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Mössbauer and magnetic properties of mononuclear, homo- and hetero-dinuclear complexes

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Abstract

A series of mononuclear, homo- and hetero-dinuclear transition metal complexes with compartmental, potentially hexadentate, Schiff bases has been synthesized and characterized by IR, Mössbauer and magnetic measurements. The mononuclear and homo-dinuclear complexes have been obtained by reaction of the preformed ligands, derived by the condensation of 2,3-dihydroxy-benzaldehyde and, respectively, 1,2-diaminoethane (H_4L_A), 1,2-diamino-2-methylpropane (H_4L_B), 1,3-diamino-2,2-dimethylpropane (H_4L_C) or 1,2-diaminobenzene (H_4L_D) with the appropriate metal salts, or by template condensation of the formyl and the appropriate amine precursor. The hetero-dinuclear complexes have been obtained by reaction of the mononuclear complexes with the desired metal salt, in the presence of base. By using iron(II) acetate, mononuclear and homo-dinuclear iron(III) complexes have also been prepared. Mononuclear, homo- and hetero-dinuclear complexes have also been prepared for the ligands obtained by reaction of ethylenediamine with 3-methoxy (H_2L_E) or 3 ethoxy-salicylaldehyde (H_2L_F), respectively. For the iron-containing compounds, the site occupancy, the oxidation state of the metal ion and the coordination geometry were verified by Mössbauer spectroscopy. The Mössbauer effect parameters of the mononuclear complexes are typical for octahedral high-spin iron(III) derivatives containing a single iron site. The presence of substituents on the ligand does not affect the isomer shift values, while it has a marked influence on the quadrupole splitting. Its value increases from 0.77 mm/s for the complex with H_4L_B to 0.98 mm/s for the derivative with H_4L_D. In the same way for the hetero-dinuclear compounds containing copper(II)–iron(III) and nickel(II)–iron(III) ions, the δ values do not change while large differences are evident in the quadrupole splitting. The Mössbauer spectra of the homo-dinuclear complexes exhibit a doublet with a large linewidth that can only be fit as a superimposition of two different doublets, one inside the other. The parameters obtained for the inner and the outer doublet are very similar to those of the mononuclear and of the hetero-dinuclear derivatives, respectively. In the di-iron derivative with the ligand H_4L_D, the outer iron is only partially oxidized, and variable amounts of a distorted octahedral high-spin iron(II) species can always be detected in the Mössbauer spectra. The magnetic properties of this class of complexes have been studied. In particular the magnetic susceptibility of the mononuclear Fe, homodinuclear Fe_2, heterodinuclear CuFe and CuMn derivatives have been measured down to 2.5 K and analyzed by means of appropriate models. The coupling for the dinuclear compounds was found to be antiferromagnetic in nature.

Introduction

The synthesis and the coordinating ability of compartmental ligands have been the goal of much research in recent years, owing to the peculiar properties of related homo- and hetero-polynuclear complexes which have been applied in bioinorganic chemistry, materials science, catalysis, separation and incapsulation processes, etc. [1–4]. Compartmental Schiff bases have been especially investigated because of the easy preparation and remarkable versatility; their coordination capability has been studied in detail and the results extensively reviewed [7–12, 15].

Recently we have verified that the potentially hexadentate Schiff bases H_4L_A–H_4L_D, obtained by condensation of 2,3-dihydroxybenzaldehyde with the appropriate amine, easily form hetero-dinuclear complexes containing a square planar d-metal ion (i.e. copper(II)

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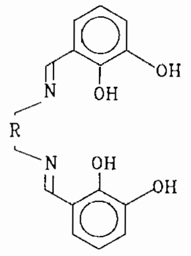
or nickel(II)) in the inner N_2O_2 coordination chamber and an f-ion (i.e. lanthanide(III) or uranyl(VI) ions) in the outer O_2O_2 coordination chamber [16–20].



R	
$-CH_2CH_2-$	H_4L_A
$-C(CH_3)_2CH_2-$	H_4L_B
$-CH_2C(CH_3)_2CH_2-$	H_4L_C
$-C_6H_4-$	H_4L_D

In these complexes, the inner N_2O_2 chamber is too small for the big f-ions, which always prefer the larger O_2O_2 compartment; in the uranyl(VI) complexes, a solvent molecule fills the fifth equatorial coordination site, with the uranium(VI) ion in a pentagonal bipyramidal geometry; the counter-anions occupy the remaining coordination sites in the lanthanide ion.

In the lanthanide complexes, the use of base causes oligomerization with the formation of tetranuclear species such as the one observed for the complexes $[CuY(L_A)(dmso)]_2$ [16]. In the di- and tetra-nuclear copper(II)–gadolinium(III) complexes, $CuGd(H_2L_A)(NO_3)_3$ and $[CuGd(L_A)(H_2O)]_2$, a ferromagnetic copper(II)–gadolinium(III) interaction was observed [17, 20], while the tetramer presents also a weak gadolinium(III)–gadolinium(III) antiferromagnetic exchange coupling, in agreement with previous finding on dinuclear gadolinium(III) complexes [17, 20].

It would be of value to quantify the magnetic interactions in hetero-polynuclear complexes with these chelating systems. During these studies, it was verified that it is difficult or even impossible to obtain homo-dinuclear copper(II) or nickel(II) complexes, possibly due to the unfavourable geometry of the outer coordination chamber towards small d-metal ions.

However by using the correct d-metal ion, it was possible to prepare homo- and hetero-dinuclear complexes and the present paper reports on the preparation and properties of a series of mononuclear, homo- and hetero-dinuclear d-metal containing complexes. We were successful in the preparation of the hetero-dinuclear species by reacting copper(II) or nickel(II) mononuclear complexes with iron(II), cobalt(II), manganese(II) and zinc(II) salts.

For the mononuclear and hetero-dinuclear complexes with compartmental ligands, the site occupancy of the metal ions has quite often been ascertained by UV or magnetic data, when it is impossible to produce crystals suitable for X-ray diffractometric investigation. When iron complexes are prepared, Mössbauer spectroscopy can be a very interesting complement to the above-mentioned measurements, in order to correctly verify the site occupancy. We have accordingly prepared, in addition to the hetero-dinuclear complexes mentioned above, a series of mononuclear and homo-dinuclear iron complexes, using iron(II) acetate as starting salt and verified that for these complexes the site occupancy, the oxidation state of the metal ion and the coordination geometry can successfully be checked by Mössbauer spectroscopy. An easy, virtually complete, oxidation of iron(II) to iron(III) was also verified for the mono- and dinuclear complexes derived from H_4L_A–H_4L_C, while only a partial oxidation was observed for the homo-dinuclear complex with H_4L_D.

The magnetic susceptibility of some of the prepared compounds was also studied, over the temperature range 3–300 K, in order to evaluate the interaction between the metal ions, and the present paper reports on the results so obtained, together with the interpretation of the experimental evidence.

Experimental

Materials

1,2-Diaminoethane, 1,2-diamino-2-methylpropane, 1,3-diamino-2,2-dimethylpropane, 1,5-diamino-3-azapentane, 2,3-dihydroxybenzaldehyde, solvents and salts are commercial products, and were used without further purification, while 1,2-diaminobenzene was recrystallized from chloroform three times before use.

The ligands H_4L_A–H_4L_D and related mononuclear copper(II) and nickel(II) complexes were prepared as already reported [16–20].

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

Preparation of the mononuclear complexes $Fe(H_2L)(OH)$

Dihydroxybenzaldehyde (2 mmol) in methanol (50 ml) was added to a methanolic solution (50 ml) of the appropriate diamine (1 mmol). The resulting yellow solution was refluxed for 1 h and then $Fe(CH_3COO)_2 \cdot H_2O$ (1 mmol) was added.

The solution turned to dark violet and was refluxed for 15 min. 2 mmol of LiOH were added and the solution refluxed for 1 h, reduced in volume, and allowed to stand overnight. The black precipitate was collected by filtration, washed with methanol and dried *in vacuo*.

TABLE 1. Elemental analyses of the prepared ligands and related complexes

Compound	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$H_4L_A \cdot 0.5MeOH$	62.98	5.75	9.08	63.06	5.13	8.91
$Cu(H_2L_A) \cdot 0.5H_2O$	52.17	3.87	7.22	51.82	4.08	7.55
$Fe(H_2L_A)(OH)$	51.52	4.25	7.64	51.50	4.59	7.51
$Fe(H_2L_A)(Cl) \cdot 0.2LiCl \cdot 2H_2O$	43.72	3.84	6.50	44.27	4.18	6.45
$Ni(H_2L_A)$	54.45	4.32	7.49	53.83	3.95	7.85
$Fe_2(L_A)(OH)_2$	43.95	3.84	6.48	43.29	3.63	6.31
$Fe_2(L_A)(Cl)_2 \cdot 0.5LiCl \cdot 2H_2O$	36.19	3.63	5.23	35.71	3.37	5.21
$CuCo(L_A) \cdot 1.5H_2O$	43.21	3.18	6.03	43.11	3.39	6.28
$CuFe(L_A)(OH)$	45.11	3.50	6.26	44.42	3.03	6.47
$CuMn(L_A) \cdot H_2O$	45.85	3.28	6.21	45.35	3.09	6.61
$CuZn(L_A) \cdot 1.5H_2O$	42.50	3.18	5.87	42.49	3.34	6.19
$NiFe(L_A)(OH)$	45.35	3.65	5.88	44.92	3.06	6.55
H_4L_B	65.29	6.31	8.44	65.84	6.14	8.53
$Fe(H_2L_B)(OH)$	54.74	4.55	6.92	54.16	4.80	7.02
$Fe_2(L_B)(OH)_2$	46.58	4.14	6.17	46.00	3.86	5.96
$H_4L_C \cdot 0.5MeOH$	65.24	6.66	8.21	65.35	6.75	7.82
$Fe(H_2L_C)(OH) \cdot MeOH$	53.75	5.56	6.17	53.95	5.66	6.29
$Fe_2(L_C)(OH)_2 \cdot 2.5MeOH$	45.40	5.17	4.75	45.78	5.36	4.97
H_4L_D	68.90	4.89	8.05	68.96	4.62	8.04
$Cu(H_2L_D) \cdot 0.5H_2O$	57.56	3.54	6.73	57.35	3.60	6.68
$Fe(H_2L_D)(OH) \cdot 1.5H_2O$	53.47	3.56	6.99	53.84	4.07	6.28
$Ni(H_2L_D) \cdot 0.3H_2O$	58.47	3.61	6.78	58.44	3.59	6.81
$CuFe(L_D)(OH) \cdot 0.7H_2O$	50.54	3.05	5.59	50.34	2.85	5.87
$CuMn(L_D) \cdot 1.5H_2O$	49.08	3.00	5.59	49.04	3.08	5.71
$CuZn(L_D) \cdot 1.5H_2O$	48.22	2.90	5.42	48.02	3.02	5.60
$Fe_2(L_D)(OH)_2 \cdot 1.5H_2O$	48.46	3.70	5.22	47.99	3.75	5.21
$NiFe(L_D)(OH) \cdot MeOH$	49.83	3.45	5.47	49.66	3.37	5.52

Preparation of $Fe(H_2L_A)(Cl) \cdot 0.2LiCl \cdot 2H_2O$

Dihydroxybenzaldehyde (2 mmol) in methanol was added to a methanolic solution of ethylenediamine (1 mmol). To the resulting solution, $FeCl_3$ (1 mmol), LiOH (2 mmol) and an excess of LiCl ($\cong$10 mmol) were added. The dark solution obtained was refluxed for 1 h, then reduced in volume and allowed to stand overnight. The black precipitate was collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of the homo-dinuclear complexes $Fe_2(L)(OH)_2 \cdot nH_2O$

Dihydroxybenzaldehyde (2 mmol) in methanol (50 ml) was added to a methanolic solution (50 ml) of the appropriate amine (1 mmol). The resulting yellow solution was refluxed for 1 h and then $Fe(CH_3COO)_2 \cdot nH_2O$ (2 mmol) and LiOH (4 mmol) were added. The resulting black suspension was refluxed for 2 h and the black precipitate was filtrated off, washed with methanol and dried *in vacuo*.

Preparation of $Fe_2(L_A)(Cl)_2 \cdot 0.5LiCl \cdot 2H_2O$

2,3-Dihydroxybenzaldehyde (2 mmol) was added to a methanolic solution of ethylenediamine (1 mmol). To the resulting solution, $FeCl_3$ (2 mmol), LiOH (4 mmol) and an excess of LiCl ($\cong$20 mmol) were added. The resulting black solution was refluxed for $\cong$3 h, partially reduced in volume and allowed to stand overnight. The black precipitate was filtered off, washed with methanol and dried *in vacuo*.

Preparation of the hetero-dinuclear complexes $MM'(L) \cdot nH_2O$ *and* $MFe(L)(OH) \cdot nH_2O$ ($M = Ni^{2+}$, Cu^{2+}; $M' = Mn^{2+}$, Co^{2+}, Zn^{2+})

The appropriate $M(CH_3COO)_2 \cdot nH_2O$ (1 mmol) and LiOH (2 mmol) were added to the mononuclear copper(II) or nickel(II) complexes in 50 ml of methanol. The resulting suspension was refluxed for 2 h and the precipitate was filtered off, washed with methanol and dried *in vacuo*.

Physicochemical measurements

IR spectra were recordered as KBr pellets on a MATTSON FTIR 3000 spectrophotometer. The homogeneity of the heteropolynuclear samples was checked with a Philips SEM XL40 model scanning electron microscope equipped with an EDAX PV99 X-ray energy dispersive spectrometer. Metal ratios were determined by the integral counting of back scattered X-ray fluorescence radiation [21].

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

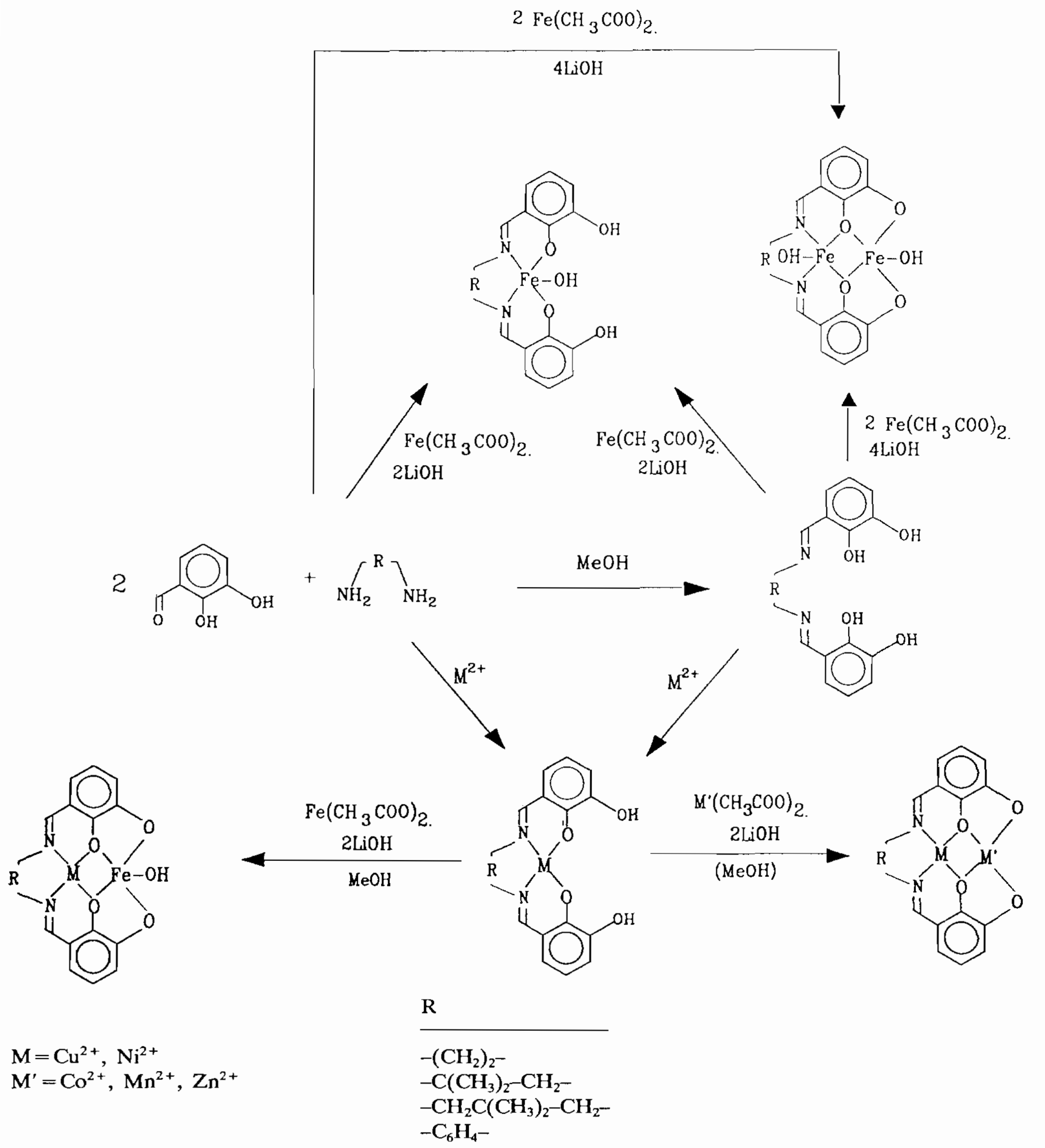
Mössbauer spectra were obtained at 80 K on a conventional constant-acceleration spectrometer, which utilizes a room-temperature rhodium matrix cobalt-57 source. The spectra were fitted to Lorentzian line shapes by using a standard least-squares computer minimization technique.

Magnetic susceptibilities were measured using a Metronique Ingegnerie SQUID magnetometer. The apparatus was calibrated by using $Gd_2(SO_4)_3$ (Aldrich, Gold Label) [22] and the data were corrected for the diamagnetism of the sample holder. Diamagnetic corrections were made by using Pascal's constants [23].

Results and discussion

The reaction procedure for the obtainment of mononuclear, homo- and hetero-dinuclear complexes is reported in Scheme 1.

Mononuclear copper(II) and nickel(II) complexes are easily prepared by reaction of the preformed ligands



Scheme 1.

with the appropriate metal(II) acetate or by template condensation of 2,3-dihydroxybenzaldehyde and the desired amine. The metal(II) ions coordinate into the inner N_2O_2 site of these compartmental ligand in a quasi square planar geometry as already ascertained by X-ray investigations [16, 20]. These complexes can act as ligands for the formation of pure hetero-dinuclear complexes, when reacted with iron(II), cobalt(II), manganese(II) or zinc(II) salts. On the contrary it is quite difficult or impossible to obtain homo-dinuclear copper(II) or nickel(II) complexes; in fact from the reaction solutions, the mononuclear complex has been recovered except $Cu_2(L_A)(MeOH)$, the only homo-dinuclear species ascertained.

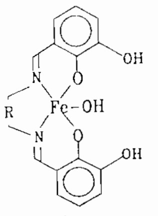
The compartmental ligands H_4L_A–H_4L_D, instead, are suitable for the formation of mononuclear and homodinuclear iron-containing complexes. The mononuclear iron $Fe(H_2\text{-}L)(OH)$ complexes are obtained as dark, quite insoluble, compounds when the ligands or the precursors are reacted with iron(II) diacetate in boiling methanol. By a similar procedure using $FeCl_3$ and an excess of LiCl, $Fe(H_2L_A)(Cl) \cdot 0.2LiCl \cdot 2H_2O$ was obtained; the excess of LiCl was added to the reaction solution in order to avoid hydrolysis of the Fe–Cl bond. The low solubility of these mononuclear complexes in non-coordinating solvents prevents or makes difficult the correct use of these species as ligands for the subsequent coordination of additional metal ions. The homodinuclear iron(III) complexes $Fe_2(L)(OH)_2$ were obtained, in a one-step reaction, by template procedure or by reaction of the preformed ligand with diacetate iron(II) salts. For the preparation of mononuclear and dinuclear complexes, iron(II) was used, but during the synthesis oxidation of the metal ion occurred with the consequent formation of iron(III) compounds (Scheme 1). Again the same experimental procedures, using $FeCl_3$ instead of iron(II) acetate, and an excess of LiCl, lead to the formation of $Fe_2(L_A)(Cl_2) \cdot 0.5LiCl \cdot 2H_2O$.

The homogeneity and the correct iron:chloride ratio in the mononuclear $Fe(H_2L_A)(Cl) \cdot 0.2LiCl \cdot 2H_2O$ or homo-dinuclear $Fe_2(L_A)(Cl)_2 \cdot 0.5LiCl \cdot 2H_2O$ complexes were also ascertained by scanning electron microscopy and X-ray fluorescence investigations. Analogously the presence of hetero-dinuclear species was checked by the same procedure: the samples appear homogeneous and a 1:1 metal ratio was observed in all the prepared complexes.

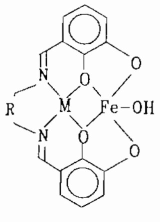
A comparison of the IR spectra of the ligands and of the complexes show that $\nu(C{=}N)$ is present as a very strong band or as a doublet at 1650–1610 cm^{-1} and that it is not significantly affected by the coordination of the metal ion. The most remarkable shift is observed on going from the free ligand to the mononuclear complexes, while the subsequent introduction of the second metal ion causes small or no further shifts.

The IR spectra rule out the presence of acetate groups as counter-anions X in the mononuclear and homo-dinuclear iron(III) complexes $Fe(H_2L)(X)$ and $Fe_2(L)(X)_2$ because of the absence of the characteristic IR absorption peaks due to the carboxylate groups. A comparison of the spectra of the free ligand and of mononuclear copper(II) and nickel(II) with the related mononuclear, homo- and hetero-dinuclear iron(III) complexes shows a remarkable similarity in the range 1650–1200 cm^{-1}. Three mean peaks are present in all the IR spectra at about 1650–1645, 1450 and 1280–1230 cm^{-1} while some differences can be observed in the smaller absorptions. Also the IR spectra of $Fe(H_2L_A)(Cl)$ and $Fe_2(L_A)(Cl)_2$ parallel those of the similar $Fe_2(H_2L_A)(X)$ and $Fe_2(L_A)(X)_2$, without remarkable differences. The similarity in the IR spectra of all the iron-containing complexes is further evidence that acetate groups are not present in the mononuclear and homo-dinuclear complexes $Fe(H_2L)(X)$ and $Fe_2(L)(X)_2$. The high magnetic moment observed at room temperature for the mononuclear iron(III) compounds ($\mu_B = 5.85$–5.89 BM) does not seem to be consistent with the presence of an Fe–O–Fe bridge: even if a single bridge was present, an antiferromagnetic coupling with a constant in the range 150–200 cm^{-1} should be operative as reported in the literature [24]. Due to the high-spin value of the iron(III) ion, a magnetic coupling of such intensity should induce relevant effects even at room temperature with a significant decrease in the magnetic moment. Therefore the X group may be OH^- and the mononuclear and homodinuclear complexes may be consequently formulated as $Fe(H_2L)(OH)$ and $Fe_2(L)(OH)_2$, respectively; analogously the hetero-dinuclear complexes are of the type $MFe(L)(OH)$ ($M = Cu^{2+}$, Ni^{2+}).

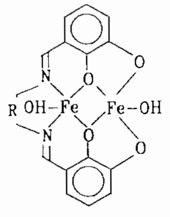
As reported above, these ligands contain an inner N_2O_2 and an outer O_2O_2 coordination site and thus the coordination of a metal ion can produce positional isomers. Magnetic and UV data can allow an identification of the site occupancy, when the samples cannot be investigated by X-ray structural diffractometry. For the iron-containing complexes Mössbauer spectroscopy can be a very useful method and thus an investigation on the three different types of iron-containing complexes has been carried out.



(A)



(B)



(C)

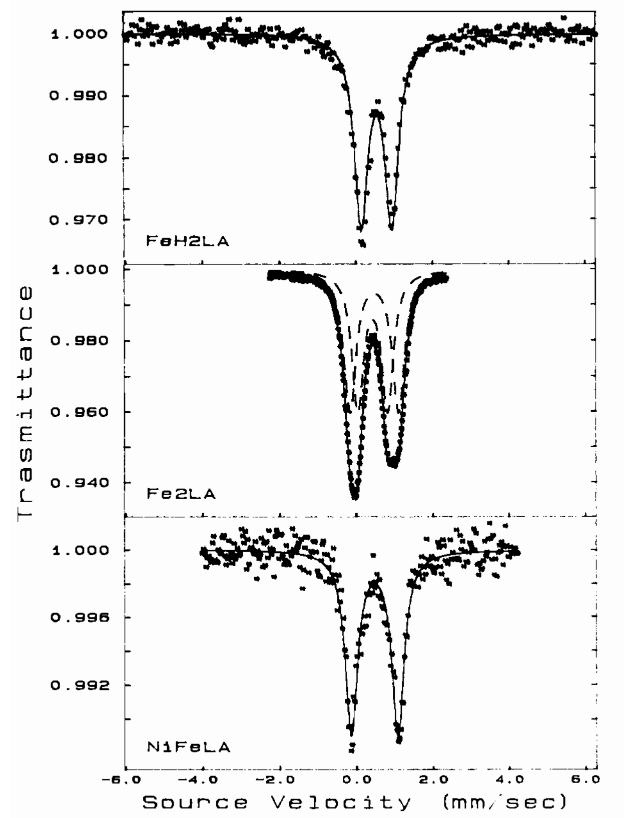


Fig. 1. Mössbauer spectra of $Fe(H_2L_A)(OH)$, $Fe_2(L_A)(OH)_2$ and $NiFe(L_A)(OH)$.

The hetero-dinuclear compounds (B) present Mössbauer effect spectra characterized by a single quadrupole split doublet with isomer shift values around 0.5 mm/s and ΔE_Q above 1 mm/s (av. 1.33 mm/s) (Fig. 1 and Table 2). In these complexes the iron atom occupies the outer O_2O_2 coordination chamber, as a consequence of the experimental procedure used in the preparation and of the ascertained quite low capability of copper(II) and nickel(II) to fill the outer O_2O_2 chamber of these ligands. As a consequence, these parameters can be considered as characteristic of this environment. On the contrary, the spectra of the homo-dinuclear complexes present Mössbauer spectra again characterized by a quadrupole split doublet, but with a too large linewidth. These spectra can only be fitted as the superimposition of two doublets, one inside the other, in a roughly 1:1 area ratio (Fig. 1 and Table 1). The parameters obtained for the outer doublet are very close to those of the hetero-dinuclear complexes and so are due to the iron present in the outer O_2O_2 chamber. The data of the inner doublet can confidently be attributed to the iron present in the inner N_2O_2 chamber, for which a lower distortion can be hypothesised. Finally for the mononuclear complexes, an iron coordination in the inner N_2O_2 chamber can be proposed on the basis of the similarity of the Mössbauer spectral data (Fig. 1 and Table 2).

The effect of the side chain is evident only on the quadrupole splitting values that increase on going from the complexes with L_A or L_B to the complexes of L_D that present the most rigid frame. No direct interaction between the two metals is evident in these spectra.

Moreover it is clear that the iron in the outer position is less available to oxidation. In fact in the $Fe_2(L_D)(OH)_2$ derivative, the outer iron is only partially oxidized, and

TABLE 2. Mössbauer effect parameters recorded at 80.0 K

Compound	Iron coordination set	δ[a] (mm/s)	ΔE_Q (mm/s)	Γ_1[b] (mm/s)	Γ_2[b] (mm/s)	Area (%)
$Fe(H_2L_A)(OH)$	N_2O_2	0.55	0.80	0.45	0.41	100
$Fe_2(L_A)(OH)_2$	N_2O_2	0.49	0.78	0.33[c]	0.33[c]	49
	O_2O_2	0.54	1.24	0.35[c]	0.35[c]	51
$NiFe(L_A)(OH)$	O_2O_2	0.48	1.22	0.38	0.40	100
$CuFe(L_A)(OH)$	O_2O_2	0.47	1.35	0.33	0.37	100
$Fe(H_2L_B)(OH)$	N_2O_2	0.50	0.77	0.30	0.36	100
$Fe_2(L_B)(OH)_2$	N_2O_2	0.51	0.75	0.31[c]	0.31[c]	46
	O_2O_2	0.55	1.25	0.30[c]	0.30[c]	54
$Fe(H_2L_C)(OH)\cdot MeOH$	N_2O_2	0.50	0.88	0.50	0.54	100
$Fe_2(L_C)(OH)_2\cdot 2.5MeOH$	N_2O_2	0.50	0.64	0.41[c]	0.41[c]	44
	O_2O_2	0.51	1.17	0.47[c]	0.47[c]	56
$Fe(H_2L_D)(OH)\cdot 1.5H_2O$	N_2O_2	0.52	0.98	0.52	0.52	100
$Fe_2(L_D)(OH)_2\cdot 1.5H_2O$	N_2O_2	0.45	0.94	0.37[c]	0.37[c]	46
	O_2O_2	0.47	1.37	0.34[c]	0.34[c]	39
		1.34	2.37	0.32[c]	0.32[c]	15
$NiFe(L_D)(OH)\cdot MeOH$	O_2O_2	0.48	1.27	0.44	0.42	100
$CuFe(L_D)(OH)\cdot 0.7H_2O$	O_2O_2	0.57	1.50	0.42	0.36	100

[a] Referred to room temperature α-Fe. [b] Linewidth for the high and the low velocity components of the doublet. [c] Γ_1 and Γ_2 values constrained to be equal for each compound.

variable amounts of a highly distorted octahedral high-spin iron(II) species can always be detected in the Mössbauer spectra (Fig. 2).

As reported above the values of the magnetic moments of the mononuclear iron(III) complexes at room temperature are fully consistent with isolated iron(III) centres; consequently the temperature dependence of the magnetic susceptibility χ of these complexes was not measured. On the contrary we have measured the temperature dependence of the magnetic susceptibility of $Fe_2(L_A)(OH)_2$ in the 2.5–280 K range. The values of the χT product steadily decrease on decreasing the temperature but observe any maximum in the pattern of the magnetic susceptibility. This behaviour can be attributed to the presence of antiferromagnetic interactions, not only to a simple intramolecular coupling. Therefore we should use a more sophisticated model: due to the absence of any structural information we did not proceed further in the analysis of the magnetic behaviour of this compound.

The magnetic susceptibilities, χ, of the hetero-dinuclear $CuMn(L_A)$ and $CuFe(L_A)(OH)$ were measured in an external field of 0.5 T down to 2.5 K. The temperature dependence of χ for the Cu–Mn derivative is shown in Fig. 3. The χ values increase on decreasing the temperature, pass through a maximum at about 4.2 K, then steadily decrease. As both the metal ions have an orbitally non-degenerate ground state an isotropic spin Hamiltonian can be used to reproduce the magnetic behaviour of the system. Further a term to account for the zero-field splitting of the Mn(II) ion was added to the $JS_1 \cdot S_2$ Hamiltonian. The parameters obtained from a least-squares fit of the $CuMn(L_A)$ data to the susceptibility expression, derived from the above described Hamiltonian, are $J = 13.7(2)$ cm^{-1} and $D = -0.87(4)$ cm^{-1} (D is the axial ZFS parameter for Mn(II) ion) with g factors fixed at 2.00 and 2.08 for Mn(II) and Cu(II), respectively. The coupling constant is indicative of an antiferromagnetic coupling as the presence of a maximum in the χ versus T curve suggests. The best fit parameters are in agreement with previously reported values for similar system [25].

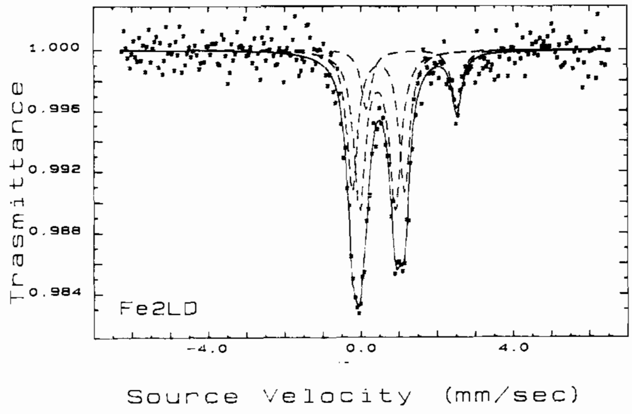


Fig. 2. Mössbauer spectrum of $Fe_2(L_D)(OH)_2 \cdot 1.5H_2O$.

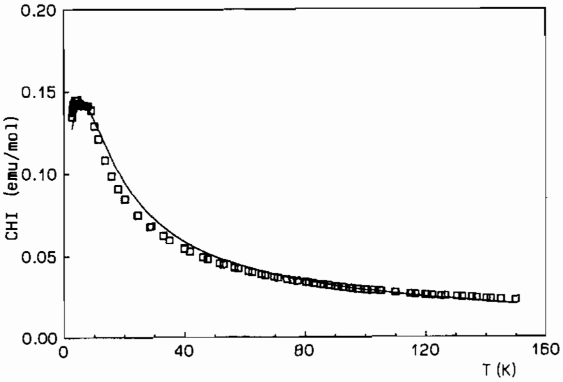


Fig. 3. Temperature dependence of χ for $CuMn(L_A) \cdot H_2O$.

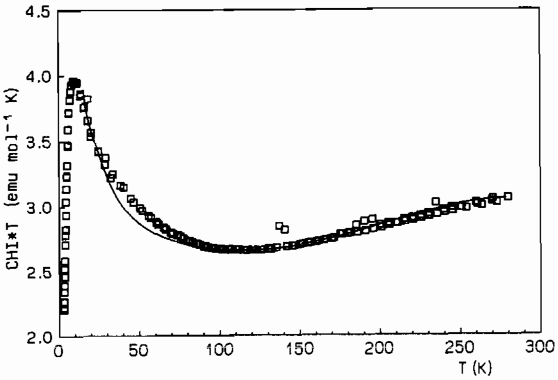


Fig. 4. Temperature dependence of χ for $CuFe(L_A)(OH)$ in the χT vs. T fashion.

The temperature dependence of the magnetic behaviour for $CuFe(L_A)(OH)$ is shown in Fig. 4 in the χT versus T fashion. Down to about 100 K the χT values decrease on lowering T, then they begin to increase and below 13 K there is a sudden decrease in the observed data. This pattern is not easy to analyze: any model which explicitly includes only metal–metal interaction and single ion terms was not able to reproduce the experimental evidence and therefore we decided to introduce a term to account for intramolecular interaction (nZJ'). The final expression for the magnetic susceptibility was derived on the basis of a spin Hamiltonian which includes the exchange isotropic parameter, a term for the ZFS of the ground spin multiplet [26], and the intramolecular interaction in the molecular field approximation [27].

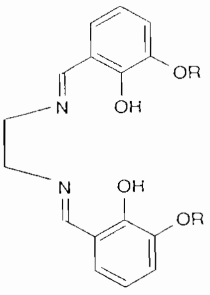
The fitting procedure to the experimental data by using the derived expression for the magnetic susceptibility was able to nicely reproduce the observed behaviour only down to 15 K and the relative parameters are $J(\text{CuFe}) = 119.1(3)$ cm^{-1}, $D = 8.8(3)$ cm^{-1}, $nZJ' = -2.7(4)$ cm^{-1} with g values fixed at 2.08 and 2.0 for Cu(II) and Fe(III), respectively. The calculated values are in good agreement with value previously observed [28] and are indicative of the presence of an antiferromagnetic Cu–Fe coupling while a weak intramolecular ferromagnetic interaction is active. We decided not to attempt an analysis of the low temperature behaviour below 15 K as any model should consider weak effects which become relevant at these temperatures, and it should be based on a detailed knowledge of the crystal structure of the system.

Both the compounds show the presence of an antiferromagnetic coupling although of different intensity; this behaviour can be rationalized considering an exchange mechanism which depends on the overlap between the magnetic orbitals on Cu(II) and on Fe(III) or Mn(II) ions probably via bridging oxygen atoms. As five unpaired electrons occupy all the 3d orbitals in the latter two ions, there is the possibility of a parallel overlap of one of these orbitals with the magnetic orbital centred on Cu(II), introducing an antiferromagnetic contribution which is, in general, the largest one [29, 30].

Finally it was also observed that it could be convenient to use 3-methoxy or 3-ethoxysalicylaldehyde as formyl precursors instead of 2,3-dihydroxybenzaldehyde in order to be certain that the external O_2O_2 coordination site behaves as a neutral tetradentate coordination entity.

Thus the use of Schiff base ligands such as H_2L_E or H_2L_F, obtained by condensation, in alcoholic solution of ethylenediamine with 3-methoxysalicylaldehyde or 3-ethoxysalicylaldehyde, respectively, precludes the dimerization observed when H_4L_A–H_4L_D are used and allows the formation of well defined and stable dinuclear entities. For instance red–brown crystals of the dinuclear complexes $\text{CuLa}(L_E)(NO_3)_3$ have easily been obtained by reaction of $\text{Cu}(L_E)$ with $\text{La}(NO_3)_3 \cdot 6H_2O$; electron microscopy and X-ray fluorescence analyses confirm the homogeneity and the correct copper:lanthanum (1:1) metal ratio in this hetero-dinuclear complex.

In addition mononuclear and dinuclear iron(III) complexes with H_2L_E have been prepared by a procedure similar to that employed for the synthesis of the analogous complexes with H_4L_A–H_4L_D. Again the oxidation of iron(II) to iron(III) and the site occupancy of the iron(III) was ascertained by Mössbauer spectroscopy [31]. According to the physicochemical data, they have been formulated as $\text{Fe}(L_E)(OH)$ and $\text{Fe}_2(L_E)(OH)_2(CH_3COO)_2$. Thus the dinuclear complex contains acetate groups as confirmed also by a comparison of the mononuclear and dinuclear complexes: strong IR bands at 1633 and 1575, and 1447 cm^{-1}, which can be associated with the antisymmetric and symmetric stretchings of the acetate groups, are clearly detectable only in the latter. Further investigations on these complexes are currently in progress.



R	
CH_3	H_2L_E
C_2H_5	H_2L_F

In conclusion it is quite easy to obtain mononuclear, homo- and hetero-dinuclear complexes containing iron ions. The inner N_2O_2 or the outer O_2O_2 site occupancy of these ions can conveniently be detected by Mössbauer spectroscopy, which reveals also that iron(II) is completely oxidized to iron(III) except for $\text{Fe}_2(L_D)(OH)_2$ in which ≅30% of the outer iron remains as iron(II).

In the prepared homo- and hetero-dinuclear complexes, an antiferromagnetic interaction between the two metal ions occurs; more complicated interactions are operative for $\text{CuFe}(L_A)(OH)$ in the range 13–25 K. The lack of structural information prevents a correct interpretation of the magnetic data in this temperature range.

By using a procedure similar to that proposed in the present paper, it becomes feasible to obtain hetero-dinuclear iron–lanthanide(III) complexes in order to study their magnetic behaviour and to use them as unconventional precursors for the formation of pure mixed oxides. Preliminary data show that iron(III)–lanthanum(III) and iron(III)–gadolinium(III) $\text{FeLn}(H_2L)(OH) \cdot (CH_3COO)_3$ complexes can be prepared with the procedure proposed for the obtainment of hetero-dinuclear complexes. These complexes can form, by thermal decomposition, pure FeLnO_3 (Ln = La, Gd) oxides.

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