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Functionalized acyclic Schiff bases and related complexes with d- and f-metal ions

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Abstract

The condensation reaction in acetonitrile of 2,6-diformyl-4-chlorophenol with tris-(2-aminoethyl)amine forms the [3 + 1] macroacyclic Schiff base **H$_3$-I** which reacts with $LnCl_3 \cdot nH_2O$ ($Ln = La^{3+}$, Dy^{3+}, Gd^{3+}) in the presence of NEt_3 giving rise to Ln(**I**)·*n*S (S = H_2O, dmf, CH_3CN; *n* = 0–1.5).

Crystals of La(**I**)(dmf), grown from a dimethylformamide/acetonitrile solution, are monoclinic, space group $P2_1/c$ with $a = 12.590(4)$, $b = 14.277(5)$, $c = 19.710(5)$ Å, $\beta = 95.45°$ and $Z = 2$. This complex is a dimeric entity and shows an inversion center in between the two lanthanum(III) ions. The organic ligand coordinates to one lanthanum ion through the four nitrogen and the three phenoxide oxygen atoms while it links the second lanthanum ion through one aldehydic oxygen atom; the other two aldehydic oxygens are not involved in the coordination and do not form significative interactions with neighboring molecules. Thus each dinuclear complex behaves as an isolated entity. The nonacoordination around each metal ion is reached through the additional coordination of the oxygen atom of a dimethylformamide molecule. The three La–N (iminic) bond distances fall between 2.70 and 2.79 Å, while the La–N (aminic) bond is longer (2.86 Å). Similarly the La–O (phenolic) bonds distances are in the range 2.41–2.47 Å, considerably shorter than the La–O (aldehydic) which is 2.72 Å, while the La–O (dimethylformamide) is 2.55 Å. Finally the two lanthanum atoms are 8.24 Å apart.

2,6-Diformyl-4-chlorophenol reacts in CH_3CN with H_2N–R–NH_2 to give the [2 + 1] acyclic Schiff bases **H$_2$-II**. The corresponding complexes containing a d (nickel(II) Ni(**II**), or manganese(III) Mn(**II**)(OH), an f (lanthanum(III), gadolinium(III), dysprosium(III)) Ln(**H$_2$-II**)$(NO_3)_3$, or the uranyl(VI) ion, UO_2(**II**)(MeOH), UO_2(**H-II**)(NO_3) and UO_2(**H$_2$-II**)$(NO_3)_2$ have also been prepared by reaction of these ligands with the appropriate metal salts or by template procedure, the different content of the nitrate in the uranyl(VI) complexes depending on the amount of base used. These complexes may be converted into the acetal analogues in alcoholic solution.

Similarly the condensation of 3-methoxy-2-hydroxybenzaldehyde or 3-ethoxy-2-hydroxybenzaldehyde with tris-(2-aminoethyl)amine in a 1:3 molar ratio afforded the [3 + 1] Schiff bases **H$_3$-IV** and **H$_3$-V** which react with lanthanide(III) salt to give rise, respectively, in the presence or in the absence of the appropriate amount of base, to Ln(**IV**)·nH_2O and Ln(**V**)·nH_2O and Ln(**H$_3$-IV**)$(X)_3 \cdot nH_2O$ or Ln(**H$_3$-V**)$(X)_3 \cdot nH_2O$ ($Ln = La^{3+}$, Gd^{3+}; $X = Cl^-$, NO_3^-; *n* = 1–5). These complexes are no longer stable in solution and hydrolyzed especially when redissolved in alcohol.

H$_3$-I, **H$_2$-II** and/or the related complexes have been engaged in further condensation reactions with 2-aminomethyl-12-crown-4 or 2-aminomethyl-15-crown-5 to give rise to the functionalized Schiff bases (**H$_3$-III** and **H$_2$-VII**) and related d- or f-complexes. Moreover the functionalized ligands **H$_3$-VI**, **H$_2$-VIII**, **H$_2$-X** and **H$_2$-XI** and/or the related d- or f-complexes have been synthesized by condensation of the appropriate formyl and amine precursors.

The ligands and the complexes have been characterized by physico-chemical measurements, especially by IR and NMR spectroscopy, SEM and EDX investigation, and FAB mass spectrometry.

Keywords: Lanthanide complexes; Actinide complexes; Schiff base complexes; Crystal structures

1. Introduction

Many efforts have been addressed in the last decade to the design and synthesis of macrocyclic or macroacyclic complexes and to the study of their physico-chemical properties [1–5]. These investigations emphasized thegreat relevance of these systems in basic and applied chemistry. Several synthetic strategies are nowadays available for the preparation of well organized molecular systems or molecular devices, especially designed to present peculiar physico-chemical properties or to have well defined performances [1,6,7].

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Sophisticated macrocyclic or macroacylic systems, containing an appropriate set of donor atoms and/or a suitable structural configuration, are capable of selective recognition of charged or neutral molecules; new chemical processes and technologies, based on this concept, are available and are already applied in the fields of activation and catalysis processes, selective separation, molecular materials, microelectronics sensors, etc. [7].

As an extension of these concepts compartmental ligands have been prepared with the idea that complexation to one of the sites can transform the second binding site. This may introduce a positive cooperativity in the binding of two metal ions and new concepts in host–guest organization. These ligands contain two similar or dissimilar compartments in close proximity and can selectively recognize two identical or different charged or neutral molecules (generally metal ions) which may mutually interact giving rise to novel and unusual devices [6,8].

In the development of the synthetic strategy of these systems an important role is played by the Schiff bases owing to their relatively easy preparation, through the well known condensation reaction of formyl or carbonyl derivatives with a primary amine, and their versatility in metal complexation. To this aim suitable keto and/or amine precursors have been prepared; they can give rise to well-defined macrocyclic or macroacyclic Schiff bases in good yield. Acyclic or symmetric cyclic compounds are quite often produced by one-step multiple condensation reaction. When the direct condensation reaction is unsuccessful, template synthesis is used; the presence of metal ion is often essential in determining the steric course of the reaction [2,4,6,8].

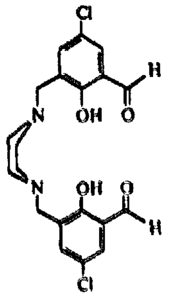
These ligands have been employed in the study of stereochemical, electronic, magnetic and catalytic properties of metal complexes [1–8]. Moreover they have successfully been proposed as models of the active sites of metal-enzymes [1,5,9].

In the recent past macrocyclic, macrobicyclic and macroacyclic compartmental Schiff bases have been prepared in one-step multiple condensation reactions of the above-mentioned formyl or keto and amine precursors [10]. The insertion of additional donor atoms (S, P, O, N) into the coordination moiety of these systems can be tuned, in order to make them suitable and selective for particular ions, especially transition metal ions. Moreover emphasis was placed on ligands incorporating oxygen donor atoms, such as crown ethers, which are considered good ligands for non-transition metal ions, especially alkaline or alkaline-earth ions [8,10].

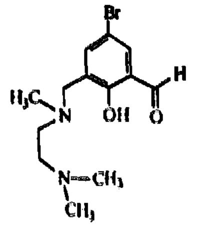
Many papers have been published on the ability of these macrocyclic ligands to mimic ion encapsulation and transport of natural systems. The ability of these synthetic ligands to act as suitable chelating agents for alkaline or alkaline-earth ions has been attributed to several factors, including the goodness of fit of the cation in the ligand cavity and the nature and the shape of the donor set.

The fusion of the Schiff base and crown-ether properties into a unique entity can give rise to polynucleating ligands with different coordination chambers in close proximity. These systems can incorporate suitable d- or f-metal ions into the Schiff base sites and non-transition ions, anions or organic substrates into the crown-ether sites [11]. The coordination of a metal ion into the crown-ether cavity can considerably modify the physico-chemical (electrochemical, optical, magnetic) properties of the metal ion bound to the Schiff base system and the mutual interaction through the ligand of the two species contemporary recognized can be applied to the development of molecular devices. To this end we have recently prepared a series of Schiff bases containing crown ether by condensation of the appropriate formyl or diformyl precursors with 4-aminobenzo-15-crown-5, 2-aminomethyl-15-crown-5 and the analogous amines containing 12-crown-4 or 18-crown-6 and tested their recognition properties towards transition metal ions [12]. It was found that they may give rise to well defined mononuclear or hetero-polynuclear complexes; moreover, under particular experimental conditions, they are interesting 'carriers' for the selective electroassisted separation of specific metal ions [13].

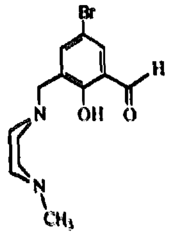
In the present work we have applied a similar synthetic strategy and we have prepared the functionalized acyclic compartmental ligands of Scheme 1 and/or related complexes containing d- or f-metal ions.



H_2-A



H-B



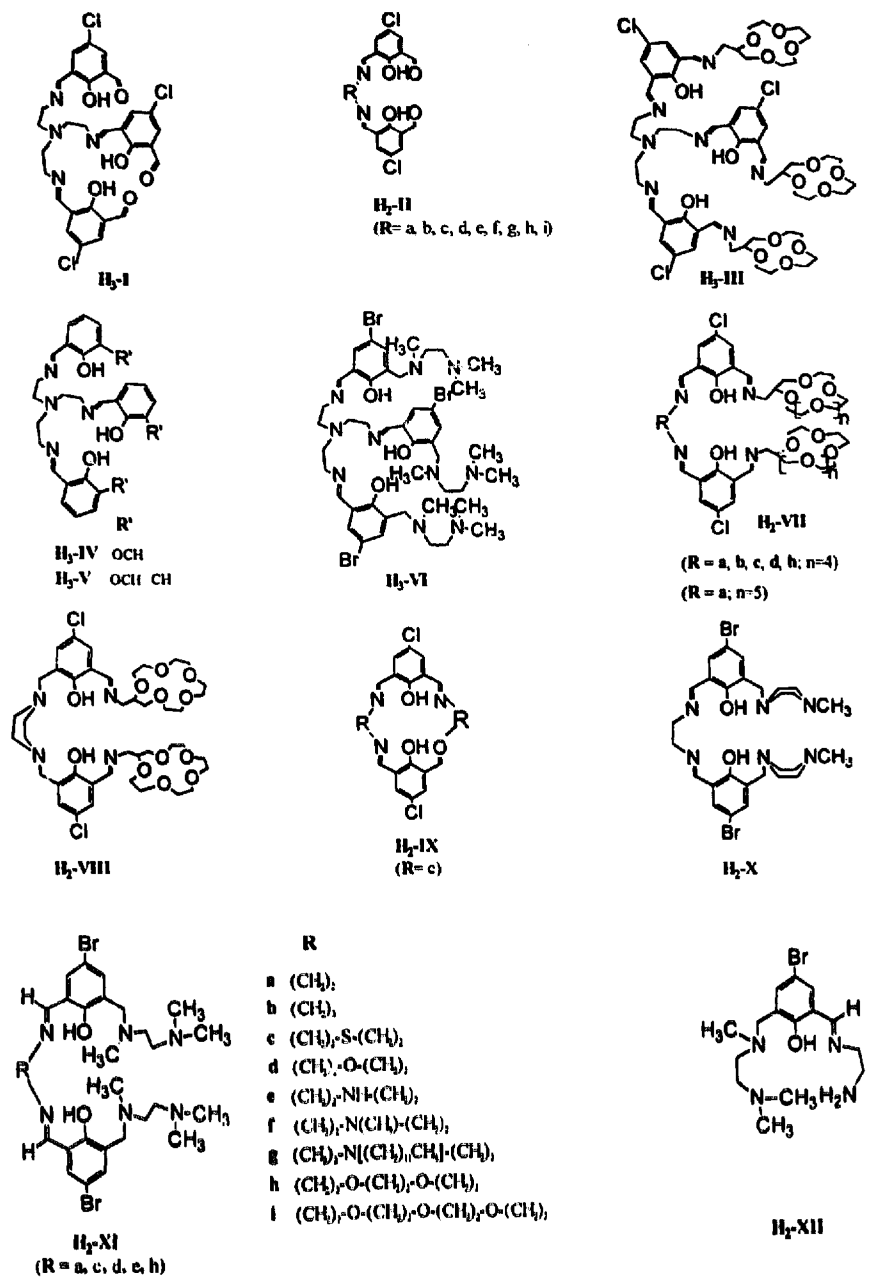
H-C

In order to obtain these compounds we had to synthesize the appropriate formyl, diformyl and triformyl precursors or by literature procedure [14,15] (H_2-A, H-B and H-C) or by condensation of 2,6-diformyl-4-chlorophenol with the appropriate polyamine (H_3-I and H_2-II). The subsequent reaction of these acyclic ligands with the appropriate primary mono- or di-amines, bearing additional donor groups (i.e. ethers, crown ethers, polyamines and polyoxyamines), gives rise to the functionalized macroacyclic systems (H_3-III···H_2-XI). The prepared ligands and related complexes have been characterized by IR or NMR spectroscopy, by mass spectrometry (FAB or EI) and by electron microscopy (SEM and EDX). For the complex La(I)(dmf), where H_3-I is the ligand derived from the condensation of 2,6-diformyl-4-chlorophenol and tris-(2-aminoethyl)amine, an X-ray investigation was also carried out and a preliminary account of the structure has already been published [16].

2. Experimental

2.1. Materials

The salts, the solvents and the reagents were commercial products (Aldrich), used without further purification. 2,6-



Scheme 1.

Diformyl-4-chlorophenol, bis[(4-chloro-6-formylphenol)-ylmethyl]piperazine (H_2-**A**), 4-bromo-2-[2-(dimethylaminoethyl)methylamino]-methyl-6-formylphenol (**H-B**) and 4-bromo-2-[2-(methylaminodiethyl)amino]-methyl-6-formylphenol (**H-C**) were prepared according to literature methods [14]; their purity was checked by elemental analyses, IR and NMR data. The acyclic ligands H_2-**IIc**···H_2-**IIg** and H_2-**III**, the symmetric cyclic ligands H_2-**IX**, and related copper(II), uranyl(VI) and lanthanum(III) complexes were also prepared and purified according to the literature [15].

The elemental analyses of the prepared ligands and complexes are reported in Table 1. The yield is 30–50% for the ligands and 60–80% for the complexes.

2.2. *Formyl precursors and related complexes*

2.2.1. *Preparation of H_3-I*

To an acetonitrile solution (50 ml) of 2,6-diformyl-4-chlorophenol (3 mmol), gently warmed, tris(2-amminoethyl)amine (1 mmol) in acetonitrile (50 ml) was added dropwise. The orange solution was refluxed for 2.5 h, then allowed to stand for 1 h. The orange-red precipitate was collected by filtration, washed with acetonitrile and dried in vacuo.

From the mother liquor, allowed to stand overnight, a further red precipitate was obtained. It was filtered off, washed with acetonitrile and dried in vacuo.

Table 1
Elemental analyses

Compound	Found (%)			Calculated (%)		
	C	H	N	C	H	N
H$_3$-I	56.14	4.29	9.06	55.79	4.21	8.67
La(**I**)·1.5H$_2$O·1.5DMF	44.32	3.55	9.15	45.12	4.12	8.39
Gd(**I**)	45.44	3.47	6.74	44.87	3.39	6.98
Dy(**I**)·2MeCN	46.68	3.87	8.90	46.02	3.41	9.47
H$_2$-IIa	55.20	3.72	7.94	54.98	3.59	7.12
Ni(**IIa**)·2H$_2$O·DMF	45.52	3.66	7.59	45.12	4.15	7.52
UO$_2$(**H$_2$-IIa**)(NO$_3$)$_2$	27.78	1.85	6.98	27.46	1.79	7.12
UO$_2$(**H-II′a**)(NO$_3$)	30.79	2.75	6.10	31.27	2.23	5.47
UO$_2$(**II′a**)(MeOH)	34.57	3.30	3.64	35.17	3.59	3.57
Mn(**IIa**)(OH)	46.88	3.61	5.85	46.68	2.83	6.05
H$_2$-IIb	50.12	3.51	5.84	50.24	3.57	6.01
La(**H$_2$-IIb**)(NO$_3$)$_3$·0.5MeCN	32.34	2.31	9.64	31.92	2.34	10.24
La(**H$_2$-IIc**)(NO$_3$)$_3$	30.81	2.69	9.60	30.87	2.33	9.00
La(**H$_2$-II′d**)(NO$_3$)$_3$	32.23	3.26	9.11	32.92	3.24	8.34
La(**H$_2$-IId**)(NO$_3$)$_3$	31.52	2.61	8.99	31.52	2.38	9.19
La$_{1.5}$(**H$_2$-IIe**)(NO$_3$)$_4$·0.5MeCN	28.82	2.74	11.32	28.49	2.33	11.86
La(**H$_2$-IIf**)(NO$_3$)$_3$	33.23	2.93	11.02	32.54	2.73	10.84
La(**H$_2$-IIg**)(NO$_3$)$_3$·0.5CHCl$_3$	39.88	4.60	8.74	39.49	4.44	8.50
H$_2$-IIh	55.34	4.79	5.76	54.90	4.61	5.82
La(**H$_2$-IIh**)(NO$_3$)$_3$·1.5CHCl$_3$·0.5MeCN	28.94	2.77	8.26	29.32	2.51	7.68
La(**III**)·3DMF·3CHCl$_3$	42.85	5.32	8.27	43.24	5.21	7.31
H$_3$-IV	65.30	6.58	10.08	65.68	6.61	10.21
La(**IV**)·H$_2$O	51.32	5.55	7.66	51.29	5.02	7.97
La(**H$_3$-IV**)(NO$_3$)$_3$·H$_2$O	39.91	4.10	10.58	40.42	4.30	11.00
La(**H$_3$-IV**)(Cl)$_3$·5H$_2$O	39.97	4.79	6.31	40.76	5.25	6.34
La(**V**)·NaCl·0.3CHCl$_3$	48.58	5.09	7.19	48.75	4.83	6.83
Gd(**V**)·2H$_2$O	51.00	5.13	7.04	50.75	5.55	7.17
La(**H$_3$-V**)(Cl)$_3$·H$_2$O	41.29	5.72	7.79	40.84	5.14	7.94
La(**H$_3$-V**)(NO$_3$)$_3$·4H$_2$O	39.56	4.54	10.74	40.13	5.10	9.93
La(**VI**)·0.5NaBr·2H$_2$O·MeOH	42.72	5.77	10.83	42.97	5.45	10.94
H$_3$-VIIh	44.61	5.55	5.33	44.37	5.13	4.87
La$_{1.5}$(**H$_3$-VIId**)(NO$_3$)$_{4.5}$·0.5CHCl$_3$	34.30	3.62	7.95	34.05	3.90	8.77
La$_2$(**VIIh**)(NO$_3$)$_3$(OH)·0.5DMF	34.74	4.23	8.71	34.76	4.18	8.30
La(**H$_3$-VIIe**)(NO$_3$)$_2$(OH)·2H$_2$O	39.40	4.42	7.38	39.91	5.02	7.35
UO$_2$(**VIIa**)(H$_2$O)	42.08	4.90	4.56	42.08	4.94	4.91
Ni(**VIIa**)·0.5CHCl$_3$	49.72	5.54	6.32	49.52	5.52	6.33
Mn(**VIIa**)(OH)·3H$_2$O	48.17	4.86	7.15	48.61	5.78	6.30
H$_3$-VIII·H$_2$O	55.81	7.07	6.15	55.81	7.14	6.20
UO$_2$(**X**)(MeOH)	35.26	4.08	8.91	35.08	4.14	9.09
H$_3$-XIa·4HBr·2.5MeOH	34.94	5.58	7.62	34.62	5.33	7.94
Na$_2$(**XIa**)·MeOH·2CHCl$_3$	40.30	4.84	9.01	40.37	5.05	9.26
Cu(**XIa**)·HBr·MeOH·H$_2$O	40.69	5.34	9.63	41.12	5.59	9.92
Cu$_2$(**XIa**)(OH)(CH$_3$COO)·HBr	38.55	4.78	8.97	38.48	4.84	8.97
Ni$_2$(**XIa**)(CH$_3$COO)$_2$·HBr·0.5H$_2$O	38.72	5.18	8.63	39.30	4.95	8.59
UO$_2$(**XIa**)(MeOH)	36.18	4.58	8.56	36.49	4.65	8.80
La$_2$(**XIc**)(NO$_3$)(OH)(Br)$_3$·4H$_2$O	28.21	4.00	6.88	27.69	4.11	7.53
La$_2$(**XId**)(NO$_3$)(OH)(Br)$_3$·1H$_2$O	28.59	3.72	8.33	29.27	3.85	7.69
La$_2$(**XIe**)(Br)$_3$(NO$_3$)$_2$·4H$_2$O	27.11	3.72	8.03	27.09	3.94	8.42
La$_2$(**XIh**)(Br)(NO$_3$)(OH)$_3$·H$_2$O	31.65	4.14	8.15	31.70	4.32	8.09
H-XII·2HBr·0.5H$_2$O·0.5MeOH	34.37	5.60	10.33	34.21	5.56	10.30

2.2.2. *Preparation of **H$_2$-IIa**, **H$_2$-IIb** and **H$_2$-IIh***

An acetonitrile solution (50 ml) of 2,6-diformyl-4-chlorophenol (2 mmol), gently warmed, was reacted with the appropriate polyamine (1 mmol) in acetonitrile. The resulting orange–yellow solution was refluxed for 3 h, then allowed to stand for 1 h. The precipitate obtained was filtered off (it appears to be the symmetric macrocyclic ligand), and the solution, reduced in volume, was allowed to stand for a week (**H$_2$-IIa**) or was evaporated to dryness to form a residue. This was treated with chloroform (**H$_2$-IIb**) or diethyl ether

(**H_2-IIh**) and stirred until a yellow solid was formed. This was filtered off, washed respectively with chloroform or diethyl ether and dried in vacuo.

2.2.3. *Preparation of Ln(**I**)·nS (Ln = La^{3+}, Gd^{3+}, Dy^{3+}; S = H_2O, dmf, CH_3CN; n = 0–1.5)*

An acetonitrile solution (50 ml) of 2,6-diformyl-4-chlorophenol (3 mmol) was reacted with tris(2-aminoethylamine) (1 mmol) in acetonitrile. To the resulting orange solution $LnCl_3 \cdot 8H_2O$ (1 mmol) in acetonitrile/dimethylformamide (30 ml) and triethylamine (3 mmol) in acetonitrile (30 ml) were added. The solution was refluxed for 4 h. The yellow precipitate obtained was filtered off, washed with acetonitrile and dried in vacuo.

Recrystallization from an acetonitrile/dimethylformamide solution gave crystals of La(**I**)(dmf), suitable for an X-ray investigation.

2.2.4. *Preparation of La(**H_2-II**)(NO_3)$_3$ (**H_2-II** ranging from **H_2-IIb** to **H_2-IIh**)*

To the yellow acetonitrile solution (50 ml) of 2,6-diformyl-4-chlorophenol (2 mmol), the appropriate polyamine (1 mmol) in acetonitrile (20 ml) was added dropwise. The resulting dark yellow solution was reacted with $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) in acetonitrile (20 ml). The solution was refluxed for 3 h, then allowed to stand for 3 h. The precipitate was filtered off, washed with acetonitrile and dried in vacuo.

For La(**H_2-IIg**)(NO_3)$_3$, the acetonitrile solution was evaporated to dryness and the residue treated with $CHCl_3$. The orange–red precipitate was collected by filtration, washed with $CHCl_3$ and dried in vacuo.

2.2.5. *Preparation of Ni(**IIa**) Mn(**IIa**)(OH), UO_2(**IIa**)(H_2O), UO_2(**H-IIa**)(NO_3) and UO_2(**H_2-IIa**)(NO_3)$_2$*

Ethylenediamine (1 mmol) in acetonitrile (10 ml) was added to a warm CH_3CN solution (50 ml) of 2,6-diformyl-4-chlorophenol (2 mmol). To the resulting yellow solution the appropriate metal acetate (1 mmol) in dimethylformamide (10 ml) (for nickel(II) or manganese(II)) or in acetonitrile (10 ml) (for uranyl(VI)) was added. The solution was refluxed for 2 h, then allowed to stand for 3 h. The precipitate was collected by filtration, washed with acetonitrile and dried in vacuo.

For the preparation of the uranyl(VI) complex $UO_2(NO_3)_2 \cdot 6H_2O$ or $UO_2Cl_2 \cdot 6H_2O$ can also be used; moreover two equivalents of base (i.e. LiOH or NEt_3) must be used. By a similar procedure but employing only one equivalent and $UO_2(NO_3)_2 \cdot 6H_2O$ the uranyl complex UO_2(**H-IIa**)(NO_3)$_2$ has been synthesized; when no base is used, UO_2(**H_2-IIa**)(NO_3)$_2$ may be recovered.

2.2.6. *Preparation of UO_2(**II′a**)(MeOH)*

A methanolic solution (10 ml) of the uranyl salt $UO_2X_2 \cdot nH_2O$ ($X = CH_3COO^-$, NO_3^-, Cl^-; $n = 2–6$) (1 mmol) was added to a methanolic solution (50 ml) of 2,6-diformyl-4-chlorophenol (2 mmol). To the resulting red solution a methanolic solution (30 ml) of LiOH (2 mmol) and ethylenediamine (1 mmol) were added in succession. The red solution was refluxed for 4 h, then allowed to stand overnight. The orange–red precipitate obtained was filtered off, washed with methanol and dried in vacuo.

When 1 mmol of LiOH is used and $UO_2(NO_3)_2 \cdot 6H_2O$ is the starting salt, [UO_2(**H-II′a**)(CH_3OH)](NO_3) is obtained, when no base is employed, the final product is UO_2(**H_2-II′a**)(NO_3)$_2$. The mother liquor separates the additional acetal-formyl complex UO_2(**H-II″a**)(NO_3).

2.3. *Tridimensional ligands and related complexes*

2.3.1. *Preparation of **H_3-IV** and **H_3-V***

To a methanolic solution (50 ml) of 3-methoxy-2-hydroxybenzaldehyde or 3-ethoxy-2-hydroxybenzaldehyde (3 mmol), tris(2-aminoethyl)amine (1 mmol) in methanol (30 ml) was added dropwise. The resulting yellow solution was refluxed for 2 h, allowed to stand for 1 h, then filtered. The solution was evaporated to dryness under reduced pressure. For **H_3-IV** the yellow oil obtained became a yellow solid on standing overnight. It was treated with a methanol/diethyl ether solution, filtered off and dried in vacuo. For **H_3-V** the yellow oil obtained was washed with petroleum ether (it is soluble in all the common organic solvents) and dried in vacuo.

2.3.2. *Preparation of La(**III**)*

An ethanol/dimethylformamide solution (70 ml) of La(**I**) (1 mmol) was reacted with 2-(aminomethyl)-12-crown-4 (3 mmol) in ethanol (30 ml). The solution was refluxed for 4 h. The precipitate was eliminated by filtration and the solution was evaporated to dryness under reduced pressure. The residue was dissolved in chloroform and precipitated with diethyl ether. The precipitate was filtered off, washed with chloroform and dried in vacuo.

2.3.3. *Preparation of Ln(**IV**)·nH_2O and Ln(**V**)·nH_2O (Ln = La^{3+}, Gd^{3+}; n = 1–2)*

A methanolic solution (50 ml) of tris(2-aminoethyl)amine (1 mmol) was added to 3-methoxy-2-hydroxybenzaldehyde or 3-ethoxy-2-hydroxybenzaldehyde (3 mmol) in methanol (50 ml). To the resulting yellow solution $LnCl_3 \cdot 7H_2O$ or $Ln(NO_3)_3 \cdot 6H_2O$ (1 mmol) and NaOH (3 mmol) in methanol (50 ml) were added in succession. The solution was stirred at room temperature for 1 h and under reflux for 1 h, then evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$ and the solution clarified by filtration. The resulting solution was evaporated to dryness and the residue was washed with diethyl ether and dried in vacuo.

2.3.4. *Preparation of* $Ln(\mathbf{H_3\text{-}IV})(X)_3 \cdot nH_2O$ *and* $Ln(\mathbf{H_2\text{-}V})(X)_3 \cdot nH_2O$ ($Ln = La^{3+}$, Gd^{3+} $X = NO_3^{6-}$, Cl^-; $n = 1$–5)

To a yellow methanolic solution (50 ml) containing tris(2-aminoethyl)amine (1 mmol) and 3-methoxy-2-hydroxybenzaldehyde or 3-ethoxy-2-hydroxybenzaldehyde (3 mmol), $LnCl_3 \cdot 7H_2O$ or $Ln(NO_3)_3 \cdot 6H_2O$ (1 mmol) in methanol (50 ml) was added dropwise. The solution was stirred for 1 h and refluxed for 1 h, then reduced in volume. The precipitate obtained by addition of diethyl ether was collected by filtration, washed with chloroform and diethyl ether and dried in vacuo.

2.3.5. *Preparation of* $La(\mathbf{VI}) \cdot 0.5NaBr \cdot 2H_2O \cdot MeOH$

A methanolic solution (30 ml) of tris(2-aminoethyl)amine (0.33 mmol) was added dropwise to the solution obtained by addition of NaOH (3 mmol) to a methanolic suspension (50 ml) of **H-B**$\cdot$2HBr (1 mmol); then $LaCl_3 \cdot 7H_2O$ (0.33 mmol) was added and the yellow solution was refluxed for 5 h. The solution obtained was clarified by filtration and evaporated to dryness under reduced pressure. The residue was treated with chloroform. The precipitated was eliminated by filtration and the solution was evaporated to dryness under reduced pressure. The yellow solid was dried in vacuo.

2.4. *Planar ligands containing crown-ethers moieties and related complexes*

2.4.1. *Preparation of* $\mathbf{H_2\text{-}VIIb}$ ($n = 4$)

An acetonitrile solution (10 ml) of 2-aminoethyl-12-crown-4 (2 mmol) was added to a yellow acetonitrile solution (50 ml) of $\mathbf{H_2\text{-}IIb}$ (1 mmol). The solution was refluxed for 3 h, then evaporated to dryness. The residue, treated with diethyl ether, separated an oil. The solution was eliminated and the oil was washed three times with diethyl ether and dried in vacuo.

2.4.2. *Preparation of* $\mathbf{H_2\text{-}VIIh}$ ($n = 4$)

A chloroform solution (50 ml) of the acyclic ligand $\mathbf{H_2\text{-}IIh}$ (1 mmol) was reacted with an excess of 2-aminomethyl-12-crown-4 (3 mmol). The solution was refluxed for 4 h then reduced in volume. By addition of an ethanol/diethyl ether solution a brown precipitate was obtained. It was collected by filtration, washed with diethyl ether and dried in vacuo.

2.4.3. *Preparation of* $\mathbf{H_2\text{-}VIII} \cdot H_2O$

0.5 mmol of 2-(aminomethyl)-15-crown-5 in methanol (30 ml) was added to a stirred solution of $\mathbf{H_2\text{-}A}$ (0.25 mmol) in methanol (50 ml). The yellow solution was refluxed for 6 h, then evaporated to dryness under reduced pressure. The dark yellow oil obtained was treated with diethyl ether. The solution was clarified by filtration, stirred and slowly evaporated. The yellow solid obtained was filtered, washed with diethyl ether and dried in vacuo.

2.4.4. *Preparation of* $M(\mathbf{VIIa})$ ($M = Ni^{2+}$, Mn^{2+}) ($n = 4$)

A dimethylformamide solution (30 ml) of the acyclic complex $M(\mathbf{IIa})$ (1 mmol) was reacted under reflux (3 h) with 2-(aminomethyl)-12-crown-4. The solution was evaporated to dryness and the residue was dissolved in chloroform (for the nickel complex) or in methanol (for the manganese complex) and clarified by filtration. The precipitate, obtained by addition of diethyl ether, was filtered off, washed with diethyl ether and dried in vacuo.

2.4.5. *Preparation of* $UO_2(\mathbf{VIIa})(H_2O)$ ($n = 5$)

To a chloroform or acetonitrile solution (50 ml) of $UO_2(\mathbf{IIa})(H_2O)$ or of $UO_2(\mathbf{II'a})(MeOH)$ (1 mmol), a chloroform solution (20 ml) of 2-(aminomethyl)-15-crown-5 (2 mmol) was added. The solution was refluxed for 3 h then evaporated to dryness under reduced pressure. The residue was dissolved in methanol and clarified by filtration. The addition of diethyl ether gave rise to an orange precipitate. It was filtered off, washed with diethyl ether and dried in vacuo.

2.4.6. *Preparation of* $La(\mathbf{H_2\text{-}VIIc})(NO_3)_3$, $La(\mathbf{H_2\text{-}VIId})(NO_3)_3$ *and* $La(\mathbf{H_2\text{-}VIIh})(NO_3)_3$ ($n = 4$)

The appropriate acyclic lanthanum complex ($La(\mathbf{H_2\text{-}IIc})(NO_3)_3$, $La(\mathbf{H_2\text{-}IId})(NO_3)_3$ or $La(\mathbf{H_2\text{-}IIh})(NO_3)_3$ (1 mmol) in dimethylformamide (30 ml) was reacted with 2-aminomethyl-12-crown-4 (or 2-aminomethyl-15-crown-5) (2 mmol). The resulting solution was refluxed for 4 h, then evaporated to dryness under reduced pressure. The residue, treated with chloroform, formed a precipitate for $La(\mathbf{H_2\text{-}VIIc})(NO_3)_3$ or a solution for $La(\mathbf{H_2\text{-}VIId})(NO_3)_3$ or $La(\mathbf{H_2\text{-}VIIh})(NO_3)_3$. The precipitate was filtered off, washed with chloroform and dried in vacuo. The solution, clarified by filtration, separated a precipitate by addition of diethyl ether for $La(\mathbf{H_2\text{-}VIId})(NO_3)_3$ or of diethyl ether/ethanol for $La(\mathbf{H_2\text{-}VIh})(NO_3)_3$. The precipitate was filtered off, washed with diethyl ether and dried in vacuo. The complexes $La(\mathbf{H_2\text{-}VIIb})(NO_3)_3$ and $La(\mathbf{H_2\text{-}VIIh})(NO_3)_3$ may be obtained by reaction of the preformed ligands $\mathbf{H_2\text{-}VIIb}$ and $\mathbf{H_2\text{-}VIIh}$ with $La(NO_3)_3 \cdot 6H_2O$ in a 1:1 molar ratio.

2.4.7. *Preparation of* $UO_2(\mathbf{VIII}) \cdot 2NaNO_3 \cdot 2CHCl_3 \cdot 3MeOH$

To $\mathbf{H_2\text{-}VIII} \cdot H_2O$ (0.08 mmol) in methanol (100 ml), NaOH (0.18 mmol) and $UO_2(NO_3)_2 \cdot 6H_2O$ (0.08 mmol) were added in succession. The solution was refluxed for 6 h, then evaporated to dryness under reduced pressure. The residue was treated with chloroform, the precipitate was eliminated by filtration and the orange solution was partially evaporated under reduced pressure. The orange precipitate obtained by addition of diethyl ether was filtered, washed with diethyl ether and dried in vacuo.

2.5. Planar ligands containing polyamine moieties and related complexes

2.5.1. Preparation of $\mathbf{H_2}$**-XIa**$\cdot 4HBr\cdot 2.5MeOH$

A methanolic solution (30 ml) of ethylenediamine (0.6 mmol) was added dropwise to a stirred suspension of **H-B**$\cdot$2HBr (1.2 mmol) in methanol (50 ml). The suspension was refluxed for 5 h and the yellow solution obtained was evaporated to dryness under reduced pressure to give a yellow solid. It was washed with diethyl ether and dried in vacuo.

2.5.2. Preparation of **H-XII**$\cdot 2HBr\cdot 0.5H_2O\cdot 0.5MeOH$

A methanolic solution (30 ml) of ethylenediamine (1 mmol) was added dropwise to a stirred suspension of **H-B**$\cdot$2HBr (1 mmol) in methanol (50 ml). The suspension was refluxed for 5 h and the yellow solution obtained was evaporated to dryness under reduced pressure. The yellow solid was treated with chloroform and the precipitate was filtered, washed with chloroform and dried in vacuo.

2.5.3. Preparation of UO_2*(X)*$\cdot MeOH$

To a methanol solution (50 ml) of **H-C** (2 mmol), ethylenediamine (1 mmol) and $UO_2(CH_3COO)_2\cdot 2H_2O$ (1 mmol) in methanol (50 ml) were added. The orange–red solution was stirred for 15 min under reflux; then LiOH (2 mmol) was added and the solution maintained under reflux for 2.5 h, then allowed to stand overnight. The orange–red solid obtained was collected by filtration, washed with methanol and dried in vacuo.

2.5.4. Preparation of UO_2*(***XIa***)*$\cdot MeOH$

To a methanol solution (50 ml) of $\mathbf{H_2}$**-XIa**$\cdot$4HBr$\cdot$2.5MeOH (0.125 mmol), an excess of NaOH (1 mmol) and $UO_2(NO_3)_2\cdot 6H_2O$ (0.125 mmol) were added in succession. The orange solution was refluxed for 5 h, then filtered and evaporated to dryness under reduced pressure. The residue was treated with chloroform; the solid obtained was eliminated by filtration while the orange solution was slowly reduced to a small volume. The precipitate was eliminated by filtration and the solution was treated with diethyl ether. The solid was filtered off and the solution was slowly evaporated to give an orange residue. It was washed with diethyl ether and dried in vacuo.

2.5.5. Preparation of Na_2*(***XIa***)*$\cdot MeOH\cdot 2CHCl_3$

To a yellow methanolic solution (50 ml) of **H-B**$\cdot$2HBr (2 mmol) and NaOH (6 mmol), a methanolic solution (30 ml) of ethylenediamine (1 mmol) was added dropwise. The resulting solution was refluxed for 6 h, then filtered and evaporated to dryness under reduced pressure. The residue was treated with chloroform, the solid was eliminated and the solution was partially evaporated under reduced pressure. The yellow precipitate obtained by addition of diethyl ether was filtered, washed with diethyl ether and dried in vacuo.

*2.5.6. Preparation of Cu(***XIa***)*$\cdot HBr\cdot H_2O\cdot MeOH$

To a methanolic solution (50 ml) of **H-B**$\cdot$2HBr (2 mmol) and NaOH (6 mmol), ethylenediamine (1 mmol) and $Cu(CH_3COO)_2\cdot H_2O$ (1 mmol) in methanol (30 ml) were added in succession. The dark green solution obtained was refluxed for 5 h, then filtered and evaporated to dryness under reduced pressure. The residue was treated with chloroform. The solid was eliminated by filtration and the green solution was evaporated to dryness under reduced pressure to give a green solid which was dried in vacuo.

2.5.7. Preparation of Cu_2*(***XIa***)*$(CH_3COO)(OH)\cdot HBr$

A methanolic solution (30 ml) of ethylenediamine (1 mmol) was added dropwise to a methanolic suspension (50 ml) of **H-B**$\cdot$2HBr (2 mmol) and NaOH (6 mmol); then $Cu(CH_3COO)_2\cdot H_2O$ (2 mmol) was added. The dark green solution was refluxed for 6 h and evaporated to dryness under reduced pressure. The residue was treated with chloroform. The precipitate was eliminated by filtration and the solution was evaporated to dryness under reduced pressure to give a green solid which was dried in vacuo.

2.5.8. Preparation of Ni_2*(***XIa***)*$(CH_3COO)_2\cdot HBr\cdot 0.5H_2O$

To a stirred methanolic suspension (50 ml) of **H-B**$\cdot$2HBr (2 mmol), a methanolic solution (30 ml) of ethylenediamine (1 mmol), NaOH (6 mmol) and $Ni(CH_3COO)_2\cdot 4H_2O$ (1 mmol) were added in succession. The clear orange solution obtained was refluxed for 5 h, then evaporated to dryness under reduced pressure. The dark orange solid obtained was treated with chloroform. The residue was eliminated by filtration and the solution was evaporated to dryness under reduced pressure. The brown solid obtained was dried in vacuo.

2.5.9. Preparation of La_2*(***XIe***)*$(Br)_2(NO_3)_2\cdot 4H_2O$

To a methanolic solution (50 ml) of **H-B**$\cdot$2HBr (2 mmol) and NaOH (6 mmol), diethylenetriamine (1 mmol) in methanol (30 ml) and $La(NO_3)_3\cdot 6H_2O$ (1 mmol) were added dropwise. The yellow solution obtained was refluxed for 6 h, then it was evaporated to dryness under reduced pressure and the residue was treated with chloroform. The solid obtained was eliminated by filtration and the solution, partially reduced in volume, was treated with diethyl ether. The obtained precipitate was filtered, washed with diethyl ether and treated with a chloroform/diethyl ether solution (1:2). The obtained precipitate was filtered, washed with diethyl ether and dried in vacuo.

2.5.10. Preparation of La_2*(***XIc***)*$(Br)_2(NO_3)(OH)\cdot 4H_2O$

Bis-2-aminoethyl-sulfide (1 mmol) in methanol (30 ml) was added dropwise to a methanolic solution (50 ml) of **H-B**$\cdot$2HBr (2 mmol) and NaOH (6.5 mmol). The resulting solution, after the addition of $La(NO_3)_3\cdot 6H_2O$ (1 mmol), was refluxed for 5 h, then evaporated to dryness under reduced pressure. The residue was treated with chloroform and the chloroformic solution was partially evaporated under reduced pressure. The solid obtained by addition of diethyl ether was filtered, washed with diethyl ether, dissolved in chloroform and treated again with diethyl ether until incipient precipitation, then allowed to stand for 2 h. The yellow solution was purified by filtration, evaporated to dryness under reduced pressure and the solid obtained was dried in vacuo.

2.5.11. *Preparation of $La_2(XIh)(Br)(NO_3)(OH)_2 \cdot H_2O$*

To a methanolic solution (50 ml) of **H-B**·2HBr (2 mmol) and NaOH (6 mmol), 1,8-diamino-3,6-dioxaoctane (1 mmol) in methanol (30 ml) and $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) were added. The yellow solution obtained was refluxed for 6 h, then clarified by filtration and evaporated to dryness under reduced pressure. The yellow solid was treated with chloroform, the precipitate was eliminated by filtration and the solution treated with diethyl ether. The precipitate obtained was filtered, washed with diethyl ether, treated with chloroform (10 ml) and precipitated with diethyl ether. The solid was filtered, washed with diethyl ether and dried in vacuo.

2.5.12. *Preparation of $La_2(XId)(Br)_2(NO_3)(OH) \cdot H_2O$*

To a methanolic solution (50 ml) of **H-B**·2HBr (2 mmol) and NaOH (6 mmol), 1,5-diamino-3-oxapentane (1 mmol) in methanol (30 ml) was added dropwise. The yellow solution obtained by the subsequent addition of $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) was refluxed for 5 h, then allowed to stand for 2 h. The precipitate was eliminated by filtration. The solution was evaporated to dryness under reduced pressure and the residue obtained was treated with chloroform. The solution was clarified by filtration and partially evaporated under reduced pressure. The precipitate obtained by addition of diethyl ether was filtered, washed with diethyl ether, dissolved in chloroform (10 ml) and treated with diethyl ether (30 ml). The solution was filtered and the solid obtained by filtration was washed with diethyl ether and dried in vacuo.

2.6. *X-ray crystallography*

Data were collected on a Philips PW1100 automatic diffractometer (FEBO System), using Mo Kα radiation ($\lambda = 0.7107$ Å) and θ–2θ scan method. Cell dimensions were determined by least-squares refinement of 25 medium angle settings. The crystals were stable under irradiation. The structure was solved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. All hydrogen atoms were introduced to calculated positions with fixed isotropic temperature factors ($U_{iso} = 0.08$ Å^2). Anisotropy was introduced for all non-hydrogen atoms. An analysis of the final distribution of $w(\Delta F)^2$ did not suggest any appropriate weighting scheme.

Crystal and intensity data and selected bond distances and angles are reported in Tables 2 and 3. All calculations were carried out on a DIGITAL ALPHA-AXP 300 computer using programs SHELX-76 and SHELX-86 [17,18]. See also Section 5.

Table 2
Crystal and intensity data for $[La(I)(dmf)]_2$

Formula	$C_{66}H_{60}N_{10}O_{14}Cl_6La_2$
FW	1707.8
Colour, shape, size	yellow, prisms, 0.20 × 0.29 × 0.21
$F(000)$	1708 (electrons)
Cell parameters	
a (Å)	12.590(4)
b (Å)	14.277(5)
c (Å)	19.710(5)
β (°)	95.45(4)
Cell volume, V (Å^3)	3527(1)
Calc. density D_c (g cm^{-3})	1.61
Molecules per cell, Z	2 (the asymmetric unit is half of the molecule)
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Absorption, μ(Mo Kα) (cm^{-1})	15.2
Wavelength, λ(Mo Kα) (Å)	0.7107
Scan method	$\theta/2\theta$
Scan speed (° min^{-1})	2
Data collected, 2θ limits (°)	5395, 5–52
Data with $I > 3\sigma(I)$	5138
No. parameters refined (obs. per parameter)	412 (12.5)
Discrepancy factor R	0.032
GOF	2.03
Corrections applied	Lp, absorption [26]
Transmission coefficient	0.980–0.867
Highest shift/e.s.d.	0.044
Highest map residual (e Å^{-3})	0.599

2.7. *Physico-chemical measurements*

IR spectra were recorded as KBr pellets on a Mattson FTIR 3000 spectrometer. ^1H and ^{13}C NMR spectra were recorded at 200.132 MHz on a Bruker AC200 spectrometer equipped with an Aspect 3000 computer at room temperature. Some of the signals were assigned by the spin decoupling technique. All the samples examined were dissolved in hot dmso-d_6 or $CDCl_3$ used also as internal references. The homogeneity of the heteropolynuclear samples was checked by using a Philips XL40 model scanning electron microscopy equipped with an EDAX PV99 X-ray energy dispersive spectrometer. Metal ratios were determined by energy dispersive X-ray spectrometry (EDX) [19]. The solvent content (H_2O or MeOH) was evaluated by thermal analysis curves using a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml min^{-1}; heating rate 5°C min^{-1}) and in air under the same conditions. Neutral alumina (Carlo Erba product) was used as reference material.

All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG analytical Ltd.) operating in electron impact (EI) (70 eV, 200 mA, ion source temperature 200°C) and fast atom bombardment (FAB) (8 KeV Xe atom bombarding a thioglycerol/acetic solution of the sample) conditions [20].

Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instru-

Table 3
Selected bond distances (Å) and bond angles (°) (standard deviation in parentheses)

La(1)–O(2)	2.421(3)	La(1)–N(1)	2.783(4)
La(1)–N(2)	2.867(3)	La(1)–N(3)	2.692(3)
La(1)–O(3)	2.408(3)	La(1)–N(4)	2.701(3)
La(1)–O(5)	2.465(3)	La(1)–O(7)	2.547(4)
Cl(1)–C(4)	1.750(3)	Cl(2)–C(16)	1.748(3)
Cl(3)–C(26)	1.753(3)	O(1)–C(1)	1.217(7)
C(1)–C(2)	1.473(6)	O(2)–C(7)	1.339(4)
C(3)–C(4)	1.395(4)	C(3)–C(2)	1.395(4)
C(4)–C(5)	1.395(4)	C(5)–C(6)	1.395(4)
C(6)–C(7)	1.395(4)	C(6)–C(8)	1.471(5)
C(7)–C(2)	1.395(4)	C(8)–N(1)	1.268(6)
N(1)–C(9)	1.482(6)	C(9)–C(10)	1.513(7)
C(10)–N(2)	1.497(6)	N(2)–C(11)	1.499(6)
N(2)–C(21)	1.481(6)	C(11)–C(12)	1.521(7)
C(12)–N(3)	1.464(5)	N(3)–C(13)	1.277(6)
C(13)–C(14)	1.462(5)	C(20)–O(4)	1.219(6)
C(18)–C(20)	1.454(6)	C(22)–N(4)	1.479(5)
C(19)–O(3)	1.337(4)	C(23)–C(24)	1.480(5)
C(21)–C(22)	1.507(6)	C(28)–C(30)	1.459(5)
N(4)–C(23)	1.278(5)	C(29)–O(5)	1.336(4)
C(30)–O(6)	1.224(5)	O(7)–C(31)	1.242(7)
C(31)–N(5)	1.325(8)	N(5)–C(32)	1.42(1)
N(5)–C(33)	1.46(1)		
O(5)–La(1)–O(7)	73.2(1)	N(4)–La(1)–O(7)	78.7(1)
N(4)–La(1)–O(5)	68.3(1)	O(3)–La(1)–O(7)	145.7(1)
O(3)–La(1)–O(5)	74.8(1)	O(3)–La(1)–N(4)	78.3(1)
N(3)–La(1)–O(7)	131.1(1)	N(3)–La(1)–O(5)	132.5(1)
N(3)–La(1)–N(4)	77.2(1)	N(3)–La(1)–O(3)	66.8(1)
N(2)–La(1)–O(7)	69.8(1)	N(2)–La(1)–O(5)	124.1(1)
N(2)–La(1)–N(4)	64.5(1)	N(2)–La(1)–O(3)	120.8(1)
N(2)–La(1)–N(3)	61.4(1)	N(1)–La(1)–O(7)	76.2(1)
N(1)–La(1)–O(5)	142.8(1)	N(1)–La(1)–N(4)	125.2(1)
N(1)–La(1)–O(3)	138.1(1)	N(1)–La(1)–N(3)	84.0(1)
N(1)–La(1)–N(2)	61.3(1)	O(2)–La(1)–O(7)	126.2(1)
O(2)–La(1)–O(5)	116.9(1)	O(2)–La(1)–N(4)	155.1(1)
O(2)–La(1)–O(3)	79.9(1)	O(2)–La(1)–N(3)	83.2(1)
O(2)–La(1)–N(2)	118.6(1)	O(2)–La(1)–N(1)	66.9(1)
La(1)–N(1)–C(8)	126.1(3)	La(1)–N(3)–C(12)	110.1(3)
La(1)–N(1)–C(9)	119.6(3)	La(1)–N(3)–C(13)	132.5(3)
La(1)–N(2)–C(10)	106.8(2)	La(1)–N(4)–C(22)	116.1(3)
La(1)–N(2)–C(11)	113.4(3)	La(1)–N(4)–C(23)	128.2(3)
La(1)–N(2)–C(21)	106.3(3)	La(1)–O(2)–C(7)	132.5(2)
La(1)–O(3)–C(19)	142.1(2)	La(1)–O(5)–C(29)	136.1(2)
La(1)–O(7)–C(31)	124.6(4)	C(8)–N(1)–C(9)	114.0(4)
C(10)–N(2)–C(21)	108.3(3)	C(11)–N(2)–C(21)	111.3(3)
C(10)–N(2)–C(11)	110.5(3)	C(12)–N(3)–C(13)	117.4(4)
C(31)–N(5)–C(33)	119.0(7)	C(22)–N(4)–C(23)	115.5(4)
C(32)–N(5)–C(33)	120.0(6)	C(31)–N(5)–C(32)	121.0(6)

ments) being calibrated with $HgCo(NCS)_4$ [21]. Diamagnetic corrections were performed [22].

3. Results and discussion

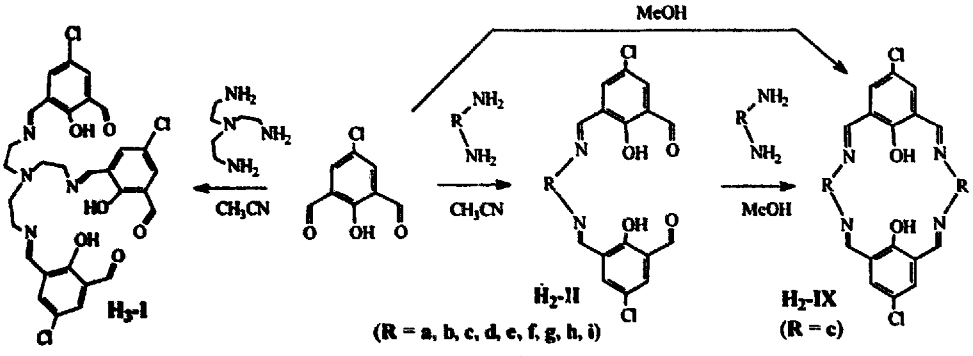
3.1. *Formyl precursors and related complexes*

In order to synthesize the functionalized tridimensional or planar compounds derived from 2,6-diformyl-4-chlorophenol, the appropriate formyl precursors $\mathbf{H_3}$-**I** and $\mathbf{H_2}$-**II** have been prepared by self condensation (Scheme 2) and/or the related complexes by template procedure.

In particular the condensation reaction in anhydrous acetonitrile of 2,6-diformyl-4-chlorophenol with tris-(2-aminoethyl)amine in a 3:1 molar ratio gives rise to the corresponding tridimensional acyclic ligand with three aldehydic functionalities ($\mathbf{H_3}$-**I**). The same reaction in methanol affords a compound where the aldehydic functionalities have been transformed into the acetal groups ($\mathbf{H_3}$-**I′**). A similar behavior was found when 2,6-diformyl-4-chlorophenol was reacted, under the same experimental conditions, with the diamines H_2N–R–NH_2 in a 2:1 molar ratio: again the diformyl compounds $\mathbf{H_2}$-**II** are obtained in anhydrous acetonitrile and the diacetal analogues $\mathbf{H_2}$-**II′** in methanol. It must be noted that the experimental conditions employed in the preparation of the acyclic ligands may favor also the formation, as by-products, of the corresponding symmetric macrocycles $\mathbf{H_2}$-**IX** (Scheme 2), identical to the genuine tetraimine macrocycles synthesized by direct self-condensation of the appropriate precursors [4,5,7,10–12]. These [2+2] macrocycles are yellow or orange–yellow solids, moderately soluble in the common organic solvents. The absence of IR bands due to $\nu(C=O)$ or $\nu(NH_2)$ and the contemporary presence of strong peaks in the range 1645–1620 cm^{-1} due to $\nu(C=N)$ confirm that the cyclic condensation reaction occurs with the consequent formation of the tetramine symmetric macrocycle. FAB or EI mass spectrometric investigations confirm these data evidencing the parent peak at the appropriate *m/z* value.

The different solubility of the acyclic and cyclic ligands or their separation by chromatography allows pure products to be obtained. The acyclic ligands have been characterized by IR, NMR and mass spectrometry. Thus the ^{1}H NMR spectrum of $\mathbf{H_3}$-**I** in dmso-d_6 does not evidence the presence of acetal groups while a peak at 8.43 ppm due to the aldehydic protons CH=O is clearly detected. The formyl compound shows additional peaks at 8.43 (CH=N), 7.61 and 7.26 (aromatic protons), 3.73 (CH_2 protons bonded with the iminic groups) and 2.92 (CH_2 protons bonded to the tertiary amine nitrogen) ppm. Moreover the IR spectrum of $\mathbf{H_3}$-**I** agrees with the NMR data showing strong bands at 1672 and 1641 cm^{-1} due respectively to $\nu(C=O)$ and $\nu(C=N)$.

In order to overcome the formation of by-products and to increase the yield, the acyclic compounds have been obtained as their complexes by the formyl and amine precursors in the presence of a suitable metal ion as templating agent. Reaction of $\mathbf{H_3}$-**I** with $LnCl_3 \cdot nH_2O$ (Ln = La^{3+}, Gd^{3+}, Dy^{3+}; n = 6, 7, 8) in the presence of NEt_3, afforded Ln(**I**) yellow solids in good yields. The same complexes were obtained when the formyl and the amine precursors were reacted in acetonitrile, using the appropriate lanthanide(III) chloride hydrate as templating agent. When recrystallized from a dimethylformamide/acetonitrile solution, the complexes Ln(**I**)(dmf) were obtained (Ln = La, Gd, Y). The homogeneity of the samples and the correct chlorine:metal 3:1 ratio were ascertained also by scanning electron microscopy (SEM) and EDX analyses.



Scheme 2.

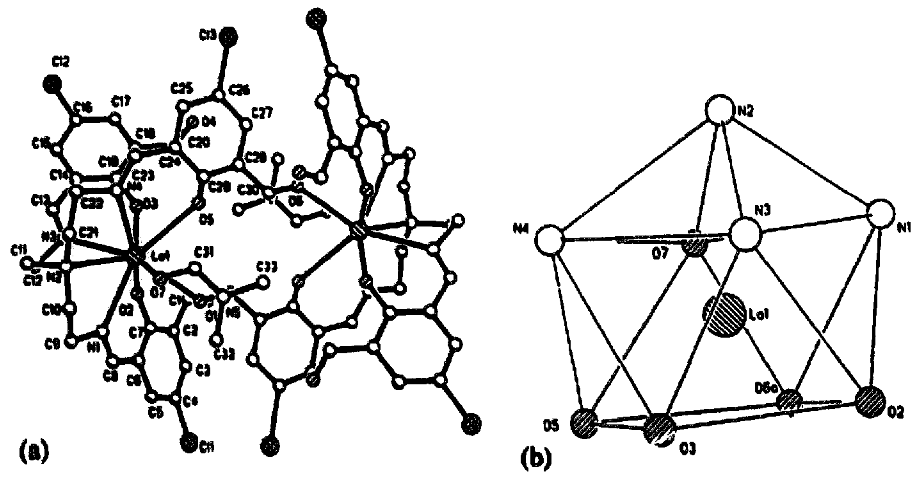


Fig. 1. View of the structure (a) and metal core (b) of [La(I)(dmf)]$_2$ with numbering scheme adopted.

The IR spectrum of the complex Ln(**I**) shows ν(C=O) at 1668–1658 cm^{-1} and ν(C=N) at 1638–1632 cm^{-1}; both absorptions are lower that those in the free ligand **H$_3$-I**.

^{1}H NMR data for La(**I**)(dmf): in dmso-d$_6$, peaks at 10.31 (s; CH=O), 8.08 (s; CH=N), 7.95, 7.35 (dd; arom.), 3.71 (t; C=NCH$_2$), 2.99 (t; NCH$_2$) ppm. ^{13}C NMR spectra (dmso-d$_6$): 189.45 (HC=O), 163.23 (HC=N), 162.27 (Car. –C=O), 140.27 (Car. –C=N), 129.51 (Car. –OH), 114.74 (Car. –Cl), 128.27, 126.42 (Car. –H), 60.00, 59.63 (=NCH$_2$, –NCH$_2$) ppm.

The ^{1}H and ^{13}C NMR spectra of the diamagnetic La(III) complex La(**I**) in solution are consistent with the occurrence of a highly symmetrical structure. In particular only one signal is observed for the three aldehyde functionalities which appears slightly shifted with respect to the position displayed by the free ligand. Interestingly the aldehyde absorption is split into two signals (2:1) in the ^{13}C CPMAS (cross polarization magic angle spinning) NMR spectrum of a solid sample. Thus this observation appears as evidence for the occurrence of different structures in solution and in solid state and prompted us to determine the X-ray structure of this complex.

Suitable crystals of La(**I**)(dmf) were obtained by recrystallization from a dimethylformamide/acetonitrile solution of the yellow reaction products La(**I**)·1.5H$_2$O. This complex is a dimeric entity and can be formulated as [La(**I**)(dmf)]$_2$. The molecular structure of [La(**I**)dmf]$_2$ is shown in Fig. 1 together with the adopted numbering scheme. The molecule is centrosymmetric and the inversion center is between the two lanthanum(III) ions that are 8.24 Å apart.

Each lanthanum ion is nine-coordinated and the coordination polyhedron can be described as a square monocapped antiprism. One square base comprises four oxygen atoms: three (O2, O3, O5) are phenolic oxygens, the fourth (O6a) is an aldeydic one generated, by symmetry, from (O6) and represents the bridge to the second part of the molecule. The second square base consists of three iminic nitrogens (N1, N3, N4) and one oxygen atom (O7) derived from the coordinated dimethylformamide molecule.

The two mean planes of the two square bases are almost parallel forming a dihedral angle of 3.5°, where the maximum deviation of the defining atoms is ±0.092 Å. The lanthanum ion is 1.343 Å above the first plane and 1.171 Å below the second one.

The aminic N(2) atom is the cap of the polyhedron and represents the longest coordination bond (2.867(3) Å) to the central ion. The other distances to the metal vary between 2.408(3) and 2.547(4) Å for the La–O and between 2.692(3) and 2.867(3) Å for the La–N bonds. The C=N iminic bonds are well localized being comprised between 1.268(6) and 1.278(5) Å; the C–O(phenolic) bonds are identical (between 1.336(4) and 1.339(4) Å); the free C=O(aldehydic) are a little shorter (C(1)–O(1), 1.217(7);

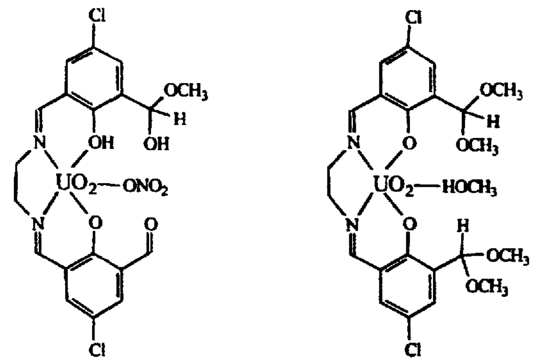
C(20)–O(4), 1.219(6) Å) than that involved in the coordination to lanthanum ion (C(30)–O(6), 1.224(5) Å).

The ligand, coordinating the lanthanum ion, forms two types of chelating rings; the five-membered rings, with N···N donor atoms, form N–La–N angles of between 61.3 and 64.5° while the six-membered rings with NO donor atoms form larger N–La–O angles of between 66.8 and 68.3°. No intermolecular interactions are present; thus the dinuclear units appear to be isolated in the crystal.

An X-ray powder diffraction investigation of the gadolinium(III) complex [Gd(**I**)(dmf)]$_2$ reveals it is isostructural with the lanthanum(III) analogue. Owing to the extremely low solubility of the complex in H_2O it was impossible to measure the relaxivity of the paramagnetic complex although the extensive broadening of the residual HDO water in DMF solution strongly indicates a direct interaction with the metal center. Likely, the two coordination sites occupied in the solid state respectively by a formylic and the amidic oxygens are substituted by H_2O in solution. The complex is then monomeric in DMF solution and might be formulated as Gd(**I**)(H_2O)$_2$. This observation is encouraging in view of the development of new, stable and water soluble compounds for NMR imaging based on the podand **H$_3$-I** ligand.

The preformed acyclic planar ligands **H$_2$-II** react with d- or f-metal ions to form the relative mononuclear complexes; the same complexes have been obtained by condensation of the formyl and amine precursors in a 2:1 molar ratio in the presence of the appropriate metal salt. The formation of these metal compounds shows the same solvent- dependent behavior: complexes containing the formyl or the acetal groups have been obtained respectively in acetonitrile or methanol. Moreover the addition of the appropriate amount of base determines, especially for the complexes derived from f-metal ions, the absence of counter anions. As examples the uranyl(VI) and lanthanum(III) complexes, UO_2(**H$_2$-II'a**)-(NO_3)$_2$ or UO_2(**H$_2$-IIa**)(NO_3)$_2$ and La(**H$_2$-II'd**)(NO_3)$_3$ or La(**H$_2$-IId**)(NO_3)$_3$, were obtained by reaction of 2,6-diformyl-4-chlorophenol respectively with ethylenediamine or 1,5-diamino-3-oxapentane in the presence of $UO_2(NO_3)_2\cdot 6H_2O$ or $La(NO_3)_3\cdot 6H_2O$ respectively in methanol or acetonitrile, while UO_2(**II"a**)(MeOH) or La(**II'd**)(OH)(S)$_n$ (S = H_2O or MeOH) were prepared when the same reactions were carried out in the presence of the appropriate amount of base.

Moreover, when a 1:1 uranyl:LiOH ratio was used, the complexes UO_2(**II'a**)(MeOH) and UO_2(**H-II"a**)(NO_3) were recovered. For UO_2(**H-II"a**)(NO_3) the structure given in Fig. 2 may be suggested on the basis of the ^1H NMR spectrum in dmso-d_6, which shows a singlet due to phenolic protons at 11.01, a singlet at 9.61 ppm due to CHO, two doublets at 9.54 and 9.48 ppm (CH=N protons coupled with aromatic protons), two multiplets at 8.09 and 7.39 ppm (aromatic protons), a peak at 5.04 ppm (OH of the acetal group), 4.60–4.49 ppm (CH_2CH_2) and 3.38 ppm (OCH_3 of the acetal group).



UO_2(**H-IIa"**)(NO_3) UO_2(**IIa'**)(CH_3OH)

Fig. 2. The proposed structure of UO_2(**II'a**)(MeOH) and UO_2(**H-II"a**)-(NO_3).

The IR spectrum shows two strong bands at 1655 and 1626 cm^{-1} respectively attributed to ν(C=O) and ν(C=N); the presence of the uranyl(VI) group is confirmed by a strong band at 905 cm^{-1} due to antisymmetric stretching ν_3(O–U–O); finally there are bands at 1453 and 1332 cm^{-1} possibly due to the nitrate group which coordinates as monodentate. An additional band at 1384 cm^{-1}, due to an ionic nitrate, may be caused by the reaction of the complex with KBr used for preparing IR samples.

A second precipitate, formulated as UO_2(**II'a**)(MeOH), obtained from the mother liquor, possibly has the structure with both formyl groups in the acetal form as shown in Fig. 2. In the ^1H NMR spectrum of this compound the signals at 11.01 and 9.61 ppm have disappeared while only one peak due to CH=N is present at 9.48 ppm. Also the aromatic signals are simplified, owing to the higher symmetry of the compound (a doublet of doublets at 7.72 and 7.60 ppm). The signal at 6.61 ppm is due to the acetal CH while the signal due to the acetalic OH is not present. Moreover the peak at 3.38 ppm is attributed to the CH_3 groups while the peak at 4.49 ppm is due to the CH_2CH_2 group. Finally the presence of a methanol molecule, possibly filling the fifth equatorial coordination site about the uranyl(VI) ion, is evidenced by a doublet at 3.17 ppm and by a quartet at 4.12 ppm. Its IR spectrum shows only a strong band at 1625 cm^{-1} due to ν(C=N) and a strong band at 902 cm^{-1} due to ν_3(O–U–O).

The high yield and purity of the complexes obtained from CH_3CN are due to the considerably enhanced solubility of the reactants in comparison with the related complexes. Thus the complexes La(**H$_2$-II**)(NO_3)$_3$ (**H$_2$-IIb**, **H$_2$-IIc**, **H$_2$-IId**, **H$_2$-IIe**, **H$_2$-IIf**, **H$_2$-IIg** and **H$_2$-IIh**) precipitate from the reaction solution as pure yellow or orange solids. SEM and EDX investigations confirm the homogeneity of these samples and the correct 1:2 lanthanum:chloride ratio. NMR and IR investigations strongly support the structure where the ligand coordinates to the central metal ion in the diformyl form. For example the ^1H NMR spectrum of La(**H$_2$-IIb**)(NO_3)$_3$ in dmso-d_6 shows signals at 14.78 (HO-phenolic), 10.18 (CH=O), 8.52 (CH=N), a doublet of doublets at 7.62–7.52

(aromatic protons) and 3.76 (methylenic protons) ppm. The IR spectrum agrees with the NMR data: the two strong bands at 1669 and 1653 cm^{-1} are due respectively to ν(C=O) and ν(C=N). It is to be noted that the NMR spectrum of La(**H_2-IIb**)$(NO_3)_3$ in dmso-d_6 progressively changes becoming in a few minutes identical to that of the free ligand showing that dimethyl sulfoxide is able to substitute the Schiff base in the coordination to the central metal ion when the Schiff base behaves as a neutral ligand. When it acts as a deprotonated ligand, it is firmly bound to the central metal ion and cannot be substituted by strong coordinating solvents.

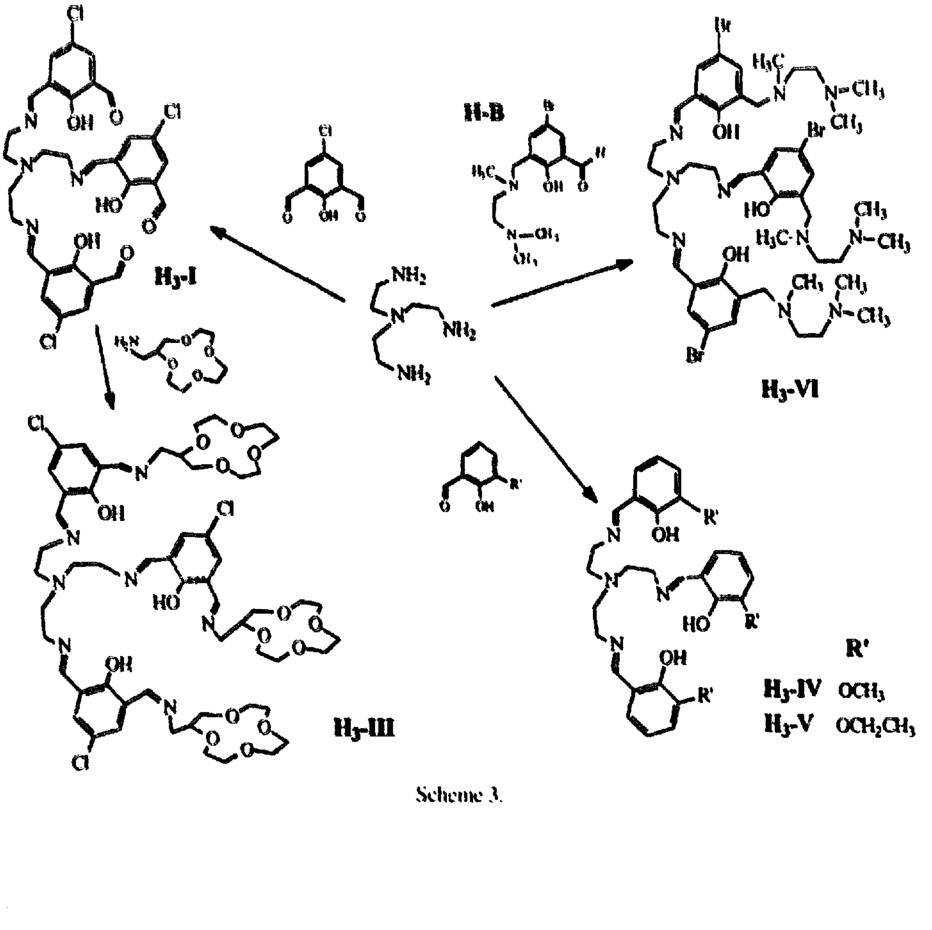
3.2. Functionalized tridimensional ligands and related complexes

The tridimensional functionalized ligands and/or their complexes have been prepared according to Scheme 3.

In particular the mononuclear lanthanide complex La(**III**) was synthesized by condensation of La(**I**) and 2-(methylamine)-12-crown-4: elemental analyses, SEM and EDX studies show the complex is homogeneous with a lanthanum:chloride ratio 1:3. In the IR spectrum the bands due to ν(C=O) are absent, indicating that the starting complex or partially condensed species are not present, while strong bands due to the iminic and crown-ether groups are clearly detectable: ν(C=N) lies at 1632 cm^{-1}, ν(C–O) at 1138 and 1106 cm^{-1}, $\nu(CH_2)$ at 2907 cm^{-1}. Accordingly the ^{1}H NMR spectra confirm the structure proposed for La(**III**) showing peaks at 8.55–8.06 (CH=N), 7.61-7.22 (aromatic protons), 3.70–3.36 and 2.92–2.63 (CH_2 protons) ppm. In addition the peaks at 10.31 ppm, due to the CH=O protons, clearly detectable in the ^{1}H NMR spectrum of La(**I**), cannot be observed in the spectrum of the functionalized lanthanum complex La(**III**).

Also it is interesting to note that the ^{13}C NMR spectrum of this complex in dmso-d_6 evidences peaks at 164–168 ppm, due to the iminic carbons, and the disappearance of peaks at 189 ppm due to the formyl carbons. Moreover the peaks due to the aromatic carbons lie at 136, 129 and 114 ppm as in the triformyl precursor La(**I**). Finally peaks due to the triamine carbon framework can be detected at 57–59 ppm and, more diagnostic, the peaks at 69–76 ppm completely absent in La(**I**), assigned to the carbons of the crown-ether moiety, are clearly detectable.

Lanthanide(III) salts react with the tridimensional pod and ligands **H_3-IV** or **H_3-V** to form Ln(**IV**)·$n$$H_2O$ or Ln(**V**)·$n$$H_2O$ (n = 1, 2) in the presence of the appropriate amount of base and Ln(**H_3-IV**)$(X)_3$·$n$$H_2O$ (X = Cl$^-$, NO_3^-; n = 1–5) in the absence of base. In Ln(**IV**)·$n$$H_2O$ or Ln(**V**)·$n$$H_2O$ the metal ion occupies the inner N_3O_3 coordination chamber; in Ln(**H_3-IV**)$(X)_3$ or Ln(**H_3-V**)$(X)_3$ only some oxygen atoms of the external O_3O_3 chamber are involved in the coordination, the other coordination sites about the metal ion being filled by the anions X [23]. The complexes Ln(**IV**)·$n$$H_2O$ and Ln(**V**)·$n$$H_2O$, when mixed with alkali salts or as a consequence of their preparation procedure, encapsulate these salts into the free outer O_3O_3 chamber and compounds formulable as Ln(**IV**)(H_2O)·nMX (n = 0.7–1; M = Na, K; X = Cl, NO_3). SEM and EDX investigations confirm the consequent formation of these het-



Scheme 3.

eropolynuclear species, evidencing the homogeneity of the samples, the presence of both metal ions and the Ln:M ratio. Ln(**H_2-IV**)(NO_3)$_3$ and especially Ln(**H_2-V**)(NO_3)$_3$ are not stable in alcoholic solution and suffer a partial hydrolysis when redissolved in these solvents; on the contrary, they are stable in air for a long period of time. Moreover in coordinating solvents, such as dimethyl sulfoxide, the demetallation reaction Ln(**H_3L**)(X)$_3$ + *n*dmso → Ln(dmso)$_n$(X)$_3$ + **H_3L** occurs; the ^{1}H NMR spectra of La(**H_3-IV**)(NO_3)$_3$ or La(**H_3-V**)(NO_3)$_3$ in dmso-d_6 clearly show the peaks due to the free ligands at 8.02 (**H_3-IV**) or 8.24 (**H_3-V**) ppm attributed to the iminic protons, peaks at 6.94–6.24 (**H_3-IV**) or 6.95–6.60 (**H_3-V**) ppm due to aromatic protons, and aliphatic ones at 3.80–2.84 (**H_3-IV**) or 3.99–1.29 (**H_3-V**) ppm. In these complexes the ligand behaves as a crown-ether-like ligand and cannot compete with strong coordinating solvents such as dimethyl sulfoxide; thus it is released in this solvent. These data also evidence that the Schiff base can be recovered from the reaction solution; thus these ligands coordinate to the lanthanide(III) ion without suffering hydrolysis. The hydrolysis occurs only when the complexes are treated with alcohol in recrystallization processes.

Finally La(VI) was prepared by template reaction of tris(2-aminoethyl)amine and 4-bromo-2-[2-(dimethylamino-ethyl)methylamino]-methyl-6-formyl-phenol in a 3:1 molar ratio, and in the presence of La(NO_3)$_3$·6H_2O and NaOH as a base (Scheme 3). The elemental analyses and SEM and EDX studies evidence the presence of $NaNO_3$ with a lanthanum:sodium:bromine ratio of 1:0.5:3.5). In the IR spectrum a strong absorption peak at 1390 cm^{-1} is diagnostic of an ionic nitrate group while the strong band at 1629 cm^{-1} is due to ν(C=N).

3.3. Planar ligands containing crown-ether moieties and related complexes

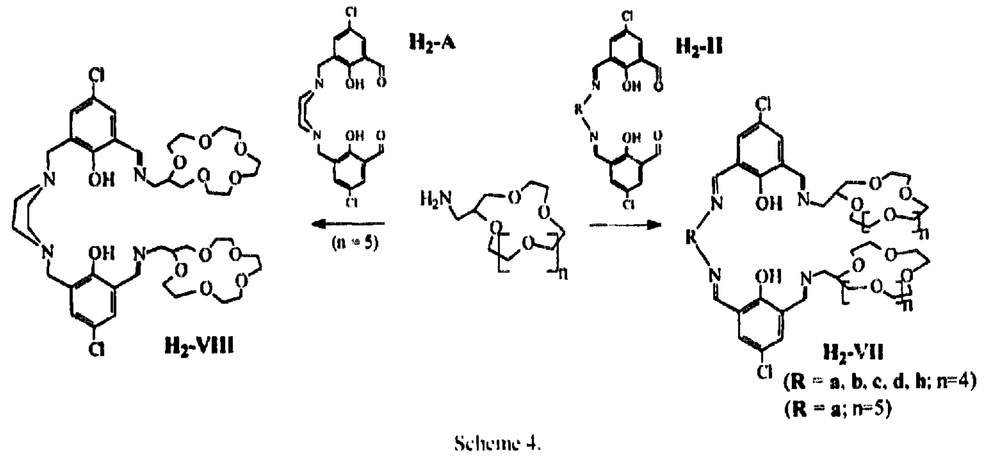
By a step by step procedure it is possible to obtain the functionalized planar acyclic ligands **H_2-VII** or **H_2-VIII** and the related complexes containing crown-ether moieties (Scheme 4).

Thus, by condensation of the acyclic ligands **H_2-IIb** and **H_2-IIh** with 2-aminomethyl-12-crown-4 in $CHCl_3$ or CH_3CN, the Schiff bases **H_2-VIIb** and **H_2-VIIh** were obtained after several purification processes and in very low yield respectively as an oil or a solid.

For **H_2-VIIb** FAB mass spectrometry shows the parent peak at 728 *m*/*z* while the ^{1}H NMR spectrum in dmso-d_6 shows peaks at 14.33 (phenolic –OH), 8.47 (CH=N protons), 7.52–7.12 (aromatic protons) and 3.85–3.54 (CH_2 aliphatic protons) ppm.

The formation of **H_2-VIIh** was also confirmed by its FAB mass spectrum, which evidences the parent peak at 856 *m*/*z*, and by its ^{1}H NMR spectrum in dmso-d_6, which shows peaks at 14.06 (OH– phenolic), 8.47 and 8.41 (CH=N iminic protons), 7.52 (aromatic protons) and 3.74–3.61 (CH_2 aliphatic) ppm. In addition IR spectroscopy evidences the absence of bands attributable to ν(C=O) and the presence of strong bands at 1640 and 1656 cm^{-1} due to ν(C=N), at 2910–2870 cm^{-1} due to ν(CH_2) and at 1131–1096 cm^{-1} due to ν(C–O). The difficulty in obtaining these compounds in high yield, by an apparently simple condensation reaction between the acyclic ligands and the appropriate primary amine bearing crown-ether moiety, is due to side reactions, such as the formation of symmetric cyclic ligands. We have tried to overcome these problems through the condensation of the acyclic ligands with a primary amine in the presence of metal salts as templating agents. Unfortunately we have observed that the hoped increased yield does not occur in a significant way; again side reactions take place. One side reaction is represented by the formation of symmetric cyclic complexes. Moreover these systems are polynucleating in nature and consequently may secure two (or more) metal ions into their coordination moiety. The consequence of these reactions is the contemporary formation of different species, quite often difficult to separate and a drastic decrease in the yield of the designed compound.

The acyclic ligands **H_2-II** and the related complexes, containing the formyl groups in the acetal form, may also undergo, under appropriate experimental conditions, further condensation reactions giving rise to functionalized com-



Scheme 4.

pounds. Thus UO_2(**II'a**)(MeOH) or UO_2(**H-II'a**)(NO_3), when reacted with 2-aminoethyl-15-crown-5, form the complexes UO_2(**VIIa**)(MeOH) ($n=5$) or UO_2(**H-VIIa**)(NO_3) ($n=5$). The IR spectra of these complexes show bands at ~ 1625 (ν(C=N)), 2902–2867 (ν(CH) aliphatic) and ~ 1117 (ν(C–O)) cm^{-1}. The IR spectra evidence also a strong and sharp band respectively at 895 and 902 cm^{-1} due to the antisymmetric ν_3(O–U–O). The ^1H NMR spectra in dmso-d_6 shows peaks at 9.12 (CH=N protons), 7.30 (aromatic protons), 4.58 (CH_2 of the ethylenediamine moiety) and 3.63 (CH_2 of the crown moiety) ppm.

As already reported [2,4,6], the uranyl(VI) ion easily forms Schiff base complexes with a pentagonal bipyramidal geometry; this is favored by the need of the linear UO_2^{2+} group to be equatorially surrounded by five donor atoms. The pentacoordination in the prepared complexes is reached by the coordination of a solvent or an anion (i.e. NO_3^-) molecule. This prevents the contemporary coordination of a second UO_2^{2+} group into the second adjacent N_2O_2 chamber. On the contrary the different coordination geometry of the lanthanide(III) ions allows the formation of dinuclear complexes in addition to the mononuclear analogues.

When the acyclic complex La(**H_2-IIc**)$(NO_3)_3$ is used as formyl precursor, the product obtained by its condensation with 2-(aminomethyl)-12-crown-4 contains an S:Cl:La ratio 1:1.5:1 as evidenced by SEM and EDX investigations; it is a mixture of the symmetric cyclic complex La(**H_2-IX**)$(NO_3)_3$ (X = S) and of the designed functionalized complex La(**H_2-VIIc**)$(NO_3)_3$ as evidenced by ^1H NMR spectra in dmso-d_6. This shows two different sets of signals: at 8.62–8.58 (CH=N), 7.69 (aromatic protons), 3.73–3.46 and 2.28 (CH_2 aliphatic) ppm due to the acyclic functionalized complex and at 8.44 (CH=N) and 7.45 (aromatic protons) ppm due to the cyclic complex (the signals due to the aliphatic CH_2 are covered by the peaks due to the aliphatic CH_2 of the functionalized compound). The IR spectrum shows the presence of ν(C=N) at 1632 and 1658, ν(CH) at 2992 and ν(C–O) 1071 cm^{-1}, while the band at 1667 (ν(C=O)) cm^{-1} present in the acyclic formyl precursors, cannot be detected. The dinuclear complex La_2(**VIIh**)$(NO_3)_4$ ($n=4$) was recovered when La(**H_2-IIh**)$(NO_3)_3$ was used as formyl precursor: SEM and EDX investigations indicate an La:Cl ratio of 1:1. The IR spectrum shows bands at 1640 and 1658 (ν(C=N)), 1071 (ν(C–O)) and 2962 (ν(CH_2)) cm^{-1}, while ^1H NMR shows signals at 8.60–8.51 (CH=N), 7.71–7.62 (aromatic protons) and 3.67–3.46 (CH_2 protons) ppm.

The formyl manganese complex Mn(**IIa**)(OH), obtained by the reaction in acetonitrile of **H_2-IIa** with manganese(II) acetate or by template reaction, was used as precursor in the formation of Mn(**VIIa**)(OH) ($n=4$) by condensation with 2-methylamino-12-crown-4. The experimental procedure used does not prevent an oxidation of the manganese as suggested by the magnetic moment found (4.20 BM). The subsequent condensation of Mn(**IIa**)(OH) with 2-methylamino-12-crown-4 gives rise to the mononuclear Mn(**VIIa**)(OH) complex which appears, on the basis of IR, SEM and EDX investigations, to be contaminated by a small amount of the related dinuclear manganese(III) complex. The IR spectrum evidences ν(C=N) at 1645 and 1653 cm^{-1} and strong bands at 1132, 1108 (ν(C=O)) and 2919, 2865 ν(CH_2) cm^{-1} due to the crown-ether moieties.

The designed mononuclear complex Ni(**VIIa**) ($n=4$) was obtained when Ni(**IIa**) was reacted with 2-methylamine-12-crown-4: SEM and EDX analyses show the complex is homogeneous with a correct 2:1 chloride:nickel ratio. The complex is diamagnetic indicating a square planar coordination about the central metal ion and the ^1H NMR spectrum parallels the proposed structure evidencing peaks at 8.64–7.80 (CH=N protons), 6.72–6.98 (aromatic protons) and 3.7 (CH_2 protons) ppm. The IR spectrum, very similar to that of the manganese analogue, shows ν(C=N) at 1625, ν(CH_2) at 2920 and ν(C–O) at 1096 cm^{-1}.

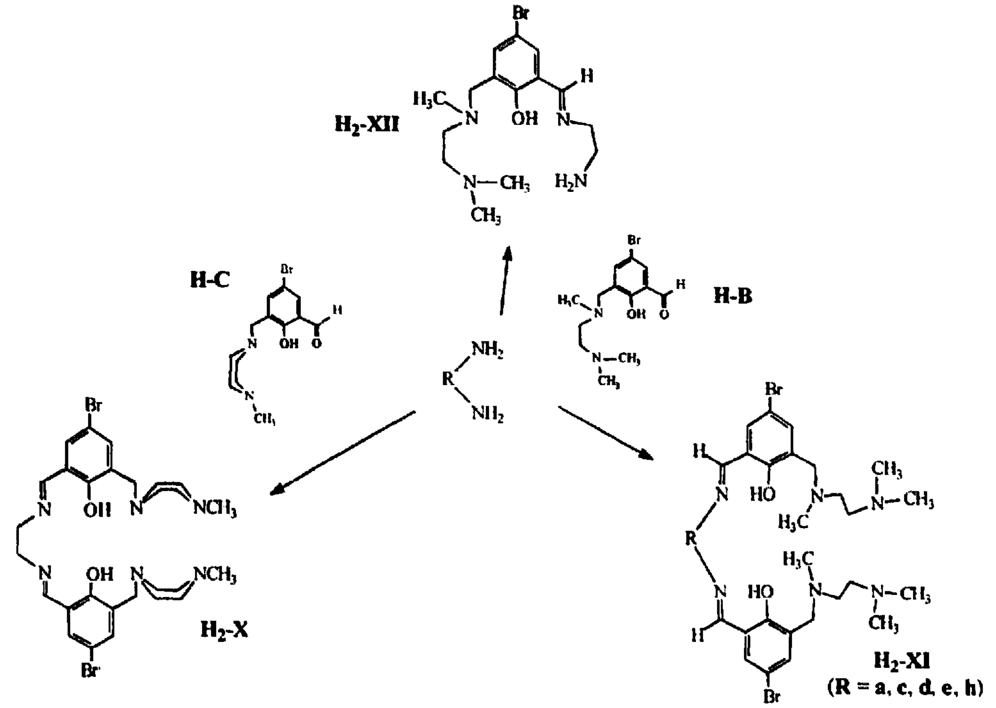
H_2-A contains two formyl groups which engage in a condensation reaction with 2-aminomethyl-15-crown-5, forming **H_2·VIII**·H_2O as a yellow powder. In this ligand a strong IR band at 1653 cm^{-1} (ν(C=N)) substitutes that at 1675 cm^{-1} (ν(C=O)) for **H_2-A**; moreover very strong bands at 2869 (ν(CH_2)) and 1121 (ν(C–O–C)) cm^{-1} give further evidence that the condensation reaction occurs. Finally an FAB mass spectrometric investigation evidences the parent peak at the appropriate m/z value.

H_2-VIII·H_2O reacts with uranyl(VI) nitrate in a chloroform/methanol solution and in the presence of NaOH to give rise to the complex UO_2(**VIII**)·$2NaNO_3$·$2CHCl_3$·3MeOH; the same complex has been obtained by condensation of **H_2-A** and 2-methylamine-15-crown-5 in the presence of $UO_2(NO_3)_2 \cdot 6H_2O$ as templating agent and NaOH. In this complex the presence of Na^+ was ascertained by SEM and EDX investigations, which evidence a 1:2:2 uranium:sodium:chlorine ratio. Moreover IR spectroscopy shows the presence of nitrate groups (a strong peak at 1384 cm^{-1}) and of an almost linear O–U–O group (ν_3 at 881 cm^{-1}). The strong peaks at 1653 and 1635 cm^{-1} are attributed to ν(C=N) of uncoordinated and coordinated azomethynic groups.

3.4. Planar ligands containing polyamine moieties and related complexes

The ligands **H_2-X** and **H_2-XI** represent a different synthetic approach to the preparation of functionalized systems. They and/or their complexes containing d- or f-metal ions were prepared by reaction of **H-B** or **H-C** with the appropriate polyamine according to Scheme 5. The starting formyl precursors **H-B** and **H-C** were obtained by Mannich reaction of 4-chloro-2-formylphenol or 4-bromo-2-formylphenol respectively with *N,N,N'*-trimethylethylenediamine or *N*-methylpiperazine in the presence of paraformaldehyde [14].

UO_2(**X**)(MeOH) was obtained as an orange–red solid by reaction in methanol of 4-bromo-2-[2-methylaminodiethyl)amino]-methyl-6-formylphenol (**H-C**) and ethylenediamine in the presence of $UO_2(NO_3)_2 \cdot 6H_2O$ and LiOH as



Scheme 5.

a base. The strong ν_3(O–U–O) IR band at 903 cm^{-1} evidences the presence of the uranyl group: in addition a band at 1632 cm^{-1} (ν(C=N)) is indicative that the condensation reaction with the consequent formation of the Schiff base occurs. Moreover the ^1H NMR in $CDCl_3$ evidences that a molecule of methanol is present and fills the fifth equatorial pentacoordination about the uranyl(VI) ion.

4-Bromo-2-[2-(dimethylaminoethyl)methylamino]-methyl-6-formyl-phenol (**H-B**) forms, by condensation with a series of polyamines or by template procedure, the corresponding Schiff bases **H_2-XI**: thus it reacts in a 2:1 molar ratio with ethylenediamine in methanol to form **H_2-XIa**·4HBr·2.5MeOH (while with an excess of ethylenediamine it forms **H-XII**).

H_2-XIa·4HBr·2.5MeOH shows ν(C=N) at 1658 cm^{-1} which is shifted to 1662 cm^{-1} in the disodium complex Na_2(**XIa**)·MeOH·2$CHCl_3$; in addition the IR bands at 2659 and 2472 cm^{-1}, attributable to ν(NH···Br), disappear in the disodium complex.

H_2-XIa·4HBr·2.5MeOH, when reacted with $UO_2(NO_3)_2\cdot 6H_2O$, in a 1:1 molar ratio and in the presence of NaOH, forms the orange–red mononuclear complex UO_2(**XIa**)(MeOH). Again strong bands at 1627 and 891 cm^{-1} respectively due to ν(C=N) and ν_3(O–U–O) can be detected in the IR spectrum.

The mononuclear Cu(**XIa**)·HBr·H_2O·MeOH and the dinuclear complexes Cu_2(**XIa**)(CH_3COO)(OH)·HBr and Ni_2(**XIa**)$(CH_3COO)_2$·HBr·0.5H_2O were prepared by template condensation of ethylenediamine and **HB**·2HBr in a 1:2 molar ratio and in the presence of the appropriate amount of metal acetate. The formulation of these complexes is based on the elemental analyses, including oxygen content, and on the metal:bromine ratio evaluated by SEM and EDX investigations. The presence of HBr is proposed on the basis of their IR spectra which evidence bands in the range 2820–2750 cm^{-1} attributed to N···H–Br bonds. Moreover, ν(C=N) lies at 1634 cm^{-1} in the mononuclear copper(II) complex and at 1625 and 1623 cm^{-1} in the dinuclear copper(II) and nickel(II) analogues, respectively. In addition the dinuclear copper(II) and nickel(II) complexes shows two strong absorption bands respectively at 1554 and 1437 cm^{-1} and at 1588 and 1431 cm^{-1} due to the ν_{asym}(COO) and ν_{sym}(COO) of bridging acetate groups [24].

The magnetic moment at room temperature of the mononuclear copper(II) (μ_B = 1.7 BM) and of the dinuclear copper(II) (μ_B = 1.7 BM per copper atom)) evidences that the interaction between the two paramagnetic centers is negligible. The corresponding dinuclear nickel(II) complex shows a μ_B = 3.3 BM (2.4 per nickel(II) atom).

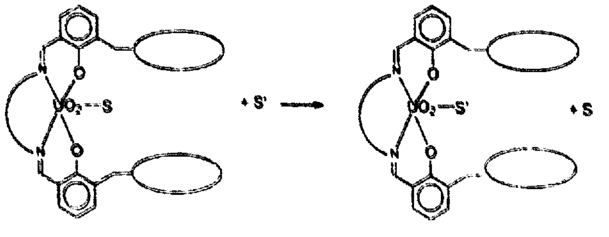
The condensation of **H-B** with $H_2N(CH_2)_2X(CH_2)_2NH_2$ (X = S, O, NCH_3) in a 2:1 molar ratio, and in the presence of $La(NO_3)_3\cdot 6H_2O$ as templating agent and of NaOH, gives rise to the corresponding dinuclear complexes La_2(**XIc**)$(Br)_2(NO_3)(OH)\cdot 4H_2O$, La_2(**XId**)$(Br)_2(NO_3)(OH)\cdot H_2O$ and La_2(**XIe**)$(Br)_2(NO_3)_2\cdot 4H_2O$. In these complexes ν(C=N) lies at 1624–1634 cm^{-1} while two bands at about 1456–1436 and 1320–1313 cm^{-1} confirm the presence of nitrate ions, possibly acting as bidentate.

By a similar synthetic procedure the template reaction **H-B** and $H_2N(CH_2)O(CH_2)_2O(CH_2)_2NH_2$, in the presence of $La(NO_3)_3\cdot 6H_2O$ and NaOH, gives rise only to the dinuclear complex La_2(**XIh**)·(Br)(NO_3)·$(OH)_2\cdot H_2O$. ν(C=N) lies at 1632 cm^{-1} while the nitrate group, possibly as bidentate, is evidenced by the peaks at 1456 and 1313 cm^{-1}; a strong peak at 3421 cm^{-1} is attributed to ν(OH). The mother liquors of all the prepared complexes deposit, on standing, the corresponding mononuclear complexes. Also for these complexes their formulation was proposed on the basis of elemental analyses, including oxygen and, where present, sulfur, and the bromine:lanthanum ratio was estimated by SEM and EDX investigations.

H-XII reacts with copper(II) acetate to form a mixture of the dinuclear Cu_2(**XII**)(CH_3COO)($Br)_2$ and of the mononuclear copper(II) complexes Cu(**XII**)(Br). They can be separated owing to their different solubility in alcoholic solution. The reduced magnetic moment for the dinuclear complex (μ_B = 1.4 BM) shows an antiferromagnetic interaction between the copper ions. The IR spectrum shows a strong peak at 1652 cm^{-1} (1648 cm^{-1} in the free ligands) due to ν(C=N) and two peaks at 1576 (ν_{asym}(COO)) and 1447 (ν_{sym}(COO)) cm^{-1} due to the acetate groups.

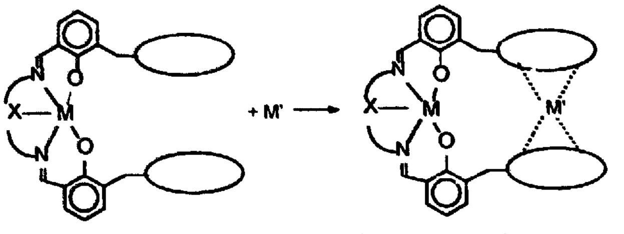
4. Conclusions

A synthetic strategy was successfully proposed for the preparation of functionalized macrocyclic and macroacyclic planar or tridimensional Schiff bases and related complexes to be used for selective recognition of neutral and/or charged molecules. These syntheses involve the preventive preparation of the acyclic compounds which must be engaged in further condensation reactions. The acyclic compounds contain formyl groups when prepared in CH_3CN but turn into the corresponding diacetals when methanol is used. The yield of the final functionalized compounds is generally low owing to the contemporary formation of symmetric cyclic species, obtained as side products. Preliminary studies on a deep comprehension of the recognition phenomena seem promising. In particular the acyclic uranyl(VI) complexes derived from **H_2-VII**, **H_2-VIII** and **H_2-X** undergo a substitution reaction of the type:



S' = Me_2SO, Ph_3PO, H_3PO_4, ecc. S = H_2O, MeOH, NO_3, Cl

showing that it is possible to design uranyl(VI) systems with enhanced selectivity toward well defined species. Moreover the complexes containing d- or f-metal ions can recognize a second metal ion or salt (i.e. Na$^+$ or $NaNO_3$), through a complexation reaction of the type:



thus acting as molecular devices for these species.

Finally a particular mention must be devoted to the lanthanide(III) complexes Gd(I) and La(III). The former complex may be considered a useful model in the preparation of contrasting agents in NMR tomography; the latter complex owing to its functionalization may be seen as a model for the design and synthesis of shift NMR reagents for the quantitative determination of sodium or potassium ions and salts. Also the podand ligand **H_3-VI** and the related lanthanide(III) complexes are promising systems capable of multiple selective recognition processes. The development of these synthetic strategies involves (i) further functionalization at the periphery of the systems, which includes hydrophilic or hydrophobic groups to enhance their solubility in particular solvents and (ii) the reduction of the less stable iminic groups CH=N to the more stable aminic analogues CH–NH. With regard to item (i) we have undertaken an investigation using calixarenes, bearing aminic or formyl groups, as precursors for the synthesis of systems of higher complexity [25]. Planar and tridimensional ligands and related d- and f-complexes have already been prepared and characterized [6]. They seem to be very promising in selective recognition and separation processes and in the preparation of molecular devices.

5. Supplementary material

Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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