New Acyclic and Cyclic Schiff Bases Derived from 2,6-Diformyl-4-Chlorophenol and their Interaction with Uranyl(VI), Copper(II) and Nickel(II) Ions

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Abstract

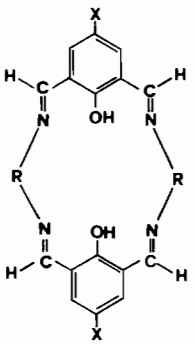
New acyclic and cyclic Schiff base compartmental ligands have been prepared, by reaction of 4-chloro-2,6-diformylphenol and polyamines of the type $NH_2-(CH_2)_2-X-(CH_2)_2-NH_2$ (X = NH, S). These ligands have two similar or dissimilar compartments in close proximity and can link two metal ions in an identical or different coordination mode.

The preparation of mono and binuclear uranyl(VI), nickel(II) and copper(II) complexes is also reported together with their physicochemical properties. For the mononuclear species, with ligands having dissimilar compartments, the site occupancy is also discussed on the basis of IR, UV and magnetic properties.

For the homobinuclear copper(II) and nickel(II) complexes an antiferromagnetic interaction between the two paramagnetic centres is suggested.

Introduction

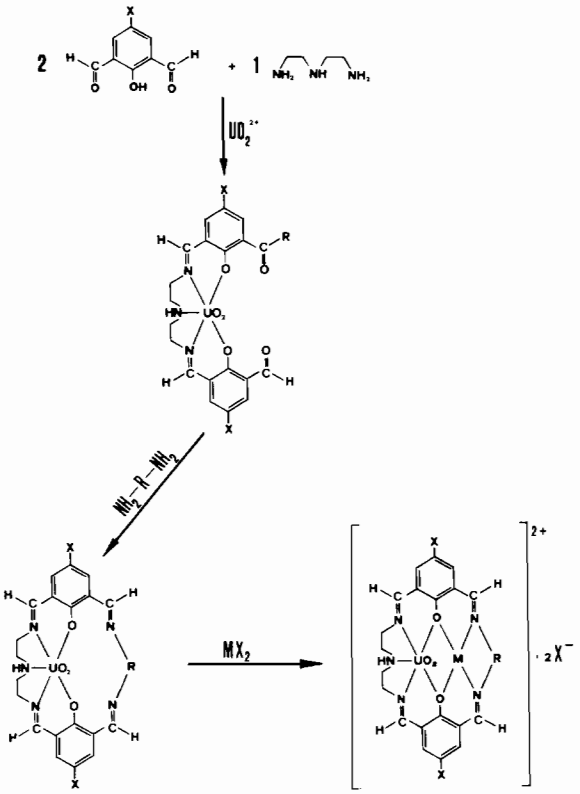
It was established, some years ago, that Schiff bases of the type:



R = $-CH_2-CH_2-$
$-CH_2-CH_2-CH_2-$

can act as binucleating ligands towards transition metal ions and a wide range of homobinuclear complexes were prepared and the related properties studied [1–5]. In particular, the magnetic interactions and the redox processes of the two metal ions have been deeply investigated [6–10].

Formerly, we prepared heterobinuclear complexes containing uranyl(VI) by the reaction scheme [11, 12]:



More recently we have obtained some interesting results concerning the synthesis of uranyl(VI) complexes containing $U-SR_2$ and $U-PR_3$ bonds, using potentially pentadentate Schiff bases of the type [13, 14]:

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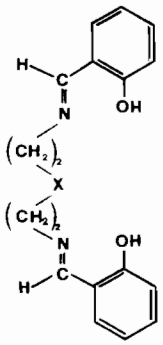
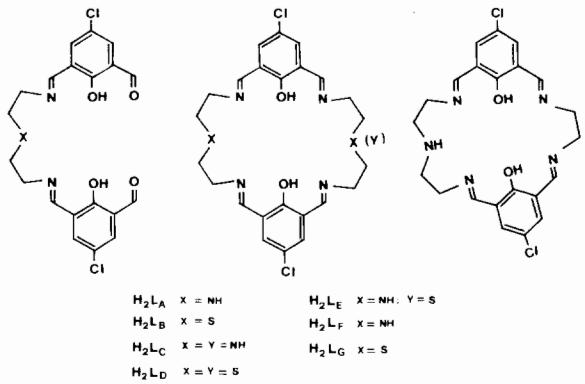


It has been found that binuclear copper(II) complexes can act better in the oxidation catalysis of phenols to quinones when the central metal ions are pentacoordinated. In these complexes [15, 16] a serious complication generally comes from the very low solubility of the complexes [15]. It could thus be useful to prepare complexes made more soluble in non-coordinating solvents by enlarging the organic ligand and/or by the addition of further functional groups.

Consequently, we studied the preparation and characterization, also by template synthesis, of a series of versatile acyclic and cyclic ligands:



which have two similar or dissimilar compartments in close proximity and can link two metal ions in an identical or in a different way.

Moreover, we investigated the interaction of these ligands with uranyl(VI), copper(II) and nickel(II) salts and this paper reports the preparation and the physico-chemical properties of a series of mononuclear and binuclear complexes.

Experimental

2,6-diformyl-4-chloro-phenol (HL) was prepared according to literature [17]; some modifications were added in order to increase the yield of the product.

The amines are commercial products (K and K) and were used without further purification.

Preparation of the Ligands

Preparation of H_2L_A and H_2L_B

To a methanolic solution of HL (2 mmol) the appropriate aliphatic polyamine was added (1 mmol). The yellow precipitate was filtered, washed with methanol and dried *in vacuo*.

Preparation of H_2L_C

To an ethanolic solution of HL (1 mmol), diethylenetriamine was added (1 mmol). The yellow solution obtained was stirred for 3 h and then evaporated to dryness. The residue was treated with MeOH. The resulting pitchy solid was filtered and treated with diethylether and stirred for 2 h. The yellow precipitate obtained was collected and dried *in vacuo*.

Preparation of H_2L_D

To an ethanolic solution of HL (1 mmol) 1,5-diamino-3-thiapentane (1 mmol) was added. The yellow precipitate was filtered, washed with ethanol and dried *in vacuo*.

Preparation of H_2L_F and H_2L_G

To the appropriate acyclic Schiff base dissolved in $CHCl_3$ (1 mmol) ethylenediamine (1 mmol) was added. The resulting yellow solution was stirred for 3 h and then evaporated to dryness. On treating the yellow oil obtained with diethylether it turned into a precipitate which was filtered and dried.

Preparation of the Complexes

Preparation of NiL_A and NiL_B

To a methanolic solution of HL (2 mmol) the appropriate aliphatic polyamine (1 mmol) was added. To the yellow precipitate dissolved in 30 ml of $CHCl_3$, 1 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$ was added. The resulting solution was stirred for 3 h. The precipitate obtained by addition of MeOH was stirred for 2 h, then filtered, washed with MeOH and dried *in vacuo*.

Preparation of CuL_A

To a methanolic solution of HL (2 mmol) $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol) and LiOH (2 mmol) were added. The green precipitate thus formed was treated with diethylentriamine (1 mmol). The solution obtained was stirred for 2 h then evaporated to dryness; the residue was dissolved in CH_2Cl_2 and precipitated with diethylether. The solid, washed with diethylether, was dried *in vacuo*.

Preparation of CuL_B and UO_2L_B

The appropriate metal diacetate (1 mmol) was added to a methanolic solution of HL (2 mmol);

to the suspension obtained LiOH (2 mmol) and, after 10 min, 1,5-diamino-3-thiapentane were added. The precipitate was collected, washed with methanol and dried *in vacuo*.

Preparation of CuL_C and NiL_C

Diethylenetriamine (1 mmol) was added to a solution of ML_A (1 mmol) (methanol for CuL_A and chloroform for NiL_A). The precipitate obtained was washed with the appropriate solvent and dried *in vacuo*.

Preparation of $M_2(L_C)(OAc)_2$ ($M = Cu^{2+}, Ni^{2+}$)

Diethylenetriamine (1 mmol) was added to an ethanolic solution of HL (1 mmol). To the yellow precipitate the metal acetate (1 mmol) was added. After stirring for 2 h the dark suspension was evaporated to dryness. The residue was dissolved with the appropriate solvent ($CHCl_3$ for copper complexes and MeOH for nickel complexes). After addition of diethylether a green (for copper) and brown-red (for nickel) precipitate was formed. The product was collected, washed with diethylether and dried *in vacuo*.

Preparation of $NiCu(L_C)(OAc)_2$

To a methanolic solution of HL (2 mmol) diethylenetriamine (1 mmol) was added. The orange solid obtained was dissolved in $CHCl_3$. To this solution $Ni(CH_3COO)_2 \cdot 4H_2O$ (1 mmol) was added. After 30 min diethylentriamine (1 mmol) and $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol) were added to the brown solution and the resulting solution was stirred for 24 h, evaporated to dryness and the residue dissolved in the minimum quantity of methanol. By addition of diethylether a green powder appeared which was filtered, washed with a methanol–diethylether mixture and dried *in vacuo*.

Preparation of NiL_D and UO_2L_D

1,5-diamino-3-thiapentane (1 mmol) was added to a solution of ML_B (MeOH for NiL_B and $CHCl_3$ for UO_2L_B). The resulting solution was stirred for 2 h, then treated with diethylether for the Ni^{2+} complex and methanol for UO_2^{2+} complex. The precipitate obtained was filtered and dried *in vacuo*.

Preparation of $Ni_2(L_D)(OAc)_2$

To a methanolic solution of HL (1 mmol) 1,5-diamino-3-thiapentane (1 mmol), $Ni(CH_3COO)_2 \cdot 4H_2O$ (1 mmol) after 15 min and LiOH(1 mmol) were added. The solution was stirred for 2 h, then evaporated to dryness and the residue, dissolved in $CHCl_3$, was filtered and treated with diethylether. The yellow precipitate obtained was collected, washed with diethylether and dried *in vacuo*.

Preparation of $Cu_2(L_D)(OAc)_2$

$Cu(CH_3COO)_2H_2O$ (1 mmol) was added to a methanolic solution of HL. A green precipitate was obtained. To the suspension, LiOH (1 mmol) and 1,5-diamino-3-thiapentane (1 mmol) were added. After stirring for 2 h the precipitate was collected, washed with MeOH and dried *in vacuo*.

Preparation of UO_2L_E

To a chloroform/dimethylformamide (70/30) solution of UO_2L_B, diethylenetriamine was added. The yellow solution was stirred for 1 h, then evaporated to dryness and the residue treated with methanol. The precipitate obtained was collected, washed with MeOH and dried *in vacuo*.

Preparation of NiL_E, NiL_G and CuL_F

To a methanolic solution of the acyclic complex (NiL_B or CuL_A) (1 mmol), the appropriate aliphatic polyamine was added. The precipitates obtained (yellow for nickel and green for copper complexes) were stirred for 20 min, filtered, washed with MeOH and dried *in vacuo*.

Preparation of UO_2L_G

To a $CHCl_3$ solution of UO_2L_B (1 mmol), ethylenediamine (1 mmol) was added. The orange solution was stirred for 2 h. The solvent was partially removed, then the solution treated with MeOH. The orange precipitate obtained was filtered, washed with methanol and dried *in vacuo*.

Preparation of NiL_F

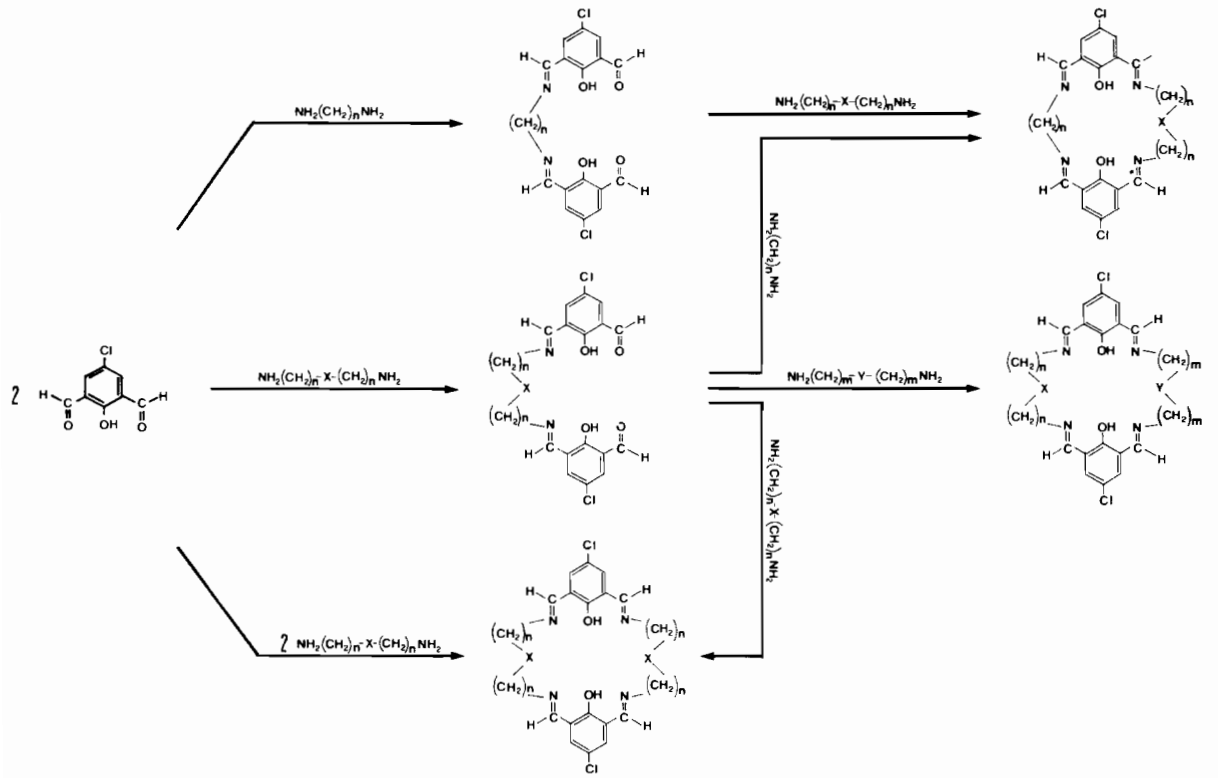
(a) to a NiL_A (1 mmol) in cloroform, ethylenediamine (1 mmol) was added and the resulting suspension stirred for 3h. The yellow solid was collected, washed with diethylether and dimethylformamide then dried *in vacuo*.

(b) To a yellow chloroformic solution of H_2L_A (1 mmol) ethylenediamine was added and after 30 min $Ni(CH_3COO)_2 \cdot 4H_2O$ (1 mmol) and LiOH (1 mmol). The color of the solution changed from yellow to dark red. By the addition of MeOH an orange precipitate was obtained, which was filtered, washed with methanol and dried *in vacuo*.

Results and Discussion

By reaction of 2,6-diformyl-4-chloro-phenol and ethylenediamine or polyamine of the type NH_2–$(CH_2)_2$–X–$(CH_2)_2$–NH_2 (X = NH, S) the series of compartmental Schiff bases (Scheme 1) has been synthesized.

As can be seen from this scheme, a direct synthesis can be employed for the symmetric cyclic ligands while for the asymmetric cyclic ligands a step-by-step synthesis must be used. The yield is good in both



Scheme 1.

cases. Particular attention must be paid to the experimental conditions in order to avoid polymeric or non-expected products. These compounds are yellow or yellow-orange solids which melt above 270 °C. They are stable and volatile enough for a mass spectrometry study. It is thus possible to identify, in addition to the peaks due to the fragmentations of the various ligands, the parent peak P^+ at the characteristic m/z values [26], this supporting the structures proposed in Scheme 1.

For the acyclic ligands, there is in their infrared spectrum a strong νC=O band at 1683 cm^{-1} (H_2L_A) and 1680 cm^{-1} (H_2L_B) which disappears upon cyclization. In the infrared spectrum of 2,6-diformyl-4-chlorophenol there are two νC=O bands at 1689 and 1668 cm^{-1}, the lowering of the second band is very probably due to the presence of hydrogen bonding between the aldehydic –C=O and the phenolic –OH groups. The band at 1603, 1580 cm^{-1} can be assigned to the absorption of the C=C groups.

The two bands at 3030 and 2875 can be attributed to νCH aromatic and νOH. The considerable lowering of the OH is further proof of the existence of strong hydrogen bonding. In all the prepared ligands there are strong absorption bands due to the stretching of the C=N and C=C groups in the range 1650–1605 cm^{-1} (see Table II). The νC=N can be seen as a very intense band at 1647–1639 cm^{-1}. There is a small shift (5–10 cm^{-1}) of the νC=N upon symmetric or asymmetric cyclization.

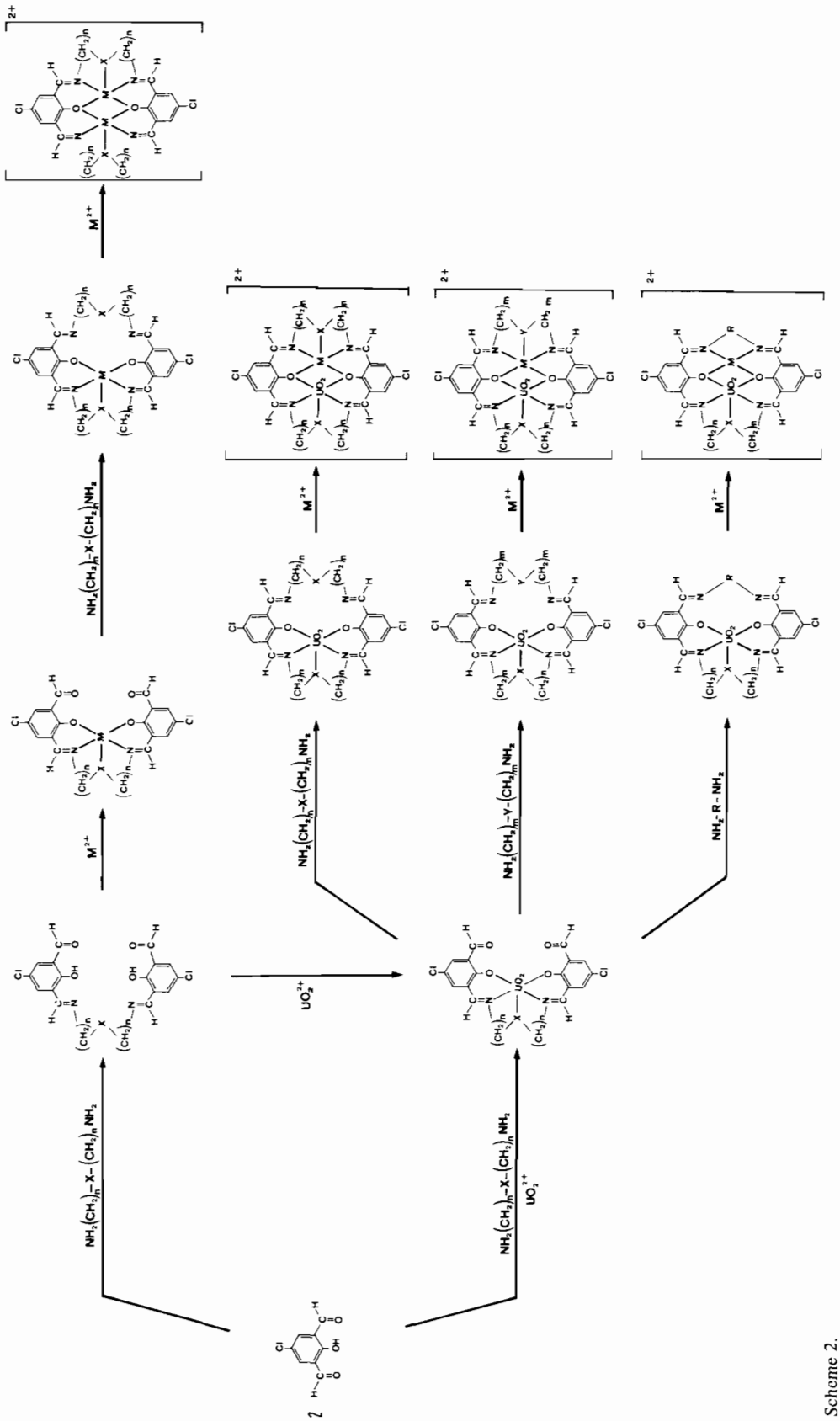
Generally there is a different solubility of the open and closed Schiff bases in methanol. The acyclic ligands precipitates from this solvent in a few minutes, while the cyclic ligands are very soluble in such a solvent.

By reaction of the preformed ligands or of the keto- and amino-precursors with uranyl(VI), copper(II) and/or nickel(II) acetate, the reaction scheme 2 has been obtained.

The infrared spectra of the mononuclear acyclic complexes show a strong IR band at about 1680 cm^{-1}, due to the νC=O of the free formyl groups. There is, in addition, a multiplicity of bands in the 1650–1600 cm^{-1} range, due to the C=N and C=C modes. The presence of the O–U–O group in the uranyl complexes can easily be detected by a strong IR band, due to the ν_3 O–U–O, in the range 920–900 cm^{-1}.

It should be noted that, in addition to the inner N_2XO_2, the acyclic ligands contain a potential outer O_2O_2 compartment. Consequently the formation of binuclear species cannot be ruled out.

We have, indeed, obtained copper complexes formulable as $Cu_2(L_A)_2\cdot(CH_3COO)_2$ where also donor atoms of the outer O_2O_2 set are involved in the coordination to the central metal ion. This



Scheme 2.

TABLE I. Elemental Analyses of the Prepared Ligands and Complexes.

	Calculated			Found		
	C%	H%	N%	C%	H%	N%
H(L)	52.17	2.72	–	52.06	2.75	–
$H_2(L_A)$	55.17	4.36	9.65	55.74	4.80	10.41
$H_2(L_B)$	52.99	3.97	6.18	52.63	4.15	6.34
$H_2(L_C)$	55.38	5.76	16.15	55.24	5.55	15.39
$H_2(L_D)$	53.64	4.84	10.43	53.57	4.94	9.88
$H_2(L_F)$	56.10	5.48	14.22	56.42	5.60	14.36
$H_2(L_G)$	53.44	4.85	11.33	53.65	4.76	11.43
$Ni(L_A)\cdot 1H_2O\cdot 1MeOH$	46.44	4.24	7.74	46.57	4.32	7.05
$Cu(L_A)\cdot 1H_2O$	46.56	3.69	8.15	46.31	3.90	8.45
$Cu(L_C)\cdot 1MeOH$	50.30	5.05	14.08	49.43	4.83	13.01
$Ni(L_C)\cdot 1MeOH$	50.68	5.07	14.19	49.76	5.68	14.98
$Cu_2(L_C)(OAc)_2\cdot 5H_2O$	40.19	5.02	10.03	40.06	4.81	10.39
$Ni_2(L_C)(OAc)_2\cdot 2H_2O$	43.51	4.66	10.85	43.59	4.79	10.20
$NiCu(L_C)(OAc)_2\cdot 3H_2O$	42.26	4.78	10.50	42.52	4.84	10.38
$Cu(L_F)\cdot 1MeOH$	49.87	4.52	12.65	49.53	4.10	12.33
$Ni(L_F)\cdot 2H_2O$	47.47	4.52	12.67	47.79	5.04	13.37
$Ni(L_B)\cdot 1MeOH$	46.52	3.69	5.18	46.22	3.72	5.28
$Cu(L_B)\cdot 1MeOH$	46.11	3.66	5.12	46.02	3.28	4.48
$UO_2(L_B)$	33.33	2.22	3.89	33.93	2.44	4.35
$Ni(L_D)\cdot 3H_2O$	44.40	4.63	8.65	43.99	4.53	9.21
$UO_2(L_D)\cdot 1H_2O$	34.90	3.19	6.80	34.40	3.02	6.65
$Ni_2(L_D)(OAc)_2\cdot 2H_2O$	41.67	4.22	6.94	41.05	3.86	6.43
$Cu_2(L_D)(OAc)_2\cdot 2H_2O$	41.18	4.16	6.86	41.79	4.16	5.14
$Ni(L_G)\cdot 1H_2O\cdot 1MeOH$	47.29	4.45	9.59	47.22	4.06	8.97
$UO_2(L_G)\cdot 1H_2O$	34.60	2.88	7.34	34.67	2.93	7.53
$Ni(L_E)\cdot 1H_2O\cdot 1MeOH$	47.87	4.95	11.16	47.79	4.57	10.54
$UO_2(L_E)\cdot 1MeOH$	36.50	3.77	8.52	36.21	3.40	8.22

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

Compound	IR frequencies in the range 1700–1500 cm^{-1} assignable to C–O, C–N and C–C	Other characteristic bands
H(L)	1689, 1668, 1606, 1581	
$H_2(L_A)$	1683, 1639, 1590, 1522	3223(N–H)
$H_2(L_B)$	1680, 1634, 1581, 1516	
$H_2(L_C)$	1647, 1589, 1573, 1531	3271(N–H)
$H_2(L_D)$	1640, 1538	
$H_2(L_F)$	1638, 1602, 1580, 1523	3250(N–H)
$H_2(L_G)$	1642, 1608, 1587, 1525, 1541	
$Ni(L_A)\cdot 1H_2O\cdot 1MeOH$	1646, 1589, 1528	3260(N–H)
$Cu(L_A)\cdot 1H_2O$	1648, 1596, 1535	3275(N–H)
$Cu(L_C)\cdot 1MeOH$	1640. 1590, 1536	3260(N–H)
$Ni(L_C)\cdot 1MeOH$	1645, 1590, 1530	3268(N–H)
$Cu_2(L_C)(OAc)_2\cdot 5H_2O$	1646, 1567, 1537	3228, 3157(N–H)
$Ni_2(L_C)(OAc)_2\cdot 2H_2O$	1646, 1569, 1557, 1540	3284(N–H)
$NiCu(L_C)(OAc)_2\cdot 3H_2O$	1646, 1568	3235(N–H)
$Cu(L_F)\cdot 1MeOH$	1635, 1539	3291(N–H)
$Ni(L_F)\cdot 2H_2O$	1667, 1640, 1591, 1530	3271(N–H)
$Ni(L_B)\cdot 1MeOH$	1636, 1588, 1532	
$Cu(L_B)\cdot 1MeOH$	1680, 1629, 1535	

(continued on facing page)

TABLE II. *(continued)*

Compound	IR frequencies in the range 1700–1500 cm^{-1} assignable to C–O, C–N and C–C	Other characteristic bands
$UO_2(L_B)$	1671, 1625, 1584, 1551	905(O–U–O)
$Ni(L_D)\cdot 3H_2O$	1631, 1591, 1533	
$UO_2(L_D)\cdot 1H_2O$	1632, 1552, 1523	896(O–U–O)
$Ni_2(L_D)(OAc)_2\cdot 2H_2O$	1643, 1570, 1550	
$Cu_2(L_D)(OAc)_2\cdot 2H_2O$	1674, 1629, 1586, 1543	
$Ni(L_G)\cdot 1H_2O\cdot 1MeOH$	1628, 1540	
$UO_2(L_G)\cdot 1H_2O$	1631, 1549	901(O–U–O)
$Ni(L_E)\cdot 1H_2O\cdot 1MeOH$	1638, 1534	3152(N–H)
$UO_2(L_E)\cdot 1MeOH$	1635, 1553	3219(N–H), 892(O–U–O)

has been generally obtained as an unexpected product, in addition to the mononuclear complexes, when the preformed Schiff base is reacted with copper or nickel acetate and can be explained with the ability of copper(II) to coordinate also the O_2O_2 site [18].

The mononuclear species were obtained as a pure product and in high yield when a template synthesis was used. With uranyl(VI) salts complexes of the type $UO_2(L)$, only obtained by template synthesis, were synthesized.

These acyclic complexes can be cyclized by reactions with polyamines. Using step-by-step reactions only mononuclear cyclic complexes can be obtained. In contrast the reaction of diformylphenol, polyamine and metal acetate in a 2:2:1 molar ratio, gives cyclic homobinuclear complexes. The same homobinuclear species have been obtained by reaction of the cyclic ligands with metal acetate in a 1:1 or 1:2 molar ratio. The ligands so formed contain two equal compartments. Consequently, the metal ion cannot discriminate between the two coordination sites giving rise to binuclear species.

The physico-chemical properties of the UO_2^{2+} ion do not favour the formation of homobinuclear cyclic complexes and mononuclear, equatorially pentacoordinated uranyl species have been obtained. In these complexes the uranyl(VI) ion is equatorially pentacoordinated in a fashion similar to that of the open complexes and of the complexes with the potentially pentadentate Schiff bases for which the crystal and molecular structure is well known [19–25]. The metal ion is thus coordinated to one of the two compartments N_2XO_2 while the other donor atoms of the other set are not involved in the coordination. Similarly, mononuclear nickel(II) and copper(II) cyclic complexes have one site available for further coordination and can thus act as ligands towards a second metal ion.

On moving from the acyclic to the cyclic mononuclear complexes the infrared spectra show remarkable analogies, apart from the disappearance of the C=O in the cyclic species. In particular, the stretching C=N lies almost at the same frequency for both open and closed mononuclear and for the binuclear complexes (1650–1640 cm^{-1}). The infrared spectra of the cyclic binuclear copper(II) and nickel(II) complexes $M_2(L_C$ or $L_D)(OAc)_2$ show in addition, significant differences from the mononuclear analogues, owing to the presence of two acetate groups. The antisymmetric and symmetric stretchings of the carboxylate groups can be assigned at 1567 and 1401 cm^{-1} for $Cu_2(L_C)(OAc)_2$, 1557 and 1405 cm^{-1} for $Ni(L_C)(OAc)_2$, 1556 and 1399 cm^{-1} for $Cu_2(L_D)(OAc)_2$, 1570 and 1423 cm^{-1} for $Ni_2(L_D)(OAc)_2$, and 1568 and 1403 cm^{-1} for $CuNi_2(L_C)(OAc)_2$. These bands lie, however, in a region where other absorptions of the ligands are present thus preventing a correct formulation of the coordination ability of these groups to the central metal ion. In the free ion both COO stretching bands appear at 1582 and 1425 cm^{-1} respectively [9]. If the acetate acts as monodentate the asymmetric and symmetric COO stretching bands will be shifted to higher and lower frequencies, respectively. If coordination occurs symmetrically, both the COO stretching bands may be shifted in the same direction, since the bond orders of both CO may be changed by the same amount [10].

The complexes are ionic in dimethylsulphoxide solution. Therefore, we may tentatively suggest that the acetate groups are not completely involved in the coordination to the central metal ion also in the solid state. However the assignment of the coordination geometry about copper or nickel from the infrared data should be considered as a proposal which needs further experimental evidence.

The electronic spectra for the nickel(II) and copper(II) complexes carried out in dimethylsulphoxide solution, show the characteristic d–d band (see Table III). We were able also to carry out the electronic spectra in non-coordinating solvents such as $CHCl_3$. For the samples with enough solubility in this solvent the d–d band at about the same

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

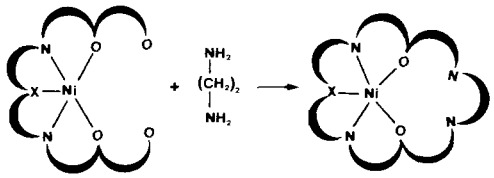
Complex	Electronic data (nm)		Magnetic moment (BM)	
	in DMSO	in $CHCl_3$	μ_{eff}	$\mu_{compl.}$
$Ni(L_A)\cdot 1H_2O\cdot 1MeOH$	970b, 515s, 435	425	2.79	
$Cu(L_A)\cdot 1H_2O$	600, 477, 413	640, 410	1.63	
$Cu(L_C)\cdot 1MeOH$	615, 560, 460s, 415	530, 407	1.71	
$Ni(L_C)\cdot 1MeOH$	ins.	950b, 535, 405	2.62	
$Cu_2(L_C)(OAc)_2\cdot 5H_2O$	600, 405	595, 400		2.93
$Ni_2(L_C)(OAc)_2\cdot 2H_2O$	935b, 438, 405	935b, 443s, 410		3.73
$NiCu(L_C)(OAc)_2\cdot 3H_2O$	970, 878, 615, 405	920, 602, 403		3.24
$Cu(L_F)\cdot 1MeOH$	585, 390	390	1.70	
$Ni(L_F)\cdot 2H_2O$	975, 600, 420	920, 430	2.11	
$Ni(L_B)\cdot 1MeOH$	970, 482, 440	940, 440	2.70	
$Cu(L_B)\cdot 1MeOH$	650, 490, 405	412	1.64	
$UO_2(L_B)$	480, 380	380		
$Ni(L_D)\cdot 3H_2O$	990, 580, 430	930, 420	3.29	
$UO_2(L_D)\cdot 1H_2O$	680, 440s, 375	470s, 375		
$Ni_2(L_D)(OAc)_2\cdot 2H_2O$	990, 585, 440, 400	965, 595, 440, 410		4.33
$Cu_2(L_D)(OAc)_2\cdot 2H_2O$	640, 405	405		1.80
$Ni(L_G)\cdot 1H_2O\cdot 1MeOH$	430	430		1.90
$UO_2(L_G)\cdot 1H_2O$	375	385		
$Ni(L_E)\cdot 1H_2O\cdot 1MeOH$	425	435		2.92
$UO_2(L_E)\cdot 1MeOH$	570s, 480s, 415	520s, 420s, 385		

wavelength as found in DMSO were observed. These data exclude that nickel(II) has a square planar coordination.

The uranyl(VI) complexes show, in the region 575–375 nm bands or shoulders due to change transfer UO_2–L and to internal transition of the O–U–O group.

In the cyclic mononuclear complexes, there is also the possibility for the central metal ion to change the coordination chamber, depending on the physico-chemical properties of the organic site and of the metal ion. The difference in the coordination ability of the two compartments is not always so high as to make one chamber selective for a particular metal ion. The physico-chemical data do not give unambiguous answers; magnetic data can, however, evidence such a change with nickel(II) when the two chambers offer the possibility of different spin states for the central metal ions.

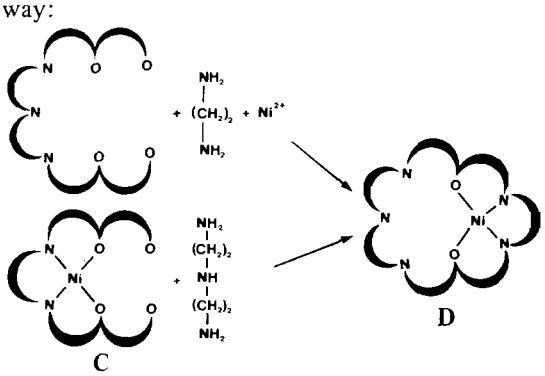
The mononuclear complexes **B**, obtained according to the reaction:



A B

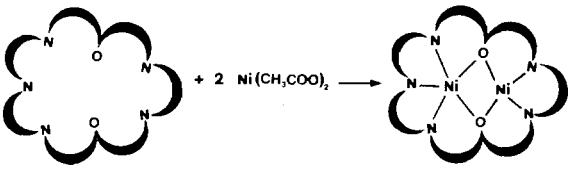
show a magnetic moment of 2.11 BM for X = NH and 1.95 BM for X = S. These values are reduced relative to the values of 2.79 and 2.70 found for the corresponding complexes of **A** and in which the nickel(II) is probably pentacoordinated.

The complex **D**, obtained by the reaction pathway:



C D

is diamagnetic, as also is **C**, and these are both proposed as having square planar N_2O_2 environments. When the preformed cyclic ligand is reacted with nickel(II) acetate the binuclear complex **E** is obtained:



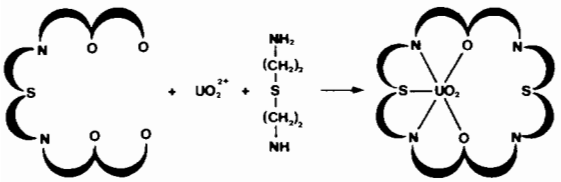
E

and the magnetic moment is 2.70 BM comparable with the nickel(II) in the N_3O_2 compartment, the

second metal being square planar and so diamagnetic. Any alternative suggestion would require an exchange between the two nickel(II) atoms.

Consequently it is possible to suggest that for the complexes B there is a mixture of positional isomers present in which the nickel is either an N_2O_2 (20%) or N_2XO_2 (80%) compartment giving rise to the reduced magnetic moment observed.

The cyclic uranyl complex $UO_2(L_D)$ obtained by the reaction of the acyclic complex $UO_2(L_B)$ with $NH_2-(CH_2)_2-S-(CH_2)_2-NH_2$, is obviously diamagnetic with an infrared spectrum identical to the sample obtained by the template reaction:



However a sample after a long period of time became paramagnetic (μ_{eff} = 2.7) without remarkable changes in the infrared spectrum. The ν_3 O–U–O, in particular, remains at 896 cm^{-1} without appreciable change in the intensity of the peak.

Attempts to reproduce the paramagnetic species failed, in all case the diamagnetic uranyl(VI) complex $UO_2(L_D)$ being obtained.

An X-ray investigation on a sample of this complex [27], confirms that the uranyl(VI) ion is equatorially coordinated by the N_2SO_2 donor atoms of one of the two identical sites; the second site is not involved at all in the coordination.

The magnetic properties of the homobinuclear nickel(II) and copper(II) complexes show that there is a magnetic interaction between the paramagnetic centres which lowers the entire magnetic moment.

The cyclic mononuclear $Ni(L_C)$ complexes have a μ_{eff} of 2.62 as the open analogue ($Ni(L_A)$, 2.79 BM). There is no appreciable difference on changing the fifth donor atom from NH to S.

The binuclear $Ni_2(L_C)(OAc)_2$ and $Ni_2(L_D)(OAc)_2$ have a μ_{eff} of 3.73 and 4.33 BM respectively.

The interaction between the two metals is weak, as obtained for other similar complexes.

For the mononuclear copper complexes we have found a μ_{eff} ranging from 1.63 to 1.71 BM while for the binuclear the μ_{eff} is 1.65 BM for $Cu_2(L_C)(OAC)_2$ and 1.80 for $Cu_2(L_D)(OAc)_2$ clearly indicating that an antiferromagnetic interaction between the two metal ions is operating.

The heterobinuclear $NiCu(L_C)(OAc)_2$ has a μ_{eff} of 3.24 BM.

Recently we obtained drastic differences in the values of the magnetic moment on changing the NH with S in the copper complexes with ligands obtained by reaction of 3-formylsalicylic acid and diethylenetriamine and 1,5-diamino-3-thiapenthane [27].

Very low values of magnetic moment have been found for mononuclear (μ_{eff} = 0.75) homobinuclear (μ_{eff} = 1.16) copper complexes and heterobinuclear uranyl–copper complexes (μ_{eff} = 0.86) with the ligand having a sulfur in the fifth inner coordination set.

Such a behaviour is not followed with the copper(II) complexes prepared in the present paper which have a magnetic moment easily explained by the interactions discussed above.

On the basis of these results it still remains difficult to explain the very surprising magnetic moment behaviour of the copper complexes with the Schiff base derived from 3-formylsalycilic and 1,5-diamino-3-thiapenthane.

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