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Cyclic and acyclic compartmental Schiff bases, their reduced analogues and related mononuclear and heterodinuclear complexes

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Abstract

[1+1] macrocyclic and [1+2] macroacyclic compartmental ligands (H_2L), containing one N_2O_2, N_3O_2, N_2O_3, N_4O_2 or $O_2N_2O_2$ Schiff base site and one O_2O_n ($n = 3, 4$) crown-ether like site, have been prepared by self-condensation of the appropriate formyl- and amine precursors. The template procedure in the presence of sodium ion afforded $Na_2(L)$ or $Na(HL) \cdot nH_2O$. When reacted with the appropriate transition metal acetate hydrate, H_2L form $M(L) \cdot nH_2O$, $M(HL)(CH_3COO) \cdot nH_2O$, $M(H_2L)(X)_2 \cdot nH_2O$ ($M = Cu^{2+}$, Co^{2+}, Ni^{2+}; $X = CH_3COO^-$, Cl^-) or $Mn(L)(CH_3COO) \cdot nH_2O$ according to the experimental conditions used. The same complexes have been prepared by condensation of the appropriate precursors in the presence of the desired metal ion. The Schiff bases H_2L have been reduced by $NaBH_4$ to the related polyamine derivatives H_2R, which form, when reacted with the appropriate metal ions, $M(H_2R)(X)_2$ ($M = Co^{2+}$, Ni^{2+}; $X = CH_3COO^-$, Cl^-), $Cu(R) \cdot nH_2O$ and $Mn(R)(CH_3COO) \cdot nH_2O$. The prepared ligands and related complexes have been characterized by IR, NMR and mass spectrometry. The [1+1] cyclic nature of the macrocyclic polyamine systems and the site occupancy of sodium ion have been ascertained, at least for the sodium (I) complex with the macrocyclic ligand containing one N_3O_2 Schiff base and one O_2O_3 crown-ether like coordination chamber, by an X-ray structural determination. In this complex the asymmetric unit consists of one cyclic molecule of the ligand coordinated to a sodium ion by the five oxygen atoms of the ligand. The coordination geometry of the sodium ion can be described as a pentagonal pyramid with the metal ion occupying the vertex. In the mononuclear complexes with H_2L or H_2R the transition metal ion invariantly occupies the Schiff base site; the sodium ion, on the contrary, prefers the crown-ether like site. Accordingly, the heterodinuclear complexes $[MNa(L)(CH_3COO)_x]$ ($M = Cu^{2+}$, Co^{2+}, Ni^2, $x = 1$; $M = Mn^{3+}$, $x = 2$) have been synthesised by reacting the appropriate formyl and amine precursors in the presence of $M(CH_3COO)_n \cdot nH_2O$ and NaOH in a 1:1:1:2 molar ratio. The reaction of the mononuclear transition metal complexes with $Na(CH_3COO) \cdot nH_2O$ gives rise to the same heterodinuclear complexes. Similarly $[MNa(R)(CH_3COO)_x]$ have been prepared by reaction of the appropriate polyamine ligand H_2R with the desired metal acetate hydrate and NaOH in 1:1:2 molar ratio.

Keywords: Compartmental ligands; Heterodinuclear complexes; Schiff base; Macrocycles; Polyamines

1. Introduction

Compartmental systems have received a growing interest in the recent past owing to their ability to give rise to compounds with unusual, although preordered, properties [1–5]. The presence of two recognition sites in close proximity confers them the capability to undergo two similar or dissimilar recognition processes, for instance the coordination of two identical or different metal ions in a well defined stereochemistry and at an appropriate distance each other. This causes a mutual influence between the two metal ions giving rise to systems with new physico-chemical properties which have been used in the design of molecular magnetic or optical devices, molecular probes for the selective recognition of charged and/or or neutral molecules or polynuclear

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catalytic systems. It was proved, in fact, that two metal ions, communicating each other through suitable bridging groups, can give rise to antiferro- or ferromagnetic interactions, to electron-transfer processes or can produce asymmetric or symmetric activation of specific molecules and hence peculiar, highly selective and efficient catalytic processes [6–13].

Moreover dinucleating systems containing a paramagnetic centre fixed in one chamber (i.e., lanthanide(III), manganese(II), etc.) can influence considerably the properties of the second metal ion coordinated to the adjacent chamber (i.e., an alkali metal ion) and hence can serve as molecular devices for its recognition and qualitative detection in the solid state and in solution [14].

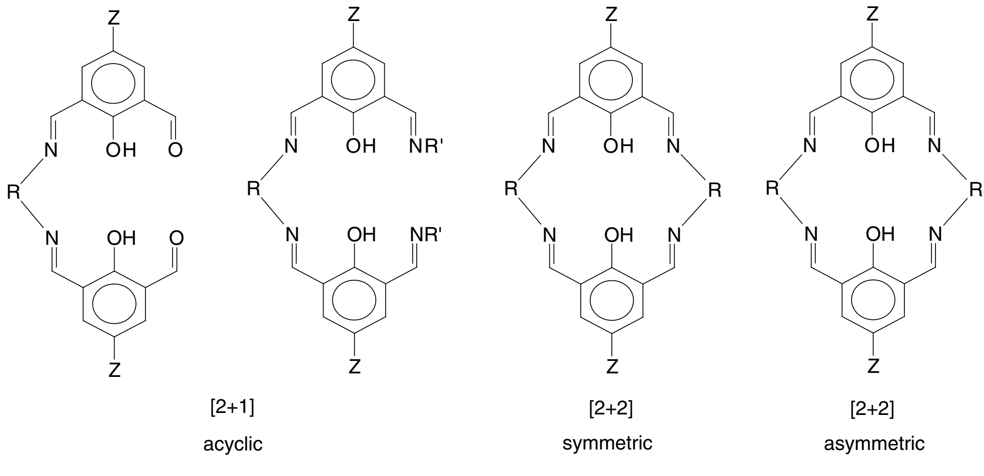
To this purpose in the recent past a large variety of acyclic and cyclic compartmental systems of the type reported in Scheme 1 have been successfully proposed. In these studies Schiff bases have been extensively studied owing to their relatively easy synthesis and their versatility in the formation of stable complexes. The acyclic [2+1] and the [2+2] macrocyclic compartmental ligands derive from the condensation reaction of 2,6-diformyl-4-substituted phenol and the appropriate amine $H_2N–R–NH_2$ in a 2:1 or 1:1 molar ratio. The asymmetric acyclic and cyclic ligands have been prepared by a step by step procedure. On changing the head or the lateral units these ligands have been conveniently diversified. As can be seen in Scheme 1 the acyclic ligands are asymmetric in nature, while the cyclic ligands can be symmetric or asymmetric [1–5].

The best way for their preparation is to carry out the condensation reaction of appropriate formyl and amine precursors in the presence of a templating agent (i.e., Na^+). Nevertheless the possibility to obtain these compounds by self-condensation of appropriate precursors has been successfully experienced in the past. They are identical to the compounds obtained by demetallation of the related Schiff bases complexes. Their cyclic or acyclic nature was inferred especially by mass spectrometry and definitively demonstrated by single crystal X-ray structural determinations [1,4,15,16].

The symmetric cyclic ligands usually form homodinuclear complexes, although hetero-dinuclear complexation was observed, using particular experimental conditions. This last complexation is generally favoured by the protonations of the nitrogens of one compartment, which makes the two sites no longer equivalent and hence accessible to two different and subsequent complexation reactions [1].

The ability to form heterodinuclear complexes is related to the possibility to synthesise stable mononuclear complexes to be used as ‘‘ligand’’ for further complexation or to have dinuclear systems capable to suffer a transmetallation process at one of the two chambers. Thus the possibility to have two well defined and different recognition processes at the two adjacent sites of the compartmental systems is especially related to the use of asymmetric compartmental ligands. The presence of different donor atoms in the two chains, R and R’, in fact, allows a different recognition process at the two chambers [1,4,14]. More recently the two chambers have been significantly diversified by the introduction of polyetheric chains. These systems form stable hetero-dinuclear complexes. No scrambling or migration processes have been observed, thus pure positional isomers are recovered. In several cases the marked differences in the two coordination chambers allows the preparation of hetero-dinuclear complexes in a one pot reaction. Thus s,f-lanthanide(III)–sodium(I) or d,f-transition metal lanthanide(III) complexes have been obtained and characterized by NMR spectroscopy or X-ray diffractometry [16–20].

Moreover, one chamber of these compartmental ligand can recognise a metal ion while the other chamber can give rise to a selective recognition process via the



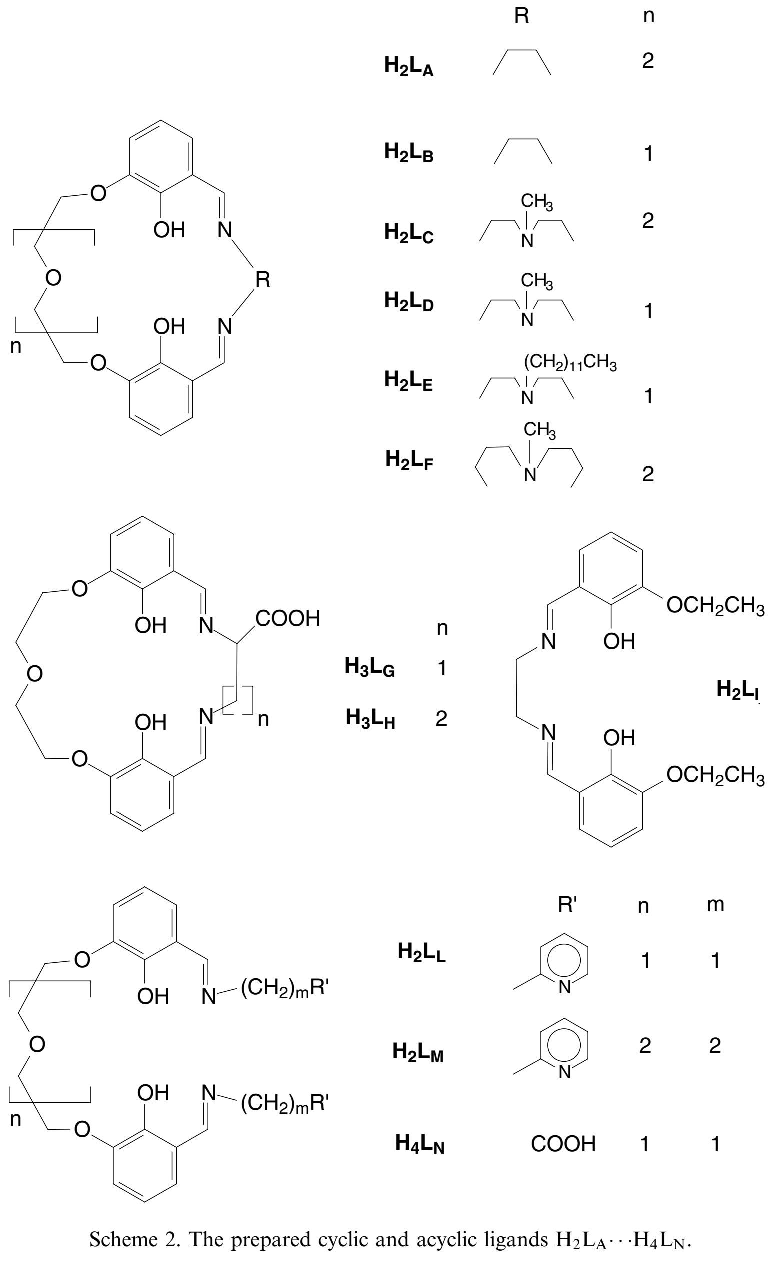
Scheme 1. [1+2] Acyclic and [2+2] macrocyclic compartmental ligands.

formation of hydrogen bonding and/or complexation of anions or organic molecule to the coordinated metal ion [21–29].

Furthermore, these Schiff bases can be reduced to the corresponding amine derivatives, which have a higher stability (they do not suffer the hydrolytic processes encountered with the Schiff base analogues), a greater flexibility, maintaining an appreciable capability to form complexes with transition metal ions. The availability of these polyamine systems allows a useful comparison between Schiff bases and their reduced analogues about the different recognition processes in consequence of the change from imine to amine groups inside the two adjacent coordinating sites.

We have already reported [18] the preparation and the properties of a series of macrocycles H_2L_A–H_4L_D, their corresponding mononuclear complexes with d metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{3+}) and the related s,d-heterodinuclear ones.

In the present paper, we have enlarged the study with other cyclic and acyclic Schiff bases (H_2L_E–H_4L_N) (Scheme 2) together with those of some reduced analogues. In particular the role of the different coordination cavity or the different donor set on the coordination of transition metal ions as Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{3+} has been studied. Also the use of the obtained mononuclear complexes as ligands for the preparation of the heterodinuclear complexes $[MNa(L)(CH_3COO)_x]\cdot nH_2O$ or



Scheme 2. The prepared cyclic and acyclic ligands $H_2L_A\cdots H_4L_N$.

$[MNa(R)(CH_3COO)_x]\cdot nH_2O$ ($M = Co^{2+}$, Ni^{2+}, Cu^{2+} $x = 1$; $M = Mn^{3+}$, $x = 2$, $n = 4$) have been successfully experienced.

For both cyclic and acyclic derivatives additional functionalities have been inserted (i.e., carboxylic or pyridine groups) in order to verify their influence in the coordination ability of the ligands towards different metal ions and to study the physico-chemical properties of the resulting mononuclear and/or heterodinuclear complexes.

2. Experimental

2.1. Materials

The hydrate metal acetates, 3-ethoxy-2-hydroxybenzaldehyde, the polyamines and the other reagents were commercial products, used as received by Aldrich. Dimethylsulfoxide was purified by standard methods [30] while the other solvents were reagent grade, used as received. The diformyl precursors 3,3-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (H_2L^I), the disodium derivative (Na_2L^I) and 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) (H_2L^{II}) were prepared by literature methods [17–33].

The preparation and the manipulation of the cobalt(II) complexes have been carried out in dry boxes or under a nitrogen atmosphere.

Caution. Although during these experiments no accidents have occurred, extreme care should be taken when perchlorates are handled, because they may explode spontaneously and may be sensitive to shock. The perchlorates should only be prepared in small quantities.

2.2. Ligands

2.2.1. Macrocyclic Schiff bases

2.2.1.1. H_2L_A, H_2L_B. The yellow ligands H_2L_A and H_2L_B were prepared according to literature (62–65% yield) [16].

2.2.1.2. H_2L_C, H_2L_D. A methanol solution (3 ml) of 1,5-diamino-3-azamethylpentane (1 mmol) was diluted with diethylether (400 ml). A $CHCl_3$ solution (5 ml) of 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) or 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) (1 mmol) was added dropwise at room temperature. The yellow precipitate was stirred for 20 min, then filtered, well washed with a diethylether/petroleum ether solution and dried in vacuo (55–60%).

Anal. Calc. for H_2L_C: C, 63.68; H, 7.05; N, 8.91. Found: C, 62.67; H, 6.88; N, 8.45%. IR (cm^{-1}): 1633 ν(C=N).

Anal. Calc. for H_2L_D: C, 62.29; H, 6.59; N, 9.47. Found: C, 62.71; H, 6.73; N, 9.28%. IR (cm^{-1}): 1634 ν(C=N).

2.2.1.3. H_2L_E, H_2L_F. To a methanolic solution (50 ml) of the appropriate diformyl derivative, 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) or 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (2 mmol), the desired polyamine,1,5-diamino-3-aza(dodecyl)pentane or 1,7-diamino-4-aza(methyl)heptane, (2 mmol) in methanol (25 ml) was added dropwise. The dark yellow solution was stirred under reflux for 2 h. The solvent was removed by distillation under reduced pression and the resulting oil or residue dissolved in $CHCl_3$ (10 ml) and precipitated with diethyl ether/petroleum ether (1:1 50 ml) this last solubilization/precipitation process being repeated three/four times. The final yellow product was collected by filtration, and washed with diethyl ether/petroleum ether and dried in vacuo. The products can be further purified by chromatography on alumina using $CHCl_3$ as eluent (yield 54–59%).

Anal. Calc. for H_2L_E: C, 68.09; H, 8.91; N, 7.01. Found: C, 68.09; H, 8.92; N, 6.74%. IR (cm^{-1}): 1633 ν(C=N).

Anal. Calc. for $H_2L_F\cdot 0.5H_2O$: C, 63.76; H, 7.53; N, 8.26. Found: C, 63.78; H, 7.64; N, 8.16%. IR (cm^{-1}): 1634 ν(C=N); 1025, 1087 ν(C–O).

$Na_2(L_D)$ was prepared according to literature [17].

2.2.1.4. $Na(H_2L_G)\cdot H_2O$, $Na(H_2L_H)\cdot H_2O$. To an aqueous solution (5 ml) of 2,3-diaminopropionic acid monochlorohydrate or 2,4-diaminobutirric acid dichlorohydrate (5 mmol), respectively, 5 and 10 mmol of NaOH in methanol (5ml) were added. The solution was stirred for 15 min, then added with a methanol solution of 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (H_2L^I), finally refluxed for 2 h. The solvent was evaporated at reduced pressure and the resulting orange-yellow or yellow residue was washed twice with ethanol, collected by filtration and dried in vacuo (69–70%).

Anal. Calc. for $Na(H_2L_G)\cdot H_2O$: C, 55.51; H, 5.10; N, 6.16. Found: C, 55.67; H, 5.33; N, 6.18%. IR (cm^{-1}): 1630 ν(C=N); 1635 ν_{asym}(COO).

Anal. Calc. for $Na(H_2L_H)\cdot H_2O$: C, 56.30; H, 5.10; N, 5.20. Found: C, 56.41; H, 5.38; N, 5.98%. IR (cm^{-1}): 1630 ν(C=N); 1636 ν_{asym}(COO).

2.2.2. Macroacyclic Schiff bases

2.2.2.1. H_2L_I. To a pale yellow $CHCl_3$ solution (60 ml) of 3-ethoxysalicylaldehyde (24.07 mmol) ethylenediamine (12.03 mmol) was added. The yellow solution was refluxed for 2 h, then reduced in volume and allowed to stand. The resulting yellow precipitate was collected by filtration, washed twice with diethylether (20 ml) and dried in vacuo (80% yield).

Anal. Calc. for $H_2L_I\cdot H_2O$: C, 64.16; H, 7.00; N, 7.48. Found: C, 64.81; H, 6.87; N, 7.70%. IR (cm^{-1}): 1634 ν(C=N), 1249, 1077 ν(C–O).

2.2.2.2. H_2L_L, H_2L_M. 2-(Aminomethyl)pyridine or 2-(2-aminoethyl)pyridine (6 mmol) was added to a pale yellow $CHCl_3$ solution (60 ml) of, respectively, 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) or 3,3′-(3,6-dioxaoctane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (3 mmol). The resulting dark yellow solution was refluxed for 2 h, then evaporated to dryness. The yellow oil obtained was treated four times with diethyl ether (4 × 100 ml). The yellow solution obtained was allowed to stand for 20 min until a yellow microcrystalline precipitate separated. This was collected by filtration, washed with diethyl ether (50 ml) and dried in vacuo (78–82%).

Anal. Calc. for H_2L_L: C, 68.43; H, 5.74; N, 10.64. Found: C, 69.40; H, 5.38; N, 10.29%. IR (cm^{-1}): 1633 ν(C=N).

Anal. Calc. for H_2L_M: C, 68.21; H, 6.40; N, 9.36. Found: C, 67.35; H, 6.38; N, 9.39%. IR (cm^{-1}): 1636 ν(C=N); 1255, 1046 ν(C–O).

2.2.2.3. $Na(HL_L)\cdot H_2O$. 2-(Aminomethyl)pyridine (10 mmol) in 10 ml of methanol was added dropwise to a methanol solution (50 ml) of Na_2L^I (5 mmol). The yellow solution obtained was refluxed for 2 h; the solvent was evaporated to dryness under reduced pressure and the brown residue was washed twice with diethyl ether, filtered and dried in vacuo (55%).

Anal. Calc. for $Na(HL_L)\cdot H_2O$: C, 63.60; H, 5.52; N, 9.89. Found: C, 62.99; H, 5.02; N, 8.98%. IR (cm^{-1}): 1633 ν(C=N).

2.2.2.4. $Na(H_3L_N)\cdot H_2O$. To a water solution (3 ml) of glycine (8 mmol), NaOH (8 mmol) in MeOH (5ml) was added dropwise. To the resulting solution 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (4 mmol) in MeOH (40 ml) was added. The resulting solution was refluxed for 2 h, then evaporated to dryness. The maroon residue was dissolved in MeOH (5 ml) filtered and precipitate with H_2O (10 ml). The maroon precipitate was collected by filtration, washed with diethyl ether and dried in vacuo (yield 64%).

Anal. Calc. for $Na(H_3L_N)\cdot H_2O$: C, 52.81; H, 5.04; N, 5.60. Found: C, 53.37; H, 4.67; N, 5.13%. IR (cm^{-1}): 1655 ν(C=N); 1611 ν_{asym}(COO).

2.2.3. Macrocyclic and macroacyclic polyamines

A general methodology was used for all the cyclic and acyclic polyamine derivatives. The desired compound was obtained by reduction of the appropriate Schiff base with an excess of $NaBH_4$.

2.2.3.1. H_2R_A, H_2R_B. A $CHCl_3$/MeOH solution (60 ml) of appropriate Schiff base (7 mmol) was reacted with an excess (36 mmol) of $NaBH_4$. The solution, turned from dark yellow to pale yellow (or cream), was stirred at room temperature for 30 min, then evaporated to dryness. The residue was treated with H_2O (100 ml), filtered off and dissolved in $CHCl_3$ or $CHCl_3$/MeOH (4:1). The resulting solution was anhydrified over molecular sieves, then evaporated to dryness. The cream or white residue was dissolved in $CHCl_3$ or MeOH and precipitated by the addition of diethyl ether or petroleum ether. The obtained cream or white precipitate was collected by filtration, washed with diethyl ether or petroleum ether and dried in vacuo (39–40% yield).

Anal. Calc. for H_2R_A: C, 63.15; H, 7.23; N, 6.69. Found: C, 63.53; H, 7.72; N, 6.24%. IR (cm^{-1}): 3291 ν(N–H); 1231, 1076 ν(C–O).

Anal. Calc. for $H_2R_B\cdot 0.5CHCl_3$: C, 56.82; H, 6.16; N, 6.46. Found: C, 56.05; H, 6.33; N, 6.39%. IR (cm^{-1}): 3302 ν(N–H); 1229, 1075 ν(C–O).

2.2.3.2. $Na(HR_D)$. To a $CHCl_3$/MeOH solution (50 ml) of $Na_2(L_D)$(1 mmol), an excess (4 mmol) of $NaBH_4$ was added. The solution, turned from yellow to a pale yellow, was stirred at room temperature for 1 h. A pale yellow precipitate formed, which was filtered, well washed with EtOH and subsequently diethyl ether, and dried in vacuo (40% yield).

Anal. Calc. for $Na(HR_D)\cdot 1CHCl_3$: C, 50.63; H, 5.49; N, 7.38. Found: C, 50.06; H, 5.85; N, 7.24%. IR: (cm^{-1}): 3279 ν(N–H).

2.2.3.3. H_2R_I, H_2R_L, H_2R_M. To a $CHCl_3$/MeOH (60 ml) solution of appropriate acyclic Schiff base H_2L_I, H_2L_L, H_2L_M (1 mmol) an excess of $NaBH_4$ (~5 mmol) was added under vigorous stirring. The solution, turned from yellow to white or pale-yellow, was maintained under stirring for 1–2 h, then reduced in volume and allowed to stand (for H_2R_I) or evaporated to dryness (for H_2R_L or H_2R_M). H_2R_I was collected from the solution by filtration, washed with methanol and dried in vacuo. The residue was treated with $CHCl_3$ (H_2R_L) or CH_2Cl_2/MeOH (H_2R_M); the solution was clarified by filtration and maintained over molecular sieves overnight, then partially evaporated (H_2R_L) or totally evaporated (H_2R_M). The subsequent addition of diethyl ether to the chloroform solution of H_2R_L produces a white precipitate which was collected by filtration and dried in vacuo. The residue of H_2R_M was dissolved in MeOH (10ml); the subsequent addition of petroleum ether to the clarified methanolic solution caused the precipitation of H_2R_M as a white oil which was collected and dried in vacuo (40–43% yield).

Anal. Calc. for $H_2R_I\cdot H_2O$: C, 63.48; H, 7.99; N, 7.40. Found: C, 64.01; H, 8.09; N, 6.96%. IR (cm^{-1}): 3291 ν(N–H); 1230–1069 ν(C–O).

Anal. Calc. for $H_2R_L\cdot H_2O$: C, 65.68; H, 6.61; N, 10.21. Found: C, 64.82; H, 6.11; N, 9.81%. IR(cm^{-1}): 3289 ν(N–H).

H_2R_M is an oil; consequently the elemental analysis was not carried out. IR (cm^{-1}): 3257 ν(N–H); 1230, 1082 ν(C–O).

2.2.3.4. $Na(HR_L) \cdot H_2O$. An excess of $NaBH_4$ (12 mmol) was added under stirring at room temperature to a methanol–chloroform solution (50 ml) of $Na(HL_L) \cdot H_2O$ (3 mmol). The cream solution obtained was stirred for 1 h, then allowed to stand for 2 h. The solvent was evaporated to dryness and the cream residue was dissolved with $CHCl_3$ (60 ml); the solution was clarified by filtration, then evaporated to dryness. The solution obtained by dissolving the residue in $CHCl_3$ (10 ml) was filtered and treated with diethyl ether (40 ml). The cream precipitate obtained was filtered and dried in vacuo (42% yield).

Anal. Calc. for $Na(HR_L) \cdot H_2O$: C, 61.32; H, 6.18; N, 9.53. Found: C, 61.70; H, 5.65; N, 8.93%. IR (cm^{-1}): 3278 ν(N–H).

2.3. Complexes

2.3.1. Mononuclear complexes with cyclic Schiff bases

2.3.1.1. $Ni(L_E) \cdot 2H_2O$. To a methanolic solution (60 ml) of 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (1 mmol), 1,5-diamino-3-aza(dodecyl)pentane (1 mmol) in methanol (10 ml) and after a stirring of 10 min, Ni(II) acetate hydrate (1 mmol) in methanol (10 ml) were added. The solution, turned into orange-red, was refluxed for 2 h, then evaporated to dryness. The residue was dissolved in ethanol and, after filtration, a orange-red precipitate was obtained by addition of diethyl ether; it was collected by filtration, washed with ethanol/diethyl ether and dried in vacuo (55% yield).

Anal. Calc. for $Ni(L_E) \cdot 2H_2O$: C, 60.45; H, 8.06; N, 6.22. Found: C, 60.19; H, 8.71; N, 6.26%. IR (cm^{-1}): 1625 ν(C=N); $\mu_{eff} = 2.2$ BM.

2.3.1.2. $Ni(H_2L_E)(CH_3COO)_2 \cdot 4H_2O$ and $Cu(HL_E)(CH_3COO)$. To a methanolic solution (50 ml) of 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (1 mmol), 1,5-diamino-3-aza(dodecyl)pentane (1 mmol) and the desired metal(II) acetate (1 mmol) in methanol (10 ml) were added in succession. The solution was refluxed for 2 h then evaporated to dryness. The residue was treated with $CHCl_3$ (5 ml). To the resulting solution, clarified by filtration, diethylether was added; the obtained precipitate was collected by filtration and dried in vacuo.

Alternatively the same complexes have been obtained by reacting a chloroform solution (60 ml) of the appropriate macrocycle (1 mmol) with the desired metal(II) acetate (1 mmol) in methanol (5 ml). The resulting solution was refluxed for 2 h then evaporated to dryness. The residue was treated with $CHCl_3$ (5 ml). The solution, clarified by filtration, separates by addition of diethylether (10 ml) a precipitate (dark green for Cu complexes, red for Ni complexes) which was filtered, washed with $CHCl_3/Et_2O$ (1:2) and dried in vacuo (50–55% yield).

Anal. Calc. for $Cu(HL_E)(CH_3COO)$: C, 61.48; H, 7.60; N, 5.97. Found: C, 61.74; H, 8.13; N, 6.82%. IR (cm^{-1}): 1636 ν(C=N); $\mu_{eff} = 2.1$ BM.

Anal. Calc. for $Ni(H_2L_E)(CH_3COO)_2 \cdot H_2O$: C, 49.94; H, 5.48; N, 4.48. Found: C, 50.13; H, 5.15; N, 5.18%. IR (cm^{-1}): 1623 ν(C=N); $\mu_{eff} = 2.3$ BM.

2.3.2. Mononuclear acyclic Schiff bases complexes

2.3.2.1. $M(L)$ ($M = Ni^{2+}, Cu^{2+}$; $H_2L = H_2L_I$, H_2L_L), $Co(H_2L_I)(CH_3COO)_2$ and $Mn(L_I)(CH_3COO) \cdot H_2O$. To a methanolic solution (30 ml) of the diformyl derivative 3-ethoxysalicylaldehyde or 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) (1 mmol), the appropriate amine (2 mmol) (respectively, ethylenediamine and 2-aminomethylpyridine) in methanol (10 ml) and, after a stirring of 15 min, the desired metal(II) acetate hydrate (1 mmol) were added. The resulting solution was refluxed for 2 h then evaporated to dryness. The residue was treated with $CHCl_3$ (5 ml); the resulting solution, clarified by filtration, separated a precipitate when treated with diethyl ether (20 ml). This was collected by filtration, washed with $CHCl_3/Et_2O$ (1:4) and dried in vacuo.

Alternatively the same complexes have been obtained by reacting equimolecular amounts of the preformed Schiff base and the appropriate metal acetate hydrate and following the same synthetic procedure (60–65% yield).

Anal. Calc. for $Ni(L_I)$ (orange red precipitate): C, 58.15; H, 5.37; N, 6.78. Found: C, 58.59; H, 5.49; N, 6.69%. IR (cm^{-1}): 1617 ν(C=N); $\mu_{eff} = 0.4$ BM.

Anal. Calc. for $Cu(L_I)$ (dark green): C, 57.48; H, 5.31; N, 6.70. Found: C, 57.21; H, 4.89; N, 6.54%. IR (cm^{-1}): 1631 ν(C=N); 1238, 1080 ν(C–O); $\mu_{eff} = 1.9$ BM.

Anal. Calc. for $Co(H_2L_I)(CH_3COO)_2$ (brick red): C, 54.04; H, 5.67; N, 5.25. Found: C, 54.04; H, 5.44; N, 5.71%. IR (cm^{-1}): 1639 ν(C=N); 1246, 1084 ν(C–O); $\mu_{eff} = 3.2$ BM.

Anal. Calc. for $Mn(L_I)(CH_3COO) \cdot H_2O$ (brown): C, 52.39; H, 5.80; N, 5.55. Found: C, 53.23; H, 5.18; N, 5.04%. IR (cm^{-1}): 1624 ν(C=N); 1253, 1083 ν(C–O); $\mu_{eff} = 6.2$ BM.

Anal. Calc. for $Ni(L_L) \cdot H_2O$ (orange-red): C, 59.93; H, 5.03; N, 9.32. Found: C, 60.77; H, 4.85; N, 8.46%. IR (cm^{-1}): 1630 ν(C=N); $\mu_{eff} = 3.0$ BM.

Anal. Calc. for $Cu(L_L) \cdot 2CHCl_3 \cdot H_2O$ (dark green): C, 45.65; H, 3.83; N, 6.65. Found: C, 44.73; H, 3.74; N, 7.61%. IR (cm^{-1}): 1639 ν(C=N); $\mu_{eff} = 1.75$ BM.

2.3.3. Mononuclear complexes with cyclic polyamine derivatives

2.3.3.1. Cu(R_A)·2H_2O, M(H_2R_A)(CH_3COO)$_2$ (M = Co^{2+}, Ni^{2+}) and Mn(R_A)(CH_3COO)·2H_2O. To a $CHCl_3$/MeOH solution (50 ml) of the appropriate polyamine (1 mmol) the desired metal(II) acetate (1 mmol) in methanol (10 ml) was added. The resulting solution was refluxed for 2 h then evaporated to dryness. The residue was treated with $CHCl_3$ (10 ml); to the resulting solution, clarified by filtration, diethyl ether (40 ml) was added and the obtained precipitate was washed with $CHCl_3$/Et_2O (1:4) and dried in vacuo (52–55% yield).

Anal. Calc. for Ni(H_2R_A)(CH_3COO)$_2$ (pale green): C, 52.46; H, 6.10; N, 4.71. Found: C, 52.57; H, 6.00; N, 4.88%. IR (cm^{-1}): 3230 ν(N–H); 1589 ν_{asym}(COO); 1400 ν_{sym}(COO), 1240, 1087 ν(C–O); $\mu_{eff} = 3.0$ BM.

Anal. Calc. for Cu(R_A)·2H_2O (green): C, 51.21; H, 6.25; N, 5.43. Found: C, 50.85; H, 5.38; N, 5.06%. IR (cm^{-1}): 3222 ν(N–H); 1223, 1071 ν(C–O); $\mu_{eff} = 1.8$ BM.

Anal. Calc. for Co(H_2R_A)(CH_3COO)$_2$ (green): C, 52.44; H, 6.09; N, 4.70. Found: C, 53.21; H, 6.62; N, 4.59%. IR (cm^{-1}): 3225, ν(N–H) 1576 ν_{asym}(COO); 1408, 1383 ν_{sym}(COO), 1228, 1065 ν(C–O); $\mu_{eff} = 3.6$ BM.

Anal. Calc. for Mn(R_A)(CH_3COO)·2H_2O (brown): C, 50.89; H, 6.23; N, 4.95. Found: C, 51.33; H, 5.42; N, 4.48%. IR (cm^{-1}): 3233 ν(N–H); 1589 ν_{asym}(COO); 1400 ν_{sym}(COO); 1240, 1021 ν(C–O); $\mu_{eff} = 5.9$ BM.

2.3.4. Mononuclear complexes with acyclic polyamine derivatives

2.3.4.1. M(H_2R_I) (CH_3COO)$_2$ (M = Co^{2+}, Ni^{2+}) and Mn(R_I)(CH_3COO)·H_2O. To a $CHCl_3$ solution (50 ml) of H_2R_I (1 mmol) the appropriate metal acetate (1 mmol) in methanol (5 ml) was added. The solution was refluxed for 2 h then evaporated to dryness. The residue was dissolved in EtOH (15 ml), clarified by filtration, and precipitated by addition of diethyl ether (50 ml). The product obtained was collected by filtration, washed twice with an ethanol/diethyl ether solution and dried in vacuo (62–65% yield).

Anal. Calc. for Ni(H_2R_I)(CH_3COO)$_2$ (pale green): C, 53.66; H, 6.38; N, 5.21. Found: C, 53.84; H, 6.65; N, 5.48%. IR (cm^{-1}): 3220 ν(N–H); 1583 ν_{asym}(COO); 1410 ν_{sym}(COO); 1056, 1227 ν(C–O); $\mu_{eff} = 3.5$ BM.

Anal. Calc. for Co(H_2R_I)(CH_3COO)$_2$·2H_2O (dark green): C, 52.73; H, 6.73; N, 4.92. Found: C, 52.53; H, 6.24; N, 5.36%. IR (cm^{-1}): 3227 ν(N=H); 1570 ν_{asym}(COO), 1393 ν_{sym}(COO); 1233, 1066 ν(C–O); $\mu_{eff} = 3.6$ BM.

Anal. Calc. for Mn(R_I)(CH_3COO)·H_2O (brown): C, 53.88; H, 6.37; N, 5.71. Found: C, 53.46; H, 6.31; N, 5.48%. IR (cm^{-1}): 3243 ν(N–H); 1566 ν_{asym}(COO); 1410 ν_{sym}(COO), 1237, 10063 ν(C–O); $\mu_{eff} = 6.1$ BM.

2.3.4.2. M(R_I)·nH_2O (M = Ni^{2+},Cu^{2+}, n = 2,3). To a $CHCl_3$ solution (50 ml) of H_2R_I (1 mmol) the appropriate metal(II) acetate (1 mmol) in methanol (5 ml) and subsequently [N(Bu)$_4$](OH) (2 mmol) were added. The solution was refluxed for 2 h then evaporated to dryness. The residue was dissolved in EtOH, clarified by filtration, and precipitated by addition of diethyl ether. The product obtained was collected by filtration, washed with an ethanol/diethyl ether solution and dried in vacuo (65% yield).

Anal. Calc. for Ni(R_I)·3H_2O (orange-red): C, 51.98; H, 6.76; N, 6.06. Found: C, 51.33; H, 5.84; N, 5.51%. IR (cm^{-1}): 3258 ν(N–H), 1229, 1059 ν(C–O); $\mu_{eff} = 3.0$ BM.

Anal. Calc. for Cu(R_I)·2H_2O (dark green): C, 52.45; H, 6.60; N, 6.12. Found: C, 52.79; H, 6.33; N, 5.41%. IR (cm^{-1}): 3224 ν(N–H); 1232, 1070 ν(C–O); $\mu_{eff} = 1.9$ BM.

2.3.4.3. Cu(R_L)·H_2O. Copper(II) acetate hydrate (1 mmol) in methanol (5 ml) was added to a $CHCl_3$ solution (50 ml) of the polyamine H_2R_L·H_2O (1 mmol). The solution was refluxed for 2 h then reduced in volume. The resulting green precipitate was collected by filtration, washed with diethylether and dried in vacuo (55% yield).

Anal. Calc. for Cu(R_L)·H_2O: C, 49.11; H, 5.81; N, 5.21. Found: C, 49.00; H, 5.80; N, 4.90%. IR (cm^{-1}): 3250 ν(N–H); $\mu_{eff} = 1.73$ BM.

2.3.5. Heterodinuclear Schiff bases complexes

2.3.5.1. MNa(L)(CH_3COO)·nH_2O (M = Co^{2+}, Ni^{2+}, Cu^{2+}; H_2L = H_2L_F, H_2L_I, H_2L_L), MNa(HL_L)(CH_3COO)$_2$·nH_2O (M = Cu^{2+}, Ni^{2+}), NiNa(L)·H_2O (H_3L = H_3L_G, H_3L_H), MNa(HL_N)·H_2O (M = Cu^{2+}, Ni^{2+}), MnNa(L_I)(CH_3COO)$_2$·nH_2O, MnNa(L_M)(CH_3COO)·H_2O. These different synthetic procedure were employed:

(A) To a methanol solution or suspension (30 ml) of the appropriate Schiff base (1 mmol) the desired metal acetate (1 mmol) in methanol (10 ml) was added. The resulting suspension, was refluxed for 15 min and, after the addition of NaOH (2 mmol) in 10 ml of MeOH, maintained under reflux for additional 2 h. Then it was allowed to stand overnight and the resulting precipitate was collected by filtration, washed with methanol and dried in vacuo.

(B) To a methanolic solution (30 ml) of the sodium derivative $Na_{2-n}(H_nL)$ (1 mmol) the desired metal acetate (1 mmol) in 10 ml of methanol was added. The resulting suspension was refluxed for 15 min and, after the addition of NaOH (2 mmol) in 10 ml of MeOH, maintained under reflux for 2 h. Then it was allowed to stand overnight and the precipitate obtained was collected by filtration, washed with methanol and dried in vacuo.

(C) Alternatively, to a methanolic solution (30 ml) of the appropriate diformyl precursor (1 mmol), the appropriate polyamine (1 mmol), metal acetate hydrate (1 mmol) and NaOH (2 mmol) were added in succession. The resulting suspension was refluxed for 2 h then allowed to stand for 3 h. The precipitate was collected by filtration, washed with methanol and dried in vacuo (50–55% yield).

Anal. Calc. for $NiNa(L_F)(CH_3COO)$ (emerald green): C, 54.57; H, 6.0; N, 6.58. Found: C, 53.85; H, 5.94; N, 6.72%. IR (cm^{-1}): 1632 ν(C=N); 1597 ν_{asym}(COO); 1324 ν_{sym}(COO); 1217, 1089 ν(C–O); $\mu_{eff} = 3.5$ BM.

Anal. Calc. for $NiNa(L_G) \cdot H_2O$ (orange): C, 49.35; H, 4.14; N, 5.48. Found: C, 49.73; H, 4.36; N, 6.16%. IR (cm^{-1}): 1617 ν(C=N); 1614 ν_{asym}(COO); $\mu_{eff} = 2.8$ BM.

Anal. Calc. for $NiNa(L_H) \cdot H_2O$ (orange-red): C, 49.26; H, 4.65; N, 4.79. Found: C, 48.34; H, 4.15; N, 5.55%. IR (cm^{-1}): 1618 ν(C=N); 1613 ν_{asym}(COO); 1314 ν_{sym}(COO); 1227, 1087 ν(C–O), $\mu_{eff} = 2.7$ BM.

Anal. Calc. for $NiNa(L_I)(CH_3COO) \cdot H_2O$ (red): C, 51.50; H, 5.30; N, 5.46. Found: C, 51.53; H, 5.27; N, 5.62%. IR (cm^{-1}): 1618 ν(C=N); 1601 ν_{asym}(COO); 1314 ν_{asym}(COO); 1227, 1087 (C–O); $\mu_{eff} = 0.3$ BM.

Anal. Calc. for $CuNa(L_I)(CH_3COO)$ (brown): C, 52.85; H, 5.04; N, 5.60. Found: C, 52.75; H, 5.05; N, 6.12%. IR (cm^{-1}): 1632 ν(C=N); 1599 ν_{asym}(COO); 1312 ν_{sym}(COO); 1238, 1081 ν(C–O); $\mu_{eff} = 2.0$ BM.

Anal. Calc. for $CoNa(L_I)(CH_3COO) \cdot H_2O$ (dark green): C, 51.47; H, 5.30; N, 5.46. Found: C, 52.10; H, 5.51; N, 6.28%. IR (cm^{-1}):1638 ν(C=N); 1604 ν_{asym}(COO); 1312 ν_{sym}(COO); 1224, 1084 ν(C–O); $\mu_{eff} = 2.1$ BM.

Anal. Calc. for $MnNa(L_I)(CH_3COO)_2$ (brown): C, 52.38; H, 5.13; N, 5.09. Found: C, 53.31; H, 5.48; N, 5.19%. IR (cm^{-1}):1625 ν(C=N); 1598 ν_{asym}(COO); 1332 ν_{sym}(COO); 1252, 1084 ν(C–O); $\mu_{eff} = 5.0$ BM.

Anal. Calc. for $NiNa(L_L)(CH_3COO) \cdot 2H_2O$ (brown): C, 56.25; H, 5.96. Found: N, 6.90; C, 56.03; H, 5.12; N, 6.90%. IR (cm^{-1}): 1635 ν(C=N); $\mu_{eff} = 3.1$ BM.

Anal. Calc. for $NiNa(HL_L)(CH_3COO)_2 \cdot 4H_2O$ (yellow-orange): C, 50.96; H, 5.91; N, 6.99. Found: C, 50.49; H, 5.56; N, 6.89%. IR (cm^{-1}): 1635 ν(C=N); $\mu_{eff} = 3.1$ BM.

Anal. Calc. for $CuNa(HL_L)(CH_3COO)_2 \cdot 2H_2O$ (hazel-brown): C, 54.43; H, 5.00; N, 7.93. Found: C, 53.89; H, 4.07; N, 7.92%. IR (cm^{-1}): 1625 (C=N); $\mu_{eff} = 1.8$ BM.

Anal. Calc. for $NiNa(L_M)(CH_3COO) \cdot 2H_2O$ (yellow): C, 55.76; H, 5.85; N, 7.22. Found: C, 56.03; H, 5.12; N, 6.90%.

Anal. Calc. for $NiNa(HL_N) \cdot H_2O$ (hazel-brown): C, 47.43; H, 4.13; N, 5.03. Found: C, 47.00 H, 4.53N, 4.90%. IR (cm^{-1}): 1639 ν(C=N); 1600 ν_{asym}(COO); $\mu_{eff} = 3.6$ BM.

Anal. Calc. for $CuNa(HL_N) \cdot H_2O$ (brown): C, 47.02; H, 4.13; N, 4.98. Found: C, 46.30 H, 4.53; N, 4.90%. IR (cm^{-1}): 1644 ν(C=N); 1601 ν_{asym}(COO); $\mu_{eff} = 1.6$ BM.

NB: SEM-EDS investigations show all the prepared heterodinuclear complexes have a M:Na = 1:1 ratio.

2.3.6. Heterodinuclear complexes with polyamine derivatives

2.3.6.1. $MNa(R)(CH_3COO) \cdot nH_2O$, $MnNa(R)(CH_3COO)_2$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}$; $H_2R = H_2R_A$, H_2R_I, H_2R_L, H_2R_M; $n = 1,2$). The complexes have been prepared following the same procedures employed for the synthesis of the analogous Schiff base complexes. To a methanol solution or suspension (30 ml) of the appropriate polyamine H_2R (1 mmol) the desired metal(II) acetate (1 mmol) in methanol (10 ml) was added. The resulting suspension was refluxed for 15 min and, after the addition of NaOH (2 mmol) in 10 ml of MeOH, was maintained under reflux for additional 2 h. Then it was allowed to stand. The resulting precipitate was collected by filtration, washed with methanol and dried in vacuo (45–50% yield).

Anal. Calc. for $NiNa(R_A)(CH_3COO) \cdot 2.5H_2O$ (orange): C, 47.87; H, 6.03; N, 4.65. Found: C, 47.16; H, 5.23; N, 4.54%. IR (cm^{-1}): 1571 ν_{asym}(COO); 1315 ν_{sym}(COO); 1246, 1091 ν(C–O) $\mu_{eff} = 2.2$ BM.

Anal. Calc. for $CuNa(R_A)(OH) \cdot H_2O$ (green): C, 49.12; H, 5.81; N, 5.21. Found: C, 48.49; H, 4.93; N, 4.65%. IR (cm^{-1}): 3226 ν(N–H); $\mu_{eff} = 1.8$ BM.

Anal. Calc. for $CoNa(R_A)(CH_3COO) \cdot 2H_2O$ (dark green): C, 48.58; H, 5.95; N, 4.72. Found: C, 48.09; H, 5.22; N, 4.24%. IR (cm^{-1}): 3232 ν(N–H); 1570 ν_{asym}(COO), 1314 ν_{sym}(COO); 1237, 1079 ν(C–O); $\mu_{eff} = 2.6$ BM.

Anal. Calc. for $MnNa(R_A)(CH_3COO)_2$ (brown): C, 50.99; H, 5.60; N, 4.57. Found: C, 50.53; H, 5.31; N, 4.32%. IR (cm^{-1}): 1569; ν_{asym}(COO); 1409 ν_{sym}(COO); 1237, 1079 ν(C–O) $\mu_{eff} = 5.0$ BM.

Anal. Calc. for $NiNa(R_I)(CH_3COO)$ (grey): C, 52.94; H, 5.86; N, 5.61. Found: C, 53.16; H, 5.75; N, 5.34%. IR (cm^{-1}): 3283 ν(N–H); 1566 ν_{asym}(COO); 1313 ν_{sym}(COO); 1228, 1064 ν(C–O); $\mu_{eff} = 3.0$ BM.

Anal. Calc. for $CuNa(R_I)(CH_3COO)$ (green): C, 52.43; H, 5.80; N, 5.56. Found: C, 53.18; H, 5.87; N, 5.71%. IR (cm^{-1}): 3226 ν(N–H); 1568 ν_{asym}(COO); 1308 ν_{sym}(COO); 1234, 1070 ν(C–O); $\mu_{eff} = 1.9$ BM.

Anal. Calc. for $CoNa(R_I)(CH_3COO) \cdot 2H_2O$ (green): C, 49.35; H, 6.21; N, 5.23. Found: C, 49.52; H, 5.73; N, 5.12%. IR (cm^{-1}): 1570, ν_{asym}(COO); 1297 ν_{sym}(COO); 1236, 1072 ν(C–O); $\mu_{eff} = 2.1$ BM.

Anal. Calc. for $MnNa(R_I)(CH_3COO)_2 \cdot H_2O$ (brown): C, 50.36; H, 5.99; N, 4.89. Found: C, 50.61; H, 5.47; N, 5.08%. IR (cm^{-1}): 3283 ν(N–H), 1570 ν_{asym}(COO); 1411 ν_{sym}(COO); 1228, 1064 ν(C–O); $\mu_{eff} = 4.7$ BM.

Anal. Calc. for $CuNa(R_L)(CH_3COO)\cdot H_2O$ (dark brown): C, 57.61; H, 4.83; N, 8.94. Found: C, 57.72; H, 4.84; N, 8.97%. IR (cm^{-1}): 3330 ν(N–H); 1580 ν_{asym}(COO); 1315 ν_{sym}(COO); $\mu_{eff} = 1.92$ BM.

Anal. Calc. for $NiNa(R_M)(CH_3COO)\cdot 1.5H_2O$ (pale green): C, 56.27; H, 6.03; N, 7.29. Found: C, 56.01; H, 5.91; N, 7.39%. IR (cm^{-1}): 3267 1570 ν_{asym}(COO); 1308 ν_{sym}(COO); 1232, 1080 ν(C–O); $\mu_{eff} = 3.5$ BM.

NB: SEM-EDS investigations show all the prepared heterodinuclear complexes have a M:Na = 1:1 ratio.

2.4. Crystal data

Crystals of $Na(HR_D)\cdot H_2O$ were grown from a methanolic solution of the crude product.

The ORTEP representation of the crystal structure is shown in Fig. 1 with the label scheme used. All geometric and intensity data were taken using an automated four-cyrcle Philips PW1100 (FEBO system) X-ray diffractometer, using the Mo Kα radiation ($\lambda = 0.7107$ Å) and $\omega - 2\theta$ method. Lattice parameters were obtained from least-squares refinement of the setting angles of 30 reflections with $10 \leqslant 2\theta \leqslant 26°$. Intensity data were reduced by routine procedures and calculations were carried out by the application of direct methods program of SHELXS-86 [30]. The refinement calculations were carried out using SHELXS-93 program [34]. The benzene rings were refined as rigid bodies, the hydrogen atoms were included in the idealised positions with fixed C–H distances (0.97 Å in CH_2 groups and 0.93 Å in CH benzenic groups).

Crystal data: $0.25 \times 0.20 \times 0.15$ mm, monoclinic, space group $P2_1/n$, $a = 14.669(5)$ Å, $b = 8.316(5)$ Å, $c = 19.470(6)$ Å, $\beta = 91.73(4)°$, $V = 2374(2)$ Å^3, $D_c = 1.266$ g cm^{-3}, $Z = 4$. μ(Mo Kα) = 0.105 mm^{-1}, $T = 293(2)$ K, 2221 reflections with $I > 4s(I)$ used, $R = 0.086$, $R_w = 0.19$.

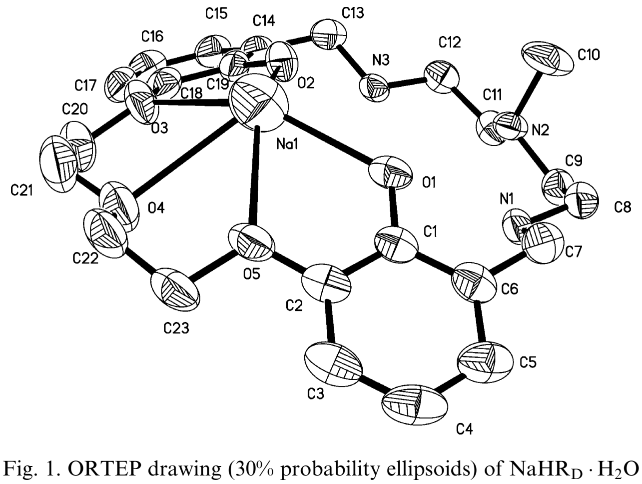


Fig. 1. ORTEP drawing (30% probability ellipsoids) of $NaHR_D \cdot H_2O$ with the atom labelling.

2.5. Physico-chemical measurements

IR spectra were recorded as KBr pellets on a Mattson 5000 FT-IR spectrometer. The same instrument, connected to a Quantum microscope equipped with a MCT detector, was used to collect the spectral data directly on the samples and avoid the risk of metathetic processes with KBr matrix.

Spectra in the UV–Vis region were collected in the solid state and in $CHCl_3$, MeOH or DMSO with a UV 500 Spectronic Unicam.

^{1}H, and ^{13}C NMR spectra and 2D COSY and NOESY experiments were recorded at 300.13 MHz on a Bruker AMX300 spectrometer at room temperature. Some of the signals were assigned by the spin decoupling technique. All the samples examined were dissolved in deuterated chloroform or methanol used also as internal references.

The morphology, homogeneity and the metal:sodium = 1:1 ratio in the complexes were checked by using a Philips XL40 model scanning electron microscopy equipped with an EDAX DX PRIME X-ray energy dispersive spectrometer [35].

The water content in the prepared samples 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; heating rate 5°C min^{-1}) and in air under the same conditions. Neutral alumina (Carlo Erba product) was used as reference material.

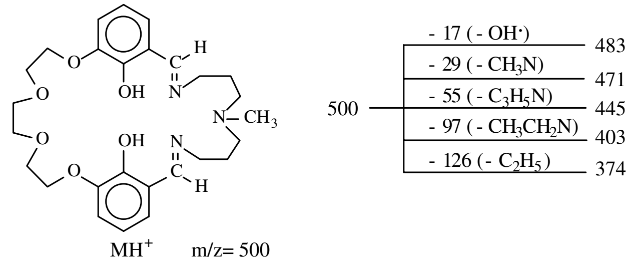
All mass spectrometric measurements were performed on a VG ZAB 217 instrument (VG analytical Ltd.) operating in fast atom bombardment (FAB) conditions (8 keV Xe atom bombarding a nitrobenzylalcohol solution of the sample) [36,37]. Also ESI-MS spectra have been recorded by using a LCQ mass spectrometry (Finnigam) and methanol solutions of the samples (10^{-5} M).

Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instruments) being calibrated with $HgCo(NCS)_4$ [38]. Diamagnetic corrections were performed [39].

3. Results and discussion

3.1. Cyclic and acyclic Schiff bases

The [1+1] cyclic Schiff bases $H_2L_A \cdots H_2L_F$, containing one N_3O_2, or N_2O_2 Schiff base site and one adjacent O_2O_3 or O_2O_4 crown-ether like site, have been prepared as yellow or yellow-orange air stable solids by self-condensation in methanol, under diluted conditions, of equimolecular amounts of the diformyl precursors 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde)



Scheme 3. Fragmentation pathway of H_2L_F.

(H_2L^I) or 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) (H_2L^{II}) and the appropriate polyamine. As we have already pointed out they can be prepared also by demetallation with guanidinium sulphate of the appropriate macrocyclic barium diperchlorate complex [16,20]. The [1+1] cyclic nature of these systems was inferred by FAB and/or ESI-MS spectra, where the formation of the parent peak $[M + H]^+$ and/or $[M + Na]^+$ at the appropriate m/z values were detected. Thus, for example, the ESI-MS spectra of H_2L_G show the formation of $[M + H]^+$ at $m/z = 500$ and a fragmentation pathway consistent with the proposed structure (Scheme 3).

A similar series of macrocyclic compounds, containing Na^+ into the crown-ether chamber, have been prepared using $Na_2(L^I)$ instead of H_2L^I as formyl precursor. It must be noted that $Na_2(L^I)$ was obtained as a yellow intermediate product during the synthesis of the diformyl precursor H_2L^I by reaction of diethyleneglicol ditosylate with 2,3-dihydroxybenzaldehyde in the presence of NaH and in anhydrous dimethylsulphoxide [25].

In these condensations the homodinuclear macrocyclic complexes $[Na_2(L)] \cdot nH_2O$ can be obtained which can evolve into the mononuclear one, $Na(HL) \cdot nH_2O$, where the sodium(I) resides into the crown-ether chamber, in solution and/or in consequence of crystallization efforts. The same occurs also when the corresponding polyamine derivatives are formed. The crystallization from methanol of the crude product gives rise to the mononuclear sodium macrocycles (see later).

Again mass spectrometry investigations confirm the [1+1] cyclic nature of these complexes. The IR spectra of these compounds show a strong band at 1634–1630 cm^{-1} due to $\nu(C{=}N)$, confirming the formation of the Schiff bases. In addition, ^1H NMR spectra of all these compounds in $CDCl_3$ show a peak at 8.50–8.15 ppm due to CH=N iminic protons, while the peak at 9.99–9.94 ppm due to the CH=O formyl protons, clearly detectable in the precursors H_2L^I, H_2L^{II} and $Na_2(L^I)$ is completely absent. Other significative variations occur also in the peaks due to the other protons when compared with those of the precursors (see Table 1).

The condensation of 2,3-diaminopropionic acid monochlorohydrate or 2,4-diaminobutirric acid dichlorohydrate with 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde in the presence of NaOH affords the [1+1] cyclic complexes $Na(H_2L_G) \cdot H_2O$ and $Na(H_2L_H) \cdot H_2O$. Their IR spectra show two strong bands at 1630 and 1635 or 1636 cm^{-1}, due, respectively, to $\nu(C{=}N)$ and $\nu_{asym}(COO)$.

3-Ethoxy-2-hydroxybenzaldehyde reacts with ethylenediamine in a 2:1 molar ratio and in alcoholic solution to form the corresponding [1+2] acyclic Schiff bases H_2L_I, as confirmed by a strong IR band at 1634 cm^{-1} $\nu(C{=}N)$ and the ^1H NMR peak at 8.29 ppm (CH=N) in $CDCl_3$. This yellow solid has an inner N_2O_2 and an outer O_2O_2 coordination chamber.

The condensation of the diformyl derivatives H_2L^I or H_2L^{II} or the sodium derivative $Na_2(L^I)$ with monoamines bearing also additional groups (i.e., $NH_2(CH_2)_n C_6H_4N$ with $n = 1$ or 2 and H_2NCH_2COOH) gives rise to the corresponding [1+2] side off acyclic compounds, H_2L_L, $Na(HL_L) \cdot H_2O$, H_2L_M and $Na(H_3L_N) \cdot H_2O$, containing one inner O_2O_3 or O_2O_4 and one outer $N_2N_2O_2$ or $N_2O_2O_2$ adjacent coordination site.

The formation of [1+2] entities for the acyclic compounds was proved by ESI-MS spectra: the fragmentation pathway is consistent with the proposed structure (Scheme 4).

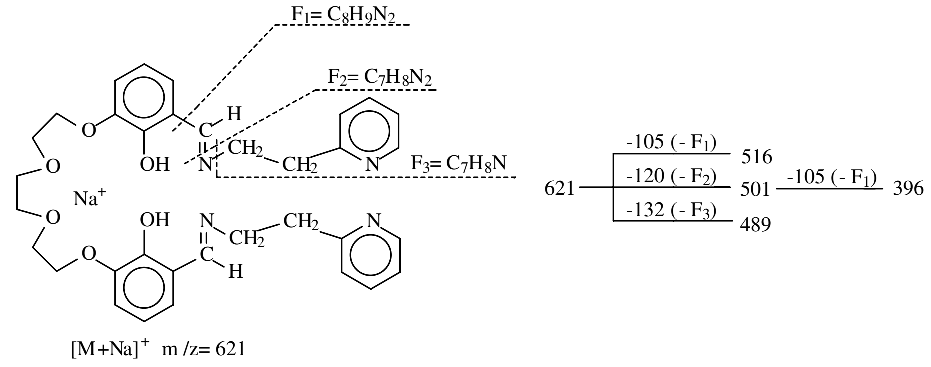
In these complexes a strong IR band at 1655–1633 cm^{-1} due to $\nu(C{=}N)$ occurs; furthermore, an additional strong IR absorption at 1611 cm^{-1}, due to the $\nu_{asymm}(COO)$, has been observed for $Na(H_3L_N) \cdot H_2O$.

Their ^1H NMR spectra in $CDCl_3$ or CD_3OD show the characteristic iminic peak at 8.54–8.19 ppm. For H_2L_L a ^1H NMR investigation in $CDCl_3$ proves the presence of a singlet at 13.72 ppm, ascribed to the phenolic OH protons, a singlet at 8.53 ppm due to the iminic protons, a doublet at 8.54 ppm, a triplet at 7.68 ppm, a doublet at 7.48 ppm and a triplet at 7.01 ppm due to the pyridine protons, while at 6.94–6.80 ppm a triplet and a doublet due to the aromatic protons occur. The singlet at 4.96 ppm is attributed to the methylenic groups bond to the Schiff base moiety and finally the two triplets at 4.25 and 4.00 ppm are due to the methylenic protons of the other crown like moiety.

Similarly the ^1H NMR spectrum in $CDCl_3$ of H_2L_M shows three multiplets at 8.53, 7.54, 7.10 ppm due to the pyridine protons, a singlet at 8.21 ppm due to the iminic protons. Furthermore, the peaks due to the aromatic protons lie in the range 6.94–6.66 ppm, while the triplet at 4.20–4.15 ppm is assigned to the aliphatic protons $ArOCH_2$. The multiplet at 4.03–3.96 ppm is due to the aliphatic protons $CNCH_2$ while the triplet at 3.90–3.85 ppm is assigned to the aliphatic protons (OCH_2CH_2OAr). Finally the singlet at 3.73 ppm and the triplet at 3.17–3.10 ppm are ascribed to the aliphatic

Table 1
^{1}H NMR data of Schiff base ligands and related complexes

	$HC{=}N$	H–Ar	CH_2O	$CNCH_2$	CH_2N	Other signals	
H_2L_C ($CDCl_3$)	8.20 s (2H)	6.88 dd (2H) 6.69 m (4H)	4.19 t (4H CH_2OAr); 3.95 m (4H); 3.86 t (4H)	3.63 m (4H)	2.78 m (4H CH_2NMe)	2.32 s (3H NCH_3)	13.91 s (2H ArOH)
H_2L_D ($CDCl_3$)	8.19 s (2H)	6.75 m (6H)	4.20 m (4H CH_2OAr); 3.95 m (4H)	3.63 m (4H)	2.78 m, m (4H CH_2NMe)	2.32 2s (3H NCH_3)	
H_2L_E ($CDCl_3$)	8.18 s (2H)	6.79 m (6H)	4.22 m (4H CH_2OAr); 3.92 m (4H)	3.63 m (4H)	2.46 m (6H)	1.18 m (20H $(CH_2)_{10}Me$)	0.82 t (3H CH_3)
$H_2L_F \cdot 0.5H_2O$ ($CDCl_3$)	8.26–8.25 d (2H)	6.94–6.59 m (6H)	4.20–4.13 m (4H CH_2OAr); 3.91–3.85 m (4H); 3.73 s (4H)	3.58 m (4H)	2.42–2.34 m (4H CH_2NMe)	2.16 s (3H NCH_3)	1.86–1.76 m (4H CH_2)
$H_2L_I \cdot H_2O$ ($CDCl_3$)	8.29 s (2H)	6.90–6.85 dd (2H); 6.82–6.78 dd (2H); 6.76–6.72 t (2H)	4.12–4.02 q (4H CH_2OAr)	3.92 s (4H)		1.41–1.15 t (6H CH_3)	13.6 s (2H ArOH)
H_2L_L ($CDCl_3$)	8.53 s (2H)	6.94–6.80 t, d, d (6H)	4.25 t (4H CH_2OAr) 4.00 t (4H)	4.96 s (4H NCH_2Pyr)		8.54–7.01 d, t, d, t (8H Pyr)	13.72 s (2H ArOH)
H_2L_M ($CDCl_3$)	8.21 s (2H)	6.94–6.90 dd (2H); 6.81–6.76 dd (2H); 6.73–6.66 t (2H)	4.20–4.15 t (4H CH_2OAr) 3.90–3.85 t (4H); 3.73 s (4H)	4.03–3.96 m (4H)	3.17–3.10 t (4H CH_2Pyr)	8.54–8.51 dd (2H Pyr); 7.59–7.50 m (2H Pyr); 7.14–7.06 m (4H Pyr)	
$Na(HL_L) \cdot H_2O$ ($CDCl_3$)	8.54 s (2H)	7.00–6.94 t, d, d (6H)	4.26 t (4H CH_2OAr) 4.00 t (4H)	4.97 s (4H NCH_2Pyr)		8.54–7.21 d, t, d, t (8H Pyr)	
$Na(H_3L_N) \cdot H_2O$ ($CDCl_3$)	8.19 s (2H)	6.92–6.45 d, d, t (6H)	4.23–3.93 3t (12H CH_2)				
$Ni(L_I)$ ($CDCl_3$)	8.54 s (2H)	7.95–7.91 dd (2H); 7.81–7.77 dd (2H); 7.63–7.55 t (2H)	5.34–5.24 q (4H $ArOCH_2$)	4.73 s (4H $CNCH_2$)		2.71 t (6H CH_3)	
$NiNa(L_I)(CH_3COO) \cdot H_2O$ (CD_3OD)	7.86 s (2H)	6.89–6.78 m (4H); 6.56–6.49 t (2H)	4.81–4.71 q (4H $ArOCH_2$)	3.53 s (4H $CNCH_2$)		1.25–1.18 t (6H CH_3)	



Scheme 4. Fragmentation pathway of H_2L_M.

protons $CH_2OCH_2CH_2OCH_2$ and CH_2Py, respectively. 2D COSY and NOESY experiments at 298K corroborate these assignments.

3.2. Polyamine derivatives

The cyclic and acyclic Schiff bases (or their sodium derivatives) have been reduced to the corresponding polyamines by reaction with an excess of $NaBH_4$. The compounds are soluble in chlorinated solvents and insoluble in H_2O and hence can be purified by extracting the residue of the reaction with $CHCl_3$.

The reduced polyamine derivatives maintain the [1+1] cyclic or [1+2] acyclic nature of the related Schiff bases as indicated by IR, NMR and mass spectrometry. The IR spectra show absorption bands at 3385–3257 cm^{-1} due to $\nu(NH)$ while the strong bands at 1636–1630 cm^{-1}, due to $\nu(C{=}N)$, characteristic of the related Schiff bases, are completely absent.

Moreover in their ^1H NMR spectra in $CDCl_3$ the singlet at 8.50–8.15 ppm due to the iminic protons (CH=N) is completely absent, while new peaks at 3.96–3.75 ppm, due to $ArCH_2N$ protons, have been detected.

Thus, the ^1H NMR spectrum of H_2R_A in $CDCl_3$, reported as an explanatory example, shows multiplets at 6.67–6.63 ppm due to the aromatic protons, at 4.14–4.10 and 3.86 ppm due to the methylenic protons of the CH_2O crown-ether chain and two singlets at 3.75 ppm and at 2.84 ppm, respectively, due to the methylenic protons $C_6H_3{-}CH_2{-}N$ and $NHCH_2$ (see Table 2).

Again, as above reported for the related Schiff bases, FAB or ESI-MS spectra confirm the cyclic or acyclic nature of the reduced compounds (see for example Scheme 5).

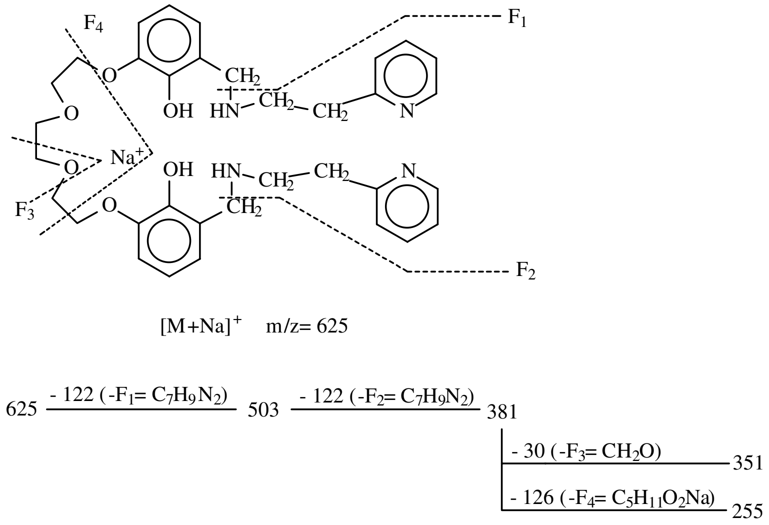
Apart from these molecular species, the FAB spectra were uninformative: no fragment ions were detected with significant abundance. In particular the $[M/2^{+\cdot}$, $[M/2+H]^+$ and $[M/2+CH_2]^{+\cdot}$ ions are completely absent, indicating a higher stability of the compounds under investigation.

3.3. Structure of $Na(HR_D)\cdot H_2O$

The reduction of these Schiff bases to the corresponding polyamine derivatives was definitively confirmed by the single-crystal X-ray structure of

Table 2
^1H NMR data of polyamines

	H–Ar	CH_2O	$NHCH_2$	$ArCH_2N$	Other signals	
H_2R_A ($CDCl_3$)	6.67–6.63 m (6H)	4.14–4.10 m (4H CH_2OAr) 3.86 m (8H)	2.84 s (4H)	3.75 s (4H)		
$H_2R_B\cdot 0.5CHCl_3$ ($CDCl_3$)	6.67–6.60 m (6H)	4.30–3.81 m (16H CH_2)				
$Na(HR_D)\cdot 1CHCl_3$ (CD_3OD)	6.91 dd (2H) 6.68 t (2H) 6.77 dd (2H)	4.20 m (4H CH_2OAr) 3.93 m (4H CH_2O)	2.64 m (4H)	3.84 s (4H)	2.48 m (4H $NMeCH_2$)	1.95 s (3H CH_3N)
$H_2R_I\cdot H_2O$ ($CDCl_3$)	6.78–6.57 m (6H)	4.10–3.99 q (4H $ArOCH_2$)	2.76 s (4H)	3.91 s (4H)	1.44–1.37 t (6H CH_3)	
H_2R_M ($CDCl_3$)	6.83–6.78 dd (2H) 6.70–6.60 m (4H)	4.18–4.13 t (4H CH_2OAr) 3.89–3.83 t (4H CH_2O)		3.96 s (4H)	3.07–2.95 m (8H $N(CH_2)_2$ Pyr)	8.50–8.47 dd (2H Pyr); 7.60–7.52 m (2H Pyr); 7.13–7.06 m (4H Pyr)



Scheme 5. Fragmentation pathway of H_2R_M.

$Na(HR_D) \cdot H_2O$. Well formed crystals of $Na(HR_D) \cdot H_2O$, suitable for an X-ray diffractometric investigation, were grown from methanol. Fig. 1 shows an ORTEP drawing of the structure. In this complex the asymmetric unit consists of one [1+1] macrocyclic molecule of the ligand coordinated to a sodium ion by five oxygen atoms present in the ligand. The coordination geometry of the metal can be described as a pentagonal pyramid with the sodium atom occupying the vertex. This constraints the whole molecule to assume a butterfly like shape with the wings, constituted by the two benzene rings, forming a dihedral angle of 48.9°. Surprisingly the sodium ion does not form other bonds or contacts, so it appears empty on the opposite side with respect to the ligand. The oxygen atoms form a plane (maximum and minimum deviations are 0.1 and 0.02 Å, respectively), from which the sodium atom displaces of 0.79 Å.

The neutralisation of the positive charge present on the sodium atom is reached by a negative charge distributed on the O(1) and O(2) atoms. The Na–O distances are 2.565(6) Å for O(2) and 2.620(7) Å for O(1), respectively, very shorter than the other Na–O(etheric) bond distances (2.904 Å mean). The bond angle O(1)–Na–O(2) is very large, (107°), with respect to all other angles to the sodium ion that are comprised between 57.2° and 59.2°. The conformation of the torsion angles O(3)–C(20)–C(21)–O(4) and O(4)–C(22)–C(23)–O(5) are g^- and g^+, identical to N(3)–C(12)–C(11)–N(2) and N(2)–C(9)–C(8)–N(1), respectively. The coordination polyhedron generated by sodium and the oxygen atoms is reported in Fig. 2.

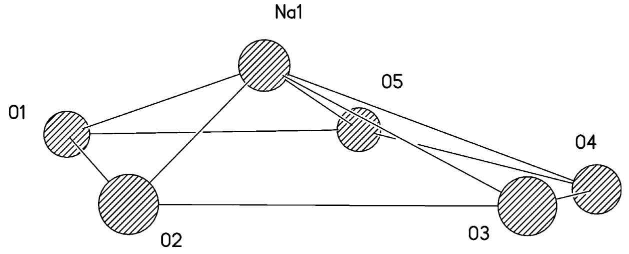


Fig. 2. Shape of the coordination polyhedron generated by the sodium and oxygen atoms.

3.4. Mononuclear complexes

The presence of a Schiff base site or of its reduced analogue in the prepared cyclic and acyclic ligands H_2L and H_2R makes the preparation of transition metal complexes highly feasible. They have been prepared by condensation of the formyl and amine precursors in the presence of these metal ions as templating agents or by reaction of the preformed ligand with the appropriate metal ion.

H_2L_A–H_2L_D react with equimolecular amounts of $M(CH_3COO)_2 \cdot nH_2O$ ($M = Cu^{2+}$, Ni^{2+}, Co^{2+}) or $Mn(CH_3COO)_3 \cdot 2H_2O$ in refluxing alcoholic solution to form, respectively, $M(L) \cdot nH_2O$ and $Mn(L)(CH_3COO) \cdot nH_2O$. The same copper(II) and nickel(II) complexes have been obtained also by template procedure [18].

The similar reaction of the preformed ligand H_2L_E with the appropriate copper(II) or nickel(II) acetate hydrate or the condensation of equimolar amount of 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde) with 1,5-diamino-3-aza(dodecyl)pentane in the presence of the same metal salt gives rise to the complexes $M(H_2L_E)(CH_3COO)_2 \cdot nH_2O$. In the nickel(II) complex the magnetic moment ($\mu_{eff} = 2.30$ BM) suggests the metal ion has probably an octahedral environment with the acetate groups acting as monodentate ligands.

Copper(II), nickel(II) and manganese(III) acetate react with the acyclic Schiff base H_2L_I in alcoholic solution and in a 1:1 molar ratio to give rise to $M(L_I)$ ($M = Cu^{2+}$, Ni^{2+}) and $Mn(L_I)(CH_3COO) \cdot H_2O$. On the contrary cobalt (II)acetate forms $Co(H_2L_I)(CH_3COO)_2$.

The IR spectra of $M(L_I)$ show a strong band at 1618–1631 cm^{-1} due to $\nu(C{=}N)$, while no bands due to acetate groups have been detected. $Ni(L_I)$ is diamagnetic while the magnetic moment of the copper complex is 1.9 BM; the electronic spectra in $CHCl_3$, in addition to band at 423 and 450 nm, show d–d bands at 556 nm for nickel(II) complex and at 564 nm for copper(II) one. These magnetic and electronic data agree with a square planar configuration about nickel(II) and copper(II).

The ^1H NMR spectrum in $CDCl_3$ of $Ni(L_I)$ shows a singlet at 8.54 ppm due to iminic protons, two doublets of doublets at 7.95–7.91 ppm and 7.81–7.77 ppm due to aromatic protons, a triplet at 7.63–7.55 ppm due to the remaining aromatic protons. Also peaks at 5.34–5.24 ppm ($ArOCH_2$), at 4.73 ppm ($CNCH_2$) and at 2.71 ppm (CH_3) due to aliphatic protons are present.

In the IR spectra of $Co(H_2L_I)(CH_3COO)_2$ and $Mn(L_I)(CH_3COO) \cdot H_2O$ in addition to the band at 1624–1640 cm^{-1} due to $\nu(C{=}N)$, the bands due to carboxylate groups at 1577–1553 cm^{-1} $\nu_{asym}(COO)$ and at 1392–1393 cm^{-1} $\nu_{sym}(COO)$ have been detected. $Co(H_2L_I)(CH_3COO)_2$ shows a magnetic moment of 3.20 BM in agreement with a severe distortion from the planarity towards an octahedral coordination about the central metal ion, in agreement with the electronic spectrum where a d–d band at 610 nm is observed.

Analogously $[Ni(L_L)]$ and $[Cu(L_L)]$ have been synthesized by reaction of H_2L_L with the appropriate metal acetate in methanol. When these reactions are carried out in $MeOH/CHCl_3$ the complexes contain also a molecule of solvent chloroform. The IR spectra show the $\nu(C{=}N)$ at 1630 and 1639 cm^{-1}, respectively. Magnetic data at room temperature ($\mu_{eff} = 3.0$ BM) evidence an octahedral coordination about the nickel(II) ion, corroborated by the solid state electronic spectra where d–d bands at 540 nm and 770 nm have been detected.

The reduced macrocycle H_2R_A forms, when reacted with $Cu(CH_3COO)_2 \cdot H_2O$ or $Mn(CH_3COO)_3 \cdot 2H_2O$ in a $CHCl_3/MeOH$ and in a 1:1 molar ratio, respectively, $Cu(R_A)2H_2O$ and $Mn(R_A)(CH_3COO) \cdot 2H_2O$. Using the same experimental conditions $Ni(CH_3COO)_2 \cdot 4H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ give rise to $Ni(H_2R_A)(CH_3COO)_2$ and $Co(H_2R_A)(CH_3COO)_2$.

In the prepared complexes the IR spectra show bands at 3216–3272 cm^{-1} due to $\nu(N–H)$ with a shift of 20–75 cm^{-1} with respect to the free ligands. In the complexes containing acetate groups an intense band at 1589–1576 cm^{-1} $\nu_{asym}(COO)$ and a less intense one at 1408–1383 cm^{-1} $\nu_{sym}(COO)$ are also observed, suggesting that also in these complexes the acetate act as monodentate ligands.

These complexes are all paramagnetic: for the nickel(II) complex the magnetic moment (3.0 BM), suggests an octahedral configuration about the central metal ion; similarly for the cobalt (II) complex a magnetic moment of 3.6 BM and a d–d band at 617 nm in the electronic spectrum in $CHCl_3$ support a strongly distorted configuration about the cobalt(II) ion in contrast with the parent Schiff base complex, where a square planar coordination was found. For $Mn(R_A)(CH_3COO)$-$2H_2O$ a magnetic moment of 5.9 BM was found; possibly a pentacoordination occurs. Finally for $Cu(R_A)$ a magnetic moment of 1.8 BM was found. The electronic spectrum in $CHCl_3$ evidences three bands at 343, 400 and 614 nm, this last d–d band suggesting a square pyramidal pentacoordination.

The acyclic complexes $Ni(R_I) \cdot 3H_2O$, $Cu(R_I) \cdot 2H_2O$, $Ni(H_2R_I)(CH_3COO)_2$, $Co(H_2R_I)(CH_3COO)_2 \cdot 2H_2O$, $Mn(R_I)(CH_3COO) \cdot H_2O$ and $Cu(R_L) \cdot H_2O$ have been prepared with a procedure similar to that above reported. The acetate groups may be eliminated by adding to the prepared complexes or to the preparation solution an equimolar amount of tetrabutyl-ammonium hydroxide, $[N(Bu)_4](OH)$. By this procedure, for instance, $Cu(R_I) \cdot H_2O$, $Ni(R_I) \cdot 3H_2O$ and $Cu(R_L) \cdot H_2O$ have been conveniently prepared. Again IR bands at 3244–3215 cm^{-1} due to $\nu(N–H)$ have been observed with a shift of 50–70 cm^{-1} with respect to the free ligand in consequence of coordination. The acetate groups, where present, show IR absorption at 1583–1566 cm^{-1} $\nu_{asym}(COO)$ and at 1410–1393 cm^{-1} $\nu_{sym}(COO)$. The magnetic moment of cobalt(II) (3.6 BM, 3.0 and 3.5 BM) and nickel(II) complexes suggest an octahedral coordination about the central metal ion. For $Cu(R_I) \cdot 2H_2O$ a square pyramidal configuration about the central metal ion may be proposed on the basis of a d–d band at 610 nm in its electronic spectrum in $CHCl_3$. Moreover a magnetic moment of 1.9 and 1.73 BM was found, respectively, for $Cu(R_I) \cdot 2H_2O$ and $Cu(R_L) \cdot H_2O$.

It must be noted that an analogous reaction of H_2R_I with $NiCl_2 \cdot 6H_2O$ gives rise to $Ni(H_2R_I)(Cl)_2 \cdot H_2O$ as confirmed also by an electron microscopy and EDX investigation, which evidences the homogeneity of the prepared complexes and the correct Ni:Cl = 1:2 ratio.

Thus, according to the above reported physicochemical data, the transition metal ion invariantly occupies the Schiff base site in the mononuclear cyclic complexes. These complexes in turn contain a free and adjustable “crown-ether-like” coordination chamber and can be used as “ligands” towards appropriate hard metal ions giving rise to pure positional isomers. It is well known, for example, the ability of crown-ethers to bind selectively alkali ions, strongly depending on the dimension and on the denticity of the coordination moiety [40,41].

3.5. Heterodinuclear complexes

As above reported the prepared mononuclear transition metal complexes contain a free crown-ether like coordination chamber; hence they can be conveniently used as ligands for further complexation reactions. In particular, taking into consideration that sodium ion prefers the crown-ether site, as ascertained also by the X-ray structure of $Na(HR_D) \cdot H_2O$, the transition metal complexes can be proposed as receptors for the recognition of Na^+. Similarly the sodium(I) complexes can be used as receptors for transition metal ions. The final products are in both cases the same d,s-heterodinuclear complexes, where the transition metal ion occupies the Schiff base site and the sodium ion the crown-ether moiety, independently from the shape of the coordination chambers.

Thus by reaction of equimolar amount of the cyclic and acyclic Schiff base (also prepared in situ) with the appropriate transition metal acetate in the presence of two equivalents of NaOH, the heterodinuclear complexes $MNa(L)(CH_3COO) \cdot nH_2O$ ($M = Cu^{2+}$, Ni^{2+}, Co^{2+}) and $MnNa(L)(CH_3COO)_2 \cdot nH_2O$ ($H_2L = H_2L_A \cdots H_2L_D$ [18] and H_2L_F, H_2L_I, $H_2L_LH_2L_M$) have been obtained. The same complexes can be prepared by the template condensation of the appropriate precursors in the presence of $M(CH_3COO)_2 \cdot nH_2O$ and NaOH.

These reactions give rise to the designed heterodinuclear complexes in high yield and in one pot owing to the above mentioned high selectivity of the two sites of the ligands, respectively, for the d transition metal ion and the sodium ion and hence to the impossibility to give rise to scrambling or migration reactions.

The same complexes have been obtained when the preformed mononuclear transition metal complexes are reacted with sodium acetate or when the reaction of the acyclic sodium complex, $Na(HL) \cdot nH_2O$ with the appropriate polyamine in the presence of the derived transition metal salt was carried out. The formation of the heterodinuclear complexes is corroborated by SEM and EDS investigations: for all the prepared complexes a M:Na = 1:1 ratio was found.

In the infrared spectra of these complexes strong absorption at 1639–1619 cm^{-1} ν(C=N), at 1604-1580 cm^{-1} ν_{asym}(COO) and at 1406–1313 cm^{-1} ν_{sym}(COO) have been observed.

The magnetic moments of the Schiff base complexes where $H_2L = H_2L_A$ and H_2L_I (0.3–0.4 BM for NiNa, 2.2–2.8 BM for CoNa and 1.8 BM for CuNa) show that the square planar N_2O_2 coordination about the transition metal ion is maintained upon Na^+ complexation. The electronic spectra parallel those of the mononuclear analogues.

On the contrary the nickel complexes, derived from the cyclic Schiff bases where $R = (CH_2CH_2)_2NCH_3$, $(CH_2CH_2)_2N(CH_2)_{11}CH_3$ (Scheme 2) are strongly paramagnetic ($\mu_{eff} = 3.1$–3.5 BM). The presence of the different donor set N_2XO_2 causes a different coordination geometry, possibly octahedral, about the nickel(II) ion.

The availability of the [1+1] cyclic functionalized sodium Schiff bases $Na(H_2L_G) \cdot H_2O$ and $Na(H_2L_H) \cdot H_2O$, obtained from the condensation of the appropriate diformyl- and -amine precursors in the presence of NaOH, allows the formation of the related complexes $NiNa(L_G) \cdot H_2O$ or $NiNa(L_H) \cdot H_2O$ by reaction of these sodium macrocyles with nickel(II) acetate in a 1:1 molar ratio. A template procedure affords the same complexes.

The strong IR bands at 1635 and 1636 cm^{-1}, present in $Na(H_2L_H) \cdot H_2O$ and $Na(H_2L_H) \cdot H_2O$, attributed to υ_{asym}COO, are shifted to 1614 and 1613 cm^{-1} in the related heterodinuclear NiNa complexes, in consequence of the coordination of the transition metal ion into the N_2O_2 Schiff base site. Ir data suggest that the carboxylate ion is also involved in the coordination. Solid state magnetic susceptibility ($\mu_{eff} = 2.7$–2.8 BM) and UV–Vis measurements (d–d bonds at 540–550 mm and 630 mm) suggest octahedral coordination about the central metal ion in these NiNa complexes.

The nickel(II)–sodium complex $NiNa(L)(CH_3COO)$ derived from the functionalised acyclic Schiff bases H_2L_L and H_2L_M, prepared by same procedure above reported, deserves further considerations. In these ligands the outer Schiff base chamber present a open N_4O_2 donor set and hence may induce a different coordination geometry about nickel(II) with respect to the acyclic ligand H_2L_I. Their IR spectrum shows bands at 1623 and 1636 cm^{-1} ν(C=N), at 1603 cm^{-1} ν_{asym}(COO) and at 1404 cm^{-1} ν_{sym}(COO). The magnetic moment found ($\mu_{eff} = 3.1$ BM) suggests an octahedral coordination about the central metal ion.

The infrared spectra of $MNa(HL_N) \cdot H_2O$ ($M = Cu^{2+}$,Ni^{2+}), prepared by the reaction of $Na(H_3L_N) \cdot H_2O$ with the appropriate metal acetate in methanol, show a shift of the ν(C=N) and ν_{asym}(COO), in consequence of the coordination of the transition metal ion into the Schiff base moiety, respectively, from 1655 and 1611 cm^{-1} in the sodium derivative to 1644 and 1601 cm^{-1} in the CuNa complex and to 1639 and 1600 cm^{-1} in the NiNa complex. The non planarity about the nickel(II) ion is confirmed by the magnetic moment ($\mu_{eff} = 3.6$ BM) which supports an octahedral coordination about the central metal ion.

Analogously the heterodinuclear complexes $MNa(R)(CH_3COO) \cdot nH_2O$ or $MnNa(R)(CH_3COO)_2 \cdot n$ H_2O have been obtained by reaction of the reduced macrocycles H_2R with the appropriate metal acetate hydrate in the presence of NaOH in a molar ratio 1:1:2. Again the obtainment of the designed complexes was verified also by SEM-EDS analysis which shows a 1:1 = M:Na ratio for all the prepared samples.

The IR bands at 3283–3226 cm^{-1} due to ν(NH), at 1560–1589 cm^{-1} ν_{asym}(COO) and at 1278–1421 cm^{-1} ν_{sym}(COO) corroborate the proposed formulation. The magnetic moment of the paramagnetic nickel(II) complexes ($\mu_{eff} = 2.2$–3.5 BM) suggest an octahedral coordination about the central metal ion, corroborated by the absorption at 555–560 and 750 nm in their electron spectra.

For the copper(II) complexes a d–d band in their electronic spectra at ≅606 or 680–690 nm coordinated by spectra at 555, 560 and 750 nm in the electronic spectra suggests a square pyramidal coordination. The magnetic moments for these complexes are 1.80–1.92 BM. For the cobalt(II) complexes with H_2R_A and H_2R_I the magnetic moment ($\mu_{eff} = 2.6$ BM and $\mu_{eff} = 2.1$ BM) and the UV–Vis d–d band, respectively, at 639 and 596 nm, seem to suggest a strongly distorted square planar configuration for the latter complex. Also for $NiNa(R_I)(CH_3COO)$ the magnetic moment of 3.5 B.M. suggest an octrahedral environment about the central metal ion. For the manganese(III)–sodium complexes magnetic moments in the range 4.7–5.0 BM were found, suggesting a high spin manganese(III) in a pentacoordinate or octahedral coordination.

In conclusion the preparation of a series of largely asymmetric acyclic and cyclic compartmental Schiff bases and their related reduced analogues together with the study of the ability of the two adjacent chambers to give rise to different metal ion recognition processes, allow to obtain pure positional mononuclear or heterodinuclear isomers.

Thus the enhanced selectivity of the Schiff base site (or of the reduced amine analogue) toward transition metal ions (i.e., copper(II), nickel(II), cobalt(II), manganese(III)) and of the crown-ether like chamber for alkali metal ions (i.e., sodium (I)) allows the formation of the same heterodinuclear complexes containing d and s metal ions in one pot, under a variety of experimental different procedures. These processes open interesting possibilities in the design and synthesis of molecular devices and sensors. Unfortunately these systems are not very soluble and stable in water. The insertion of appropriate functionalities inside the coordination moiety or at the periphery of these ligands could confer the appropriate physico-chemical properties to these complexes. Preliminary investigations are very promising.

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