text{U}$)	37.3 (37.4)	4.4 (4.5)	4.5 (4.6)		45.0	> 270	Brick red
7	$[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + 2\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} + \text{LiOH}$	$(\text{CuL}^1)_2\text{UO}_2(\text{OH}_2) \cdot 9\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{54}\text{N}_4\text{O}_{18}\text{Cu}_2\text{U}$)	37.4 (37.4)	4.3 (4.5)	4.5 (4.6)		40.0	> 270	Brick red
8	$2[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + \text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} + \text{LiOH}$	$\{[\text{UO}_2\text{L}^1(\text{OH}_2)_2]_2\text{Cu}\} \cdot 4.5\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{51}\text{N}_4\text{O}_{18.5}\text{CuU}_2$)	32.5 (32.6)	3.6 (3.7)	3.9 (4.0)		40.0	> 270	Brick red
9	$\text{H}_3\text{L}^2 + \text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$ ($\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_7.5\text{U}$)	40.3 (40.2)	3.6 (3.7)	4.1 (4.1)		78.0	228	Orange
10	$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + 2\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	$[(\text{NiL}^2)_2\text{UO}_2(\text{OH}_2)]$ ($\text{C}_{46}\text{H}_{40}\text{N}_4\text{O}_9\text{Ni}_2\text{U}$)	48.1 (48.1)	3.4 (3.5)	4.8 (4.9)		50.0	260	Yellowish orange
11	$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + \text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$[\text{HL}^2\text{Ni}] \cdot \text{H}_2\text{O}$ ($\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_4\text{Ni}$)	61.7 (61.5)	4.9 (4.9)	6.2 (6.2)	12.9 (13.1)	90.0	250 ^b	Brownish yellow
12	$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + 2\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	$[(\text{CuL}^2)_2\text{UO}_2(\text{OH}_2)] \cdot 8\text{H}_2\text{O}$ ($\text{C}_{46}\text{H}_{56}\text{N}_4\text{O}_{17}\text{Cu}_2\text{U}$)	42.5 (42.4)	4.1 (4.3)	4.3 (4.3)		55.0	> 270	Brick red
13	$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O} + \text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$[\text{HL}^2\text{Cu}] \cdot 0.5\text{H}_2\text{O}$ ($\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_{3.5}\text{Cu}$)	61.9 (62.1)	4.7 (4.8)	6.3 (6.3)	14.5 (14.3)	90.0	240 ^b	Brown
14	$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2 + 2\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} + \text{LiOH}$	$[(\text{CuL}^2)_2\text{UO}_2(\text{OH}_2)] \cdot 4\text{H}_2\text{O}$ ($\text{C}_{46}\text{H}_{48}\text{N}_4\text{O}_{13}\text{Cu}_2\text{U}$)	44.8 (44.9)	3.8 (3.9)	4.5 (4.6)		40.0	248	Brick red

a) Found/(Calculated); b) The same melting point for the corresponding complexes previously prepared by a different procedure [13]; c) Decomposition temperature was not determined due to the presence of explosive ClO_4^- ion.

assigned to $\nu(\text{OH})$ of the coordinated water molecules. The DTA diagrams of the parent uranyl complexes exhibited a weak endothermic peak in the range 140–190 °C which corresponded to a mass loss of two water molecules for each uranyl molecule. The ^1H NMR spectrum of the uranyl complex of ligand H_3L^2 (Table 4) showed the absence of the signal assigned to the phenolic proton of the ligand which indicated that deprotonation of the phenolic group occurred on $\text{UO}_2(\text{VI})$ complexation and that the phenolic oxygen takes part in the complex formation. Thus, according to the ^1H NMR data along with the IR and thermal data discussed above, it was deduced that the $\text{UO}_2(\text{VI})$ ions bind to the outer O_2O sites of the ligands and are coordinated to the oxygen atoms of both the phenolic and ketonic groups.

The ligands thus behave as dibasic tridentate ones towards the $\text{UO}_2(\text{VI})$ ions. Casellato *et al.* [7, 8] have previously reported that $\text{UO}_2(\text{VI})$ ions prefer to bind to outer O_2O_2 coordinating sites of ligands which pos-

sess in addition inner N_2O_2 sites. As the $\text{UO}_2(\text{VI})$ ion prefers the equatorial pentagonal coordination, then when the chelating ability of the ligands does not allow this coordination number to be reached, the free sites of $\text{UO}_2(\text{VI})$ ion are filled by the solvent molecules.

The two parent mononuclear $\text{UO}_2(\text{VI})$ complexes of ligands H_3L^1 and H_3L^2 were used as ligands towards Cu(II) and Ni(II) ions. Different products were obtained according to the type of the counter anion of the metal ion and the addition of LiOH as a deprotonating reagent. The reactions of the parent complexes with either Cu(II) or Ni(II) acetates in methanol yielded the heterotrinary metal complexes of the type *f* (Fig. 1) whether LiOH was added or not.

The IR spectra of the products show a shift of the azomethine group vibration by 20 cm^{-1} to lower frequencies indicating its involvement in metal coordination. The diamagnetic behaviour of the Ni(II) products (Table 2) indicates a square-planar coordination

Table 2. Other Data of the Metal Complexes

Complexes	UV VIS Spectra ^a		Magnetic moments		Conductance ^a
	λ/nm		$\frac{\mu_{\text{eff}}^b}{\text{B.M.}}$	$\frac{\mu_{\text{compl}}^c}{\text{B.M.}}$	$\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
1		340, 245	Diamag.		8.0
2	547		Diamag.		10.0
3	547		Diamag.		10.0
4	547		Diamag.		125.0
5	550		Diamag.		15.0
6	546		1.95	2.76	10.0
7	535		1.84	2.60	10.0
8	540		1.98		10.0
9		340, 240	Diamag.		10.0
10	535, 404	320	Diamag.		10.0
11	540, 400	312	Diamag.		2.0
12	535, 424	380, 330	2.20	3.11	12.0
13	532, 360	312	2.24		5.0
14	535		1.82	2.48	10.0

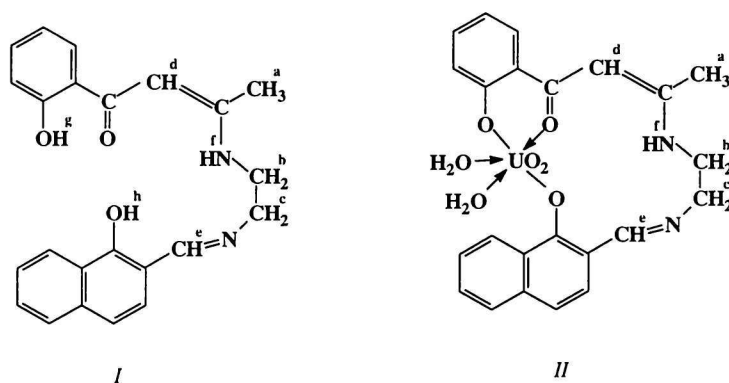
a) 10^{-3} M solution of the complex in DMF; b) μ_{eff} is the magnetic moment of one cationic species in the complex; c) μ_{compl} is the total magnetic moment of all cations in the complex.

Table 3. IR Spectral Data ($\bar{\nu}/\text{cm}^{-1}$) of the Parent Ligands, the Mononuclear $\text{UO}_2(\text{VI})$ Complexes, and the Product Metal Complexes

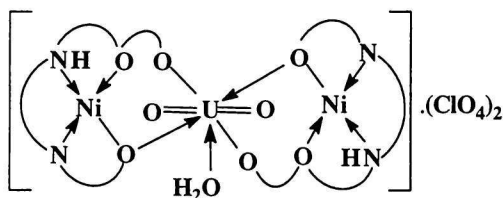
Ligands and Complexes	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{C})$	$\nu(\text{C}-\text{N})$	$\nu_3(\text{O}=\text{U}=\text{O})$	$\nu(\text{ClO}_4)$	$\nu(\text{OH})(\text{phenolic or water})$
H_3L^1	1625	1600	1565	1515	—	—	3400
$[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$	1655	1600	1540	1500	900	—	3460
$[(\text{NiL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 10\text{H}_2\text{O}$	1628	1595	1540	1460	905	—	3460
$[(\text{NiL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 10\text{H}_2\text{O}$	1622	1590	1544	1460	900	—	3455
$[(\text{NiHL}^1)_2\text{UO}_2(\text{OH}_2)](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	1633	1595	—	1475	910	1100	3415
$\{[\text{UO}_2\text{L}^1(\text{OH}_2)_2]_2\text{Ni}\} \cdot 6.5\text{H}_2\text{O}$	1622	1595	1550	1460	900	—	3425
$[(\text{CuL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 9\text{H}_2\text{O}$	1633	1595	1545	1467	900	—	3435
$[(\text{CuL}^1)_2\text{UO}_2(\text{OH}_2)] \cdot 9\text{H}_2\text{O}$	1639	1595	1550	1462	900	—	3425
$\{[\text{UO}_2\text{L}^1(\text{OH}_2)_2]_2\text{Cu}\} \cdot 4.5\text{H}_2\text{O}$	1633	1590	1550	1500	900	—	3425
H_3L^2	1630	1590	1565	1515	—	—	3380
$[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$	1650	1600	1550	1500	900	—	3460
$[(\text{NiL}^2)_2\text{UO}_2(\text{OH}_2)]$	1630	1605	1550	1510	900	—	3460
$[\text{HL}^2\text{Ni}] \cdot \text{H}_2\text{O}$	1625	1600	1545	1485	—	—	3470
$[(\text{CuL}^2)_2\text{UO}_2(\text{OH}_2)] \cdot 8\text{H}_2\text{O}$	1622	1590	1535	1467	925	—	3440
$[\text{HL}^2\text{Cu}] \cdot 0.5\text{H}_2\text{O}$	1635	1605	1545	1505	—	—	3460
$[(\text{CuL}^2)\text{UO}_2(\text{OH}_2)] \cdot 4\text{H}_2\text{O}$	1640	1605	1550	1510	900	—	3460

geometry around the Ni(II) ions. Besides, the visible spectra of both Cu(II) and Ni(II) products show a broad absorption band in the range $\lambda = 535\text{--}547$ nm which further indicates a square-planar coordination geometry around both Cu(II) and Ni(II) ions [15, 16]. It could be concluded that in this type of reaction the introduction of two metal ions, either Cu(II) or Ni(II), in the inner N_2O_2 sites of two parent molecules is accompanied by the loss of one of the uranyl ions while the one left is coordinated to the outer O—O atoms of the two parent molecules and is further coordinated to a water molecule to reach its favourable heptacoordination geometry. These complexes are identical with those prepared from the starting mononuclear Cu(II) or Ni(II) complexes by reacting them with uranyl acetate [13].

On the other hand, the reactions of the parent uranyl complex $[\text{HL}^1\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$ with Cu(II) or Ni(II) perchlorates in the presence and absence of LiOH yielded different heterotrimeric metal complexes. In the presence of LiOH, either Cu(II) or Ni(II) ions were coordinated to the N_2N_2 sites of two parent ligand molecules through their rear positions (Fig. 3), this might be only a suggestion to explain the behaviour in spite of that it was not described before. To the knowledge of the author this is a novel type of coordination which was not met before with ligands incorporating both nitrogen and oxygen coordinating sites. LiOH thus deprotonates the imine groups, NH, and the nitrogen atoms become more basic and form strong coordinating bonds to either Cu(II) or Ni(II) ions. This linkage is however similar to that observed

Table 4. The ^1H NMR Data of the Free Ligand H_3L^2 (*I*) and its $\text{UO}_2(\text{VI})$ Complex (*II*) in $(\text{CD}_3)_2\text{SO}$ 

δ									
H_3L^2	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H_{arom}
<i>I</i>	2.10 (s)	3.75 (m)	5.65 (s)	8.95 (s)	11.20 (br)	13.40 (s)	13.9 (br)	6.85—7.90 (m)	
<i>II</i>	2.30 (s)	2.95 (m)	6.05 (s)	8.85 (s)	12.10 (br)	—	—	6.85—8.60 (m)	

**Fig. 4.** A heterotrimeric metal complex of ligand H_2L^1 .

in macrocyclic tetradentate N_2N_2 ligands [17, 18].

However, if the same reaction was carried out without LiOH, nickel(II) perchlorate was only tested and yielded another heterotrimeric metal product where two Ni(II) ions occupy the inner N_2O_2 sites of two parent molecules, one uranyl ion is removed and the remaining one is coordinated to the outer O—O atoms of the parent molecules besides a further water molecule. This product is similar to those illustrated as the type *f* (Fig. 1), however, here the imine groups are not deprotonated due to the presence of the stronger acidic medium produced by the production of perchloric acid and thus a cationic complex is produced (Fig. 4) instead of the neutral complexes prepared in the presence of the weaker acetic acid by-product of the type *f* (Fig. 1).

The IR spectrum of the latter complex (Fig. 4) shows a broad absorption peak at 1100 cm^{-1} which is characteristic of an ionic perchlorate group [19]. Its molar conductance in DMF was $125\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ (Table 2) which indicates that the complex is ionic and 1 : 2 electrolyte. The IR spectra of the three previous complexes (Figs. 3 and 4) show a shift of the band due to the azomethine group to lower frequencies, which indicates its involvement in metal coordination. Both

Ni(II) complexes (Figs. 3 and 4) are diamagnetic and their electronic spectra show bands at 550 and 547 nm, respectively, also the Cu(II) complex (Fig. 3) shows *d*—*d* transition at 540 nm. These results indicate that Cu(II) and Ni(II) ions in these complexes have square-planar coordination geometry.

The products of the reactions of the parent mononuclear $\text{UO}_2(\text{VI})$ complex of ligand H_3L^2 , $[\text{HL}^2\text{UO}_2(\text{OH}_2)_2] \cdot 0.5\text{H}_2\text{O}$ with $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Cu}(\text{II})$ or $\text{Ni}(\text{II})$) are rather surprising. Transmetalation between Cu(II) or Ni(II) ions and the $\text{UO}_2(\text{VI})$ ion does occur and mononuclear Cu(II) or Ni(II) complexes are produced, $[\text{HL}^2\text{M}]$, where these ions are incorporated in the inner N_2O_2 sites of the parent ligand (Fig. 2). These complexes were previously obtained by the reaction of the parent ligand with either Cu(II) or Ni(II) acetates [13]. IR spectra of the products were devoid of the UO_2 vibration absorption band and showed a shift of the azomethine absorption bands to lower frequencies. The electronic spectra of the products showed absorption bands at 532 and 540 nm, respectively, besides the Ni(II) complex was diamagnetic. These results indicate that both Cu(II) and Ni(II) complexes have square-planar coordination geometry.

A further reaction similar to the latter ones was carried out using Cu(II) perchlorate in the presence of LiOH and yielded a product similar to the prepared complex using Cu(II) acetate of the type *f* (Fig. 1).

Thus, it seems that the presence of a strong acidic medium such as perchloric acid, which is produced as a by-product in some of the previous reactions, would lead to unexpected products. On the other hand, the presence of a weak acidic medium, such as acetic acid, which is also produced as a by-product in other reactions, would lead to the expected $[(\text{ML})_2\text{UO}_2(\text{OH}_2)]$

complexes. It is also concluded that LiOH while having no effect on the reaction products when metal acetates are used, has an effect when using metal perchlorates. The presence of coordinated and hydrated water molecules in the metal complexes has been confirmed by new bands appearing at 3250–3420 cm^{-1} in the IR spectra of the complexes. Also, the rocking mode of coordination water molecules appeared as a weak vibrational band [20] at 820–840 cm^{-1} . In the other cases, the band observed at about 605–660 cm^{-1} indicates the presence of hydrated water molecules [20]. The metal–ligand vibrations is expected below 600 cm^{-1} and the presence of bands between 330–410 and 470–550 cm^{-1} is due to bonding of the metal cation to the nitrogen and oxygen atoms of the ligand, respectively.

Attempts to study the previous reactions using metal chlorides failed to give distinctive products, as mixtures of products not separable by means of organic solvents were obtained.

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