

Preparation, properties and coordination behaviour of planar or tridimensional compartmental Schiff bases

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Abstract

Planar compartmental Schiff bases containing an inner N_2O_2 or N_3O_2 and an outer O_2O_2 chamber were prepared by condensation of 3-methoxysalicylaldehyde with 1,2-diaminoethane (H_2L_A) or 4-*N*-dodecyldiethylenetriamine (H_2L_B). Mononuclear and homodinuclear complexes were synthesized by reaction of the ligands with metal salts or by template procedure; heterodinuclear complexes were obtained by step by step reactions. Tridimensional compartmental ligands, containing an inner N_4O_3 and an outer O_3O_3 chamber, obtained by condensation of tris(2-ethylamine)amine with 3-methoxy- (H_3L_C) or 3-hydroxysalicylaldehyde (H_6L_D) form with $M(CH_3COO)_2 \cdot nH_2O$ ($M = Mn^{2+}, Fe^{2+}$) the mononuclear iron(III) and manganese(III) complexes, $M(L_C)$ or $M(H_3L_D)$. In these complexes the oxidation of the central metal ion occurs as ascertained by Mössbauer and X-ray structural determinations. The crystal molecular structure of the manganese(III) complex, MnL_C was established by X-ray diffraction methods. This complex crystallizes in the monoclinic system, space group $P2_1/c$ in a cell of dimensions $a = 10.910(4)$, $b = 12.382(4)$, $c = 21.196(6)$ Å and $\beta = 90.91(6)^\circ$, with $Z = 4$. The structure was refined to the conventional agreement index $R = 0.057$ with 1880 observed reflections. The manganese(III) ion coordinates in the inner chamber, giving rise to an octahedral complex with the N_3O_3 donor set formed by the phenolate oxygen and the imine nitrogen donor atoms. The apical amine nitrogen is not involved in the coordination. Bond lengths in the octahedral coordination polyhedron are comprised between 1.897(5) and 2.081(6) Å for the three oxygens and 2.075(7) and 2.317(7) Å for the three nitrogen donors to the metal ion. The possibility of using this manganese(III) complex (MnL_C) as a ligand towards $Ln(X)_3$ or KBr has also been studied.

Key words: Crystal structures; Iron complexes; Manganese complexes; Compartmental ligand complexes; Schiff base complexes

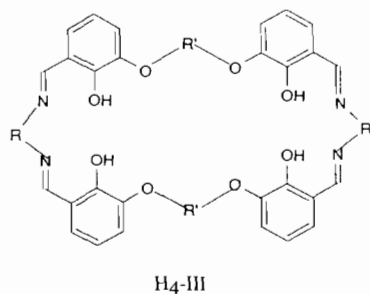
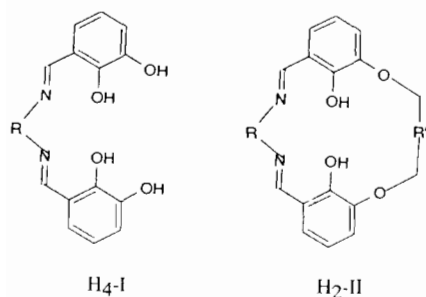
Introduction

Several papers have been published on the preparation and properties of mononuclear and homo- or heteropolynuclear complexes with the compartmental macroacyclic or macrocyclic Schiff bases [1–8] H_4-I , H_2-II and H_4-III . H_4-I and H_2-II contain an N_2O_2 and an O_2O_2 chamber, while H_4-III presents two N_2O_2 and one O_2O_2 chambers.

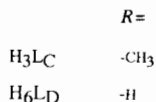
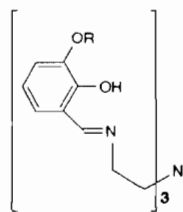
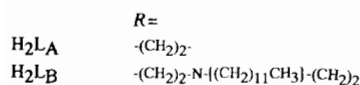
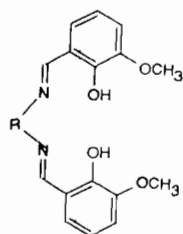
In these ligands the differences in the coordination sites facilitate the formation of pure heteropolynuclear compounds: the ligands H_4-I and H_2-II give rise to dinuclear complexes, while H_4-III easily produces trinuclear species. H_4-I can also form tetranuclear complexes, owing to the ability of the external phenolate groups to bridge two dinuclear entities [1–3]. Thus the

mononuclear complexes $M(H_2-I)$ ($M = Cu^{2+}, Ni^{2+}$), where the metal ion coordinates the inner N_2O_2 chamber, form the heterodinuclear $MLn(H_2-I)(NO_3)_3$ but the heterotetranuclear $[MLn(I)(NO_3) \cdot (S)]_2$ ($S = CH_3OH, H_2O, (CH_3)_2SO$), when treated with the appropriate lanthanide(III) nitrate, in the absence or presence of 2 equiv. of LiOH, respectively.

Under particular experimental conditions, as for instance a prolonged reflux of the reaction solution, the use of particular counter anions, etc., deprotonation of the 3-OH phenol groups occurs and consequently the external coordination chamber of the mononuclear complexes $M(H_2-I)$ can act as dinegative O_2O_2 site, even in the absence of a base, giving rise to mixtures of dinuclear and tetranuclear complexes. To avoid this possibility, we have used 3-methoxysalicylaldehyde, in



addition to 2,3-dihydroxybenzaldehyde, as formyl precursors in the [2+1] or [3+1] condensation reaction with 1,2-diaminoethane, 4-*N*-dodecyldiethylenetriamine or tris(2-ethylamine)amine to form the planar or tridimensional ligands H₂L_A, H₂L_B, H₃L_C and H₆L_D.



These ligands show an internal N₂O₂, N₃O₂ or N₄O₂ Schiff base chamber and an external 'crown-like' O₂O₂ or O₃O₃ chamber. Very recently the preparation and properties of mononuclear nickel(II) and heteropolynuclear nickel(II)-tin(IV) complexes with H₂L_A were reported [9]. In particular, it was verified that the external O₂O₂ chamber can recognize oxygen donor molecules, especially H₂O; this recognition ability seems to be a general trend of this donor set as it was already found in Ni(H₂-I)(MeOH) (R = CH₂CH₂) and in the similar UO₂(H₂-I)·dmf (R = CH₂CH₂NHCH₂CH₂) [3, 10]. The ability of H₂L_A, H₂L_B, H₃L_C and H₆L_D to encapsulate d (i.e. copper(II), nickel(II), iron(III), manganese(III)) or f (i.e. lanthanide(III)) or

uranyl(VI)) ions into their inner Schiff base chamber has been verified. Moreover, the possibility of the resulting mononuclear complexes to act as ligands towards a second metal ion through their outer 'crown-like' chamber has been tested.

In particular we have prepared the mononuclear manganese(III) complex with H₃L_C and determined its X-ray structure to verify if the external chamber, O₃O₃, has the correct geometry for a further encapsulation of metal ions.

Experimental

Materials

3-Hydroxy- or 3-methoxysalicylaldehyde, 1,2-diaminoethane, 4-*N*-dodecyldiethylenetriamine, 2,2',2''-tri-aminotriethylamine, the salts and the solvents were commercial products used without further purification.

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

Ligands

H₂L_A, H₂L_B, H₃L_C and H₆L_D

A methanolic solution (50 ml) of the appropriate amine (1 mmol) was added to 3-methoxysalicylaldehyde (2 mmol) in methanol (50 ml). Fe(CH₃COO)₂ (1 mmol) in methanol was added to a stoichiometric amount of the formyl precursor (2 or 3 mmol) in methanol. The solution was stirred for 2 h and then reduced in volume (30 ml). The yellow compound so obtained was collected by filtration, washed with a methanol/diethyl ether solution and dried *in vacuo*.

H₂L_B was obtained as a yellow oil, soluble in the most common organic solvents.

Mononuclear complexes

M(L_A) (M = Cu²⁺, Ni²⁺)

A methanolic solution of ethylenediamine (1 mmol) was added to a methanolic solution of 3-methoxysalicylaldehyde. The appropriate metal(II) acetate (1 mmol) and LiOH (2 mmol) were added to the resulting yellow solution. The solution was stirred for 3 h under reflux. The precipitate obtained by reducing the solution, or by leaving it to stand overnight, was filtered out, washed with methanol and dried *in vacuo*. The same complex can be obtained by reaction of the preformed ligand (1 mmol) with the appropriate metal acetate (1 mmol) and LiOH (2 mmol) in methanol.

Fe(L_A)(OH)

The complex was obtained by using the same procedure employed for Cu(L_A) or Ni(L_A). The dark red precipitate was filtered, washed with diethyl ether and dried *in vacuo*.

TABLE 1. Elemental analysis of ligands and related complexes

	Calc.			Found		
	C	H	N	C	H	N
H ₂ L _A	65.84	6.14	8.53	65.86	6.46	8.42
Cu(L _A)	53.00	4.94	6.87	52.87	5.26	7.01
Ni(L _A)	53.64	4.99	6.95	54.28	4.80	6.86
Fe(L _A)(OH)	54.16	4.79	7.02	53.77	5.23	7.07
Mn(L _A)(CH ₃ COO)·1.5H ₂ O	51.40	5.17	5.99	51.65	5.27	5.60
Fe ₂ (L _A)(CH ₃ COO) ₂ (OH) ₂	44.62	4.76	4.73	46.42	4.96	4.78
CuLa(L _A)(NO ₃) ₂ ·H ₂ O	29.50	2.75	9.55	30.04	2.87	9.59
Fe(L _B)(OH)·0.5H ₂ O	62.04	7.96	6.78	61.74	7.81	6.15
UO ₂ (L _B)·3H ₂ O	44.60	6.19	4.88	44.63	5.99	4.90
UO ₂ La(L _B)(NO ₃) ₂ ·(OH)·3H ₂ O	31.93	4.51	6.98	31.87	4.32	6.20
La ₂ (L _B)(NO ₃) ₂ (OH) ₂ ·3H ₂ O	35.27	5.08	7.71	35.15	5.24	8.02
FeLa(L _B)(NO ₃) ₂ (OH)·5H ₂ O	37.48	5.69	8.19	37.09	4.94	8.31
H ₃ L _C	65.68	5.96	11.06	65.84	6.39	11.70
Fe(L _C)·H ₂ O	58.07	5.84	9.03	58.29	5.44	8.83
Mn(L _C)·2H ₂ O	56.51	6.00	8.77	56.69	5.47	8.60
H ₆ L _D	64.02	5.96	11.06	63.84	6.39	11.70
Fe(H ₃ L _D)	57.98	4.86	10.02	57.59	5.14	9.92
Mn(H ₃ L _D)·2H ₂ O	54.55	5.26	9.42	54.00	4.81	9.33

Mn(L_A)(CH₃COO)·1.5H₂O

The complex was obtained by using the same procedure employed for Cu(L_A) or Ni(L_A). The reaction solution, containing the formyl and amine precursor, turned from yellow to red and then dark green, when Mn(CH₃COO)₂ (1 mmol) and LiOH (2 mmol) were added. The resulting solution was refluxed for 2 h and allowed to stand overnight. The solvent was removed, the residue treated with a methanol/diethyl ether solution and stirred for 2 h. The precipitate was filtered, washed with methanol/diethyl ether and dried *in vacuo*.

Fe(L_B)(OH)·0.5H₂O

A methanolic solution (50 ml) of 4-*N*-dodecyl-diethylenetriamine (1 mmol) was added to 3-methoxysalicylaldehyde (2 mmol) in methanol (50 ml). Fe(CH₃COO)₂ (1 mmol) in methanol was added to the resulting yellow solution, which turned to black and, after the addition of LiOH (2 mmol), it was refluxed for 2 h. The solution was filtered, evaporated to dryness under reduced pressure and the residue dissolved in CHCl₃. The resulting solution was filtered off, evaporated to dryness under reduced pressure and the residue was dissolved in *n*-hexane. A black precipitate, obtained by addition of diethyl ether, was filtered off, washed with diethyl ether and dried *in vacuo*.

UO₂(L_B)·3H₂O

A methanolic solution (50 ml) of 3-methoxysalicylaldehyde (2 mmol) was treated with 4-*N*-dodecyl-diethylenetriamine (1 mmol). UO₂(CH₃COO)₂·2H₂O (1

mmol) and LiOH (2 mmol) were added to the resulting yellow solution. The red solution was stirred for 3 h under reflux. The solvent was removed at reduced pressure and the red oil dissolved in CHCl₃. The solution was maintained overnight over anhydrous MgSO₄. The solvent was removed and the residue was treated with diethyl ether. The red precipitate was filtered, washed with diethyl ether and dried *in vacuo*.

M(L_C)·nH₂O (*M* = Mn³⁺, Fe³⁺; *n* = 1, 2)

A methanolic solution (50 ml) of tris(2-aminoethyl)amine (1 mmol) was added to 3-methoxysalicylaldehyde (3 mmol) in methanol. To the yellow solution, refluxed for 30 min, the appropriate M(CH₃COO)₂·*n*H₂O (1 mmol) and LiOH (3 mmol) in methanol were added. The red solution was refluxed for 2 h and allowed to stand overnight. The precipitate so obtained was filtered off, washed with methanol and dried *in vacuo*.

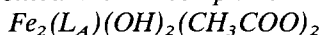
NB. By this procedure green crystals of the manganese(III) complex, suitable for X-ray investigation were obtained.

M(H₃L_D)·nH₂O (*M* = Mn³⁺, Fe³⁺; *n* = 0, 2)

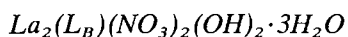
A methanolic solution (50 ml) of tris(2-aminoethyl)amine (1 mmol) was added to 2,3-dihydroxybenzaldehyde (3 mmol) in methanol. To the yellow solution, refluxed for 30 min, the appropriate M(CH₃COO)₂·*n*H₂O (1 mmol) and LiOH (3 mmol) in methanol were added. The solution was refluxed for 2 h, then allowed to stand overnight. The precipitate so obtained was

collected by filtration, washed with methanol and dried *in vacuo*.

Homodinuclear complexes

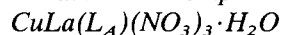


A methanolic solution (50 ml) of 4-*N*-dodecyldiethylenetriamine (1 mmol) was added to 3-methoxysalicylaldehyde (2 mmol) in 50 ml of methanol. To the resulting yellow solution, after a reflux of 30 min, $\text{Fe}(\text{CH}_3\text{COO})_2$ (2 mmol) and LiOH (2 mmol) were added. The resulting black-red solution was refluxed for 3 h, then reduced in volume at low pressure and allowed to stand overnight. The black precipitate was collected by filtration, washed with methanol and dried *in vacuo*.

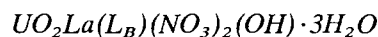


A methanolic solution of the formyl precursor (2 mmol) was reacted with 4-*N*-dodecyldiethylenetriamine (1 mmol). To the resulting yellow solution $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2 mmol) and LiOH (2 mmol) were added. The yellow solution was refluxed for 2 h, allowed to stand overnight and then filtered. The solvent was removed at reduced pressure and the yellow residue treated with a methanol/diethyl ether solution and dried *in vacuo*.

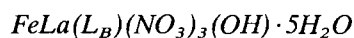
Heterodinuclear complexes



To a methanolic solution (50 ml) of the appropriate mononuclear copper(II) complex $\text{Cu}(\text{L}_A)$ (1 mmol), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) in methanol was added. The resulting solution was refluxed for 3 h and the precipitate filtered off, washed with methanol and chloroform and suspended in refluxing methanol. The solution, obtained by filtration, separated crystals of the heterodinuclear copper(II)-lanthanum(III) complex.



To $\text{UO}_2(\text{L}_B)$ (1 mmol) dissolved in methanol (50 ml) $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) in 50 ml of methanol was added. The red solution was stirred under reflux for 2 h. The solvent was removed at reduced pressure and the yellow-orange residue treated with a methanol/diethyl ether solution. The suspension was stirred for 2 h and the precipitate collected by filtration, washed with a methanol/diethyl ether solution and dried *in vacuo*.



A methanolic solution (50 ml) of $\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol) was added to a methanol/dimethylformamide solution (50 ml) of the mononuclear complex $\text{Fe}(\text{L}_B)(\text{OH})$ (1 mmol). The solution was refluxed for 2 h, then evaporated to dryness. The residue was dissolved with methanol and precipitated by the addition

of diethyl ether. The precipitate was filtered off, washed with a methanol/diethyl ether solution and dried *in vacuo*.

Physicochemical measurements

IR spectra were recorded as KBr pellets on a Mattson FTIR 3000 spectrometer. The homogeneity of the heteropolynuclear samples was checked with a Philips SEM KL40 model scanning electron microscopy equipped with an EDAX PV99 X-ray energy dispersive spectrometer. Metal ratios were determined by energy dispersive X-ray spectrometry (EDX) [11].

The solvent content (H_2O or MeOH) was evaluated by thermal analysis curves using a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml/min^{-1} ; heating rate $5 \text{ }^\circ\text{C min}^{-1}$) and in air under the same conditions. Neutral alumina (Carlo Erba product) was used as reference material.

Mössbauer spectra were obtained at 80 and 4.5 K on a conventional constant-acceleration spectrometer, which utilizes a room-temperature rhodium matrix cobalt-57 source. The spectra were fitted to Lorentzian line shapes by using a standard least-squares computer minimization technique.

Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instruments) being calibrated with $\text{HgCo}(\text{NCS})_4$ [12]. Diamagnetic corrections were performed [13].

X-ray structure determinations

The data were collected on a Philips PW1100 diffractometer with the control and computing systems modified by the firm DATA 5 [14]. Lattice parameters were determined from a least-square refinement of 25 reflection settings obtained from an automatic centring routine. Lorentz and polarization corrections and a semi-empirical absorption correction [15] were applied. Table 2 reports the data collection conditions.

Atomic scattering factors for neutral atoms and correction parameters were taken from International Tables [17]. The phenyl carbons were refined as rigid bodies and isotropic owing to the low number of observed reflections (Table 2); the hydrogen atom positions were calculated and refined positionally, thermal parameters being fixed isotropically at $U = 0.08 \text{ \AA}^3$. See also 'Supplementary material.'

Results and discussion

The mononuclear and the homo- and heterodinuclear complexes were prepared according to the reactions shown in Scheme 1.

TABLE 2. Data collection conditions

Formula	C ₃₀ H ₃₃ N ₄ O ₆ Mn
Molecular weight	600.5
<i>F</i> (000) (electrons)	1256
<i>a</i> (Å)	10.910(4)
<i>b</i> (Å)	12.382(4)
<i>c</i> (Å)	21.196(6)
β (°)	90.91(6)
<i>U</i> (Å ³)	2861.6
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>D</i> _{calc} (g/ml)	1.39
<i>Z</i>	4
Radiation, λ (Å)	0.71073
Absorption coefficient μ (cm ⁻¹)	4.61
Crystal size (mm)	0.3 × 0.2 × 0.2
Scan range (°)	3 > θ > 25
Unique data collected	5500
Observed data (<i>I</i> > 3 σ <i>I</i>)	1880
Largest non-solved resonance (e/Å ³)	0.54
<i>R</i> ($R = \sum F_o - F_c / F_o $)	0.057
Computing program package	SHELX76 [16]

The mononuclear complexes were obtained by template procedure or by reaction of the preformed ligand with the appropriate metal salt. With H₂L_A the metal ions coordinate the inner N₂O₂ site; the copper(II) and nickel(II) ions are square planar, as confirmed by UV, magnetic and X-ray measurements [9]. An oxidation of iron(II) to iron(III) occurs in the mononuclear iron Fe(L_A)(OH), as ascertained by Mössbauer spectroscopy. The Mössbauer spectrum of this complex shows values ($\delta = 0.40$, $\Delta E_Q = 0.83$, $\Gamma = 0.30$ mm/s), very close to those of already reported adducts (i.e. Fe(H₂-I)(OH)) and points to an N₂O₂ coordination (Fig. 1(a)) [4].

The magnetic moment value ($\mu_B = 3.25$ BM) is considerably lower than that found in the very similar Fe(H₂-I)(OH) ($\mu_B = 5.85$ – 5.89 BM) and may be attributed to an intermolecular antiferromagnetic interaction between two monomeric units. This dimeric aggregation might be due to Fe–O–Fe or Fe–OH–Fe bridges already found in similar Schiff base systems [18]. However for iron(III) Schiff bases or other systems containing the FeOFe bridges considerably lower magnetic moments have been found ($\mu_B = 1.5$ – 1.9 BM); consequently we propose for the prepared compound the formulation [Fe(L_A)(OH)].

For formation of the mononuclear uranyl(VI) complex, UO₂L_B, it is necessary to enlarge the inner coordination chamber to N₃O₂, by using H₂N–CH₂CH₂N(CH₂)₁₁CH₃CH₂CH₂NH₂ as the amine precursor, in order to allow the uranyl(VI) group to reach its usual equatorial pentacoordination [19–23] and to obtain a very soluble compound.

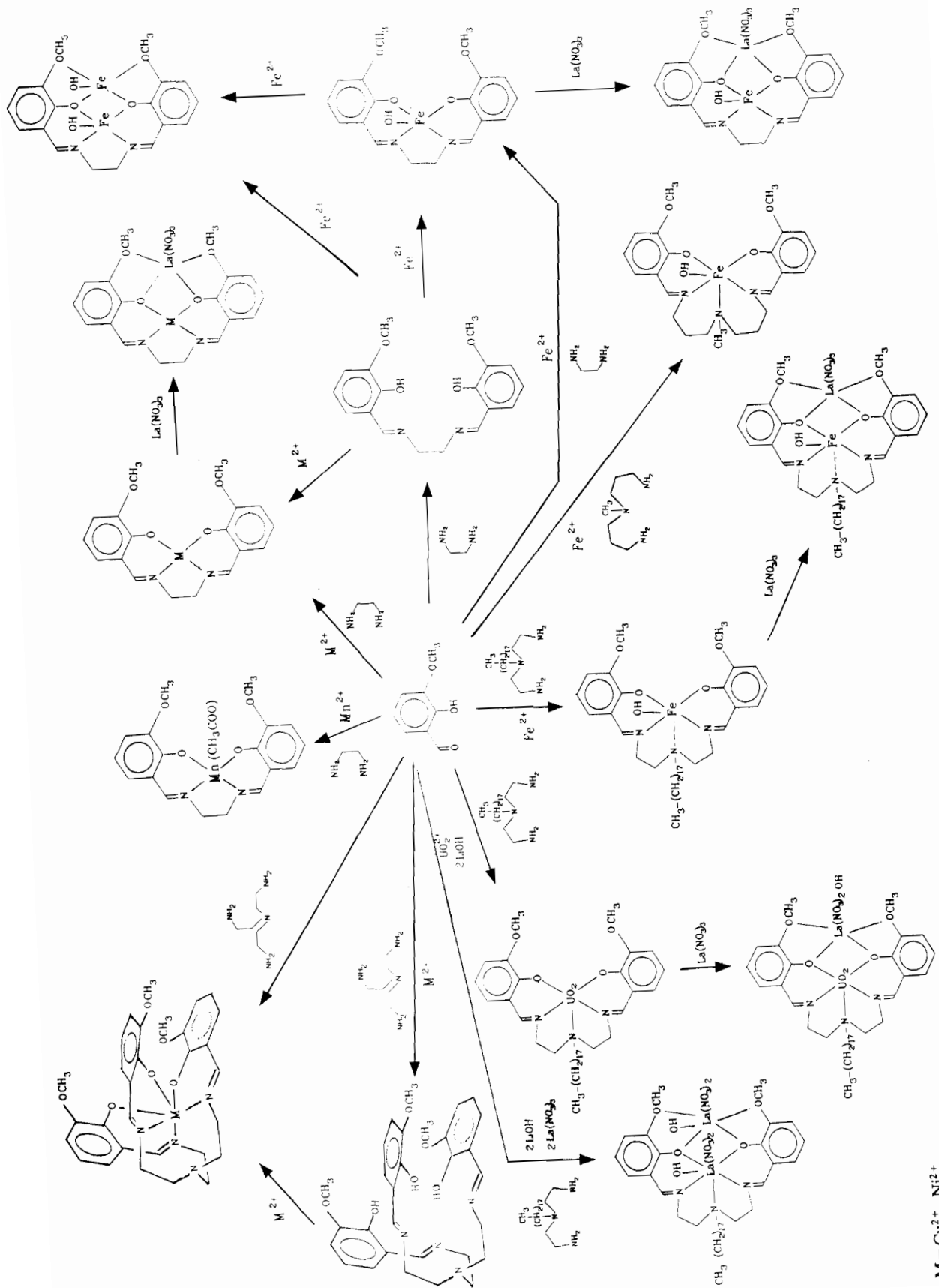
Analogously, in order to overcome the low solubility encountered with Fe(L_A)(OH) and to make a mononuclear complex suitable for further metal complexation,

the mononuclear Fe(L_B)(OH) was prepared by template condensation of 3-methoxysalicylaldehyde and 4-*N*-do-decyldiethylenetriamine. The magnetic moment of this complex ($\mu_B = 4.85$ BM) is again lower, although not as dramatically as Fe(L_A)(OH), than expected for a mononuclear iron(III) complex. From the Mössbauer spectrum of Fe(L_B)(OH) (Fig. 1(b)) values in line with an N₂O₂ coordination of iron(III) were found ($\delta = 0.40$, $\Delta E_Q = 0.72$, $\Gamma = 0.39$ mm/s).

The homodinuclear complexes Fe₂(L_A)(OH)₂·(CH₃COO)₂ and La₂(L_B)(NO₃)₂(OH)₂ were prepared by reaction of the appropriate formyl and amine precursors in the presence of a stoichiometric amount of metal salt and LiOH. Again iron(III) ions are present in the dinuclear complex, which shows a $\mu_B = 4.18$ BM, consistent with a polymeric species where probably dinuclear entities are interacting with each other, possibly through OH and/or acetate bridges.

The mononuclear copper complex, Cu(L_A), forms the heterodinuclear complex, CuLa(L_A)(NO₃)₃, when treated with a stoichiometric amount of the lanthanum(III) nitrate hexahydrate. By recrystallization from methanol of the crude product, which does not show a satisfactory 1:1 copper:lanthanum metal ratio, a pure crystalline complex was obtained. UO₂(L_B) and Fe(L_B)(OH) also form the heterodinuclear UO₂La(L_B)(NO₃)₂(OH) and FeLa(L_B)(NO₃)₃(OH) complexes when treated with La(NO₃)₃·6H₂O.

The magnetic moment of FeLa(L_B)(NO₃)₃(OH) ($\mu_B = 4.93$ BM) and the values obtained from the Mössbauer spectrum (Fig. 1(c)) ($\delta = 0.39$, $\Delta E_Q = 0.88$, $\Gamma = 0.53$ mm/s) parallel those of the mononuclear Fe(L_B)(OH). In particular the Mössbauer spectra of both compounds, Fe(L_B)(OH) and FeLa(L_B)(OH)(NO₃)₃, are typical of high spin iron(III) species in octahedral environments. By comparison with already reported spectra [4], some structural hypotheses for these complexes may be proposed. The similarity of the hyperfine parameters with those due to iron coordinated in the inner N₂O₂ chamber ($\delta = 0.47$ – 0.53 , $\Delta E_Q = 0.64$ – 0.94 mm/s) [4] suggests a similar situation is also very likely in these compounds. Therefore the iron(III) is in the N₃O₂ inner chamber provided that the third nitrogen of the ligand is not bonded. Such an arrangement is highly probable because of the difficulty for that atom to occupy the axial coordination position around the iron centre. This configuration is maintained in the lanthanum derivative, that is so bonded in the outer O₂O₂ chamber. The δ value for the mononuclear adduct is somewhat lower than that found for complexes with other related ligands [4], probably due to the presence of the third non-coordinated nitrogen atom, and decreases on coordination of the second metal, as expected. The quadrupole splitting of the mononuclear compound is the lowest reported in the literature for this kind of ligand [4]



$M = Cu^{2+}, Ni^{2+}$
 Scheme 1.

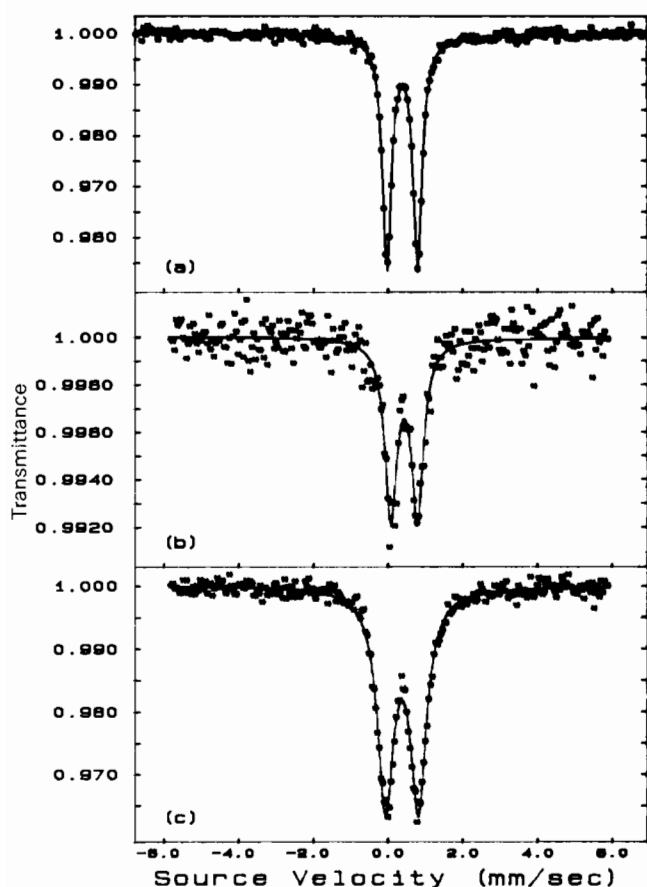


Fig. 1. Mössbauer spectra of $\text{Fe}(\text{L}_A)(\text{OH})$ (a), $\text{Fe}(\text{L}_B)(\text{OH})$ (b) and $\text{FeLa}(\text{L}_B)(\text{NO}_3)_3(\text{OH})$ (c).

and increases on lanthanum coordination. This implies that the presence of the second metal in the outer chamber increases the distortions around the iron centre, while in the cases of the already reported compounds [4] there was a decrease of the ΔE_Q values. This inversion may be due to the different atomic hindrance of the metal or may be an indication that lanthanum is bonded to the ligand only by a water molecule.

The correct 1:1 metal ratio and the homogeneity of these heterodinuclear complexes were ascertained by electron microscopy and EDX analyses. As an example the EDX spectra for $\text{CuLa}(\text{L}_A)(\text{NO}_3)_3$ and $\text{FeLa}(\text{L}_B)(\text{NO}_3)_3(\text{OH})$ are reported in Fig. 2.

Apparently similar experimental conditions produce complexes with a different composition. As an explanation of this behaviour, an encapsulation of the $\text{Ln}(\text{NO}_3)_3(\text{H}_2\text{O})_n$ moiety into the outer O_2O_2 chamber through the oxygen atoms of water molecules may be supposed. This recognition process, already found in $[\text{Ni}(\text{L}_A)_3 \cdot (\text{H}_2\text{O})\text{Sn}(\text{Cl})_2(\text{CH}_3)_2]$ [9], may give rise to dinuclear or polynuclear species of the type A or B reported in Scheme 2. Moreover a sandwich structure of type C in Scheme 2 may also be taken into account.

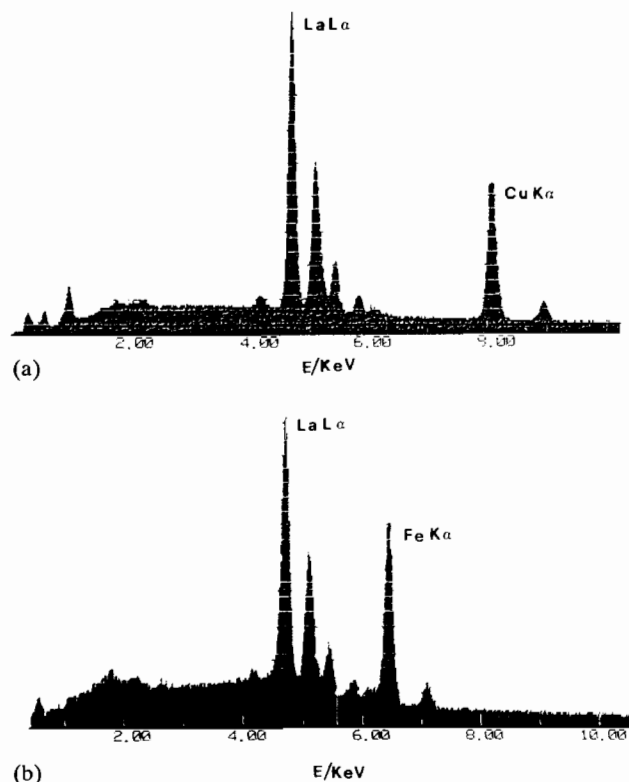
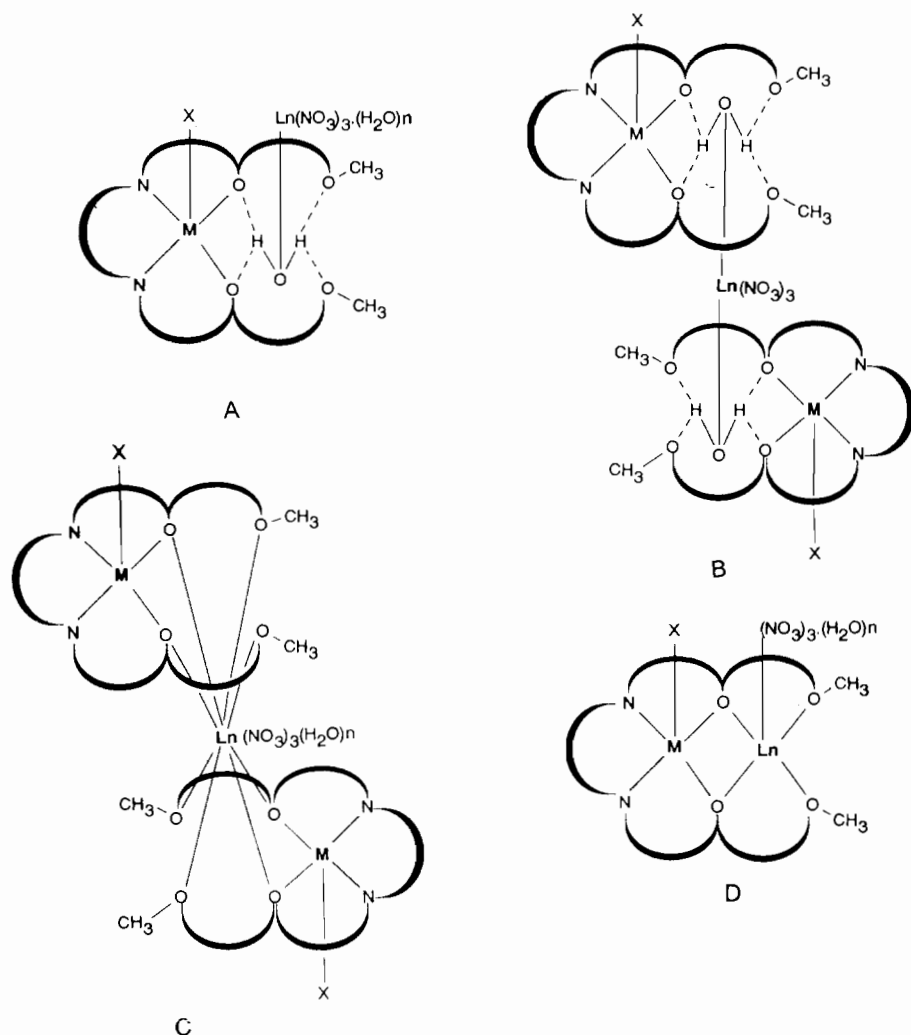


Fig. 2. EDX spectra of $\text{CuLa}(\text{L}_A)(\text{NO}_3)_3$ (a) and $\text{FeLa}(\text{L}_B)(\text{NO}_3)_3(\text{OH})$ (b).

Further information has been obtained from the Mössbauer spectrum of the similar iron(III) complex with the Schiff base derived by condensation of 3-methoxysalicylaldehyde and 1,9-diamino-5-methylazonane in the presence of iron(II) acetate. In this complex again the oxidation of iron(II) to iron(III) has completely taken place. One apical position is filled with the oxygen of an acetate group. A comparison of the IR spectra of the free ligand and related iron(III) complex shows that $\nu(\text{C}=\text{N})$ at 1632 cm^{-1} in the free ligand shifts to 1619 cm^{-1} in the complex. Two new bands at 1449 and 1317 cm^{-1} , present only in the spectrum of the complex, seem to be indicative of the presence of an acetate group asymmetrically bonded to the central metal ion.

The hyperfine parameters ($\delta=0.46$, $\Delta E_Q=1.00$ and $I=0.46\text{ mm/s}$) are slightly different from those obtained for the analogous derivative with H_2L_B and are found on the border-line of the range typical for an N_2O_2 coordination. The lengthening of the aliphatic chain increases the flexibility of the whole molecule, especially around the central aminic nitrogen atom. In this way it may approach the metal centre from an apical position: it is therefore possible to hypothesize the presence of such an interaction that will surely affect both the isomer shift and quadrupole splitting. The interaction between the neutral nitrogen atom and the iron ion



Scheme 2.

should give rise to a more distorted structure than that obtained when the apical position is occupied by small groups such as OH or H₂O, with the consequent increase of ΔE_Q . The experimental value $\Delta E_Q = 1.00$ observed in the complex with the more flexible ligand derived from 1,9-diamino-5-methylaza-nonane, compared to 0.72 found for the Fe(L_B)(OH) agrees well with this hypothesis.

Preliminary data show that the reaction of Ni(L_A) and Fe(L_A)(OH) with Ln(NO₃)₃·6H₂O (Ln = La(III), Gd(III), Eu(III), Tb(III)) does not form only the expected complex, formulated in agreement with CuLa(L_A)(NO₃)₃ or FeLa(L_B)(NO₃)₃(OH) as NiLn(L_A)(NO₃)₃(OH) and FeLa(L_A)(NO₃)₃(OH). According to the elemental analyses, electron microscopy and EDX data complexes formulated as Ni₂La(L_A)(NO₃)₃·4H₂O and Fe₂Ln(L_A)(NO₃)₃(OH)·3H₂O have also been detected. Again in the iron-containing complexes a complete oxidation to iron(III) has been ascertained by Mössbauer spectroscopy.

These possible types of coordination, in addition to the most usual metal ion coordination into the O₂O₂ chamber (compound D of Scheme 2) may cause the different stoichiometries encountered for the complexes prepared under similar experimental procedures or during the attempts to recrystallize the crude products for the obtainment of crystals suitable for X-ray determinations.

A comparison of the IR spectra of H₂L_A with those of the related mononuclear and dinuclear complexes gives useful information, especially about the iron(III) complexes. $\nu(\text{C}=\text{N})$ present as a strong band at 1633 cm⁻¹ in the free ligand lies at 1642 cm⁻¹ in the copper(II), 1622 cm⁻¹ in the nickel(II), 1622 cm⁻¹ in the iron(III) and 1628 cm⁻¹ in the manganese(III) complexes, respectively. It remains at the same frequency (1623 cm⁻¹) in the dinuclear iron complex.

In addition in Mn(L_A)(CH₃COO) and Fe₂(L_A)(OH)₂(CH₃COO)₂, strong bands at 1597 and 1300 cm⁻¹ for the former and at 1633, 1575 and 1447 cm⁻¹ for

the latter, which can be associated with the antisymmetric and symmetric stretchings of the acetate groups, are clearly detectable. In $\text{Mn}(\text{L}_A)(\text{CH}_3\text{COO})$ the intensity of the asymmetric $\nu(\text{COO})$ is much higher than that attributed to the symmetric $\nu(\text{COO})$; this may be ascribed to a monodentate coordination or to the very asymmetric bidentate nature of the acetate group. These bands are not present in the mononuclear iron(III) complex; this enforces the above formulation, $\text{Fe}(\text{L}_A)(\text{OH})$.

For $\text{Fe}(\text{L}_B)(\text{OH})$ $\nu(\text{C}=\text{N})$ lies at 1624 cm^{-1} while $\text{UO}_2(\text{L}_B)$ shows $\nu(\text{C}=\text{N})$ at 1623 cm^{-1} and a strong $\nu_3(\text{O}-\text{U}-\text{O})$ band at 897 cm^{-1} . These two bands lie at 1620 and 909 cm^{-1} in the heterodinuclear $\text{UO}_2\text{La}(\text{L}_B)(\text{NO}_3)_2(\text{OH})$. $\nu(\text{C}=\text{N})$ was observed at 1637 and 1621 cm^{-1} for $\text{CuLa}(\text{L}_A)(\text{NO}_3)_3$ and $\text{FeLa}(\text{L}_B)(\text{NO}_3)_3(\text{OH})$, respectively. In the heterodinuclear complexes bands have been found at 1457 and 1288 cm^{-1} for $\text{CuLa}(\text{L}_A)(\text{NO}_3)_3$, at 1456 and 1311 cm^{-1} for $\text{FeLa}(\text{L}_B)(\text{NO}_3)_3(\text{OH})$ and at 1455 , 1480 and 1304 cm^{-1} for $\text{UO}_2\text{La}(\text{L}_B)(\text{NO}_3)_2(\text{OH})$, due to bidentate nitrate groups. Analogously, the homodinuclear $\text{La}_2(\text{L}_B)(\text{NO}_3)_2(\text{OH})$ shows bands, attributable to nitrate groups, at 1489 , 1478 , 1457 , 1438 and 1304 cm^{-1} . For this complex $\nu(\text{C}=\text{N})$ lies at 1652 cm^{-1} .

Mononuclear manganese(III) and iron(III) complexes with the ligands H_3L_C and H_3L_D were prepared by template procedure or by reaction of the preformed ligand with the metal(II) acetate. Both metal ions coordinate in the inner coordination chamber, forming octahedral complexes with the N_3O_3 donor set; the phenolate oxygen and the imine nitrogen donor atoms are thus involved in the coordination to the metal ion. The apical amine nitrogen is not involved in the coordination as confirmed by the X-ray investigation on the complex $\text{Mn}(\text{L}_C)$ (*vide post*).

$\nu(\text{C}=\text{N})$ found at 1630 and 1630 cm^{-1} in the IR spectrum of H_3L_C and H_3L_D lies at 1659 and 1629 cm^{-1} in the $\text{Fe}(\text{L}_C)$ and $\text{Fe}(\text{H}_3\text{L}_D)$ complexes and at 1611 and 1633 cm^{-1} in $\text{Mn}(\text{L}_C)$ and $\text{Mn}(\text{H}_3\text{L}_D)$, respectively. Again the oxidation of iron(II) to iron(III) was ascertained by Mössbauer spectroscopy.

$\text{Fe}(\text{L}_C)$ and $\text{Fe}(\text{H}_3\text{L}_D)$ present Mössbauer spectra at 80.0 and 4.5 K characterized by a very broad single line (Fig. 3(a) and (b)). Both can be ascribed to paramagnetic relaxation effects due to fluctuations of magnetic fields arising from flips of electronic spins whose rate may present the same order of magnitude as the Mössbauer effect in all the temperature intervals. In the case of high-spin iron(III) compounds the contribution to the relaxation rate is mainly due to the spin-spin interactions. The relaxation time increases with the iron-iron distance and decreases on increasing the temperature. Thus the difference between the two spectra can be ascribed to the presence of the methyl

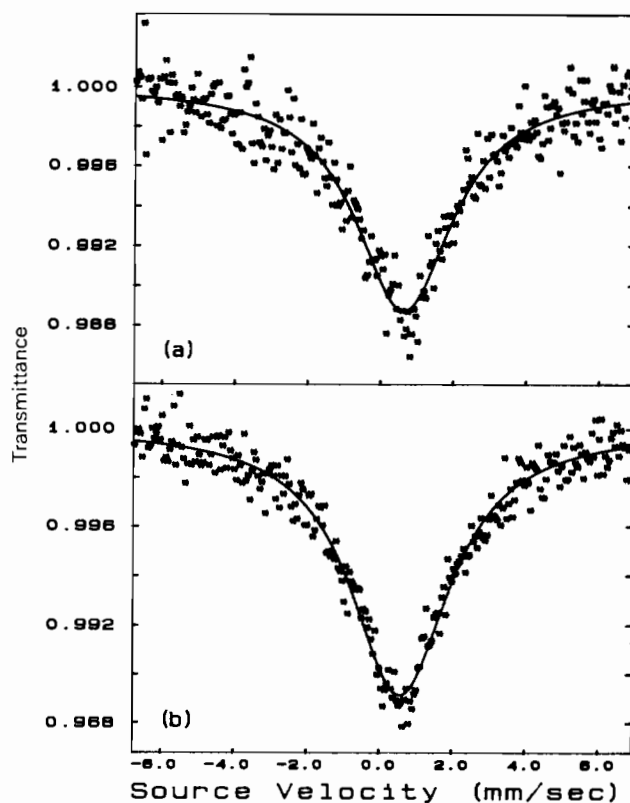


Fig. 3. Mössbauer spectra of $\text{Fe}(\text{L}_C)$ (a) and $\text{Fe}(\text{H}_3\text{L}_D)$ (b) at 4.5 K .

groups that probably increases the iron-iron distance. Experiments to obtain spectra at lower and higher temperatures are in progress in order to fully clarify the mechanism of the paramagnetic relaxation in these complexes.

The magnetic moment of the iron(III) complex $\text{Fe}(\text{L}_C)$ is normal ($\mu_B = 5.82\text{ BM}$) while it is lower than expected for $\text{Fe}(\text{H}_3\text{L}_D)$ ($\mu_B = 5.63\text{ BM}$); both values may be considered in line with a high-spin iron(III) complex.

The magnetic moment of $\text{Mn}(\text{H}_3\text{L}_D)$ ($\mu_B = 5.84\text{ BM}$), although high, may be considered as due to the manganese(III) ion, while the value found for $\text{Mn}(\text{L}_C)$ ($\mu_B = 3.7\text{--}3.9\text{ BM}$) is low and one might suggest a magnetic intermolecular interaction as an explanation for this value. To elucidate this magnetic behaviour a single crystal X-ray investigation on $\text{Mn}(\text{L}_C)$ was carried out, and we can anticipate that, according to the results obtained by X-ray diffractometry, no metal-metal interaction can be proposed.

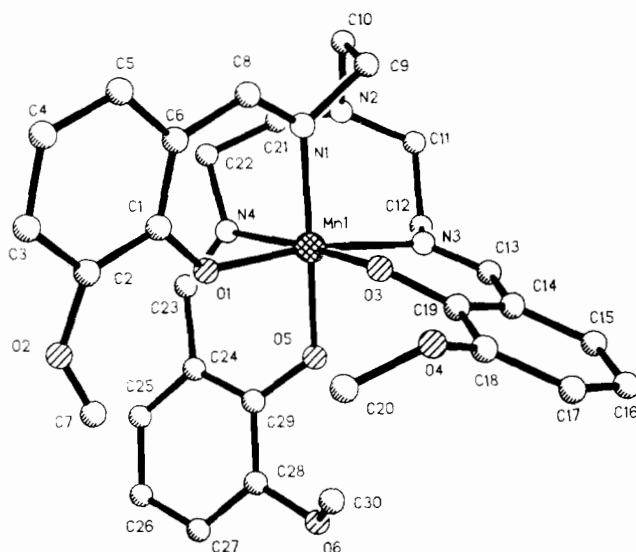
The final atomic parameters of the non-H atoms are given in Table 3. The identification of the atoms and the configuration of the manganese complex are shown in the ORTEP [24] drawing of Fig. 4 while selected bond distances and angles are reported in Tables 4 and 5.

TABLE 3. Fractional coordinates with isotropic (denoted by *) or equivalent isotropic thermal parameters (\AA^2)

Atom	x	y	z	$U_{\text{iso/eq}}^a$
Mn(1)	0.0625(1)	0.2509(1)	0.07654(6)	0.0487(4)
O(1)	0.1895(5)	0.3182(4)	0.1245(3)	0.071(2)
C(3)*	0.3660(4)	0.5525(6)	0.1715(3)	0.098(4)
C(4)*	0.2844(4)	0.6358(6)	0.1570(3)	0.082(3)
C(5)*	0.1690(4)	0.6122(6)	0.1313(3)	0.069(3)
C(6)*	0.1353(4)	0.5051(6)	0.1201(3)	0.052(2)
C(1)*	0.2170(4)	0.4217(6)	0.1346(3)	0.056(3)
C(2)*	0.3323(4)	0.4454(6)	0.1604(3)	0.091(3)
O(2)	0.4136(10)	0.3686(8)	0.1786(9)	0.261(9)
C(7)	0.4382(10)	0.2592(10)	0.1754(8)	0.148(8)
C(8)	0.0187(8)	0.4887(7)	0.0901(4)	0.057(3)
N(1)	-0.0295(6)	0.3980(5)	0.0728(3)	0.048(3)
C(9)	-0.1525(9)	0.4059(7)	0.0432(4)	0.059(4)
C(10)	-0.2484(8)	0.3652(8)	0.0894(5)	0.066(4)
N(2)	-0.2234(6)	0.2547(8)	0.1069(3)	0.063(3)
C(11)	-0.2599(9)	0.1702(8)	0.0630(5)	0.074(4)
C(12)	-0.1527(9)	0.0998(8)	0.0471(5)	0.064(4)
N(3)	-0.0531(6)	0.1625(5)	0.0175(4)	0.051(3)
C(13)	-0.0310(8)	0.1379(7)	-0.0394(5)	0.065(4)
C(15)*	0.0699(5)	0.1303(4)	-0.1390(3)	0.077(3)
C(16)*	0.1631(5)	0.1602(4)	-0.1798(3)	0.092(3)
C(17)*	0.2488(5)	0.2380(4)	-0.1613(3)	0.095(3)
C(18)*	0.2414(5)	0.2860(4)	-0.1019(3)	0.072(3)
C(19)*	0.1482(5)	0.2561(4)	-0.0611(3)	0.061(2)
C(14)*	0.0625(5)	0.1783(4)	-0.0796(3)	0.053(2)
O(3)	0.1424(5)	0.3056(5)	-0.0061(3)	0.065(2)
O(4)	0.3185(8)	0.3710(7)	-0.0919(4)	0.104(4)
C(20)	0.3997(11)	0.3626(10)	-0.0456(8)	0.140(8)
C(21)	-0.2229(8)	0.2269(8)	0.1733(4)	0.070(4)
C(22)	-0.1036(7)	0.2582(9)	0.2048(4)	0.067(3)
N(4)	-0.0016(6)	0.2014(6)	0.1761(3)	0.058(3)
C(23)	0.0661(8)	0.1418(7)	0.2103(4)	0.058(4)
C(25)*	0.2402(5)	0.0319(5)	0.2404(2)	0.069(3)
C(26)*	0.3463(5)	-0.0257(5)	0.2264(2)	0.070(3)
C(27)*	0.3853(5)	-0.0330(5)	0.1642(2)	0.071(3)
C(28)*	0.3182(5)	0.0172(5)	0.1159(2)	0.063(3)
C(29)*	0.2121(5)	0.0748(5)	0.1298(2)	0.052(3)
C(24)*	0.1731(5)	0.0822(5)	0.1921(2)	0.054(2)
O(5)	0.1480(5)	0.1157(4)	0.0809(3)	0.054(2)
O(6)	0.3591(6)	0.0017(6)	0.0570(3)	0.080(3)
C(30)	0.3865(9)	0.0975(10)	0.0225(5)	0.094(6)

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

The coordination polyhedron (Fig. 5) resembles a somewhat distorted octahedron and this distortion seems to be caused more by the constraints of the ligand geometry than by other effects. As already found for the complex $\text{Mn}(\text{L}_{\text{E}}) \cdot 3\text{H}_2\text{O}$ with a similar ligand [25], the 'tren' moiety imposes an enlargement of the N_3 triangular face with $\text{N} \cdots \text{N}$ contacts comprised between 3.15(1) and 3.43(1) \AA and a 'compression' of the O_3 face with the $\text{O} \cdots \text{O}$ contacts ranging between 2.71(1) and 2.99(1) \AA . The bond angles around the Mn atom also confirm this distortion; in fact the

Fig. 4. The configuration of $\text{Mn}(\text{L}_{\text{C}})$, with atom labels as used in Tables 3, 4 and 5.TABLE 4. Selected bond distances (\AA)

Mn(1)–O(1)	1.897(6)	Mn(1)–N(1)	2.081(7)
Mn(1)–N(3)	2.075(7)	Mn(1)–O(3)	2.081(6)
Mn(1)–N(4)	2.317(7)	Mn(1)–O(5)	1.918(5)
O(1)–C(1)	1.333(9)	O(2)–C(7)	1.38(2)
C(2)–O(2)	1.35(1)	N(1)–C(9)	1.47(1)
C(8)–N(1)	1.29(1)	C(10)–N(2)	1.44(1)
C(9)–C(10)	1.53(1)	N(2)–C(21)	1.45(1)
C(11)–C(12)	1.50(1)	N(2)–C(11)	1.45(1)
N(3)–C(13)	1.27(1)	C(13)–C(14)	1.43(1)
C(18)–O(4)	1.36(1)	C(19)–O(3)	1.317(8)
O(4)–C(20)	1.32(2)	C(21)–C(22)	1.50(1)
C(22)–N(4)	1.46(1)	N(4)–C(23)	1.26(1)
C(28)–O(6)	1.345(8)	O(6)–C(30)	1.43(1)
C(29)–O(5)	1.340(7)		

$\text{N}–\text{Mn}–\text{N}$ angles are comprised between 96.6 and 106°, while the $\text{O}–\text{Mn}–\text{O}$ angles are close to the theoretical 90° as the oxygen atoms are not subjected to severe constraints. The two triangular faces, N_3 and O_3 , are nearly parallel, their dihedral angle being 5°, and are twisted by about 61°. The fourth (tripodal) nitrogen atom is not bonded to the central ion, its distance to the Mn atom being 3.196(2) \AA , (3.229(6) \AA in the complex $\text{Mn}(\text{L}_{\text{C}})$ and 3.245(4) \AA in a similar complex $\text{Mn}(\text{L}_{\text{E}}) \cdot \text{MeOH}$, recently published [26]).

The coordination lengths compare well with those found in similar complexes. $\text{Mn}–\text{O}$ bonds, comprised between 1.897(5) and 2.081(6) \AA (mean 1.965 \AA), are in accordance with those found in $\text{Mn}(\text{L}_{\text{E}}) \cdot 3\text{H}_2\text{O}$ and in $\text{Mn}(\text{L}_{\text{E}}) \cdot \text{MeOH}$ (1.965(3) and 1.964(3) \AA , respectively), and in other $\text{Mn}(\text{III})$ derivatives [27–30]. $\text{Mn}–\text{N}$

TABLE 5. Selected bond angles (°)

N(4)–Mn(1)–O(5)	83.0(2)	O(3)–Mn(1)–O(5)	96.6(2)
O(3)–Mn(1)–N(4)	171.6(3)	N(3)–Mn(1)–O(5)	81.9(2)
N(3)–Mn(1)–N(4)	102.7(3)	N(3)–Mn(1)–O(3)	85.6(3)
N(1)–Mn(1)–O(5)	179.4(3)	N(1)–Mn(1)–N(4)	96.6(3)
N(1)–Mn(1)–O(3)	83.8(2)	N(1)–Mn(1)–N(3)	98.6(3)
O(1)–Mn(1)–O(5)	90.4(2)	O(1)–Mn(1)–N(4)	81.8(3)
O(1)–Mn(1)–O(3)	89.8(3)	O(1)–Mn(1)–N(3)	170.5(3)
O(1)–Mn(1)–N(1)	89.1(3)	Mn(1)–O(1)–C(1)	132.0(5)
C(1)–C(6)–C(8)	123.7(7)	O(1)–C(1)–C(6)	122.3(6)
C(6)–C(8)–N(1)	127.4(8)	C(8)–N(1)–C(9)	115.3(7)
Mn(1)–N(1)–C(8)	123.8(6)	Mn(1)–N(1)–C(9)	120.6(5)
C(10)–N(2)–C(21)	118.2(8)	C(10)–N(2)–C(11)	118.1(8)
C(11)–N(2)–C(21)	116.6(8)	C(12)–N(3)–C(13)	115.4(7)
Mn(1)–N(3)–C(12)	117.6(6)	N(3)–C(13)–C(14)	129.0(8)
Mn(1)–N(3)–C(13)	125.1(6)	C(14)–C(19)–O(3)	121.9(6)
C(13)–C(14)–C(19)	123.7(6)	Mn(1)–O(3)–C(19)	128.3(4)
Mn(1)–N(4)–C(22)	119.7(6)	C(22)–N(4)–C(23)	119.1(7)
Mn(1)–N(4)–C(23)	119.6(6)	N(4)–C(23)–C(24)	127.9(8)
C(24)–C(29)–O(5)	122.9(5)	C(23)–C(24)–C(25)	116.7(5)
C(23)–C(24)–C(29)	123.2(6)	C(28)–O(6)–C(30)	115.6(7)
Mn(1)–O(5)–C(29)	127.9(4)		

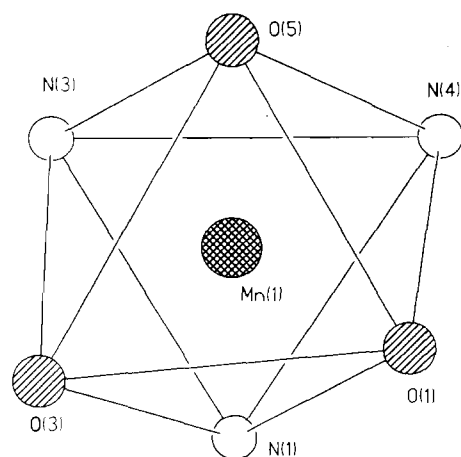
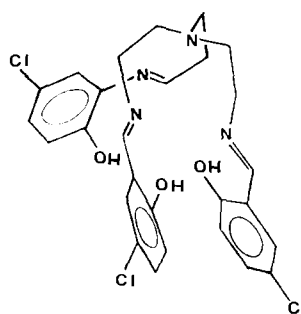


Fig. 5. The coordination polyhedron about the manganese(III) ion.

distance values, comprised between 2.075(7) and 2.317(7) Å (mean 2.158 Å), are similar to the values of 2.137(4) and 2.173(4) Å found in $\text{Mn}(\text{L}_E) \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{L}_E) \cdot \text{MeOH}$ complexes, respectively, and in the range of those found in the above cited compounds.

The three non-bonded oxygen atoms, O(2), O(4) and O(6), could be potential donor atoms to a second metal ion, in an O_6 coordination. In fact the O1...O2, O3...O4 and O5...O6 'bites' are in the range 2.76–2.79 Å. This second coordination does not seem to be favoured by the rigidity of the salicylaldimine moiety that imposes a non-favourable spatial direction of the ethereal oxygens. The other ligand details are normal and in accordance with similar organic fragments.

 H_2L_E

The formation of heterodinuclear (or heteropolynuclear) complexes follows the trend already found with similar systems: the mononuclear complex, sparingly soluble in methanol, is completely solubilized by the coordination of the second metal ion in the outer chamber.

The structure can account for the formation of different dinuclear or polynuclear complexes. Thus complexes such as $\text{MnLn}_{1.5}(\text{L}_C)(\text{NO}_3)_{4.5}$ have also been isolated when $\text{Mn}(\text{L}_C)$ is reacted with $\text{Ln}(\text{NO}_3)_3$ in methanol.

By a similar procedure, using KBr , $\text{MnK}(\text{L}_C)(\text{Br})$ has been obtained. With both metal ions, the external coordination chamber seems to act only as an O_2O_2 tetradentate site; the third arm cannot coordinate to the same metal ion and thus polynuclear species with lanthanide ions can also be obtained.

Conclusions

Both planar and tridimensional compartmental Schiff bases have been used to obtain mononuclear complexes containing d- or f-transition metal ions. These ions always occupy the inner coordination chamber and can conveniently be used as 'ligands' for further complexation.

In all the iron-containing complexes a complete oxidation of iron(II) to iron(III) occurs; a similar oxidation of manganese(II) to manganese(III) has been observed in the mononuclear $\text{Mn}(\text{L}_C)$ and $\text{Mn}(\text{H}_3\text{L}_D)$ complexes.

Certainly, when good crystals are available, the site occupancy can be detected by single-crystal X-ray diffractometric investigations; when it is impossible to grow crystals UV and magnetic data can be diagnostic. With iron-containing complexes it was verified that Mössbauer spectroscopy can be used as a useful technique for such an investigation: the parameters associated with the coordination of iron(III) to the inner or to the outer chamber of the compartmental Schiff bases are different enough to give good information on the site occupancy.

Besides the information on the coordination site, the hyperfine parameters which are very sensitive to minor variation of the organic ligand, indicate a progressive increase of the relaxation time related to the steric hindrance of the Schiff base.

In conclusion Schiff bases are of great value as precursors in the formation of well defined heterodinuclear complexes, which are essential models for a correct comprehension of the physico-chemical phenomena associated with metal-metal interaction.

Supplementary material

Observed structure amplitudes and calculated structure factors are available from the authors on request.

Acknowledgement

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