Macrocyclic and macroacyclic compartmental Schiff bases: synthesis, characterization, X-ray structure and interaction with metal ions

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Abstract

Acyclic, potentially hexadentate (H_4L_A–H_4L_D) or decadentate (H_6L_E) compartmental Schiff bases have been obtained by reaction in methanol of 2,3-dihydroxybenzaldehyde and 1,2-diaminoethane, 1,2-diamino-2-methylpropane, 1,3-diamino-2,2-dimethylpropane, 1,2-diaminobenzene or tris(2-aminoethyl)amine in a 2:1 or 3:1 molecular ratios as appropriate. The reaction of 2,6-diformyl-4-Z-phenol (Z = Cl–, CH_3–) with 1,2-diaminobenzene in methanol produced the partially reduced macrocycles (H_2L_F and H_2L_G). Similarly symmetric tetraimine macrocyclic ligands have been synthesized by cyclo-condensation of the same 2,6-diformyl-4-substituted phenols and 1,5-diamino-3-azapentane (H_2L_H) or 1,4-bis(3-aminopropyl)piperazine (H_2L_I). A step by step procedure has been employed for the preparation of the asymmetric macrocycle (H_2L_L). The ligands are yellow or yellow–orange solids and have been characterized by elemental analyses, IR, ^{1}H NMR spectroscopy and electron impact (EI) or fast atom bombardment (FAB) mass spectrometry. The X-ray crystal structures of H_4L_C and H_2L_F have also been solved. Crystals of H_4L_C, grown from $CHCl_3$, are monoclinic, space group $P2_1/c$ with $a = 6.767(4)$, $b = 14.106(5)$, $c = 18.163(5)$ Å, $\beta = 91.05(4)°$ for $Z = 4$. The molecule is composed of two identical dihydroxybenzaldimine moieties connected by the carbon atom C(9). Three hydroxylic oxygens are protonated while the fourth is negatively charged. An intermolecular hydrogen system, involving the hydroxyl groups, gives rise to the formation of polymer chains parallel to *c* axis. Crystals of H_2L_F, grown from $CHCl_3$, are monoclinic, space group $P2_1/a$ with $a = 22.481(7)$, $b = 8.989(5)$, $c = 11.911(5)$ Å, $\beta = 93.28(5)°$ for $Z = 4$. The molecule shows some unexpected bond lengths and angles. Two nitrogen atoms of each molecule are iminic, the other two aminic in character. A reduction of two C=N bonds occurs during the synthetic procedures with the consequent formation of the partially reduced Schiff base. The coordination properties of the acyclic and cyclic ligands towards d and/or f metal ions have been tested, and the results are discussed in detail.

Introduction

Recently much effort has been devoted to the design and synthesis of multidentate ligands capable of coordinating selectively to particular metal ions [1–17]. The availability of a wide variety of planar or tridimensional ligands, with different donor atoms or cavities, offers the opportunity to study in detail metal ion recognition, encapsulation, transport and separation, catalytic processes, new molecular devices, etc. and many papers have been published on these topics [18–23].

Previous studies on the coordination properties of metal ions have shown that it is possible to choose the correct coordination size and/or donor set of the ligands in order to enhance selectivity. Thus it is possible to synthesize new ligands particularly suitable for d or f metal ions or for the simultaneous presence of different metal ions in a preordered geometry and/or at a well defined distance from each other. As a consequence it is now becoming feasible to obtain homo- and/or heteropolynuclear compounds which, owing to their unusual properties, can act as molecular devices [14–17, 22, 23].

In the recent past we have prepared compartmental macrocyclic and macroacyclic Schiff bases capable of securing, in close proximity, two equal or different metal ions and studied their coordinating ability toward d and f metal ions [12, 24–26].

We have expanded the range of available ligands to include the new macroacyclic and macrocyclic Schiff bases H_4L_A–H_2L_L (Scheme 1), and the present paper reports their preparation, characterization and chemical behaviour.

For the acyclic H_4L_C and the macrocyclic H_2L_F compounds the X-ray structure is reported; both compounds show some interesting and unexpected features. In particular the expected macrocyclic tetraimine under-

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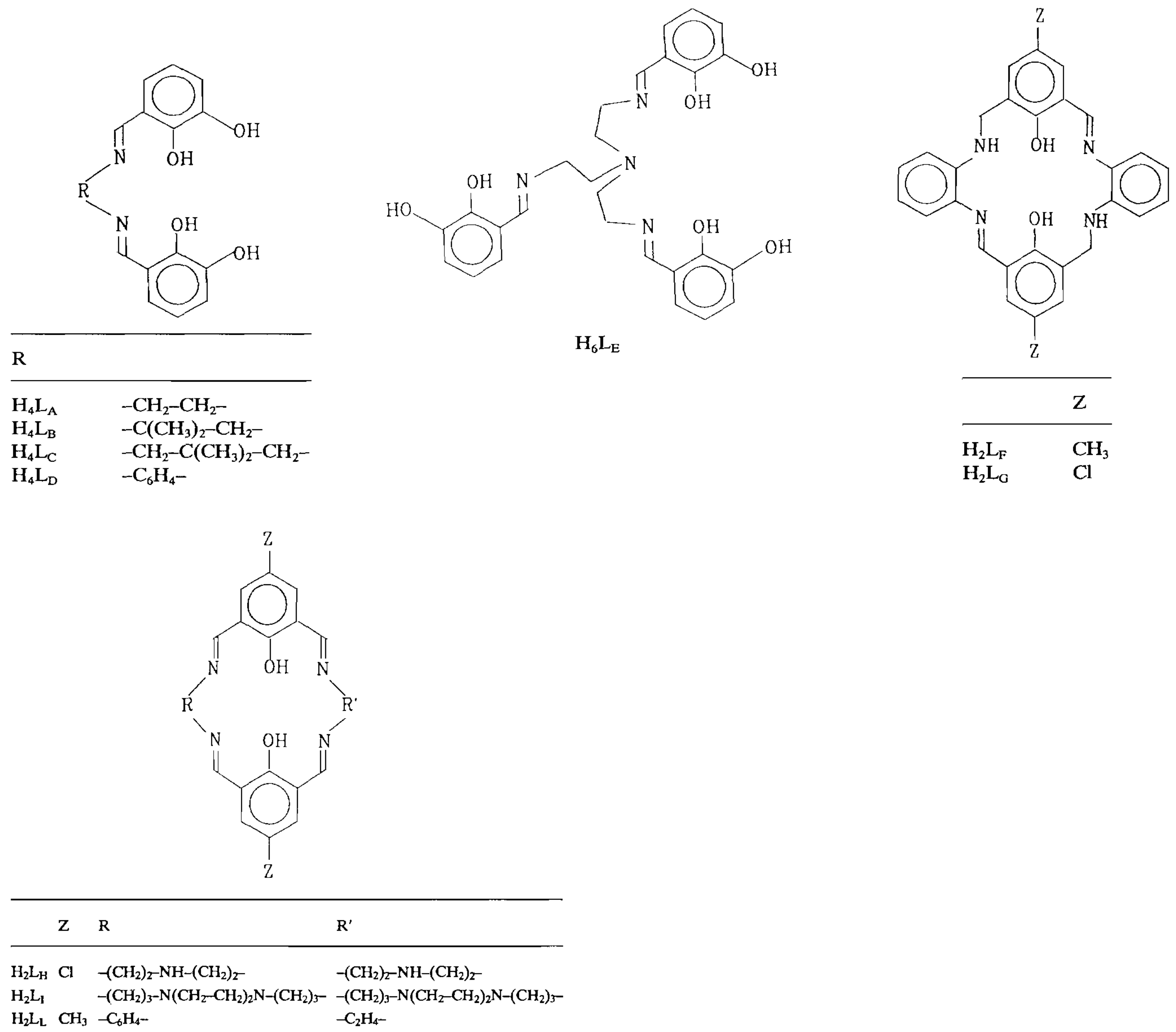


R	
H_4L_A	$-CH_2-CH_2-$
H_4L_B	$-C(CH_3)_2-CH_2-$
H_4L_C	$-CH_2-C(CH_3)_2-CH_2-$
H_4L_D	$-C_6H_4-$

	Z
H_2L_F	CH_3
H_2L_G	Cl

	Z	R	R'
H_2L_H	Cl	$-(CH_2)_2-NH-(CH_2)_2-$	$-(CH_2)_2-NH-(CH_2)_2-$
H_2L_I		$-(CH_2)_3-N(CH_2-CH_2)_2N-(CH_2)_3-$	$-(CH_2)_3-N(CH_2-CH_2)_2N-(CH_2)_3-$
H_2L_L	CH_3	$-C_6H_4-$	$-C_2H_4-$

Scheme 1. The prepared macroacyclic and macrocyclic compartmental ligands.

goes, during the synthetic procedures, a reduction of two $-HC{=}N-$ groups to $-CH_2-NH-$, giving rise to the partially reduced Schiff base H_2L_F. An analogous behaviour has been observed for H_2L_G. For both macrocycles extensive NMR investigations show that such reduction takes place during the preparation procedure and not during the recrystallization processes.

Experimental

Materials

1,2-Diaminoethane, 1,2-diamino-2-methylpropane, 1,3-diamino-2,2-dimethypropane, 1,5-diamino-3-azapentane, 1,4-bis(3-aminopropyl)piperazine, tris(2-aminoethyl)amine, 2,3-dihydroxybenzaldehyde, the solvents and the salts are commercial products, used without further purification, while 1,2-diaminobenzene was recrystallized from chloroform three times before use.

2,6-Diformyl-4-Z-phenols ($Z=Cl$, CH_3) were prepared according to literature procedures [27]; their purity was checked by elemental analysis, IR and NMR spectroscopy. Mononuclear and heterodinuclear complexes with the macroacyclic ligands (H_4L_A–H_4L_C) were prepared, as already reported [28], following a procedure similar to that used for the complexes derived from H_4L_D. The macroacyclic complex [*N*,*N*′-phenylene-bis-(3-formyl-5-chlorosalicylideneiminato]copper(II) was prepared according to the literature [7].

The elemental analyses of the ligands and complexes prepared are reported in Table 1.

TABLE 1. Elemental analysis of the prepared ligands and complexes

Compound	Calc. (%)			Found (%)		
	C	H	N	C	H	N
$H_4L_A \cdot 0.5MeOH$	62.65	5.74	8.86	62.98	5.75	9.08
H_4L_B	65.84	6.14	8.53	65.29	6.31	8.44
H_4L_C	66.65	6.48	8.18	66.39	6.62	8.21
H_4L_D	68.69	4.62	8.04	68.90	4.89	8.05
H_6L_E	64.02	5.97	11.06	63.84	6.39	11.70
H_2L_F	76.26	5.11	11.85	76.48	5.02	11.42
$H_2L_G \cdot 0.5MeOH$	64.66	3.80	10.58	64.61	4.38	10.77
H_2L_H	55.38	5.76	15.12	55.24	5.55	15.39
$(H_6L_I)(ClO_4)_4$	39.47	4.59	10.22	39.04	5.31	9.91
H_2L_L	73.57	5.69	13.20	73.42	5.82	13.42
$Cu(H_2L_D) \cdot 0.5H_2O$	57.35	3.60	6.68	57.17	3.53	6.65
$Ni(H_2L_D) \cdot 0.5H_2O$	58.44	3.59	6.81	58.47	3.61	6.78
$CuLa(H_2L_D)(NO_3)_3$	30.53	2.30	8.90	30.98	2.32	9.00
$Cu(L_G) \cdot 2H_2O$	59.82	5.01	10.73	59.64	4.70	12.58
$Cu_2(L_G)(Ac)_2 \cdot 4H_2O$	48.71	4.90	7.57	48.33	4.30	7.10
$CuNi(L_G)(Ac)_2 \cdot 4H_2O$	47.86	5.08	7.44	48.98	4.68	6.34
$Cu_2La(L_G)(NO_3)_2(OH)$	46.54	4.12	10.43	46.59	3.84	10.12
$LiLa(L_F)_2 \cdot 5H_2O$	61.23	4.62	9.52	61.64	4.35	9.02
$[La(L_F)(NO_3)]_n$	53.51	3.59	10.40	53.82	3.46	10.22

Preparation of H_4L_A–H_4L_D

To a methanolic solution (50 ml) of 2,3-dihydroxybenzaldehyde (2 mmol), the appropriate diamine (1 mmol) in methanol (30 ml) was added. The yellow solution was refluxed for 2 h. The solvent was partially evaporated under reduced pressure and the yellow (H_4L_A–H_4L_C) or red (H_4L_D) precipitate collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of H_6L_E

To a methanolic solution (50 ml) of 2,3-dihydroxybenzaldehyde (3 mmol) tris(2-aminoethyl)amine (1 mmol) in methanol (50 ml) was added. The resulting yellow solution was refluxed for 2 h. The solvent was then partially removed and the yellow precipitate was filtered, washed with methanol and dried *in vacuo*.

Preparation of the symmetric, partially reduced, macrocyclic ligands H_2L_F *and* H_2L_G

To 2,6-diformyl-4-Z-phenol (Z = Cl, CH_3) (2 mmol), 1,2-diaminobenzene (2 mmol) was added in methanol (100 ml). The solution was refluxed for 2 h, reduced in volume and the orange–red precipitate filtered, washed with methanol and dried *in vacuo*.

Recrystallization of H_2L_F from $CHCl_3$ produces orange–red crystals suitable for X-ray determinations.

Preparation of the symmetric macrocyclic ligands (H_2L_H *and* $[H_6L_I](ClO_4)_4$)

To 2,6-diformyl-4-chlorophenol (2 mmol), 1,5-diamino-3-azapentane (2 mmol) was added in methanol (100 ml). The solution was refluxed for 2 h, reduced in volume and the orange–yellow precipitate obtained was collected by filtration, washed with methanol and dried *in vacuo*.

Metal-free H_2L_H was obtained as a yellow–orange solid also during attempts to obtain lanthanide complexes, by template effect.

H_2L_I was obtained as the tetraprotonated compound $[H_6L_I](ClO_4)_4$ during attempts to obtain the related lanthanium(III) perchlorate complex by template condensation of 2,6-diformyl-4-chlorophenol and 1,4-bis(2-aminopropyl)piperazine in the presence of $La(ClO_4)_3 \cdot 6H_2O$.

Caution: care must be taken when perchlorate salts are used, as they sometimes explode.

Preparation of the non-symmetric macrocyclic ligand H_2L_L

To 2,6-diformyl-4-methylphenol (2 mmol), ethylenediamine (1 mmol) was added in methanol (100 ml). The solution was refluxed for 2 h, reduced in volume and the precipitate filtered, washed with methanol and dried *in vacuo*. The compound, partially dissolved in methanol, was treated with 1,2-diaminobenzene (1 mmol). The solution turning from yellow to red, was refluxed for 2 h, then reduced in volume and the precipitate collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of $M(H_2L_D)$(M = *Cu(II); Ni(II)*)

To a methanolic solution (50 ml) of 2,3-dihydroxybenzaldehyde (2 mmol), 1,2-diaminobenzene (1 mmol), the appropriate metal(II) acetate (1 mmol) and LiOH

(2 mmol) in methanol (50 ml) were added in order. The resulting solution or suspension was refluxed for 2 h. The precipitate was collected by filtration, washed with methanol and dried *in vacuo*.

The same mononuclear complex can be prepared when the preformed ligand H_4L_D is used instead of the formyl and amine precursors.

Preparation of $CuLa(H_2L_D)(NO_3)_3$

Method A. To a methanolic solution (50 ml) of $Cu(H_2L_D)$ (1 mmol), $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) in methanol (50 ml) was added. The solution was gently heated, then stirred for 2 h. The obtained precipitate was filtered, washed with methanol and dried *in vacuo*.

Method B. To a methanolic solution (50 ml) of the precursors (or of H_2L_D), 1 mmol of copper(II) acetate and $La(NO_3)_3$ were added in order. The solution was gently refluxed then stirred for 2 h. The precipitate was filtered, washed with methanol and dried *in vacuo*.

Preparation of $Cu(L_L) \cdot 2H_2O$

Method A. To H_2L_L (1 mmol) in methanol (50 ml), copper(II) acetate (1 mmol) and LiOH (2 mmol) in methanol (50 ml) were added. The resulting suspension was refluxed for 2 h, the precipitate was filtered, washed with methanol and dried *in vacuo*.

Method B. To the acyclic ligand, obtained by condensation in methanol of 2,6-diformyl-4methylphenol (2 mmol) and ethylenediamine (1 mmol), copper(II) acetate (1 mmol) and LiOH (2 mmol) were added. The solution was gently refluxed and then stirred for 2 h. To the precipitate, partially dissolved in methanol, 1,2-diaminobenzene (1 mmol) was added. The suspension was refluxed for 2 h and the precipitate collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of $CuM(L_L)(CH_3COO)_2 \cdot 4H_2O$ $(M = Cu^{2+}, Ni^{2+})$

To the mononuclear complex $Cu(L_L) \cdot 2H_2O$ (1 mmol) in 50 ml of methanol, a methanolic solution (50 ml) of the appropriate metal(II) acetate (1 mmol) was added. The resulting suspension was refluxed for 2 h and the precipitate collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of $Cu_2La(L_L)(NO_3)_2(OH)$

To a methanolic solution of the acyclic complex [*N*,*N*′-phenylenebis(3-formyl-5-chlorosalicylideneiminato]-copper(II) (2 mmol), $La(NO_3) \cdot 6H_2O$ (1 mmol) and ethylenediamine (1 mmol) in methanol (50 ml) was added. The solution was stirred for 2 h and the yellow–brown precipitate, collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of $LiLa(L_F)_2 \cdot 5H_2O$

To a methanolic solution (50 ml) of H_2L_F (2 mmol) and LiOH (4 mmol), $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) in methanol (50 ml) was added. The solution was gently heated and stirred for 2 h. The yellow precipitate obtained was filtered, washed with methanol and dried *in vacuo*.

Precipitation of $[La(L_F)(NO_3)]_n$

To a methanolic solution (50 ml) of H_2L_F (1 mmol) and LiOH (2 mmol), $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) in methanol (50 ml) was added. The solution was refluxed for 2 h and the precipitate collected by filtration, washed with methanol and dried *in vacuo*.

X-ray structure determination

The crystal and molecular structures of (H_4L_C) and (H_2L_F) were determined by X-ray diffraction methods. The measurements were performed on a Philips PW1100 diffractometer. The crystals are stable under irradiation. Accurate lattice parameters were obtained from the setting of 25 medium-angle reflections. The intensities were measured with a scan speed of 2°/min with $\omega/2\theta$ scan and were corrected for Lorentz and polarization effects, but not for absorption. In fact, a series of Ψ-scans at $\cong 90°$, for both compounds, showed that the relative transmission coefficient was nearly unity and therefore the absorption correction was judged unnecessary.

The structures were determined by the symbolic-addition procedure and refined by least-squares methods. The hydrogen atoms, apart from those of hydroxyl groups, were introduced in calculated positions using a fixed isotropic parameter ($U_{iso} = 0.07$ Å^2), and the regular hexagons of carbon atoms were refined as rigid bodies.

In the case of the compound H_4L_C one of the last Fourier maps showed the presence of three residual maxima corresponding to hydroxylic hydrogens, well positioned near the oxygen atoms apart from the one corresponding to the O(2) atom; a maximum was instead present near the N(1) (imminic) atom. The successive introduction and refinement of hydrogen atoms (with fixed $U_{iso} = 0.07$ Å^2) in these found positions, lowered the final *R* factor from 6.2 to 5.4% and no residuals were found around the O(2) atom.

Physicochemical measurements

IR spectra were recorded as KBr pellets on a Philips PU 9624 FTIR spectrophotometer, ^1H NMR spectra on a Bruker AC 200 spectrometer equipped with an Aspect 3000 computer (solvent $CDCl_3$, acetone-d_6 or dimethyl sulfoxide-d_6, concentration 1 mg sample per 1 ml solvent). Mass spectrometric measurements were performed on a VG ZAB-ZF instrument operating in electron impact (EI) [70 eV (*c.* 1.12×10–17 J), 200 μA, ion-source temperature 200 °C or in fast atom bombardment (FAB) (8 KeV Xe atom bombarding a sulfolane acid solution of the sample) conditions [29].

Metal and chlorine ratios were determined by the integral counting of X-ray fluorescence radiation from a Philips SEM model XL40 scanning electron microscope equipped with an EDAX PV99 energy dispersive X-ray spectrometer. Samples suitable for scanning electron microscopy (SEM) analysis were prepared by suspending the microcrystalline powders in light petroleum (30–40 °C). Some drops of the resulting suspension were placed on a graphite disc and, after evaporation of the solvent, the samples were carbon coated by means of a Balzers MED 010 evaporating unit [30].

Results and discussion

Synthesis and characterization of the ligands

The preparation of the Schiff base ligands was carried out by the condensation of the relevant amines and aldehydes [31, 32]. The reactions are quite facile, almost quantitative and produce yellow–orange or red solids, stable in air and soluble in common organic solvents. In particular acyclic compartmental ligands have been obtained by condensation in methanol of 2,3-dihydroxybenzaldehyde with the appropriate polyamines.

The electron impact (EI) mass spectra of the ligands show peaks of both molecular and fragmentation products confirming the structures proposed in Scheme 1. In the IR spectra, strong νC=N absorptions are present at 1640 cm^{-1} for H_4L_A, at 1655 and 1634 cm^{-1} for H_4L_B, at 1651 cm^{-1} for H_4L_C and at 1616 cm^{-1} for H_4L_D, while bands due to νOH lie at about 3400 and 3290–3259(br) cm^{-1}; only H_4L_C shows a sharp band at 3226 cm^{-1}. H_6L_E shows an IR spectrum similar to those of the other acyclic ligands with sharp bands at 1661 (νC=N) and at 3258 (νOH) cm^{-1}.

The ^1H NMR spectra of the acyclic ligands H_4L_A–H_6L_E have been recorded in $CDCl_3$, acetone-d_6 or dimethyl sulfoxide-d_6 and the chemical shift (ppm) and coupling constant data are reported in Table 2. The aromatic protons of the ligands containing the –HC=N–CH_2–R groups lie at the same chemical shifts, while their coupling constants depend on R. In addition for H_4L_B and H_4L_C a coupling between the iminic –HC=N proton and the methylene protons occurs (J = 1.07 Hz). The signals due to the hydroxylic protons are not detectable in $CDCl_3$, broad in dmso-d_6 and sharp in acetone-d_6. It must be noted that in dimethyl sulfoxide and acetone the integration is half than expected.

Symmetric and non-symmetric macrocyclic compartmental ligands have been obtained by condensation in methanol of 2,6-diformyl-4-Z-phenol (Z = Cl, CH_3–) with the appropriate polyamine. For the asymmetric macrocycle H_2L_L a step by step procedure is necessary and particular care must be devoted to its purification in order to eliminate the presence of the symmetric species.

While the mass spectra of the acyclic compounds H_4L_A–H_6L_E show, under EI conditions, the formation of both molecular ions and fragmentation products well related to their original structures, the mass spectra (EI) of the cyclic compounds do not give reliable results. In such ionization conditions it is possible to obtain the production of ionic species at low mass values only with high probe temperatures and without any evidence of molecular ions production. The FAB ionization technique, as already observed [33, 34], shows the parent peaks at the appropriate values, although due to highly specific decomposition pathways, the drawing of a general fragmentation pattern for the macrocyclic compounds is impossible [35].

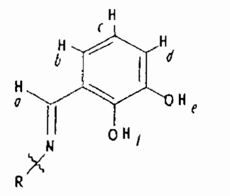
The IR spectra show a strong absorption band at about 1640 cm^{-1} due to νC=N while the bands at 1690–1680 cm^{-1}, due to νC=O, present in the diformyl and acyclic precursors, are not detectable in the cyclic compounds.

The orange–red H_2L_F, and H_2L_G compounds, on the basis of their physicochemical properties, can be formulated as the partially reduced macrocycles, where two C=N groups have been reduced to –CH_2–NH– ones. In H_2L_F and H_2L_G the νC=N lies at 1617 and 1611 cm^{-1}, respectively, while a sharp band at 3405 and 3396 cm^{-1}, respectively can be ascribed to the νNH groups.

^1H NMR spectra of H_2L_F and H_2L_G have been carried out using $CDCl_3$ and dmso-d_6 as solvent respectively; the chemical shifts of the protons are reported in Table 3. Both macrocyclic Schiff bases show an analogous reduction at two –HC=N– groups with the consequent formation of –CH_2–NH– groups as evidenced by the presence of a broad triplet at 6.30 (H_2L_F) and 6.17 (H_2L_G) ppm, due to NH, coupled with a sharp doublet at 4.39 (J = 5.2 Hz) (H_2L_F) and 4.46 (J = 4.2 Hz) (H_2L_G) ppm, attributed to –CH_2–. For a fully assignment of all peaks of the ^1H NMR of both samples, 2D COSY experiments were done and in Fig. 1 the contour plot of H_2L_F is reported. These experiments evidence that the inductive effect of –CH_3–, with respect to –Cl^-, markedly enhances the chemical coupling among the protons of the phenolic, –CH_2– and –HC=N– spin systems. The contour plot for H_2L_F, in addition to the expected coupling between the –CH_3 and the CH of the phenolic ring (line 1 of Fig. 1) shows cross peaks due to the links of –CH_2– and OH with the same protons (line 2). The coupling between the OH and this aromatic proton, five bonds away, is indicative of

TABLE 2. ^{1}H NMR data for the acyclic ligands H_4L_A–H_6L_E

	H_4L_A				H_4L_B				H_4L_C				H_4L_D				H_6L_E			
	$CDCl_3$				$CDCl_3$				$CDCl_3$				acetone-d_6				dmso-d_6			
	ppm	mo	int	J(Hz)	ppm	mo	int	J(Hz)	ppm	mo	int	J(Hz)	ppm	mo	int	J(Hz)	ppm	mo	int	J(Hz)
a	8.28	s	2		8.25	t	1	H^aH^g 1.1	8.24	t	2	H^aH^g 1.2	8.88	s	2		8.21	s	3	
**a*					8.21	s	1													
b	6.94	q	2	H^bH^c 7.4	6.95	q	1	H^bH^c 7.4	6.98	q	2	H^bH^c 7.9	7.11	q	2	H^bH^c 7.8	6.77	q	3	H^bH^c 7.8
**b*					6.93	q	1	H^bH^c 7.8												
c	6.63	t	2	H^cH^d 7.9	6.70	t	1	H^cH^d 7.9	6.63	t	2	H^cH^d 7.9	6.63	t	2	H^cH^d 7.8	6.63	t	3	H^cH^d 7.8
**c*					6.61	t	1	H^cH^d 8.0												
d	6.82	q	2	H^dH^b 2.1	6.78	q	1	H^dH^b 1.9	6.80	q	2	H^dH^b 1.8	7.00	q	2	H^dH^b 1.9	6.41	q	3	H^dH^b 2.2
**d*					6.74	q	1	H^dH^b 1.7												
e													7.79	s shp	1		13.70	s brd	1.5	
f													13.26	s shp	1		8.77	s brd	1.5	
g	3.93	s	2		3.73	d	2	H^gH^a 1.1	3.51	d	4	H^gH^a 1.2					3.59	t	6	H^gH^h 5.6
h																	2.85	t	6	
i					1.46	s	6		1.09	s	6									
l–m													7.43	m	4					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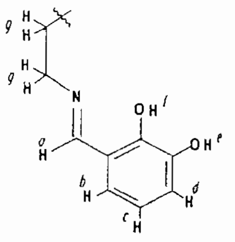
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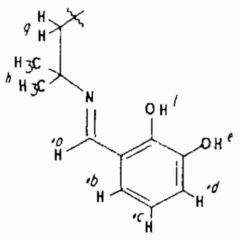
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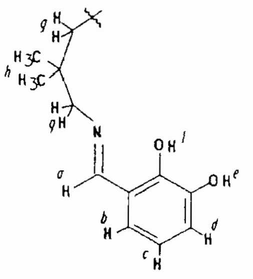
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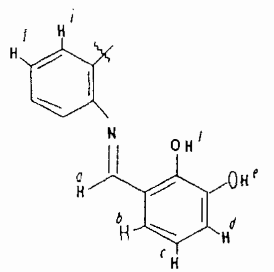
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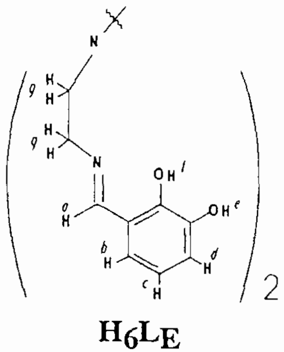
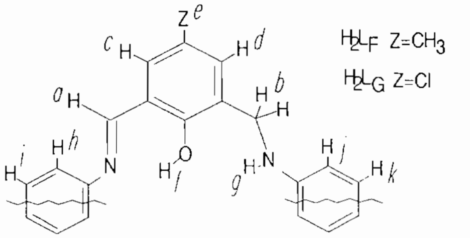

H6LE

TABLE 3. ^1H NMR data for the acyclic ligands H_2L_F and H_2L_G

Protons	H_2L_G			H_2L_F		
	ppm	Integral	Multiplet	ppm	Integral	Multiplet
f	14.08	6		13.50	6	
e				2.28	6	s
b	4.46	4	d	4.39	4	d
g	6.17	2	t	6.30	2	t
a	8.92	2	s	8.54	2	s
d	6.5–7.7	2		7.13	2	m
c	7.62	2		7.17	2	s
k	6.5–7.7	2		6.76	2	m
i	6.5–7.7	2		7.23	2	m
j	6.5–7.7	2		7.02	2	m
h	6.5–7.7	2		6.92	2	m

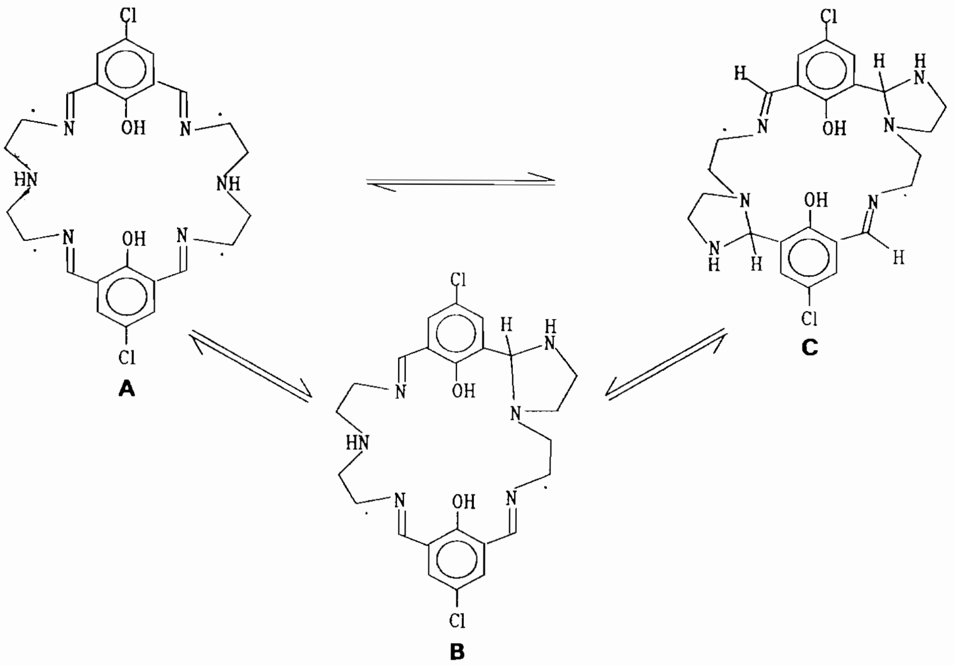


the higher electronic density on the half of the phenolic ring bonded to the –CH$_2$– group. The additional coupling of the –NH– protons with the close *o*-CH– protons of the diamino benzene ring, facilitates the correct assignment of the remaining protons (line 3).

The Schiff base H_2L_H has two secondary NH groups that may undergo addition reactions with adjacent imine groups, as indicated in Scheme 2.

The complex ^1H NMR spectra indicate the presence of more than one compound in solution, which is attributed to the ability of the ligand to adopt more than one structural conformation, thus resulting in a mixture of isomers as shown in Scheme 2.

A bidimensional COSY experiment (in $CDCl_3$) was performed to confirm the presence of the different isomers in solution facilitating the connection of individual spin systems. The contour plot shows the presence of a peak at 4.83 ppm, due to the CH group of the imidazolidine ring, coupled to the benzenic ring protons (7.39 ppm). Two peaks at 8.21 and 7.65 ppm assigned to non-equivalent carboximine protons (CH=N) are coupled (see the long range correlation peaks in Fig. 2) to the methylenic spin system (=N–CH$_2$) at 3.93 ppm. The lines a and b in Fig. 2 of contour plot demonstrate the presence of two different alkylic chains; the line a is due to the non-equivalent methylenic protons of the imidazolidine rings (2.5–3.4 ppm) of the isomer **C** of Scheme 2. Otherwise the line b (–NH–C*H*$_2$ at 3.03 ppm) can be assigned to the isomer **A** of the same scheme. The ratio between the **A** and **C** isomers, as obtained from the integration of the peaks assigned to the different structures present in solution, is 4/6. The presence of the isomer **B** cannot be ruled out; the correct assignment of the peaks due to the protons of this species is quite difficult, due to the overlap of these signals with those of the isomers **A** and **C**.



Scheme 2. Behaviour in solution proposed for H_2L_H.

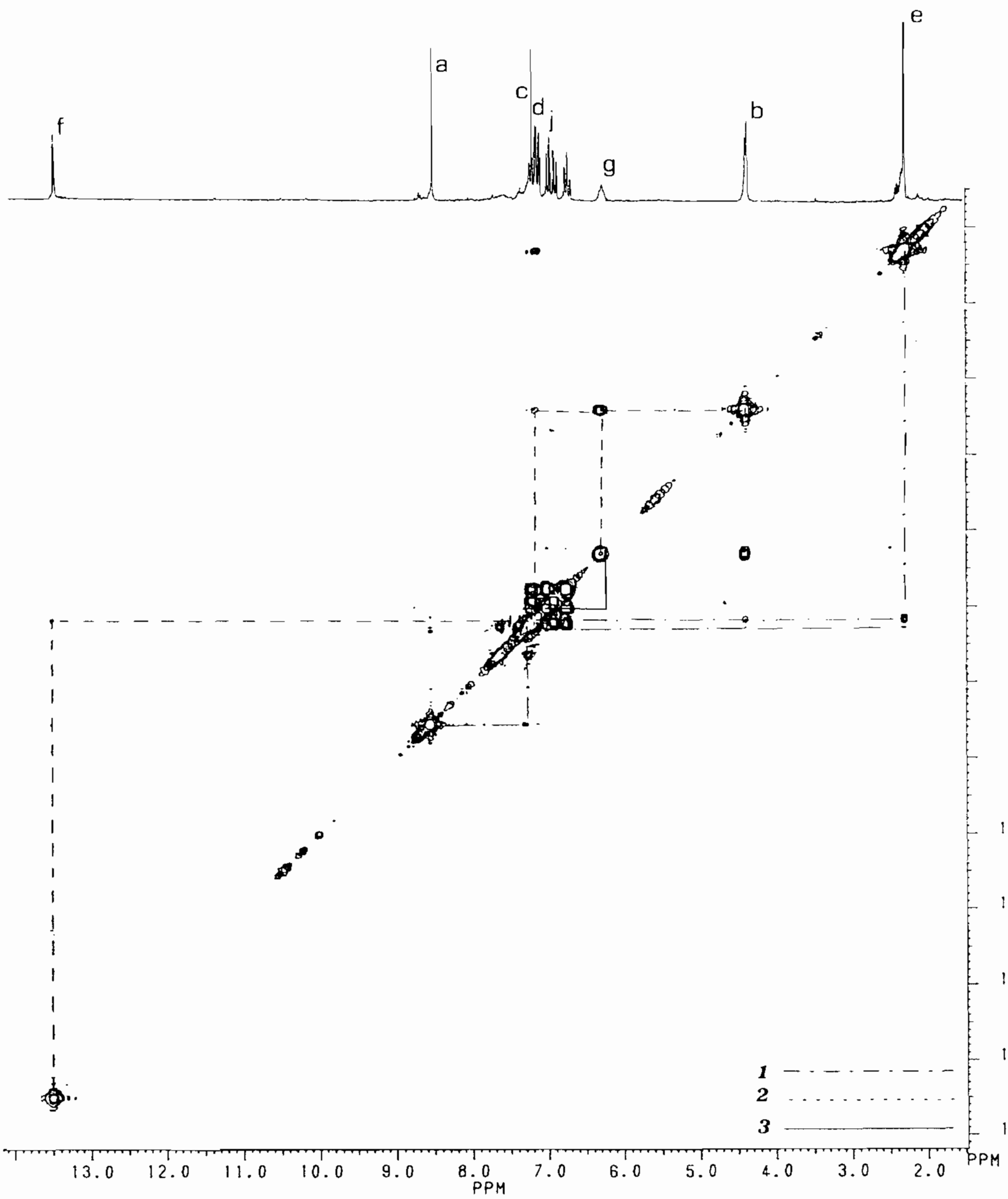


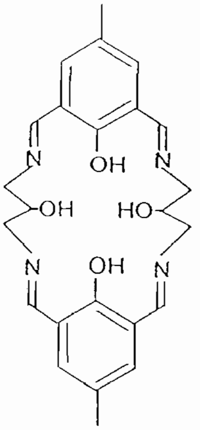
Fig. 1. The 2D ^1H NMR COSY contour plot of H_2L_F in $CDCl_3$. Lines 1, 2 and 3 show the connection between the different spin systems (for the meaning of the labels of the peaks see Table 3).

Indeed analogous ligands, derived by condensation of furan-2,5-dicarboxaldehyde or 2,6-diacetylpyridine with 1,5-diamino-3-azapentane have been found to behave in a similar manner [36–39]; X-ray investigations show that in the solid state, a ring closure with the formation of two imidazoline rings occurs; consequently these ligands exist only in the **C** form of Scheme 2 in the solid state, while in solution isomers **A** and **B** are also present.

FAB mass spectrum of the macrocycle shows fragmentation patterns, arising from the various isomers proposed in Scheme 2 [35]. In addition, the presence of one of these isomers (**B**) has been identified by X-ray crystallography, although as a lanthanide complex [40, 41].

The reaction of 2,6-diformyl-4-chlorophenol and 1,4-bis(3-aminopropyl)piperazine in the presence of $La(NO_3)_3 \cdot 6H_2O$ (also under different experimental conditions) leads only to the mononuclear complex $La(L_I)(NO_3) \cdot MeOH$. An investigation by scanning electron microscopy and X-ray microprobe analysis was carried out on this complex. By integration of backscattered X-rays, the lanthanum to chlorine ratio has been evaluated, thus allowing the sample homogeneity to be checked. This technique gives multielement analyses on small volumes of the samples (about 1 μm^3 depending of the average atomic composition) [32, 33]. The complex is homogeneous with 1:2 lanthanum to chlorine ratio.

The obtainment of the mononuclear species is probably due to its very high insolubility in organic solvents. On using $La(ClO_4)_3 \cdot 6H_2O$ instead of $La(NO_3)_3 \cdot 6H_2O$ the tetraprotonated ligand $(H_6L_I)(ClO_4)_4$ has been obtained, in addition to unidentified lanthanum complexes. This is not an entirely unexpected result since such a reaction has already been observed during the condensation reaction of 2,6-diformyl-4-methylphenol with 1,3-diamino-2-hydroxypropane in the presence of $Pb((ClO_4)_2 \cdot 6H_2O$. The diaquo complex of the partially protonated macrocycle $[(H_6L_M)(H_2O)_2](ClO_4)_2$ is one of the products obtained, together with mono and dinuclear lead(II) complexes [42].



H_4L_M

Positive ion FAB mass spectrometric data on $[H_6L_I](ClO_4)_4$ do not show the parent peak for the protonated tetraperchlorate compound M, however the species $[M+H-HClO_4]^+$, $[M+H-2HClO_4]^+$, $[M+H-3HClO_4]^+$ and $[M+H]^+$ together with other fragmentation species related to the proposed formulation are observed.

The IR spectrum of $[H_6L_I][ClO_4]_4$ shows a strong $\nu C{=}N$ at 1667 and 1640 cm^{-1}, while a very strong broad band centered at 1090 cm^{-1} and a sharp band at 628 cm^{-1} can be ascribed to the ν_3 and ν_4 of ionic ClO_4^- groups. $La(L_I)(NO_3)$ shows $\nu C{=}N$ at 1642 cm^{-1} and bands due to a coordinated nitrate group at 1472 and 1285 cm^{-1}. The band at 1392 cm^{-1}, ascribed to ionic NO_3^-, can be due to an exchange with KBr used for IR recording.

Structure of the acyclic H_4L_C and cyclic H_2L_F ligands

The most relevant crystallographic data and data processing information for the acyclic H_4L_C and the cyclic H_2L_F ligands are reported in Table 4. The molecular structure of H_4L_C is displayed in Fig. 3, together with the atom numbering scheme adopted and shows the intramolecular hydrogen bonds involving the hydroxyl groups and the iminic nitrogen atoms; fractional coordinates are listed in Table 5, selected bond distances and angles in Table 6.

The molecule is composed of two identical dihydroxybenzaldimine moieties connected by the C(9) atom; the bond lengths and angles compare very favourably. The N=C double bonds are fully localized and practically identical; the C(7)=N(1) (protonated) distance (1.292(5) Å) is in agreement with the corresponding C(13)=N(2) bond distance (1.284(6) Å). The intramolecular bond system is summarized in Table 7. As already stated in the experimental data, three hydroxyl oxygens retain their hydrogen atoms but the fourth, O(2), does not and so is negatively charged. The two external C–OH bonds are similar (C(1)–O(1): 1.357(4) Å; C(18)–O(3): 1.362(4) Å and a small difference is present between the C(6)–O(2) (1.329(4)) and C(19)–O(4) (protonated) (1.346(4) Å) bond distances. Protonation of the iminic nitrogen atom has already been observed in crystal structure determinations of other Schiff base compounds [45, 46].

An intermolecular hydrogen bond system is also present (Table 7); the O(1)–H10 and O(3)–H30 groups act as donors to the oxygen atoms O(2) and O(4), respectively, of the symmetry-related molecules at $-x$, y, $-z$ and $1-x$, $2-y$, $1-z$, respectively. These interactions give rise to the formation of polymeric chains parallel to the c axis.

A perspective view of H_2L_F and the atom labelling scheme are shown in Fig. 4. Fractional coordinates are reported in Table 8; selected bond distances and angles and torsion angles are given in Table 9. The asymmetric unit consists of two halves of two independent and chemically equivalent molecules (A and B, Fig. 4) positioned around the special positions 0, 0, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, respectively.

H_2L_F has crystallographic imposed $\bar{1}$ molecular symmetry and the four nitrogen atoms are necessarily coplanar, while the bonded aromatic rings are approximately so (the dihedral angle with each N_4 system plane is 8.3° for the C(9)–C(14) ring and 6.9° for the C(24)–C(29) ring).

The interplanar spacing between the mean planes of the phenyl rings C(1)–C(6) and C(16)–C(21) and of their centrosymmetrically related atoms is 2.96(1) and 3.01(1) Å, respectively. These rings make dihedral angles, with their own N_4 planar system, of 36.2 and 36.9°, respectively. The molecules, considered overall, adopt a two-step-like conformation. Only one, but a very significant, remark has to be made concerning the bond lengths and angles in the molecules. The two nitrogen atoms of each molecule present different char-

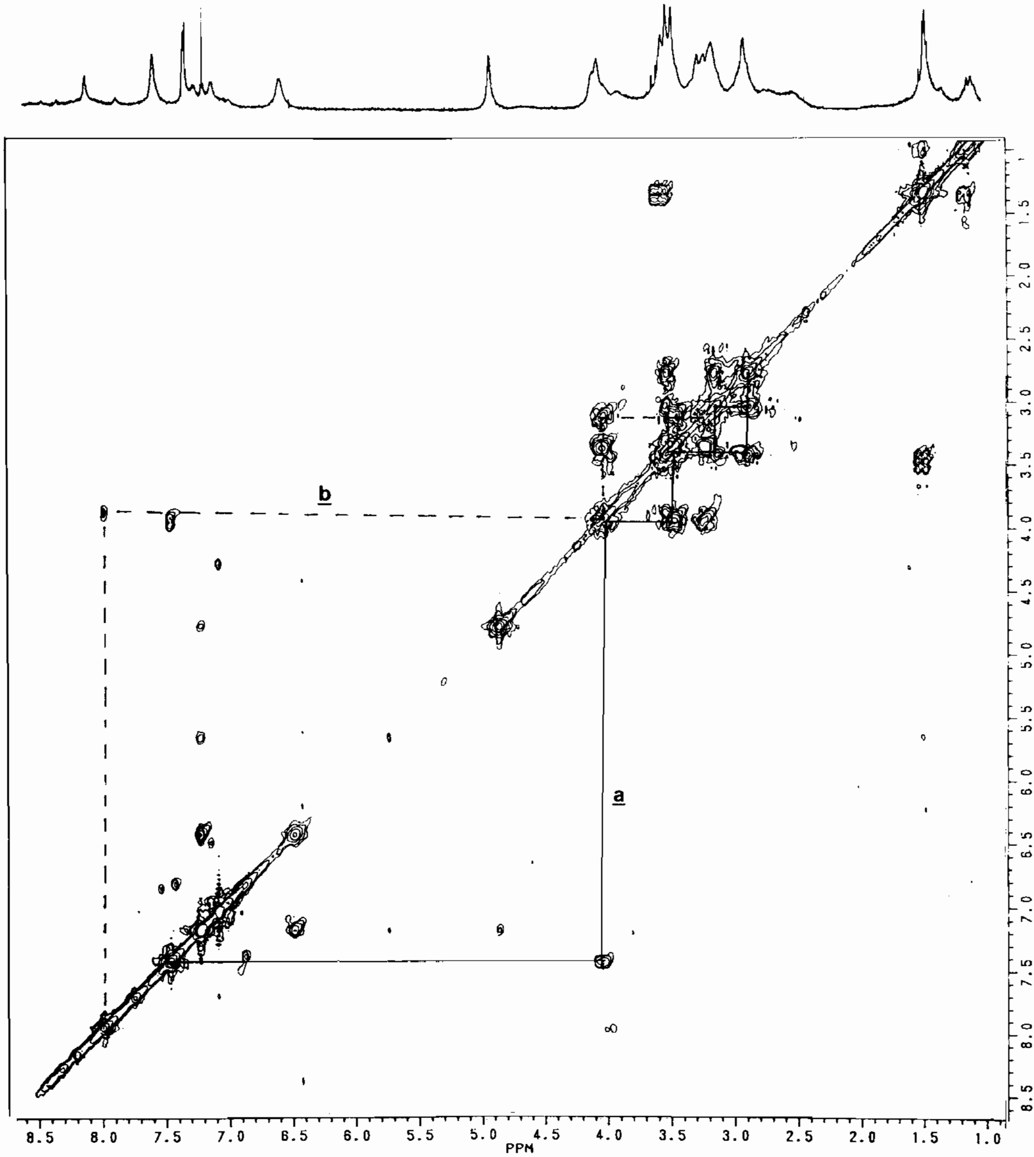


Fig. 2. The 2D ^{1}H NMR COSY contour plot of the mixture of isomers of the ligand H_2L_H in $CDCl_3$. Lines a and b show the presence of isomers C and A (see 'Discussion').

acteristics, one iminic, the other aminic. The N(1)–C(8) and N(4)–C(30) bond lengths are 1.48(1) and 1.49(1) Å, respectively, as expected for aminic groups but the bond lengths of N(2)–C(15) and N(3)–C(23) are 1.30(2) and 1.28(2) Å, respectively, typical of iminic groups. The bond and torsion angles (see Table 6) indicate the presence of sp^3 hybridization for C(8) and C(30) atoms and sp^2 hybridization for C(15) and C(23) atoms, suggesting that a partial reduction, involving the N(1)–C(8) and N(4)–C(30) systems, occurred during the synthesis.

Complexation behaviour

The acyclic ligands H_4L_A–H_4L_D are particularly designed for the simultaneous coordination of a d ion (i.e. Cu^{2+}, Ni^{2+}, etc.) into the inner N_2O_2 chamber and an f ion (i.e. Ln^{3+}, UO_2^{2+}, etc.) in the larger outer O_2O_2 site, while the Schiff base H_6L_E has been designed for the encapsulation of a lanthanide(III) ion also in the inner N_4O_3 cavity in addition to the coordination of a lanthanide or another metal ion in the outer O_3O_3 chamber. Thus H_4L_A–H_4L_D readily form square planar mononuclear complexes with copper(II) and nickel(II) salts and related heterodinuclear or heterotetranuclear d, f copper(II)–lanthanide(III), nickel(II)–lanthanide(III), copper(II)–uranyl(VI) and nickel(II)–uranyl(VI) complexes. The enhanced selectivity of the two chambers of these ligands towards the different metal ions is evidenced by their capability to form pure heterodinuclear complexes also when a tran-

TABLE 4. Crystallographically important data collection and data processing information[a]

Compound	H_4L_C	H_2L_F
Molecular formula	$C_{19}H_{22}N_2O_2$	$C_{30}H_{28}N_4O_2$
Molecular weight	342.2	474.5
$F(000)$	728	1008
Crystal system	monoclinic	monoclinic
Z	4	4
Space group	$P2_1/c$	$P2_1/a$
Cell dimensions		
(MoKα, $\lambda=0.7107$ Å) a (Å)	6.767(4)	22.481(7)
b (Å)	14.106(5)	8.998(5)
c (Å)	18.163(5)	11.911(5)
β (°)	91.05(4)	93.28(5)
Unit cell volume (Å^3)	1733(1)	2405(1)
D_x	1.31	1.30
Scanning range for 2θ (°)	4.5–50	4.8–50
No. independent unique reflections	3045	3498
No. reflections above three standard deviations	1506	1208
Final $R=\Sigma(\|F_o\|-\|F_c\|)/\|F_o\|$	0.054	0.075

[a]Common data: function minimized, $\Sigma w(|F_o|-|F_c|)^2$; weighting scheme, $w=1$; program package, SHELX-76 System [43].

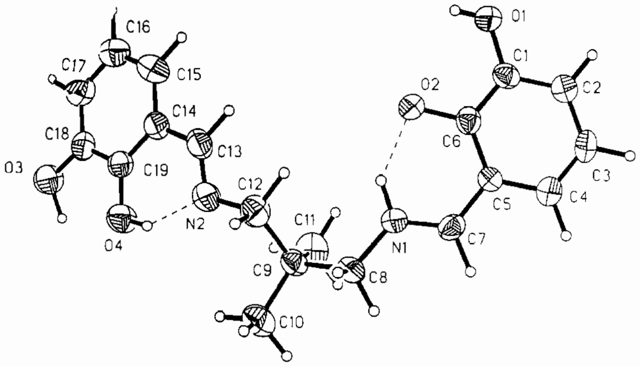


Fig. 3. An ORTEP drawing [44] of the molecular structure of H_4L_C; the thermal ellipsoids are drawn at the 50% level.

sition metal ion (i.e. copper(II) or nickel(II)) and an f metal ion (i.e. lanthanum or uranyl(VI)) are added in sequence to the ligands without previous separation and purification of the mononuclear species. The transition metal ion always occupies the inner and the f ion the outer chamber.

TABLE 5. Fractional coordinates with equivalent isotropic thermal parameters (Å^2) for H_4L_C

Atom	x	y	z	$U_{iso/eq}$[a]
O(1)	−0.1279(5)	0.9052(3)	−0.0793(2)	0.052(1)
O(2)	0.2008(4)	0.9332(2)	0.0099(2)	0.047(1)
O(3)	0.2506(5)	1.0787(3)	0.5267(2)	0.059(1)
O(4)	0.4607(5)	1.0294(3)	0.4037(2)	0.053(1)
N(1)	0.5464(5)	0.8747(3)	0.0538(2)	0.040(1)
N(2)	0.4774(6)	1.0258(3)	0.2588(2)	0.049(2)
C(2)	0.0180(4)	0.7672(2)	−0.1271(1)	0.046(2)
C(3)	0.1771(4)	0.7047(2)	−0.1312(1)	0.052(2)
C(4)	0.3461(4)	0.7196(2)	−0.0876(1)	0.050(2)
C(5)	0.3562(4)	0.7970(2)	−0.0400(1)	0.037(2)
C(6)	0.1971(4)	0.8596(2)	−0.0359(1)	0.036(1)
C(1)	0.0281(4)	0.8447(2)	−0.0794(1)	0.038(2)
C(7)	0.5257(7)	0.8066(3)	0.0067(2)	0.039(2)
C(8)	0.7152(6)	0.8854(4)	0.1041(2)	0.042(2)
C(9)	0.6536(7)	0.9042(3)	0.1837(2)	0.041(2)
C(10)	0.8415(8)	0.8987(4)	0.2316(3)	0.063(2)
C(11)	0.5041(8)	0.8303(4)	0.2087(3)	0.061(2)
C(12)	0.5669(8)	1.0051(4)	0.1874(2)	0.050(2)
C(13)	0.3035(8)	1.0622(3)	0.2590(3)	0.047(2)
C(15)	0.0118(4)	1.1277(2)	0.3181(1)	0.056(2)
C(16)	−0.0928(4)	1.1513(2)	0.3810(1)	0.057(2)
C(17)	−0.0106(4)	1.1336(2)	0.4506(1)	0.056(2)
C(18)	0.1761(4)	1.0924(2)	0.4574(1)	0.045(2)
C(19)	0.2807(4)	1.0687(2)	0.3945(1)	0.043(2)
C(14)	0.1986(4)	1.0864(2)	0.3249(1)	0.043(2)

[a]U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Several potentially heptacoordinated N_4O_3 Schiff bases, prepared by condensation of tris(2-aminoethyl)amine and acetylacetone (H_3L_N) or substituted hydroxyacetophenone (H_3L_O), are believed to act as heptadentate trinegative chelating agent when reacted with lanthanide salts containing poorly coordinating anions such as Cl^- and an early, large lanthanide ion such as lanthanum(III), or praseodymium(III), and to act as neutral tridentate O_3 chelating agents when the anion is NO_3^-. The resulting complexes are $Ln(L_N)$ or $Ln(L_O)$ and $Ln(H_3L_N)(NO_3)_3$ or $Ln(H_3L_O)(NO_3)_3$, respectively [47]. The ligand H_6L_E, which resembles these Schiff bases, reacts with $La(NO_3)_3\cdot 6H_2L$ (in a 1:1 or 1:2 molar ratio) or $LaCl_3\cdot 8H_2O$, in alcoholic solution, to give the mononuclear $La(H_4L_E)(NO_3)\cdot 2H_2O$, the dinuclear $La_2(H_2L_E)(NO_3)_2\cdot MeOH$ and $La(H_3L_E)$, respectively. It seems that in the nitrate complexes one of the three coordinating arms of the ligand does not participate in the coordination of the

TABLE 6. Selected bond distance (Å) and angles (°) for H_4L_C

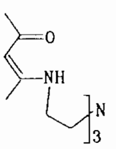
O(1)–C(1)	1.357(4)	O(2)–C(6)	1.329(4)
O(3)–C(18)	1.362(4)	O(4)–C(19)	1.346(5)
N(1)–C(7)	1.292(6)	N(1)–C(8)	1.457(6)
N(2)–C(12)	1.471(6)	N(2)–C(13)	1.284(7)
C(2)–C(3)	1.395(4)	C(2)–C(1)	1.395(4)
C(3)–C(4)	1.395(4)	C(4)–C(5)	1.395(4)
C(5)–C(6)	1.395(4)	C(5)–C(7)	1.420(5)
C(6)–C(1)	1.395(4)	C(8)–C(9)	1.536(6)
C(9)–C(10)	1.529(7)	C(9)–C(11)	1.528(7)
C(9)–C(12)	1.542(7)	C(13)–C(14)	1.443(6)
C(15)–C(16)	1.395(4)	C(15)–C(14)	1.395(4)
C(16)–C(17)	1.395(4)	C(17)–C(18)	1.395(4)
C(18)–C(19)	1.395(4)	C(19)–C(14)	1.395(4)
C(7)–N(1)–C(8)	124.5(4)	C(12)–N(2)–C(13)	118.2(4)
C(4)–C(5)–C(7)	118.3(3)	C(6)–C(5)–C(7)	121.6(3)
O(2)–C(6)–C(5)	121.4(3)	O(2)–C(6)–C(1)	118.6(3)
O(1)–C(1)–C(6)	122.3(3)	O(1)–C(1)–C(2)	117.6(3)
N(1)–C(7)–C(5)	122.8(4)	N(1)–C(8)–C(9)	112.6(4)
C(8)–C(9)–C(12)	108.1(4)	C(8)–C(9)–C(11)	110.8(4)
C(8)–C(9)–C(10)	106.8(4)	C(11)–C(9)–C(12)	111.3(4)
C(10)–C(9)–C(12)	109.6(4)	C(10)–C(9)–C(11)	110.1(4)
N(2)–C(12)–C(9)	112.6(4)	N(2)–C(13)–C(14)	124.1(4)
O(3)–C(18)–C(17)	117.4(3)	O(3)–C(18)–C(19)	122.6(3)
O(4)–C(19)–C(18)	117.9(3)	O(4)–C(19)–C(14)	122.1(3)
C(13)–C(14)–C(19)	121.1(4)	C(13)–C(14)–C(15)	118.9(3)

TABLE 7. Hydrogen bond system in H_4L_C

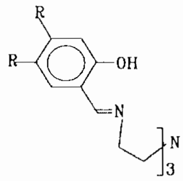
Donor atom D	Acceptor atom A	D···A (Å)	H···A (Å)	<D–H···A (°)
Intramolecular				
N(1)	O(2)	2.592(5)	1.799(6)	139(1)
O(4)	N(2)	2.636(5)	1.782(5)	144(1)
Intermolecular				
O(1)	O(2′)	2.656(4)	1.894(5)	155(1)
O(3)	O(4″)	2.765(4)	1.914(5)	137(1)

Symmetry codes: ′ $-x, y, -z$; ″ $1-x, 2-y, 1-z$.

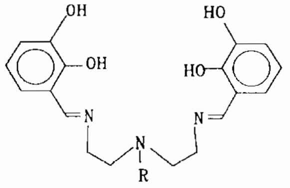
central metal ion; thus the ligand behaves as the similar dinucleating ligands H_3L_P [47]. In contrast, in the complex obtained from lanthanum(III) chloride, the ligand appears to coordinate with the three arms and the encapsulation of the metal ion into the N_4O_3 compartment can be proposed on the basic of the results reported for the related heptadentate Schiff bases H_3L_N and H_3L_O.



H_3L_N



H_3L_O



H_3L_P

The two N_2O_2 coordination chambers of the compartmental macrocycles are suitable to form mono-, homo- and heterodinuclear complexes containing d metal ions, and homodinuclear copper(II) or heterodinuclear copper(II)–nickel(II) diacetate complexes have been prepared with the asymmetric H_2L_L and symmetric H_2L_F ligands. These ligands, however, are too small for the coordination into their cavity of larger metal ions such as lanthanide(III) ions. Thus by template condensation of [*N*,*N*′-phenylene-bis(3-formyl-5-chlorosalicylideneiminato]copper(II) with 1,2-diaminoethane in the presence of $La(NO_3)_3 \cdot 6H_2O$ or by reaction of H_2L_F, H_2L_G with $La(NO_3)_3 \cdot 6H_2O$ under appropriate conditions, the heterotrinuclear copper(II)–lanthanum(III), $Cu_2La(L_L)(NO_3)_2OH$, the mononuclear $[La(L_F)_2]^-$ and polynuclear lanthanum(III) $[La(L_L)(NO_3)]_n$ complexes can be obtained. In these compounds, the ligands, owing to the reduced cavity, are believed to coordinate the lanthanum(III) ion through oxygen and nitrogen atoms above and below the equatorial plane, as already found for other similar complexes [48]. It must be noted that lanthanide(III) ions coordinated the larger Schiff base H_2L_H approximately in their equatorial plane through the five donor set N_3O_2 of one compartment [40, 41]. In the heterotrinuclear copper(II)–lanthanum(III) complex $Cu_2La(L_L)(NO_3)_2(OH)$ the X-ray microprobe analysis shows the metal atoms ratio is 2:1 in agreement with the formulation proposed.

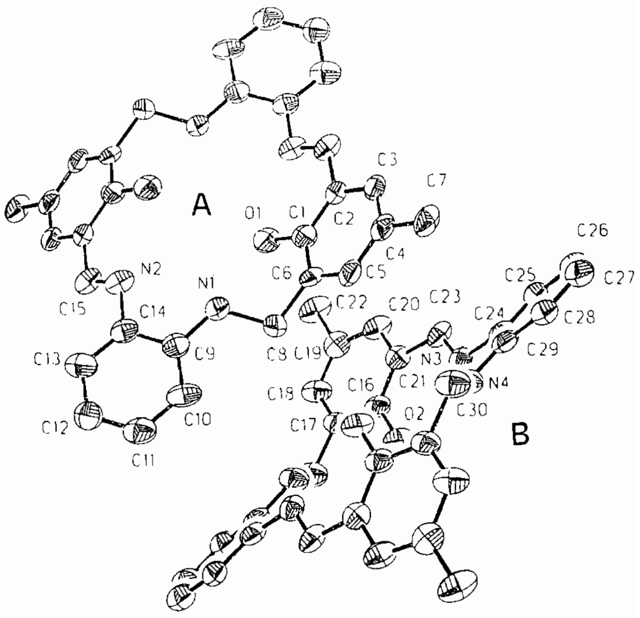
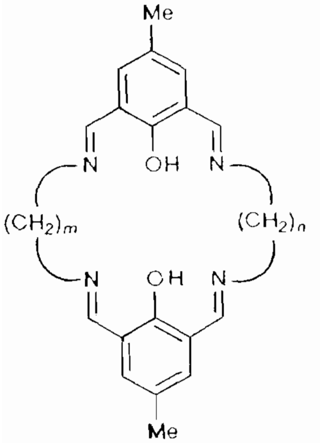


Fig. 4. An ORTEP [44] view of the molecular structure of H_2L_F. Thermal ellipsoid are scaled to enclose 50%.

Unfortunately the macrocyclic compounds containing lanthanum(III) are unstable in solution and break into their components. In particular the free ligand H_2L_F can be recovered from chloroform solution of $[La(L_F)(NO_3)]_n$, or of $LiLa(L_F)_2 \cdot 5H_2O$, as ascertained by the X-ray structural investigations reported above. This solution lability prevents a detailed study of these compounds; thus the structures proposed, especially for the complexes containing only lanthanum(III), must be considered as tentative.

Very recently the template synthesis and the X-ray structure of nickel(II)–lead(II) and copper(II)–lead(II) heterotrinuclear complexes with the similar macrocycles H_2L_Q have been reported [49].



H_2L_Q: $m=2, 3$; $n=2, 5$

The trinuclear complexes, $[Pb(ML_Q)_2](X)_2$ (M = Cu, Ni; X = ClO_4^-, PF_6^-, BPh_4^- or BF_4), were obtained by the condensation of [*N*,*N'*-ethylene] or [*N*,*N'*-propane-1,3-diylbis(3-formyl-5-methylsalicylideneiminato]metal(II) with ethylenediamine, propane-1,3-diamine, butane-1,4-diamine or pentane-1,5-diamine in the presence of lead(II) ions. In $[Pb(CuL_Q)_2](ClO_4)_2$ ($n=m=3$), each copper ion is bound at one of the N_2O_2 donor sites and the lead ion is sandwiched by the vacant N_2O_2 site of two CuL_Q entities, providing a square-antiprismatic environment [47]. A very similar structural configuration is proposed for the $Cu_2La(L_L)(NO_3)_2(OH)$ complexes prepared. The lability of these complexes in solution can be caused by the N_2O_2 site not involved in the coordination to the copper(II) ion: it could be too small and not flexible enough for a strong coordination to the 4f ion. The complexes prepared however indicate that a synthetic approach using macrocyclic ligands with a small cavity for the synthesis of polynuclear compounds containing lanthanide(III) ions, can be reasonably proposed and the synthesis and characterization of trinuclear complexes with larger and more flexible macrocyclic compartment ligands is under investigation.

Finally, we cannot explain the formation of the reduced macrocycles H_2L_F and H_2L_G when the ligands are prepared. Reactions at the C=N groups are not uncommon; for example attempts to recrystallize alkaline or alkaline earths complexes with analogous macrocycles derived by condensation of 2,6-diformyl pyridine or 2,5-diformyl furan with 1,2-diaminobenzene produce metal-free macrocycles which can be described as bis adducts, with the alcohol used (generally methanol) for the recrystallization having added to the imine bonds [50]. However the easy condensation reaction under the same experimental conditions employed to obtain H_2L_F and H_2L_G, of 2,3-dihydroxybenzaldehyde and 1,2-diaminobenzene with the formation of the expected acyclic Schiff base H_4L_D makes any possible explanation at this stage doubtful.

TABLE 8. Fractional coordinates with isotropic (denoted by *) or equivalent isotropic thermal parameters ($Å^2$) for H_2L_F

Atom	x	y	z	$U_{iso/eq}$[a]
O(1)	0.5466(3)	0.1141(7)	0.9342(5)	0.054(3)
C(7)	0.6133(6)	−0.0359(11)	0.4938(9)	0.061(5)
C(3)*	0.6269(2)	−0.0524(6)	0.7053(5)	0.041(3)
C(4)*	0.5957(2)	0.0089(6)	0.6118(5)	0.047(3)
C(5)*	0.5483(2)	0.1056(6)	0.6264(5)	0.047(3)
C(6)*	0.5320(2)	0.1411(6)	0.7344(5)	0.040(3)
C(1)*	0.5632(2)	0.0799(6)	0.8279(5)	0.041(3)
C(2)*	0.6107(2)	−0.0168(6)	0.8134(5)	0.035(2)
C(8)	0.4781(5)	0.2416(11)	0.7474(9)	0.051(5)
N(1)	0.4341(4)	0.1607(8)	0.8126(7)	0.051(3)
C(10)*	0.3488(3)	0.3030(7)	0.7323(5)	0.048(3)
C(11)*	0.2899(3)	0.3494(7)	0.7388(5)	0.056(3)
C(12)*	0.2569(3)	0.3022(7)	0.8278(5)	0.056(3)
C(13)*	0.2827(3)	0.2086(7)	0.9102(5)	0.055(3)
C(14)*	0.3416(3)	0.1622(7)	0.9037(5)	0.038(3)
C(9)*	0.3747(3)	0.2094(7)	0.8147(5)	0.041(3)
N(2)	0.3718(4)	0.0757(9)	0.9913(8)	0.050(4)
C(15)	0.3588(5)	0.0982(11)	1.0952(10)	0.046(5)
O(2)	0.5455(3)	0.6181(7)	0.5752(5)	0.055(3)
C(22)	0.6123(6)	0.4648(11)	1.0299(8)	0.059(5)
C(18)*	0.5470(3)	0.6075(7)	0.8840(5)	0.042(3)
C(19)*	0.5949(3)	0.5122(7)	0.9087(5)	0.046(3)
C(20)*	0.6265(3)	0.4526(7)	0.8218(5)	0.047(3)
C(21)*	0.6103(3)	0.4885(7)	0.7103(5)	0.038(2)
C(16)*	0.5624(3)	0.5838(7)	0.6857(5)	0.040(3)
C(17)*	0.5307(3)	0.6434(7)	0.7725(5)	0.041(3)
C(23)	0.6401(5)	0.4099(10)	0.6235(10)	0.046(4)
N(3)	0.6278(4)	0.4287(8)	0.5178(8)	0.045(4)
C(25)*	0.7185(3)	0.3026(7)	0.4588(5)	0.050(3)
C(26)*	0.7462(3)	0.2122(7)	0.3822(5)	0.058(3)
C(27)*	0.7144(3)	0.1625(7)	0.2855(5)	0.058(3)
C(28)*	0.6548(3)	0.2031(7)	0.2653(5)	0.056(3)
C(29)*	0.6271(3)	0.2934(7)	0.3419(5)	0.041(3)
C(24)*	0.6589(3)	0.3432(7)	0.4386(5)	0.039(2)
N(4)	0.5669(4)	0.3397(8)	0.3274(7)	0.053(3)
C(30)	0.5230(5)	0.2572(11)	0.2523(10)	0.056(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

While cyclic compartmental Schiff bases have been the focus of extensive studies, half reduced or fully reduced macrocycles are now receiving an increasing interest as binucleating ligands, owing to their flexibility [51]. H_2L_F and H_2L_G can be thus the starting compounds for the obtainment of complexes with unusual magnetic, electrochemical or catalytic properties.

TABLE 9. Selected bond distances and angles for H_2L_F

Molecule A		Molecule B	
Bond distances (Å)			
O(1)–C(1)	1.376(9)	O(2)–C(16)	1.383(8)
C(6)–C(8)	1.53(1)	C(17)–C(30″)	1.52(1)
C(15)–C(2′)	1.45(1)	C(21)–C(23)	1.45(1)
C(8)–N(1)	1.48(1)	N(4)–C(30)	1.49(1)
N(1)–C(9)	1.41(1)	C(29)–N(4)	1.42(1)
N(2)–C(15)	1.30(2)	C(23)–N(3)	1.28(2)
C(14)–N(2)	1.44(1)	N(3)–C(24)	1.43(1)
C(7)–C(4)	1.54(1)	C(22)–C(19)	1.53(1)
Bond angles (°)			
C(6)–C(8)–N(1)	108.6(7)	C(17″)–C(30)–N(4)	108.4(7)
C(8)–N(1)–C(9)	121.2(7)	C(29)–N(4)–C(30)	121.4(7)
N(1)–C(9)–C(14)	117.8(6)	C(24)–C(29)–N(4)	116.6(6)
N(1)–C(9)–C(10)	122.2(6)	C(28)–C(29)–N(4)	123.4(6)
C(14)–N(2)–C(15)	118.8(8)	C(23)–N(3)–C(24)	119.3(8)
C(9)–C(14)–N(2)	117.8(6)	N(3)–C(24)–C(29)	118.1(6)
C(13)–C(14)–N(2)	122.0(6)	N(3)–C(24)–C(25)	121.8(6)
N(2)–C(15)–C(2′)	120.7(7)	C(21)–C(23)–N(3)	123.6(8)
Torsion angles (°)			
C(9)–N(1)–C(8)–C(6)	165.5(8)	C(29)–N(4)–C(30)–C(17″)	164.2(8)
C(14)–N(2)–C(15)–C(2′)	178.1(7)	C(24)–N(3)–C(23)–C(21)	177.9(7)

Symmetry codes: ′: $-x$, $-y$, $1-z$; ″: $1-x$, $1-y$, $1-z$.

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