

## Mono-, di- and tri-nuclear metal complexes of new pentadentate schiff bases

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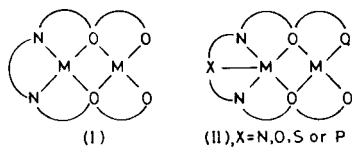
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New pentadentate schiff bases containing  $N_2O_3$  coordination sites have been prepared in two steps. In the first step, the ligand half-unit is obtained by condensing 1-(*o*-hydroxyphenyl)butane-1,3-dione and 1,2-diaminoethane, which is condensed in the second step with a bidentate aromatic aldehyde or ketone such as *o*-hydroxyacetophenone, salicylaldehyde, or 2-hydroxy-1-naphthaldehyde to obtain the schiff bases. These ligands react with transition metals to yield mono-, bi- and tri-nuclear complexes.

Much interest has been evinced in the last few years in the study of symmetrical and unsymmetrical multidentate schiff bases as ligands and preparation of transition metal complexes incorporating two similar or different metal ions<sup>1-3</sup>. The interest in these complexes arises from their similarity to the systems found in the living organisms, e.g., enzymes and proteins which develop their activity in the presence of two or more metal ions<sup>4-6</sup>.

Acyclic and cyclic ligands containing six coordination sites have been synthesized which usually coordinate to two similar or different cations. Mainly ligands of this type have  $N_2O_4$  sites<sup>1,2</sup> (structure I). Later on, these ligand systems were further extended to systems containing seven coordination sites ( $XN_2O_4$ ) (structure II). The interest in the latter type of ligands arose from the need of the uranyl cation to coordinate with five donating atoms to complete its seven-coordination sphere.



In this work some pentadentate schiff bases have been prepared by reacting the condensation product of 1-(*o*-hydroxyphenyl)butane-1,3-dione and 1,2-diaminoethane, with a bidentate aromatic aldehyde or ketone such as *o*-hydroxyacetophenone, salicylaldehyde, or 2-hydroxy-1-naphthaldehyde. The resulting ligands have five coordination sites,  $N_2O_3$ , which are capable of coordinating to two adjacent metal ions. These ligands also coordinate with one metal ion to form mononuclear complexes.

The interest in these ligands arises from the fact that they would offer more space to accommodate two adjacent cations without severe distortion. Previous studies on hexadentate ligands (I) showed distortion of both Cu(II) and Ni(II) symmetries if dioxouranium (VI) is attached to the outer compartment<sup>7,8</sup>.

### Materials and Methods

*o*-Hydroxyacetophenone, ethyl acetate, salicylaldehyde, 2-hydroxy-1-naphthaldehyde and ethylenediamine were either Merck or BDH reagents of AR grade. Ethylenediamine was distilled over NaOH pellets. Copper acetate monohydrate, nickel acetate tetrahydrate, uranyl acetate dihydrate, thorium nitrate tetrahydrate, copper chloride dihydrate and nickel chloride hexahydrate were BDH reagents. Organic solvents were reagent grade chemicals.

### Preparation of ligands

*o*-Acetoacetylphenol was prepared by the method of Wittig<sup>9</sup>. The preparation was carried out by condensing *o*-hydroxyacetophenone with ethylacetate in the presence of sodium metal under reflux. The resulting sodium phenolate was stirred with glacial acetic acid and the product was extracted with acetone and crystallized from benzene, yield 15%, m.p. 90.5-91.5 °C. Reaction of the  $\beta$ -ketophenol with a solution of ethylenediamine in  $CHCl_3$  yielded the corresponding half-unit<sup>10</sup>, yield 84%, m.p. 75°C. The preparation of the new schiff bases was carried out by condensing under reflux the half-unit, dissolved in  $CHCl_3$ , with either *o*-hydroxyacetophenone, salicylaldehyde or 2-hydroxy-1-naphthaldehyde dissolved in ethanol; yields ranged between 60 and 95%, m.p.'s: 167°C,

94°C and 135°C changed colour to dark brown), respectively.

#### Preparation of mononuclear complexes

The metal acetate [Ni(II) or Cu(II)] or nitrate [Th(IV)] was dissolved in hot ethanol and added gradually to a stirred hot solution of the schiff base ligand dissolved in hot chloroform (molar ratio 1:1). The resulting solution was refluxed for 3-4 hours. The mononuclear complex either precipitated immediately or after reducing the volume of the solution. The solution was then cooled, filtered, the product washed with small amounts of chloroform and ethanol and then air-dried. Yields were about 70%.

Uranyl complexes were prepared by adding a methanolic solution of uranyl acetate dropwise to a stirred solution of the ligand in chloroform at room temperature. An orange precipitate appeared after a short time and its quantity increased with time (6 hr) during which period stirring was continued. The solution was concentrated *in vacuo* and the precipitate obtained was filtered and washed with small amounts of chloroform and methanol.

#### Preparation of binuclear and trinuclear complexes

A hot methanolic solution of LiOH was added gradually to a stirred solution of the mononuclear Cu(II) or Ni(II) complex dissolved in hot chloroform (molar ratio 1:1): After 15 min, a hot methanolic solution of the hydrated metal chloride was added gradually to the previous solution, in the molar ratio 1:1. The resulting solution was refluxed for 15-20 hr when bi- or tri-nuclear complexes precipitated. After reducing the volume, products were separated by filtration, washed with small amounts of methanol and chloroform and finally air-dried. Yields were 60-80%.

In the case of dioxouranium (VI) products, trinuclear complexes containing one  $\text{UO}_2^{2+}$  cation and either two  $\text{Cu}^{2+}$  or two  $\text{Ni}^{2+}$  cations were obtained; these precipitated after refluxing for a shorter time and without reducing the volume of the solutions.

The pentadentate ligand derived from *o*-hydroxyacetophenone yielded a trinuclear complex containing three  $\text{Cu}^{2+}$  cations instead of the usual binuclear products. However, the binuclear complex which contains only two  $\text{Cu}^{2+}$  cations was

Table 1—Elemental analyses of the ligands and their complexes

Compound	Colour	Found (Calc.) %				
		C	H	N	Cl	M
$\text{H}_3\text{L}_a$	Yellow	70.6 (71.0)	6.6 (6.6)	8.3 (8.3)	—	—
$[\text{Cu}(\text{HL}_a)]$	Brown	60.0 (60.1)	4.7 (5.0)	6.8 (7.0)	—	15.9 (15.9)
$[\text{Ni}(\text{HL}_a)] \cdot 0.5\text{H}_2\text{O}$	Golden	59.0 (59.4)	5.2 (5.2)	6.8 (6.9)	—	14.5 (14.5)
$[\text{UO}_2(\text{HL}_a)(\text{OH}_2)_2]$	Orange red	37.3 (37.3)	3.6 (3.7)	4.2 (4.4)	—	—
$\text{Th}(\text{HL}_a)(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$	Yellow	30.4 (30.3)	4.0 (4.0)	7.1 (7.1)	—	—
$[\text{Ni}(\text{CuL}_a)\text{Cl}] \cdot 0.5\text{H}_2\text{O}$	Red	47.7 (47.8)	4.0 (4.0)	5.6 (5.6)	7.1 (7.1)	—
$[\text{Ni}_2\text{LaCl}] \cdot 0.5\text{H}_2\text{O}$	Red	48.3 (48.3)	4.0 (4.0)	5.6 (5.6)	7.0 (7.1)	23.5 (23.6)
$[\text{Cu}_2\text{L}_a\text{Cl}] \cdot 2.5\text{H}_2\text{O}$	Green	44.2 (44.2)	4.5 (4.5)	5.1 (5.2)	6.2 (6.5)	23.4 (23.4)
$[\text{Cu}_3\text{L}_a\text{Cl}_3] \cdot 5\text{H}_2\text{O}$	Greenish brown	33.3 (33.3)	4.1 (4.1)	3.9 (3.9)	14.4 (14.7)	26.4 (26.4)
$[(\text{NiL}_a)_2\text{UO}_2(\text{OH}_2)] \cdot 5\text{H}_2\text{O}$	Brownish yellow	40.9 (41.2)	3.9 (4.3)	4.7 (4.8)	—	—
$[(\text{CuL}_a)_2\text{UO}_2(\text{OH}_2)] \cdot \text{H}_2\text{O}$	Brick red	43.5 (43.5)	3.8 (3.8)	5.0 (5.1)	—	—
$\text{H}_3\text{L}_b$	Yellow	70.6 (70.6)	6.0 (5.9)	8.6 (8.7)	—	—

(contd.)

Table 1—Elemental analyses of the ligands and their complexes —*Contd*

Compound	Colour	Found (Calc.) %				
		C	H	N	Cl	M
[Cu(HL <sub>b</sub> )]	Brown	59.1 (59.1)	4.7 (4.7)	7.3 (7.3)	—	16.4 (16.5)
[Ni(HL <sub>b</sub> )]	Brownish yellow	59.5 (59.9)	4.8 (4.8)	7.4 (7.4)	—	15.5 (15.4)
[UO <sub>2</sub> (HL <sub>b</sub> )(OH <sub>2</sub> ) <sub>2</sub> ]	Orange	36.3 (36.3)	3.5 (3.5)	4.4 (4.5)	—	—
[Ni(CuL <sub>b</sub> )Cl].0.5H <sub>2</sub> O	Red	46.6 (46.8)	3.7 (3.7)	5.6 (5.7)	7.2 (7.3)	—
[Cu <sub>2</sub> L <sub>b</sub> Cl].0.5H <sub>2</sub> O	Brown	46.3 (46.3)	3.7 (3.7)	5.7 (5.7)	7.2 (7.2)	25.3 (25.8)
[(NiL <sub>b</sub> ) <sub>2</sub> UO <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ].7H <sub>2</sub> O	Red	38.4 (38.9)	4.0 (4.3)	4.7 (4.8)	—	—
[(CuL <sub>b</sub> ) <sub>2</sub> UO <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ].6.5H <sub>2</sub> O	Brick red	38.9 (38.9)	4.0 (4.2)	4.6 (4.8)	—	—
H <sub>3</sub> L <sub>c</sub>	Greenish yellow	73.5 (73.8)	5.6 (5.9)	7.4 (7.5)	—	—
[Cu(HL <sub>c</sub> )]	Dark brown	62.9 (63.4)	4.6 (4.6)	6.2 (6.4)	—	14.6 (14.6)
[Ni(HL <sub>c</sub> )].H <sub>2</sub> O	Dark brownish yellow	61.5 (61.5)	4.9 (4.9)	6.2 (6.2)	—	13.1 (13.4)
[UO <sub>2</sub> (HL <sub>2</sub> )(OH <sub>2</sub> ) <sub>2</sub> ]	Orange	40.7 (40.7)	3.6 (3.6)	4.1 (4.1)	—	—
Th(HL <sub>c</sub> )(NO <sub>3</sub> ) <sub>2</sub> .9.5H <sub>2</sub> O	Brown	30.7 (30.7)	4.1 (4.4)	6.1 (6.2)	—	—
[Ni(CuL <sub>c</sub> )Cl].1.5H <sub>2</sub> O	Dark red	49.3 (49.7)	4.0 (4.0)	5.0 (5.0)	6.2 (6.4)	—
[(CuL <sub>c</sub> ) <sub>2</sub> UO <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ].7H <sub>2</sub> O	Brick red	42.5 (43.0)	4.2 (4.2)	4.4 (4.4)	—	—

obtained by the reaction of the ligand with CuCl<sub>2</sub>.2H<sub>2</sub>O in the presence of LiOH keeping the molar ratio 1:1:1.

IR spectra were recorded on a Perkin-Elmer 598 spectrophotometer using KBr discs. Electronic spectra were recorded in dimethylformamide (10<sup>-3</sup> M solutions) using a Perkin-Elmer 550 spectrophotometer. Either the solvent or ligand solution, of the same concentration as that of the complex, was used as a reference. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Varian EM-390 90 MHz NMR spectrometer with Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard. Magnetic susceptibilities were measured by the Gouy method. Diamagnetic corrections were calculated from Pascal's constants. Conductivities of solutions of the complexes in dimethylformamide (10<sup>-3</sup> M solutions) were measured using a conductivity meter, Mod. LBR 40A (West Germany).

Microanalyses for carbon, hydrogen nitrogen and

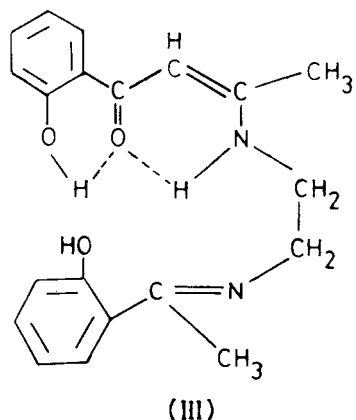
chlorine were carried out at the Fine Microanalyses Centre, Giza, Egypt. Metal contents of complexes were analyzed by dissolving the solid complexes in hot conc. HCl, diluting with water and filtering to remove the precipitated ligand. Aqueous solutions of the metals were then titrated with EDTA. The analytical data are given in Table 1.

### Results and Discussion

*Schiff bases:* Three pentadentate schiff bases were prepared. The schiff bases derived from *o*-hydroxyacetophenone, salicylaldehyde and 2-hydroxy-1-naphthaldehyde, are designated as L<sub>a</sub>, L<sub>b</sub> and L<sub>c</sub> respectively. Structure III shows the L<sub>a</sub> schiff base as a representative of this group of ligands.

These ligands were characterized on the basis of chemical analyses (Table 1), UV spectra (Table 2) and IR spectra. The UV spectral peaks of the ligands are characterized by their high extinction coefficients. These bands could be assigned to π-π\* transitions of

the aromatic rings overlapping with absorptions due to carbonyl and imine groups.



The IR spectra showed a band at  $\sim 1630 \text{ cm}^{-1}$  assigned to the  $\nu \text{C}=\text{N}$  mode and another band at  $1515 \text{ cm}^{-1}$  assigned to the  $\nu \text{C}=\text{N}$  mode originating from the H-bonded inner ring due to conjugation. The  $\nu \text{C}=\text{O}$  band appeared at low frequency ( $1590\text{--}1620 \text{ cm}^{-1}$ ) due to its conjugation with the  $\nu \text{C}=\text{C}$ . The  $^1\text{H NMR}$  spectra of ligands  $L_a$  and  $L_b$  are shown in Table 3 together with their assignments.

*Mononuclear metal complexes:* The prepared Schiff bases have two dissimilar donor sets,  $\text{N}_2\text{O}_2$  and  $\text{O}_2\text{O}$  (see structure III) available for metal coordination. Previous studies have shown that  $\text{Ni(II)}$  prefers the  $\text{N}_2\text{O}_2$  set while  $\text{UO}_2^{2+}$  tends to occupy the outer  $\text{O}_2\text{O}$  set.  $\text{Cu(II)}$  can coordinate through either the inner  $\text{N}_2\text{O}_2$  set or the outer  $\text{O}_2\text{O}$  set depending on the reaction conditions<sup>11</sup>.

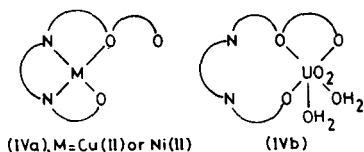
Table 2—Electronic, magnetic and conductance data of the ligands and their complexes

Compound	UV-Visible bands (nm)			Magnetic moments			
				$\mu_{\text{eff}}$ (B.M.)	$\mu_{\text{coml.}\dagger}$ (B.M.)		
$\text{H}_3\text{L}_a$			355	260	—		
$[\text{Cu}(\text{HL}_a)]$	530		345	260	2.04		
$[\text{Ni}(\text{HL}_a) \cdot 0.5\text{H}_2\text{O}]$	540		320	260	2.81		
$[\text{UO}_2(\text{HL}_a)(\text{OH}_2)_2]$		420			—		
$\text{Th}(\text{HL}_a)(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$			395		—		
$[\text{Ni}(\text{CuL}_a)\text{Cl}] \cdot 0.5\text{H}_2\text{O}$	495sh	460	415	320	240	3.05	
$[\text{Ni}_2\text{L}_a\text{Cl}] \cdot 0.5\text{H}_2\text{O}$	490		385	305	255	—	
$[\text{Cu}_2\text{L}_a\text{Cl}] \cdot 2.5\text{H}_2\text{O}$	540		395			312	
$[\text{Cu}_3\text{L}_a\text{Cl}_3] \cdot 5\text{H}_2\text{O}$	525	490		340	245	1.97	
$[(\text{NiL}_a)_2\text{UO}_2(\text{OH}_2)] \cdot 5\text{H}_2\text{O}$	540					3.82	
$[(\text{CuL}_a)_2\text{UO}_2(\text{OH}_2)] \cdot \text{H}_2\text{O}$	525	475		345	255	Diamagnetic	
$\text{H}_3\text{L}_b$			335	235	—	3.18	
$[\text{Cu}(\text{HL}_b)]$	540		335	245	1.92	—	
$[\text{Ni}(\text{HL}_b)]$	535		300	240	Diamagnetic	—	
$[\text{UO}_2(\text{HL}_b)(\text{OH}_2)_2]$			340	245	—	—	
$[\text{Ni}(\text{CuL}_b)\text{Cl}] \cdot 0.5\text{H}_2\text{O}$	485		300	235	—	2.66	
$[\text{Cu}_2\text{L}_b\text{Cl}] \cdot 0.5\text{H}_2\text{O}$	555		335	245	1.73	2.45	
$[(\text{NiL}_b)_2\text{UO}_2(\text{OH}_2)] \cdot 7\text{H}_2\text{O}$	540	425sh	400			2.01	
$[(\text{CuL}_b)_2\text{UO}_2(\text{OH}_2)] \cdot 6.5\text{H}_2\text{O}$	530		395			2.84	
$\text{H}_3\text{L}_c$			405sh	340	240	—	—
$[\text{Cu}(\text{HL}_c)]$	515		285			1.94	—
			340			—	—
$[\text{Ni}(\text{HL}_c)] \cdot \text{H}_2\text{O}$	530		290			Diamagnetic	—
$[\text{UO}_2(\text{HL}_c)(\text{OH}_2)_2]$			295		240	—	—
			340			—	—
			290			—	—
$\text{Th}(\text{HL}_c)(\text{NO}_3)_2 \cdot 9.5\text{H}_2\text{O}$			395			—	—
$[\text{Ni}(\text{CuL}_c)\text{Cl}] \cdot 1.5\text{H}_2\text{O}$	520	420				—	4.25
$[(\text{CuL}_c)_2\text{UO}_2(\text{OH}_2)] \cdot 7\text{H}_2\text{O}$	515		410			2.28	3.22

\* $\mu_{\text{eff}}$  is the magnetic moment of one cationic species in the complex.

† $\mu_{\text{coml.}}$  is the total magnetic moment of all cations in the complex.

The reactions of the three schiff bases, prepared in this work, with Ni(II), Cu(II) and dioxouranium (VI) acetates yielded  $N_2O_2$  type of products with the first two metal ions (structure IVa) and an  $O_2O$  product with dioxouranium (VI) (structure IVb). In the latter complex, the  $UO_2^{2+}$  cation is coordinated to two water molecules also to complete its favoured seven coordination sphere. Th(IV) reacts with  $L_a$  and  $L_c$  to give complexes where the cation is coordinated to the  $N_2O_2$  set. Earlier, some workers showed that Th(IV) is coordinated to both nitrogen and oxygen donor atoms in arsenoazo complexes<sup>12</sup>.



Conductance measurements of solutions of the mononuclear complexes in dimethylformamide show that they are non-conducting ( $\Lambda_M = 0.45 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) except for thorium complexes with  $L_a$  ( $\Lambda_M = 110$ ) and  $L_2$  ( $\Lambda_M = 180$ ) ligands which are 1:1 and 2:1 electrolytes respectively indicating that one of the nitrate anions is coordinated to the thorium cation in the first complex.

IR spectra of the complexes indicate that Cu(II) and Ni(II) are coordinated to the inner  $N_2O_2$  compartment. The  $\nu C \equiv N$  and  $\nu C - N$  vibrations, which appear at  $\sim 1630$  and  $1515 \text{ cm}^{-1}$ , respectively, in the case of free ligands, are shifted to  $1610$ - $1620$  and  $1485$ - $1498 \text{ cm}^{-1}$ , respectively, in these complexes. The  $\nu C = O$ , which is conjugated with  $\nu C = C$  and which appears at  $1620$ - $1590 \text{ cm}^{-1}$  in the free ligands, is also shifted to lower frequencies in these complexes. The presence of water of crystallization in some of these complexes is confirmed by a broad band at  $3390$ - $3420 \text{ cm}^{-1}$ . In the case of dioxouranium (VI) complexes no shift is observed in the imine vibrations indicating that this group does not take part in coordination and that the uranyl cation is linked to the outer  $O_2O$  compartment. The carbonyl vibrations are shifted to lower frequencies which agree with the suggested configuration. The  $\nu_3$  mode of dioxouranium (VI) appears as a strong band at  $\sim 890 \text{ cm}^{-1}$ . The stretching vibrations of the coordinated water molecules appear at  $\sim 3400$  and  $3200 \text{ cm}^{-1}$ . Th(IV) complexes show decrease in both frequencies of the imine and carbonyl groups indicating that thorium cation is linked to  $N_2O_2$  donating atoms.

The electronic spectra of the Cu(II) complexes show a band at  $515$ - $540 \text{ nm}$  which is similar to that of Cu(acacen)<sup>13</sup>. These results coupled with the magnetic moments of the complexes which are in the

Table 3— $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , p.p.m.)

$L_a$	$L_b$
2.05 [s, 3H, $\text{CH}_3$ (a)]	2.02 [s, 3H, $\text{CH}_3$ (a)]
2.31 [s, 3H, $\text{CH}_3$ (b)]	
3.74 [multiplet, 4H, $\text{CH}_2$ (c/d)]	3.67 [multiplet, 4H, $\text{CH}_2$ (b,c)]
5.62 [s, 1H, CH(e)]	5.85 [s, 2H, CH(d'e)]
6.85 [multiplets, CH(phenyl groups)]	6.85
7.24	7.20 [multiplets, CH(phenyl groups)]
7.52	7.49
11.11 [br, 1H, NH]	11.01 [br, 1H, NH]
13.34 [br, 2H, OH]	13.28 [br, 2H, OH]

$L_a$

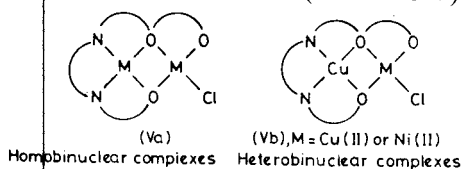
$L_b$

range  $1.92$ - $2.04 \text{ B.M.}$  (Table 2) indicate square planar geometry around Cu(II) ions. Ni(II) complexes show a band at  $\sim 540 \text{ nm}$  similar to that of Ni(acacen)<sup>14</sup>. The Ni(II) complexes of  $L_b$  and  $L_c$  are diamagnetic and this fact agrees with square planar arrangement of  $N_2O_2$  around the Ni(II) ion. The Ni(II) complex with  $L_a$  is paramagnetic and thus acquires octahedral symmetry in the solid state through oligomerization. Dioxouranium (VI) and Th(IV) complexes show an absorption band at  $420$  and  $395 \text{ nm}$ , respectively, which may be due to charge transfer transition. UV bands due to ligands were shifted in the case of complexes indicating the effect of the attached metal on ligand transitions.

**Binuclear metal complexes:** These complexes were prepared by the reaction of mononuclear ( $N_2O_2$ ), Ni(II) or Cu(II) complexes with hydrated metal chloride in the presence of LiOH as a deprotonating agent. Either homo- or hetero-binuclear complexes were obtained. Generally, Cu(II) mononuclear complexes accept Ni(II) in its outer  $O_2O$  compartment but the reverse reaction proved to be not possible. Reaction of Ni(II) mononuclear complexes with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  yielded the unchanged starting materials. The mono-nuclear Ni(II) complex of ligand  $L_a$  accepted another Ni(II) cation in its outer compartment. However, carrying out the same reaction in the case of ligand  $L_b$  did not give pure dinickel complex and a mixture of mononuclear and binuclear complexes was always obtained.

The reaction of the mononuclear Cu(II) complex of ligand  $L_a$  with  $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  yielded a trinuclear

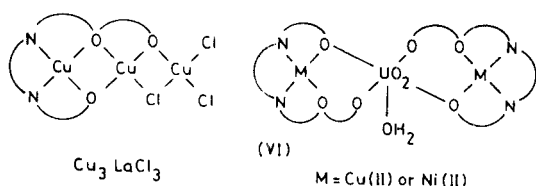
complex (discussed latter); however, the binuclear Cu(II) complex was prepared by reaction of the hydrated copper (II) chloride with the ligand in the presence of LiOH. This reaction was carried out initially to investigate the possibility of preparing an O<sub>2</sub>O isomer of the mononuclear Cu(II) complex. The corresponding reaction using hydrated nickel chloride yielded again the N<sub>2</sub>O<sub>2</sub> Ni(II) complex. Thus, no isomeric mononuclear Cu(II) or Ni(II) complexes could be prepared in this work. The metal cation in the outer O<sub>2</sub>O compartment is further coordinated to a chloride ion (structure V).



IR spectra of the complexes indicate that the second incorporated metal ion, which is attached to the outer O<sub>2</sub>O compartment, does not alter the bands of the starting mononuclear complexes. The disappearance of the band at  $\sim 3400\text{ cm}^{-1}$  due to phenolic O-H group, which is present in the ligands and mononuclear complexes, is not clearly observed in the binuclear complexes due to the presence of the stretching vibrations of water molecules.

Conductance measurements showed these complexes to be non-conducting. Electronic spectra and magnetic moments of the complexes are also shown in Table 2. The homobinuclear copper complexes show a band at 540 or 555 nm similar to that of the mononuclear complex which indicates square planar geometry around copper (II) ions. The magnetic moment of L<sub>b</sub> complex indicates slight antiferromagnetic interaction between the two copper cations. The homobinuclear nickel complex of L<sub>a</sub> shows bands at 490 and 395 nm. The bands are different from those of the mononuclear complex and indicate that the outer Ni(II) cation may have six-coordination through oligomerization. The magnetic data favour this suggestion. The heterobinuclear complexes, incorporating both copper (II) and nickel (II) cations show variable bands in the range 460-520 nm and may also indicate octahedral geometry of the outer Ni(II) cation. Their magnetic moments, though vary, emphasize this conclusion.

**Trinuclear metal complexes:** The reaction of the mononuclear Cu(II) complex of L<sub>a</sub> with CuCl<sub>2</sub>·2H<sub>2</sub>O (molar ratio 1:1) yielded a trinuclear Cu(II) complex rather than a binuclear one. Two Cu(II) cations are linked to the N<sub>2</sub>O<sub>3</sub> donating atoms in both the inner and outer compartments and chloride ions link the outermost two Cu(II) ions (structure VI).



The reactions of either mononuclear Cu(II) or Ni(II) complexes with dioxouranium (VI) yielded a trinuclear complex where the UO<sub>2</sub><sup>+</sup> cation is linked to two mononuclear units by replacing the phenolic protons (structure VI).

IR spectra of these complexes are similar to those of the binuclear complexes and thus indicate the occupancy by the metals of the inner and outer compartments. Solutions of these complexes in DMF are non-conducting and the visible-UV spectra (Table 2) are similar to those of mononuclear complexes indicating the square planar geometry of the Ni(II) and Cu(II) cations. Magnetic measurements (Table 2) indicate that Cu(II) complexes have somewhat higher magnetic moments than normal which may be due to distortion of the square planar symmetry by steric effects of the phenyl and naphthyl groups<sup>15</sup>. The trinuclear complex of L<sub>a</sub> incorporating two Ni<sup>2+</sup> and one UO<sub>2</sub><sup>+</sup> cations is diamagnetic.

The trinuclear Cu(II) complex of ligand L<sub>a</sub> conducts electricity to a certain extent which may be due to H<sub>2</sub>O-Cl<sup>-</sup> exchange.

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