

TEMPLATE SYNTHESIS OF MONONUCLEAR, HOMONUCLEAR AND HETERODINUCLEAR COMPLEXES FROM 2,6-DIFORMYLPYRIDINE AND 2,6-DIFORMYL-4-CHLOROPHENOL

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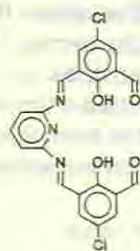
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ABSTRACT. Various acyclic or cyclic Schiff bases have been prepared by condensation of a diamine (2,6-diaminopyridine or ethylenediamine) with a dialdehyde (2,6-diformylpyridine or 2,6-diformyl-4-chlorophenol). These ligands have two similar or dissimilar compartments in close proximity and can react with metal ion to give mononuclear (Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , SnR_2^{2+} and UO_2^{2+}), homonuclear (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) and heterodinuclear ($M_1 = Ni^{2+}$, $M_2 = Cu^{2+}$, Zn^{2+} , UO_2^{2+} ; $M_1 = Cu^{2+}$, $M_2 = Zn^{2+}$, UO_2^{2+}) complexes.

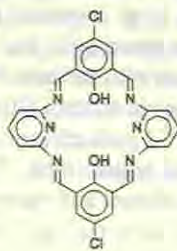
For the mononuclear acyclic and unsymmetric cyclic complexes, the occupied site is discussed on the basis of the infrared and electronic data.

INTRODUCTION

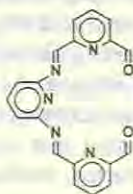
In recent years the chemistry of homo and hetero-polynuclear complexes from Schiff bases containing two similar or dissimilar compartments has been investigated by a large number of authors [1-7]. In an effort to develop new polynuclear complexes we have studied the metal complexation of polyfunctional Schiff base ligands derived from 2,6-diformylpyridine (L_1) or 2,6-diformyl-4-chlorophenol (HL) and 2,6-diaminopyridine or ethylenediamine. In the present work we have studied the preparation and characterisation of acyclic and cyclic ligands which can be used to link one or two metal ions in close proximity.



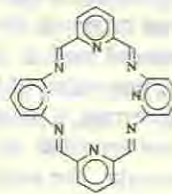
H₂LA



H₂LB



LC



LD

The occupied compartment for the acyclic or dissymmetric cyclic ligand is discussed on the basis of the infrared data.

The mononuclear complexes can act as ligands for another metal ion. Therefore we have investigated the ability of interaction of mononuclear species of nickel(II), copper(II), zinc(II) and uranyl(VI) with another metal ion. We have also obtained some mononuclear diorganotin complexes.

The preparation, IR and UV data of a series of mononuclear, homodinuclear and heterodinuclear complexes are discussed below.

EXPERIMENTAL

2,6-Diformyl-4-chlorophenol(HL) was prepared by improving the method described in the literature [8,9]. Modifications were made in order to increase the yield and the purity of the compounds.

2,6-Diformylpyridine(L₁), metal diacetates, diphenyltin dichloride, dimethyltin dichloride and the amines were purchased from Aldrich and were used without further purification.

All of the manganese(II) and cobalt(II) complexes were prepared under argon. IR spectral data were obtained with a JASCO FT/IR-5300 infrared spectrometer. Electronic spectra were recorded on a Beckman DU-64 spectrophotometer. Elemental analysis were performed by the Service Central de Microanalyse du CNRS, Vernaison, France.

Preparation of the ligands

Preparation of H₂L_A. To a solution of HL (0.37 g) in ethanol (25 mL) was added, dropwise, with stirring, a solution of 2,6-diaminopyridine (0.11 g) in ethanol (10 mL). The solution first turned brownish and within *ca* 1 min a red solid had formed. The stirring was continued overnight. The solid was collected, washed with chloroform and ethanol and vacuum dried.

Preparation of H₂L_B. To a solution of HL (0.18 g) in methanol (30 mL) was added dropwise, with stirring, a solution of 2,6-diaminopyridine (0.11 g) in methanol (10 mL). The solution first turned brownish and within *ca* 5 min a red solid had formed. The stirring was continued overnight. The solid was collected, washed with hot chloroform and methanol and vacuum dried.

Preparation of L_C. To a solution of L₁ (0.28 g) in methanol (25 mL) was added dropwise, with stirring, a solution of 2,6-diaminopyridine (0.11 g) in ethanol (10 mL). The solution first turned brownish and within *ca* 5 min an emerald green solid had formed. The stirring was continued for 3 h. The solid was collected, washed with methanol and vacuum dried.

Preparation of L_D. To a solution of L₁ (0.14 g) in ethanol (20 mL) was added dropwise, with stirring, a solution of 2,6-diaminopyridine (0.11 g) in ethanol (10 mL). The solution first turned brownish and within *ca* 1 min a red solid had formed. The stirring was continued overnight. The solid was collected, washed with ethanol and vacuum dried.

Preparation of the mononuclear complexes

Preparation of MnL_A·6H₂O. To a solution of HL (0.37 g) in ethanol (20 mL) under argon atmosphere was added solid LiOH (0.05 g) with stirring, followed by the addition of a solution of Mn(OAc)₂·4H₂O (0.24 g) in ethanol (20 mL). After the solution was stirred for 30 min, a solution of 2,6-diaminopyridine (0.11 g) in ethanol(10 mL) was added dropwise with stirring. The resulting solution was stirred overnight. The green solid was collected by

vacuum filtration, washed with ethanol and vacuum dried.

Preparation of $\text{CoL}_A\cdot 4\text{H}_2\text{O}$. The preparation of this complex was identical with that of $\text{MnL}_A\cdot 6\text{H}_2\text{O}$ discussed above, except that $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.25 g) was substituted for $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$. The resulting crystals were orange.

Preparation of $\text{UO}_2\text{L}_A\cdot 6\text{H}_2\text{O}$. The preparation of this complex was identical with that of $\text{MnL}_A\cdot 6\text{H}_2\text{O}$, except that $\text{UO}_2(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.42 g) was substituted for $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$. The resulting orange solid was washed with ether and air dried.

Preparation of $(\text{SnMe}_2)_\text{L}_B\cdot 2\text{MeOH}$. To a solution of HL (0.37 g) in methanol (20 mL) was added solid LiOH (0.05 g) with stirring, followed by the addition of a solution of SnMe_2Cl_2 (0.22 g) in methanol (10 mL). After the solution was stirred for 30 min, a solution of 2,6-diaminopyridine (0.22 g) in methanol (10 mL) was added dropwise with stirring. The resulting precipitate was stirred overnight. The red product was collected by vacuum filtration, washed with methanol and vacuum dried.

Preparation of $(\text{SnPh}_2)_\text{L}_B\cdot 5\text{H}_2\text{O}$. The preparation of this complex was identical with that of $(\text{SnMe}_2)_\text{L}_B\cdot 2\text{MeOH}$ discussed above, except that SnPh_2Cl_2 (0.34 g) was substituted for SnMe_2Cl_2 .

Preparation of $\text{UO}_2\text{L}_B\cdot 6\text{H}_2\text{O}$. Method A: The preparation of this complex was conducted following the same procedure discussed above for $(\text{SnMe}_2)_\text{L}_B\cdot 2\text{MeOH}$, except that $\text{UO}_2(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.42 g) was substituted for SnMe_2Cl_2 . The brown solid was washed with ether and air dried.

Method B: To a solution of $\text{UO}_2\text{L}_A\cdot 6\text{H}_2\text{O}$ (0.82 g) in methanol (20 mL) was added, with stirring, a solution of 2,6-diaminopyridine (0.11 g) in methanol (10 mL). Meanwhile the orange suspension disappeared and a brown precipitate was collected after 18 h.

Preparation of $\text{NiL}_E\cdot 2\text{MeOH}$. To a solution of HL (0.37 g) in methanol (25 mL) was added solid LiOH (0.05 g) with stirring, followed by the addition of a solution of $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.25 g) in methanol (10 mL). After the solution was stirred for 30 min, a solution of ethylenediamine (0.06 g) in methanol (5 mL) was added. Stirring continued for another 30 min. At this point a solution of 2,6-diaminopyridine (0.11 g) in methanol (10 mL) was added dropwise with stirring. The resulting suspension was stirred overnight. The orange product was collected by vacuum filtration, washed with methanol and vacuum dried.

Preparation of $\text{ZnL}_E\cdot 6\text{H}_2\text{O}$. This complex was prepared following the same method discussed above for the preparation of $\text{NiL}_E\cdot 2\text{MeOH}$, except that $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.22 g) was substituted for $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$. The resulting solid was orange.

Preparation of $\text{UO}_2\text{L}_E\cdot 6\text{H}_2\text{O}$. This complex was prepared following the same method discussed above for the preparation of $\text{NiL}_E\cdot 2\text{MeOH}$, except that $\text{UO}_2(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.42 g) was substituted for $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$. The resulting orange crystals were washed and dried.

Preparation of $(\text{SnPh}_2)_\text{L}_E\cdot 6\text{H}_2\text{O}$. This complex was prepared following the same method discussed above for the preparation of $\text{NiL}_E\cdot 2\text{MeOH}$, except that SnPh_2Cl_2 (0.34 g) was substituted for $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$. The resulting solid was yellowish.

Preparation of the homodinuclear complexes

Preparation of $\text{Mn}_2\text{L}_C(\text{OAc})_4\cdot 2\text{H}_2\text{O}$. To a solution of L_1 (0.29 g) in ethanol (20 mL) under argon atmosphere was added a solution of $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.53 g) in ethanol (20 mL). After the solution was stirred for 10 min, a solution of 2,6-diaminopyridine (0.11 g) in ethanol (10 mL) was added dropwise with stirring. The resulting solution was stirred overnight. The orange solid was collected by vacuum filtration, washed with ethanol and vacuum dried.

Preparation of $\text{Co}_2\text{L}_C(\text{OAc})_4\cdot 2\text{MeOH}$. The preparation of this complex was identical with

that employed for $Mn_2L_C(OAc)_4 \cdot 2H_2O$, except that $Co(OAc)_2 \cdot 4H_2O$ (0.54 g) was substituted for $Mn(OAc)_2 \cdot 4H_2O$. The resulting solid was brown.

Table 1. Elemental analyses data of the prepared ligands and complexes.

Compound	Calculated (%)				Found (%)			
	C	H	N	Cl	C	H	N	Cl
HL	52.06	2.73		19.21	52.01	2.76		19.11
H_2L_A	57.03	2.96	9.50	16.03	57.05	3.02	9.46	16.04
H_2L_B	60.60	3.13	16.31	13.76	60.54	3.12	16.30	13.62
L_C	66.47	3.82	20.40		66.45	3.85	20.41	
L_D	69.22	3.87	26.91		69.19	3.90	27.02	
$MnL_A \cdot 6H_2O$	41.81	3.84	6.96		41.76	3.69	6.98	
$CoL_A \cdot 4H_2O$	44.16	3.35	7.36		44.63	3.03	7.94	
$UO_2L_A \cdot 6H_2O$	30.82	2.83	5.13		30.23	2.62	5.38	
$SnPh_2L_B \cdot 5H_2O$	52.08	3.91	9.59	8.09	52.32	4.05	9.76	8.58
$SnMe_2L_B \cdot 2MeOH$	49.62	3.89	11.57	9.76	49.49	3.96	11.69	9.91
$UO_2L_B \cdot 6H_2O$	35.03	2.94	9.43	7.95	34.75	2.74	9.02	7.98
$SnPh_2L_B \cdot 6H_2O$	49.73	4.41	8.28	8.39	50.77	3.88	8.48	8.50
$NiL_E \cdot 2MeOH$	51.15	3.95	11.93	12.08	50.80	4.63	11.09	12.35
$ZnL_E \cdot 6H_2O$	43.31	4.27	10.98	11.12	43.36	4.22	11.60	11.01
$UO_2L_E \cdot 6H_2O$	32.79	3.23	8.31	8.42	33.11	3.25	8.45	8.50
$Mn_2L_C(OAc)_4 \cdot 2H_2O$	44.70	4.03	9.65		44.09	4.10	10.02	
$Co_2L_C(OAc)_4 \cdot 2MeOH$	45.74	4.37	9.20		45.13	4.28	8.85	
$Ni_2L_B(OAc)_2 \cdot 5H_2O$	42.95	3.60	10.02		42.67	2.99	10.06	
$Cu_2L_B(OAc)_2 \cdot 2H_2O$	45.35	3.04	10.58		45.84	2.91	10.34	
$Zn_2L_B(OAc)_2 \cdot 2H_2O$	45.14	3.03	10.53		45.20	3.15	11.06	
$NiCuL_B(OAc)_2 \cdot 4H_2O$	43.64	3.42	10.17	8.59	43.03	3.84	9.86	8.80
$NiZnL_B(OAc)_2 \cdot 4H_2O$	43.54	3.41	10.15		43.42	3.24	10.32	
$NiUO_2L_B(OAc)_2$	37.53	2.10	8.75		37.07	2.28	8.83	
$CuZnL_B(OAc)_2 \cdot 2H_2O$	45.25	3.04	10.55		45.55	2.92	10.80	
$CuUO_2L_B(OAc)_2$	37.34	2.09	8.71		37.30	2.20	8.07	

Preparation of $Cu_2L_B(OAc)_2 \cdot 2H_2O$. To a solution of HL (0.18 g) in ethanol (20 mL) was added solid LiOH (0.025 g) with stirring, followed by the addition of a solution of $Cu(OAc)_2 \cdot H_2O$ (0.20 g) in ethanol (15 mL). The mixture was stirred for 30 min. and a

solution of 2,6-diaminopyridine (0.11 g) in ethanol (10 mL) was added dropwise. The resulting suspension was stirred overnight. The brown compound was collected by vacuum filtration, washed with ethanol and vacuum dried.

Preparation of $Ni_2L_B(OAc)_2 \cdot 5H_2O$. This complex was prepared following a method similar to that employed for the preparation of $Cu_2L_B(OAc)_2 \cdot 2H_2O$ above, except that $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g) was substituted for $Cu(OAc)_2 \cdot H_2O$. The resulting solid was reddish.

Preparation of $Zn_2L_B(OAc)_2 \cdot 2H_2O$. This complex was prepared following a method similar to that employed for the preparation of $Cu_2L_B(OAc)_2 \cdot 2H_2O$ above, except that $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g) was substituted for $Cu(OAc)_2 \cdot H_2O$. The resulting solid was yellow-brown.

Preparation of the heterodinuclear complexes

Preparation of $NiCuL_B(OAc)_2 \cdot 4H_2O$. To a solution of HL (0.37 g) in ethanol (15 mL) was added solid LiOH (0.05 g) with stirring, followed by the addition of a solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g) in ethanol (15 mL). The resulting solution stirred for 30 min, and a solution of $Cu(OAc)_2 \cdot H_2O$ (0.20 g) in ethanol (15 mL) was added. After 30 min, a solution of 2,6-diaminopyridine (0.22 g) in ethanol (10 mL) was added dropwise. The resulting precipitate was stirred overnight. The brown product was collected by vacuum filtration, washed with ethanol and ether and vacuum dried.

Preparation of $NiZnL_B(OAc)_2 \cdot 4H_2O$. This complex was prepared following a similar procedure discussed above for the preparation of $NiCuL_B(OAc)_2 \cdot 4H_2O$, except that $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g) was substituted for $Cu(OAc)_2 \cdot H_2O$. The resulting solid was reddish.

Preparation of $NiUO_2L_B(OAc)_2$. This complex was prepared following a similar procedure discussed above for the preparation of $NiCuL_B(OAc)_2 \cdot 4H_2O$, except that $UO_2(OAc)_2 \cdot 2H_2O$ (0.42 g) was substituted for $Cu(OAc)_2 \cdot H_2O$. The resulting red crystals were washed with ether and air dried.

Preparation of $CuZnL_B(OAc)_2 \cdot 2H_2O$. This complex was prepared following a similar procedure discussed above for the preparation of $NiCuL_B(OAc)_2 \cdot 4H_2O$, except that $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g) was substituted for $Ni(OAc)_2 \cdot 4H_2O$. The resulting solid was brown.

Preparation of $CuUO_2L_B(OAc)_2 \cdot 2H_2O$. This complex was prepared following a similar procedure discussed above for the preparation of $NiCuL_B(OAc)_2 \cdot 4H_2O$, except that $UO_2(OAc)_2 \cdot 2H_2O$ (0.42 g) was substituted for $Ni(OAc)_2 \cdot 4H_2O$. The resulting red crystals were washed with ether and air dried.

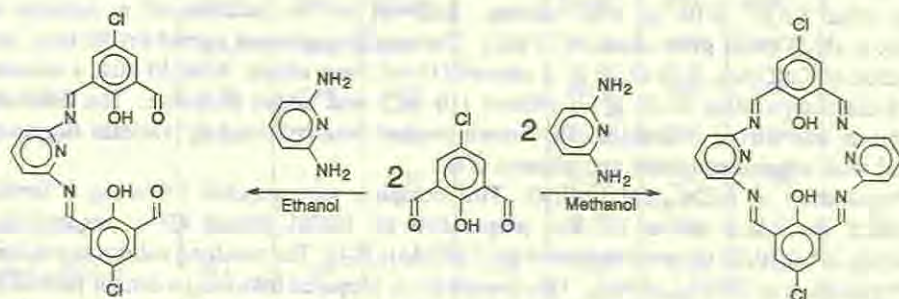
RESULTS AND DISCUSSION

The nuclear complexes were synthesized by the template condensation reaction of HL with various diamines as shown in Scheme 2. Okawa and co-workers [1,2,10] found that the metal ions bound preferentially to the N_2O_2 site. The addition of another $M_2(II)$ salt solution results in the complexation of $M_2(II)$ in the vacant O_2O_2 inner chamber.

The choice of 2,6-diaminopyridine and ethylenediamine as co-ligands was suggested by the ability of the ligands to adopt a solid configuration as well as to induce inertness of the metal macrocycles complexes toward the scrambling dissociation ($2 M_1M_2L^{2+} \rightleftharpoons M_1M_1L^{2+} + M_2M_2L^{2+}$). No macrocycles displacement reaction were observed using other 3d metal ions. It is particularly important to point out that the $[M_1M_2L_B]^{2+}$ species are stable toward metal exchange. Subsequent addition of 2 equivalent of $M_3(II)$ salt in methanol

suspension containing $[M_1M_2L_B]^{2+}$ salt confirms the stability of these complexes. No complexes containing metal ion of M_3 were observed in this case.

By reaction of 2,6-diformyl-4-chlorophenol or 2,6-diformylpyridine with 2,6-diaminopyridine, the series of compartmental Schiff bases have been synthesized. The yield was good in both cases ($> 80\%$). The solid compounds obtained from 2,6-diformyl-4-chlorophenol are red and when 2,6-diformylpyridine was used a green solid was isolated. All of these products melting points above 270° . Generally the open and closed Schiff bases showed different solubility in methanol [12]. In those cases that we have investigated both acyclic and cyclic ligands precipitate from this solvent in a few minutes. The ligand route is detailed in Scheme 1.



Scheme 1. Reaction pathway for the formation of Schiff base ligands H_2L_A and H_2L_B .

IR study

For the acyclic ligand (H_2L_A) there is in its IR spectrum a strong $\nu C=O$ band at 1683 cm^{-1} which disappears upon cyclization (H_2L_B). In all the prepared ligands there are strong absorption bands due to stretching of the $C=N$ and $C=C$ groups in the range $1660\text{--}1650\text{ cm}^{-1}$. There is a small shift of the $\nu C=N$ upon cyclization. In the IR spectrum of 2,6-diformyl-4-chlorophenol two $\nu C=O$ bands appeared at 1689 and 1664 cm^{-1} . The shift of the second band to a lower frequency was probably due to the formation of hydrogen bonding between the phenolic OH and the aldehydic $C=O$ groups [10,11].

In the infrared spectra of the acyclic ligand L_C , derived from 2,6-diformylpyridine, there is a strong $\nu C=O$ band at 1707 cm^{-1} which disappears upon cyclization (L_D). In all ligands of these kinds very intense $\nu C=N$ bands were observed at 1589 cm^{-1} .

The reaction pathway described in Scheme 2 has been formulated for the reaction of the aldehyde precursors and diamines with metal(II) salts and/or uranyl(VI) acetate and dialkyl tin derivatives.

Table 2. IR spectral data for the prepared ligands and complexes.

Compound	IR frequencies in the range of 1750-1500 cm^{-1} assignable to C=O, C=N and C=C	Other characteristic bands (cm^{-1})
HL	1689, 1664, 1608, 1582	
H_2L_A	1683, 1653, 1609, 1559	
H_2L_B	1655, 1609, 1559	
L_C	1707, 1589	
L_D	1589	
$\text{MnL}_A \cdot 6\text{H}_2\text{O}$	1647, 1620, 1559, 1520	
$\text{CoL}_A \cdot 4\text{H}_2\text{O}$	1638, 1620, 1559, 1526	
$\text{UO}_2\text{L}_A \cdot 6\text{H}_2\text{O}$	1699, 1659, 1620, 1559, 1535	891(O-U-O)
$\text{SnPh}_2\text{L}_B \cdot 5\text{H}_2\text{O}$	1618, 1552, 1533	
$\text{SnMe}_2\text{L}_B \cdot 2\text{MeOH}$	1613, 1557, 1520	567(C-Sn-C)
$\text{UO}_2\text{L}_B \cdot 6\text{H}_2\text{O}$	1620, 1566, 1535	907(O-U-O)
$\text{SnPh}_2\text{L}_E \cdot 6\text{H}_2\text{O}$	1622, 1566, 1535	
$\text{NiL}_E \cdot 2\text{MeOH}$	1622, 1568, 1537	
$\text{ZnL}_E \cdot 6\text{H}_2\text{O}$	1640, 1564, 1537	
$\text{UO}_2\text{L}_E \cdot 6\text{H}_2\text{O}$	1626, 1564, 1547	893(O-U-O)
$\text{Mn}_2\text{L}_C(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$	1650, 1622, 1558, 1541	
$\text{Co}_2\text{L}_C(\text{OAc})_4 \cdot 2\text{MeOH}$	1645, 1622, 1558, 1522	
$\text{Ni}_2\text{L}_B(\text{OAc})_2 \cdot 5\text{H}_2\text{O}$	1626, 1566, 1530	
$\text{Cu}_2\text{L}_B(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	1612, 1566, 1534	
$\text{Zn}_2\text{L}_B(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	1611, 1571, 1531	
$\text{NiCuL}_B(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	1614, 1566, 1535	
$\text{NiZnL}_B(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	1618, 1572, 1531	
$\text{NiUO}_2\text{L}_B(\text{OAc})_2$	1615, 1559, 1534	910(O-U-O)
$\text{CuZnL}_B(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	1626, 1564, 1533	
$\text{CuUO}_2\text{L}_B(\text{OAc})_2$	1622, 1559, 1539	920(O-U-O)

Mononuclear complexes derived from H_2L_A

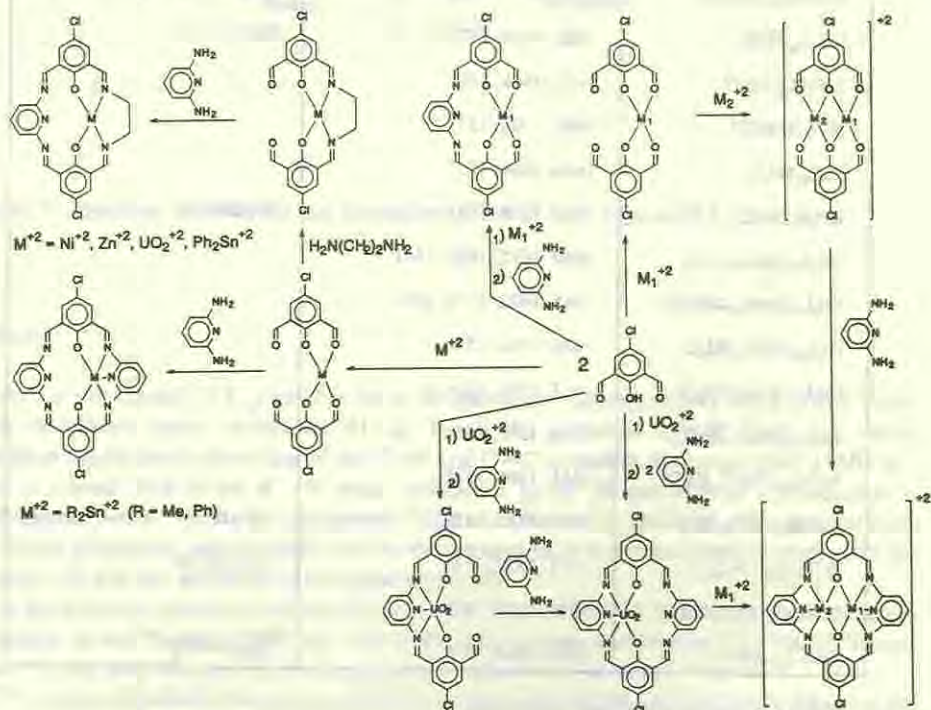
The infrared spectra of the mononuclear acyclic complexes derived from H_2L_A , show a strong IR band in the range 1700-1638 cm^{-1} , due to the $\nu\text{C}=\text{O}$ of the formyl groups. This band appeared at 1699 cm^{-1} for the uranyl(VI) complex attesting the freedom of the formyl groups. In the Mn(II) and Co(II) complexes the $\nu\text{C}=\text{O}$ bands appeared at 1647 and 1638 cm^{-1} ,

respectively. The observed shift in the $\nu\text{C}=\text{O}$ in these complexes is due to the interaction between metal(II) ion and the aldehydic $\text{C}=\text{O}$ groups. There is, in addition, a multiplicity of bands in the range $1660\text{--}1560\text{ cm}^{-1}$, due to the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ vibrations. The presence of the $\text{O}-\text{U}-\text{O}$ group in the uranyl(VI) complex was easily detected by the intense IR band at 891 cm^{-1} due to the $\nu_3(\text{O}-\text{U}-\text{O})$ mode.

It should be noted that the acyclic ligands contain one N_3O_2 inner chamber and an outer O_2O_2 compartment. Consequently the IR study leads to the assumption that the uranyl group is coordinated to the N_3O_2 while the $\text{Mn}(\text{II})$ and $\text{Co}(\text{II})$ ions are coordinated to the O_2O_2 sites [5,13].

Mononuclear complexes derived from H_2L_B

On moving from the acyclic to the mononuclear complexes the IR spectra show remarkable analogies, apart from the disappearance of the $\nu\text{C}=\text{O}$ in the cyclic complexes. There is a small shifts of the $\nu\text{C}=\text{N}$ mode. The IR spectra of the cyclic dimethyltin derivative show, in addition, significant differences, owing to the presence of the $\nu_{15}\text{ SnC}_2$ indicating a linear skeleton [14]; there is also a small shift (16 cm^{-1}) of the $\nu_3(\text{O}-\text{U}-\text{O})$ for the uranyl(VI) complex [12]. The metal ion is coordinated to one of the two N_3O_2 , while the other donor atoms of the other inner chamber are not involved in the coordination.



Scheme 2. Reaction pathways for the formation of the complexes from the Schiff base ligands.

Mononuclear complexes derived from L_E

These mononuclear species were obtained as pure products and in high yield, by template synthesis using step-by-step reaction; only mononuclear asymmetric cyclized complexes were synthesized. The ligand so formed contains two different sites, N₃O₂ and N₂O₂. Consequently, the ionic species can discriminate between the two coordination compartments giving dissymmetric mononuclear complexes [15]. But the difference in the coordination ability of the N₃O₂ and N₂O₂ inner chambers was not always so high as to make one compartment selective for a particular metal. The IR spectra of these complexes show remarkable analogies apart from the shifting of the ν C=N to higher frequencies in the case of ZnL_E.6H₂O. The stretching ν C=N lies almost in the same frequency range (1640-1620 cm⁻¹) for both symmetric and asymmetric closed mononuclear complexes.

Dinuclear complexes derived from L_C

Mononuclear acyclic complexes of Mn(II) and Co(II) derived from H₂L_A have one site available for further coordination and can act as ligands towards a second metal ions. Similarly L_C can react with one or two metal ions, leading to dinuclear complexes. The IR spectra of these complexes present good similarities with those of MnL_A and CoL_A apart from the difference owing to the presence of the acetate groups. The antisymmetric and the symmetric modes of vibrations of the carboxylates groups can be seen in the range 1580-1350 cm⁻¹. These bands lie in the region where other absorptions of the ligands were present. Thus the correct formulation of the coordination of these species to the metal ions was impossible [16].

Homo and heterodinuclear complexes derived from H₂L_B

The dinuclear complexes were isolated as pure products in good yield. Using step-by-step reaction, homo and heteronuclear complexes were synthesized. Particular attention must be paid to the experimental conditions, in the case of heterodinuclear synthesis, in order to avoid the scrambling dissociation.

The symmetric cyclic ligand contains two N₃O₂ compartments. Every one of the two metal ions is thus coordinated to one of the two sites and all the donor atoms were involved in the coordination. The IR spectra of these multinuclear complexes present good similarities. The ν (C=N) band appeared in the range (1630-1610 cm⁻¹). In addition there were significant difference owing to the presence of acetate groups which have a symmetric and an antisymmetric stretching in the range 1585-1420 cm⁻¹. In the IR spectra of these complexes other absorptions of the ligand were present in this region making the correct assignment of the carboxylate groups impossible. Thus, the formulation of the coordination geometry from the IR spectra is not unambiguous and needs further experimental evidence. The ν_3 (O-U-O) for the uranyl(VI) complex appeared at 910 cm⁻¹ for NiUO₂L_B(OAc)₂ and 920 cm⁻¹ for CuUO₂L_B(OAc)₂.2H₂O.

UV study

Most of the complexes are only soluble in DMSO. Therefore we were not able to compile the electronic data in a non coordinating solvent. The electronic data obtained in DMSO show

only d-d bands. The uranyl complex shows shoulders due to the charge transfer UO_2 -Ligand or internal transition of O-U-O.

The complexes are ionic in DMSO and the characteristic d-d bands exclude the possibility of coordination in apical position to the central metal ion. These data show that nickel(II) has a square planar coordination.

Table 3: Electronic spectral data for the prepared complexes.

Complexes	λ_{max} (nm) in DMSO
$\text{MnL}_A \cdot 6\text{H}_2\text{O}$	480, 395
$\text{CoL}_A \cdot 4\text{H}_2\text{O}$	425, 400
$\text{UO}_2\text{L}_A \cdot 6\text{H}_2\text{O}$	485, 395, 365
$\text{UOL}_B \cdot 6\text{H}_2\text{O}$	485, 435, 375
$\text{NiL}_E \cdot 2\text{MeOH}$	ins
$\text{UO}_2\text{L}_E \cdot 6\text{H}_2\text{O}$	390, 355
$\text{Mn}_2\text{L}_C(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$	ins
$\text{Co}_2\text{L}_C(\text{OAc})_4 \cdot 2\text{MeOH}$	430, 400
$\text{Ni}_2\text{L}_B(\text{OAc})_2 \cdot 5\text{H}_2\text{O}$	438
$\text{Cu}_2\text{L}_B(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	430
$\text{Zn}_2\text{L}_B(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	425, 400
$\text{NiCuL}_B(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	430, 395
$\text{NiZnL}_B(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	420
$\text{NiUO}_2\text{L}_B(\text{OAc})_2$	435, 410
$\text{CuZnL}_B(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	435
$\text{CuUO}_2\text{L}_B(\text{OAc})_2$	425, 400

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