Inorg. Chem. **1982**, *21*, 1396–1402

Contribution from the Dipartimento di Chimica and Istituto di Mineralogia e Cristallografia,
Università di Perugia, 06100 Perugia, Italy

Exchange Interaction in Multinuclear Transition-Metal Complexes. 1. Synthesis, X-ray Structure, and Magnetic and Spectroscopic Properties of Di-μ-methoxy-dichloro[1,4-piperazinebis(*N*-ethylenesalicylaldiminato)]diiron(III), $Fe_2L(OCH_3)_2Cl_2$

B. CHIARI, O. PIOVESANA,* T. TARANTELLI, and P. F. ZANAZZI

Received February 18, 1981

Two dinuclear iron(III) derivatives of $Fe_2L(OCH_3)_2Cl_2$ and Fe_2LCl_4 stoichiometries, where L^{2-} is the anion of the novel hexadentate Schiff base 1,4-piperazinebis(*N*-ethylenesalicylaldimine), have been obtained. The crystal structure of the methoxy complex has been determined by X-ray methods. The compound crystallizes in the monoclinic space group $P2_1/n$ with eight formula units in a cell of dimensions a = 25.924 (3) Å, b = 18.923 (3) Å, c = 12.496 (3) Å, and β = 90.19 (2)°. Least-squares refinement of 1727 observed reflections and 282 parameters has led to a final R factor of 0.087. The asymmetric unit is formed by two independent but quite similar dinuclear molecules. Each complex consists of two iron(III) ions that are symmetrically bridged by two methoxy groups. The geometry around the iron atoms is roughly octahedral. Three coordination sites are occupied by one oxygen and two nitrogens (cis) of hexadentate L^{2-} and the remaining three by the two bridging methoxy groups and a terminal chlorine atom. The average Fe–O(bridging) bond length is 1.99 Å, the mean Fe–Fe separation is 3.106 Å, and the FeOFe angle averages 103°. The magnetic susceptibilities of powdered samples of $Fe_2L(OCH_3)_2Cl_2$ and Fe_2LCl_4 have been examined in the temperature ranges 7–289 and 90–300 K, respectively. The methoxy compound exhibits an antiferromagnetic exchange interaction with the best fit to the Van Vleck equation yielding $J = -16.3$ cm^{-1}, with $g = 2.00$ and TIP = 0. The effective magnetic moment of Fe_2LCl_4 is essentially temperature independent, 5.8 ± 0.2 μ_B, and closely corresponds to the spin-only value (5.9 μ_B) expected for an exchange-noninteracting high-spin system. A comparison of the magnetic and structural properties of $Fe_2L(OCH_3)_2Cl_2$ to those of the other X-ray structurally determined iron(III) compounds containing Fe–O–Fe–O rings does not indicate any correlation between J and the bridging angle at oxygen or the electron density at the bridging atom. Infrared, ESR, and UV–vis spectral data for both $Fe_2L(OCH_3)_2Cl_2$ and Fe_2LCl_4 are reported.

Introduction

Magnetic multinuclear complexes are receiving continuing attention.[1] One reason these materials are so interesting is that they enable the exchange coupling between metal atoms, which is just incipient chemical bond formation, to be deduced from experimental measurements without resorting to the approximations necessary in treating materials that have collective properties. Additional interest derives from the antiferromagnetism of metalloproteins[2] and other biological iron compounds.[3]

Observable spin exchange necessarily implies the presence of very weak interactions between electrons. These are generally given in terms of the exchange coupling constant, J, which, at least for metal atoms in single-ion orbital singlet ground states, can be easily evaluated from the temperature dependence of the magnetic susceptibility.[1]

However, a quantitative interpretation of the sign and magnitude of the J parameter, particularly as they relate to other molecular properties, is difficult because it requires the calculation of small energy differences (<1000 cm^{-1}) in large many-electron systems, and because it is necessary to take account of electron correlation,[4] an arduous task by means of current MO approaches.[5] Actually, attempts at theoretical calculations of J have been very limited in number,[4] and in general, our knowledge of how the extent of magnetic interaction depends on the nature of the metal ion, the nature of the terminal and bridging ligands, and the molecular geometry is still essentially empirical. It mainly derives from systematic experimental studies of the effect of small variations in molecular structure on exchange coupling for series of related compounds that differ in a controlled manner.

Considerable experimental evidence has been presented supporting the view that J is correlated to the MOM bridging angle,[6,7] and to the electron density at the bridging oxygen atoms[8,9] in Cu(II) or Cr(III) complexes containing four-membered M–O–M–O rings. Semiempirical MO arguments in agreement with these effects have also been presented.[10-14] In contrast, the origin of the variations in weak antiferromagnetic coupling that have been reported for the Fe(III) analogues[15-24] remains unknown.[15]

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*To whom correspondence should be addressed at the Dipartimento di Chimica.

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We here report the results of our synthetic, structural, magnetic, and spectroscopic investigations of magnetically coupled, dimethoxo-bridged $Fe_2L(OCH_3)_2Cl_2$, where L^{2-} is the anion of the novel, hexadentate Schiff base 1,4-piperazinebis(*N*-ethylenesalicylaldimine). The synthesis and properties of the related Fe_2LCl_4 compound, which is magnetically noninteracting, are also reported.

Experimental Section

Syntheses. LH_2. Solid 1-amino-2-bromoethane hydrobromide (41 g, 0.2 mol) was added to a solution of NaOH in water (20 g in 150 mL) at 0 °C. The addition was made over a period of 15 min, with stirring. The aqueous solution was extracted with two 50-mL portions of cold benzene. These were added to a solution of salicylaldehyde in benzene (25 g, 0.2 mol, in 25 mL). The resulting solution was evaporated to dryness by distillation under vacuum. Recrystallization of the residue from methanol afforded the novel, yellow, crystalline Schiff base *N*-salicylidene-2-bromoethylamine (32 g, 70%), mp 55–57 °C. Anal. Calcd for $C_9H_{10}NBrO$: C, 47.39; H, 4.43; N, 6.14; Br, 35.03. Found: C, 47.32; H, 4.51; N, 6.20; Br, 34.84.

N-Salicylidene-2-bromoethylamine (2.3 g, 10 mmol) dissolved in benzene (25 mL) was added to a solution of piperazine (1.7 g, 20 mmol) in the same solvent (25 mL). The reaction mixture was heated under reflux for ~1 h, with stirring, cooled at 0 °C, and then filtered to remove solid piperazine dihydrobromide. The filtrate was evaporated to dryness by distillation under vacuum. The residue was treated with an aqueous solution of Na_2CO_3 (2 g in 50 mL). After ~1 h of stirring, solid LH_2 was collected by filtration and washed with water. Recrystallization from methanol afforded yellow prismatic crystals (0.75 g, 40%), mp 149–151 °C. Anal. Calcd for $C_{22}H_{28}N_4O_2$: C, 69.43; H, 7.43; N, 14.73. Found: C, 69.60; H, 7.41; N, 14.75.

Triethylenetetramine (trien) of commercial source was reported by Bergsted and Widmark[25] to contain 1,4-piperazinebis(ethylenamine) as a byproduct. In agreement with these authors, we have found that LH_2 can be obtained from technical trien. In a typical experiment, salicylaldehyde dissolved in boiling methanol (11 g, 90 mmol in 20 mL) was added to a boiling solution of technical trien (BDH, Chemicals Ltd., Poole, England) in the same solvent (7.3 g in 20 mL). The clear solution was allowed to cool at room temperature, and it was then stirred for 1 h before crystalline LH_2 was collected by filtration, washed with methanol, and dried in air. Magnetic stirring at room temperature could not be prolonged for more than 1 h, in order to avoid progressively increasing contamination of LH_2 by the tetrahydroimidazole derivative produced by the reaction of trien with salicylaldehyde.[26] Yields corresponding to 5–10% by weight of 1,4-piperazinebis(ethylenamine) in trien were obtained.

$Fe_2L(OCH_3)_2Cl_2$. $FeCl_3{\cdot}6H_2O$ dissolved in methanol (0.54 g, 2 mmol, in 15 mL) was added to 20 mL of a 0.1 M solution of sodium methoxide in methanol. To the resulting solution was added 0.38 g (1 mmol) of LH_2 dissolved in 30 mL of methanol. The reaction mixture was heated under reflux for about 5 min, and after filtration of a dark solid impurity, for an additional 2 h. After cooling of the solution to room temperature, crystallization was allowed to continue for about 24 h before brown, crystalline $Fe_2L(OCH_3)_2Cl_2$ was collected by filtration, washed with methanol, and dried in air; yield 0.4 g (64%). The product could not be recrystallized unaltered from organic solvents (mp >350 °C). Anal. Calcd for $Fe_2C_{24}H_{32}N_4Cl_2O_4$: Fe, 17.92; C, 46.25; H, 5.19; N, 8.89; Cl, 11.38. Found: Fe, 17.82; C, 45.96; H, 5.22; N, 9.01; Cl, 11.24.

Fe_2LCl_4. A solution of LH_2 in methanol (0.38 g, 1 mmol, in 30 mL) was added to a boiling solution of $FeCl_3{\cdot}6H_2O$ in the same solvent (0.54 g, 2 mmol, in 20 mL). The resulting solution was heated under reflux for ~1 h, filtered, and then allowed to stand at room temperature overnight. A brown microcrystalline material separated, which was filtered and washed with methanol; yield 0.3 g (47%). The compound could not be recrystallized due to its insolubility in organic solvents (mp >350 °C). Anal. Calcd for $Fe_2C_{22}H_{26}N_4Cl_4O_2$: Fe, 17.67; C, 41.81; H, 4.15; N, 8.87; Cl, 22.44; O, 5.06. Found: Fe, 17.61; C, 42,12; H, 4.28; N, 9.08; Cl, 22.41; O, 5.19.

Table I. Crystal Data for $Fe_2L(OCH_3)_2Cl_2$

$C_{24}H_{32}O_4N_4Cl_2Fe_2$
mol wt = 622.6
monoclinic, space group $P2_1/n$
$a = 25.924\ (3)$ Å
$b = 18.923\ (3)$ Å
$c = 12.496\ (3)$ Å
$\beta = 90.12\ (2)°$
$V = 6130.0$ Å^3
$Z = 8$
$d_{\text{calcd}} = 1.349$ g/cm^3
$d_{\text{obsd}}{}^a = 1.29$ g/cm^3
μ(Mo Kα) = 11.2 cm^{-1}
cryst dimens:
0.06 × 0.06 × 0.85 mm

[a] By the flotation method.

Chemical Analyses. These were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Molecular Weight Measurements. Molecular weights were determined by using a Mechrolab Model 301 A vapor pressure osmometer.

Infrared Spectra. Infrared spectra were recorded, in the region 5000–250 cm^{-1}, with a Perkin-Elmer 521 spectrophotometer. The compounds were studied as KBr pellets or Nujol mulls.

Visible–UV Spectra. Both solution and Nujol mull spectra were recorded on a Cary 17 spectrophotometer.

ESR Spectra. These were measured with a Varian E-9 spectrometer, operated at the X band, and with diphenylpicrylhydrazyl (DPPH) free radical as internal reference.

Frozen-solution spectra were obtained with a Dewar finger filled with liquid nitrogen, which fitted into the instrument sample cavity.

Conductivity Measurements. These were made with a Philips PW 9501 apparatus.

Magnetic Measurements. The magnetic susceptibility of Fe_2LCl_4 was measured by the Gouy method on solid polycrystalline samples, at temperatures between ~90 and ~300 K and at several field strengths. For $Fe_2L(OCH_3)_2Cl_2$, magnetic measurements, in the liquid-helium- to room-temperature range, were carried out on a Faraday balance system (Oxford Instruments cryogenic system) similar in principle to that described by Gardner and Smith.[27] The magnetic field H_z and the field gradient dH/dz were generated by two different superconducting NbTi coils, allowing both H_z and dH/dz to be set independently of each other. The changes in weight were measured on an electronically controlled vacuum microbalance (Sartorius) with a resolution of 1 μg. The temperature was measured with a gold (+0.03% Fe) vs. chromel P thermocouple. The main field was calibrated, with dH/dz remaining constant at 1000 G/cm, by using mercury tetrakis(thiocyanato)cobaltate(II) as a susceptibility standard. All measurements were made at a field strength of 9000 G.

Diamagnetic corrections of 153×10^{-6} and 150×10^{-6} cgsu per iron ion were used for $Fe_2L(OCH_3)_2Cl_2$ and Fe_2LCl_4, respectively; these were calculated from Pascal's constants.[28]

X-ray Data and Structure Solution. A crystal of $Fe_2L(OCH_3)_2Cl_2$ was mounted on a PW1100 four-circle diffractometer equipped with Mo radiation monochromatized by graphite. The crystal is monoclinic. Lattice dimensions were determined with a least-squares procedure, with use of the values of the setting angles of 25 reflections. From the systematic extinctions, the space group was found to be $P2_1/n$. Crystal data are listed in Table I. The intensity data were collected in the range 3–15° of the ϑ angle, with the ϑ–2ϑ scan technique. Beyond this limit no reflections with measurable intensities were detected. Each reflection was measured with a scan width of 1.2°, a scan speed of 0.04° s^{-1}, and two background measurements for 10 s on each side of the peak. As a check of instrumental and crystal stability, three reflections were monitored every 180 min: a total decay in intensity of about 10% was detected during data collection. A correction for this effect, due to partial decomposition of the crystal under the X radiation, was applied to the data.

A total of 5549 reflections were measured, but owing to the low diffraction power of the crystal, 3827 reflections had intensity I less than $3[\sigma(I)]$[29] and were considered as "unobserved". Data were

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Table II. Fractional Atomic Coordinates and Thermal Parameters for Nonhydrogen Atoms of $Fe_2L(OCH_3)_2Cl_2$[a]

atom	x/a	y/b	z/c	U, Å^2	atom	x/a	y/b	z/c	U, Å^2
				Molecule A					
Fe(1)	0.5608 (2)	0.2741 (3)	0.6825 (3)	[b]	C(7)	0.6378 (14)	0.3354 (16)	0.8321 (27)	0.058 (11)
Fe(2)	0.4757 (2)	0.3271 (3)	0.5277 (3)	[b]	C(8)	0.5555 (12)	0.3325 (17)	0.9107 (27)	0.058 (11)
Cl(1)	0.5809 (4)	0.1622 (5)	0.7409 (8)	[b]	C(9)	0.5212 (13)	0.2734 (17)	0.9078 (26)	0.061 (11)
Cl(2)	0.4258 (3)	0.4276 (5)	0.5430 (7)	[b]	C(10)	0.4601 (11)	0.2100 (15)	0.8011 (22)	0.031 (10)
O(1)	0.6254 (8)	0.2899 (10)	0.6117 (15)	0.050 (7)	C(11)	0.4340 (12)	0.2003 (16)	0.6912 (23)	0.052 (11)
O(2)	0.5116 (7)	0.3541 (11)	0.3984 (16)	0.057 (7)	C(12)	0.4036 (12)	0.3190 (17)	0.7424 (26)	0.060 (12)
O(3)	0.5183 (7)	0.2428 (10)	0.5598 (15)	0.038 (6)	C(13)	0.4537 (12)	0.3347 (17)	0.8052 (27)	0.070 (12)
O(4)	0.5281 (7)	0.3628 (10)	0.6330 (14)	0.036 (6)	C(14)	0.3693 (12)	0.2642 (16)	0.5806 (24)	0.049 (11)
N(1)	0.5911 (11)	0.3202 (13)	0.8209 (20)	0.052 (9)	C(15)	0.3841 (12)	0.2282 (17)	0.4751 (25)	0.048 (11)
N(2)	0.4891 (9)	0.2707 (13)	0.8084 (19)	0.041 (8)	C(16)	0.4126 (12)	0.2942 (16)	0.3258 (28)	0.049 (11)
N(3)	0.4163 (10)	0.2680 (13)	0.6502 (20)	0.042 (8)	C(17)	0.4449 (9)	0.3452 (12)	0.2648 (14)	0.045 (11)
N(4)	0.4223 (10)	0.2742 (13)	0.4261 (22)	0.054 (9)	C(18)	0.4259 (9)	0.3663 (12)	0.1653 (14)	0.064 (12)
C(1)	0.6721 (9)	0.3009 (11)	0.6532 (18)	0.036 (10)	C(19)	0.4524 (9)	0.4169 (12)	0.1056 (14)	0.052 (11)
C(2)	0.7138 (9)	0.2872 (11)	0.5860 (18)	0.063 (12)	C(20)	0.4979 (9)	0.4463 (12)	0.1455 (14)	0.052 (11)
C(3)	0.7640 (9)	0.3000 (11)	0.6215 (18)	0.069 (13)	C(21)	0.5169 (9)	0.4252 (12)	0.2451 (14)	0.059 (11)
C(4)	0.7725 (9)	0.3265 (11)	0.7243 (18)	0.092 (14)	C(22)	0.4904 (9)	0.3746 (12)	0.3047 (14)	0.051 (12)
C(5)	0.7308 (9)	0.3401 (11)	0.7915 (18)	0.059 (12)	C(23)	0.5282 (15)	0.1874 (22)	0.4935 (32)	0.095 (15)
C(6)	0.6806 (9)	0.3273 (11)	0.7559 (18)	0.041 (11)	C(24)	0.5492 (11)	0.4315 (16)	0.6282 (23)	0.039 (10)
				Molecule B					
Fe(3)	0.2752 (2)	0.5958 (3)	0.8049 (4)	[b]	C(31)	0.3685 (13)	0.6731 (16)	0.7135 (25)	0.038 (11)
Fe(4)	0.2671 (2)	0.4625 (3)	0.9499 (3)	[b]	C(32)	0.3375 (12)	0.5789 (16)	0.5998 (25)	0.051 (11)
Cl(3)	0.2122 (4)	0.6646 (5)	0.7226 (7)	[b]	C(33)	0.2852 (12)	0.5527 (17)	0.5729 (25)	0.058 (11)
Cl(4)	0.3195 (3)	0.3625 (5)	0.9565 (6)	[b]	C(34)	0.2930 (12)	0.4449 (16)	0.6696 (25)	0.047 (11)
O(5)	0.3004 (7)	0.6702 (10)	0.8951 (15)	0.046 (7)	C(35)	0.2635 (11)	0.3842 (16)	0.7140 (24)	0.044 (11)
O(6)	0.2832 (7)	0.4948 (10)	1.0900 (15)	0.051 (7)	C(36)	0.1851 (13)	0.4621 (18)	0.7414 (26)	0.062 (12)
O(7)	0.2273 (7)	0.5466 (10)	0.9055 (15)	0.042 (7)	C(37)	0.2096 (11)	0.4970 (16)	0.6430 (24)	0.043 (10)
O(8)	0.3188 (8)	0.5190 (9)	0.8704 (14)	0.039 (6)	C(38)	0.1976 (12)	0.3472 (16)	0.8475 (25)	0.054 (11)
N(5)	0.3362 (10)	0.6243 (14)	0.6975 (21)	0.057 (9)	C(39)	0.1671 (11)	0.3770 (16)	0.9419 (24)	0.047 (11)
N(6)	0.2638 (10)	0.5126 (13)	0.6637 (19)	0.043 (8)	C(40)	0.2026 (12)	0.3856 (16)	1.1143 (27)	0.047 (11)
N(7)	0.2217 (10)	0.4104 (14)	0.7960 (20)	0.052 (9)	C(41)	0.2408 (8)	0.4084 (12)	1.1950 (17)	0.062 (12)
N(8)	0.2047 (9)	0.4114 (12)	1.0154 (21)	0.045 (8)	C(42)	0.2396 (8)	0.3687 (12)	1.2891 (17)	0.068 (12)
C(25)	0.3345 (8)	0.7183 (11)	0.8860 (21)	0.053 (11)	C(43)	0.2775 (8)	0.3787 (12)	1.3673 (17)	0.068 (12)
C(26)	0.3371 (8)	0.7705 (11)	0.9646 (21)	0.070 (12)	C(44)	0.3165 (8)	0.4283 (12)	1.3514 (17)	0.068 (12)
C(27)	0.3767 (8)	0.8205 (11)	0.9626 (21)	0.079 (13)	C(45)	0.3177 (8)	0.4679 (12)	1.2573 (17)	0.041 (10)
C(28)	0.4137 (8)	0.8182 (11)	0.8819 (21)	0.071 (13)	C(46)	0.2798 (8)	0.4580 (12)	1.1791 (17)	0.043 (11)
C(29)	0.4111 (8)	0.7660 (11)	0.8032 (21)	0.064 (12)	C(47)	0.1870 (13)	0.5778 (17)	0.9636 (27)	0.062 (12)
C(30)	0.3715 (8)	0.7160 (11)	0.8053 (21)	0.048 (11)	C(48)	0.3720 (13)	0.5205 (16)	0.8916 (24)	0.048 (10)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{12}	U_{23}		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.057 (4)	0.079 (5)	0.013 (4)	0.006 (4)	−0.001 (3)	−0.001 (3)	Cl(1)	0.090 (9)	0.084 (8)	0.058 (8)	0.029 (7)	0.019 (6)	0.016 (7)
Fe(2)	0.052 (4)	0.074 (4)	0.011 (4)	0.002 (3)	0.007 (3)	0.003 (3)	Cl(2)	0.065 (7)	0.076 (8)	0.031 (7)	0.002 (6)	0.005 (5)	0.004 (6)
Fe(3)	0.055 (4)	0.079 (5)	0.016 (4)	0.009 (3)	0.017 (3)	0.006 (3)	Cl(3)	0.081 (8)	0.093 (8)	0.035 (7)	0.034 (7)	0.018 (6)	0.008 (6)
Fe(4)	0.049 (4)	0.069 (4)	0.006 (3)	−0.003 (3)	0.005 (3)	−0.001 (3)	Cl(4)	0.070 (8)	0.086 (8)	0.023 (6)	0.016 (6)	−0.001 (5)	0.004 (6)

[a] Estimated standard deviations in parentheses refer to the last digit. [b] The anisotropic temperature factors of Fe and Cl atoms are given in the bottom section of the table and are in the form $\exp(-2\pi^2(\Sigma_i\Sigma_j h_i h_j a^*_i a^*_j U_{ij}))$.

corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by the direct multisolution method with MULTAN.[30] The E map for the best solution showed the positions of the Fe atoms and part of the coordination sphere around these atoms. The structure was completed by successive Fourier syntheses. The refinement was carried out with the full-matrix least-squares method employing the SHELX system of programs.[31] The phenyl rings of the salicylic residues were constrained to perfect hexagons having C–C distances of 1.395 Å and CCC angles of 120° and refined with their H atoms as rigid groups. The other H atoms were included at their computed positions. C–H bond lengths were imposed to be 1.08 Å. An overall isotropic thermal parameter was refined for the hydrogen atoms: this parameter converged to the value $U = 0.11$ Å^2. All the nonhydrogen atoms were refined isotropically, with the exception of the Fe and Cl atoms, for which anisotropic thermal parameters were refined. The refinement was stopped when all the shift/esd ratios were less than 0.1. The R[32] value converged to 0.087 for 1722 observed reflections and 282 parameters. R_w was 0.094. These rather high figures are probably due to the poor quality of the data, and to the not completely adequate model assumed for the constraints during the refinement. However, the results concerning the main structural features of chemical interest maintain their validity.

The atomic scattering factors of neutral Cl, O, N, C, and H were those of the SHELX system of programs; Fe scattering factors were taken from ref 33. A correction for anomalous dispersion was applied. Positional and thermal parameters of nonhydrogen atoms are listed in Table II.

Results

Both $Fe_2L(OCH_3)_2Cl_2$ and Fe_2LCl_4 are air stable. The former species is soluble in common organic solvents whereas the latter is so sparingly soluble as to prevent significant solution measurements. A molecular weight of 1200 ± 30 was measured for $Fe_2L(OCH_3)_2Cl_2$ (calculated 623) in dichloromethane (0.62%) or acetone (0.15%). Conductivity measurements in these solvents showed a strictly nonelectrolytic behavior. We are at this time unable to account for the nature of the molecular association that appears to occur in solution.

Description of the Structure of $Fe_2L(OCH_3)_2Cl_2$. The crystal structure of $Fe_2L(OCH_3)_2Cl_2$ is built up by discrete dinuclear

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(32) The R index is defined as $\sum(|F_o| - |F_c|)/\sum|F_o|$ and R_w as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w is $1/(\sigma^2(F) + 0.0032F^2)$.

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Table III. Bond Lengths (Å) in $Fe_2L(OCH_3)_2Cl_2$

molecule A		molecule B	
Fe(1)-Cl(1)	2.30 (1)	Fe(3)-Cl(3)	2.33 (1)
Fe(2)-Cl(2)	2.31 (1)	Fe(4)-Cl(4)	2.33 (1)
Fe(1)-O(1)	1.92 (2)	Fe(3)-O(5)	1.92 (2)
Fe(1)-O(3)	1.98 (2)	Fe(3)-O(7)	2.01 (2)
Fe(1)-O(4)	1.98 (2)	Fe(3)-O(8)	2.00 (2)
Fe(2)-O(2)	1.94 (2)	Fe(4)-O(6)	1.90 (2)
Fe(2)-O(3)	1.98 (2)	Fe(4)-O(7)	1.98 (2)
Fe(2)-O(4)	2.01 (2)	Fe(4)-O(8)	1.98 (2)
Fe(1)-N(1)	2.09 (3)	Fe(3)-N(5)	2.15 (3)
Fe(1)-N(2)	2.44 (2)	Fe(3)-N(6)	2.38 (2)
Fe(2)-N(3)	2.44 (3)	Fe(4)-N(7)	2.46 (2)
Fe(2)-N(4)	2.13 (3)	Fe(4)-N(8)	2.06 (2)
O(1)-C(1)	1.33 (3)	O(5)-C(25)	1.27 (2)
O(2)-C(22)	1.35 (2)	O(6)-C(46)	1.32 (3)
C(6)-C(7)	1.47 (4)	C(30)-C(31)	1.41 (4)
C(7)-N(1)	1.25 (3)	C(31)-N(5)	1.26 (3)
N(1)-C(8)	1.48 (3)	N(5)-C(32)	1.49 (3)
C(8)-C(9)	1.43 (4)	C(32)-C(33)	1.48 (4)
C(9)-N(2)	1.49 (3)	C(33)-N(6)	1.48 (3)
N(2)-C(10)	1.38 (3)	N(6)-C(34)	1.49 (3)
N(2)-C(13)	1.52 (3)	N(6)-C(37)	1.46 (3)
C(10)-C(11)	1.54 (3)	C(34)-C(35)	1.49 (3)
C(11)-N(3)	1.45 (3)	C(35)-N(7)	1.57 (3)
N(3)-C(12)	1.54 (3)	N(7)-C(36)	1.52 (3)
C(12)-C(13)	1.54 (4)	C(36)-C(37)	1.54 (4)
N(3)-C(14)	1.50 (3)	N(7)-C(38)	1.50 (3)
C(14)-C(15)	1.53 (4)	C(38)-C(39)	1.53 (4)
C(15)-N(4)	1.45 (3)	C(39)-N(8)	1.49 (3)
N(4)-C(16)	1.33 (3)	N(8)-C(40)	1.33 (3)
C(16)-C(17)	1.49 (4)	C(40)-C(41)	1.48 (3)
O(3)-C(23)	1.36 (4)	O(7)-C(47)	1.40 (3)
O(4)-C(24)	1.41 (3)	O(8)-C(48)	1.40 (3)
Fe(1)-Fe(2)	3.097 (7)	Fe(3)-Fe(4)	3.115 (7)

molecules. The asymmetric unit is formed by two independent molecules whose structures as well as atomic numbering are shown in Figure 1. A comparison of bond distances and angles for both molecules (Tables III and IV) shows that they are strikingly similar.

In each dinuclear unit the Fe(III) ions are symmetrically bridged by two methoxy groups. The geometry around the iron atoms is roughly octahedral. One oxygen and two nitrogens (cis) of hexadentate L^{2-} occupy three coordination sites; the remaining three are occupied by the two bridging methoxy groups and a terminal chlorine atom. The whole molecule has a nearly perfect noncrystallographic twofold rotation axis perpendicular to the plane of the four-membered iron-oxygen ring. The Fe-O-Fe-O ring is only approximately planar, the two iron atoms being out of the least-squares plane by 0.09 Å, on the same side of the plane, toward the nitrogen atoms of the piperazine ring. The dihedral angle between the Fe(1)O(3)O(4) and Fe(2)O(3)O(4) planes is 167°; that between the Fe(3)O(7)O(8) and Fe(4)O(7)O(8) planes is 169°. Angles at oxygen and iron average 103 and 76.6°, respectively, and are typical for a symmetrical Fe-O-Fe-O ring.[15,18-20,22,34] The Fe-O(bridging) (1.98 (2)-2.01 (2) Å) and the Fe-O(terminal) (1.90 (2)-1.94 (2) Å) distances are also in the ranges normally observed for iron(III)-Schiff base complexes.[18-20,22,34-36] The mean Fe···Fe separation is 3.106 Å. The N-Fe distances fall into two groups, averaging 2.11 and 2.43 Å for bonds involving azomethine and piperazine nitrogen atoms, respectively. Both values agree with those reported in the literature for secondary and tertiary amine-Fe(III) bond lengths, respectively.[36,37] The Cl-Fe distance averages 2.33 Å. The methoxy carbon atoms (C(23), C(24), C(47), and C(48)) are considerably out of the plane of the four-membered iron-oxygen ring, the mean deviation from this plane being 0.70 Å, on the opposite side of the iron atoms. The preference of the Fe-O-Fe-O ring for an OFeO angle close to 77° and the steric requirements for the hexadentate ligand, particularly the N···N separation in the piperazine ring (e.g., the N(2)···N(3) separation is 2.73

Table IV. Bond Angles (Deg) in $Fe_2L(OCH_3)_2Cl_2$

molecule A		molecule B	
Cl(1)-Fe(1)-O(1)	95.3 (6)	Cl(3)-Fe(3)-O(5)	95.0 (6)
Cl(1)-Fe(1)-O(3)	95.5 (6)	Cl(3)-Fe(3)-O(7)	95.8 (6)
Cl(1)-Fe(1)-O(4)	167.6 (6)	Cl(3)-Fe(3)-O(8)	167.5 (6)
Cl(1)-Fe(1)-N(1)	92.2 (7)	Cl(3)-Fe(3)-N(5)	95.8 (7)
Cl(1)-Fe(1)-N(2)	86.7 (7)	Cl(3)-Fe(3)-N(6)	87.5 (6)
O(1)-Fe(1)-O(3)	100.0 (8)	O(5)-Fe(3)-O(7)	100.6 (8)
O(1)-Fe(1)-O(4)	95.6 (8)	O(5)-Fe(3)-O(8)	95.8 (7)
O(1)-Fe(1)-N(1)	89.5 (10)	O(5)-Fe(3)-N(5)	86.2 (10)
O(1)-Fe(1)-N(2)	165.6 (9)	O(5)-Fe(3)-N(6)	164.2 (9)
O(3)-Fe(1)-O(4)	76.9 (8)	O(7)-Fe(3)-O(8)	75.9 (8)
O(3)-Fe(1)-N(1)	167.2 (10)	O(7)-Fe(3)-N(5)	166.0 (9)
O(3)-Fe(1)-N(2)	93.9 (8)	O(7)-Fe(3)-N(6)	94.7 (8)
O(4)-Fe(1)-N(1)	93.7 (9)	O(8)-Fe(3)-N(5)	91.3 (8)
O(4)-Fe(1)-N(2)	84.1 (8)	O(8)-Fe(3)-N(6)	83.8 (8)
N(1)-Fe(1)-N(2)	76.3 (10)	N(5)-Fe(3)-N(6)	78.0 (10)
Cl(2)-Fe(2)-O(2)	97.1 (6)	Cl(4)-Fe(4)-O(6)	95.9 (6)
Cl(2)-Fe(2)-O(3)	163.5 (6)	Cl(4)-Fe(4)-O(7)	165.4 (6)
Cl(2)-Fe(2)-O(4)	92.7 (6)	Cl(4)-Fe(4)-O(8)	93.5 (6)
Cl(2)-Fe(2)-N(3)	88.3 (6)	Cl(4)-Fe(4)-N(7)	88.9 (6)
Cl(2)-Fe(2)-N(4)	94.2 (7)	Cl(4)-Fe(4)-N(8)	93.7 (7)
O(2)-Fe(2)-O(3)	96.4 (8)	O(6)-Fe(4)-O(7)	96.4 (8)
O(2)-Fe(2)-O(4)	97.6 (8)	O(6)-Fe(4)-O(8)	98.1 (8)
O(2)-Fe(2)-N(3)	161.6 (9)	O(6)-Fe(4)-N(7)	162.4 (8)
O(2)-Fe(2)-N(4)	86.6 (9)	O(6)-Fe(4)-N(8)	87.4 (9)
O(3)-Fe(2)-O(4)	76.2 (8)	O(7)-Fe(4)-O(8)	77.2 (8)
O(3)-Fe(2)-N(3)	81.8 (8)	O(7)-Fe(4)-N(7)	81.6 (8)
O(3)-Fe(2)-N(4)	96.0 (9)	O(7)-Fe(4)-N(8)	94.5 (9)
O(4)-Fe(2)-N(3)	99.7 (8)	O(8)-Fe(4)-N(7)	98.4 (8)
O(4)-Fe(2)-N(4)	171.5 (9)	O(8)-Fe(4)-N(8)	170.4 (9)
N(3)-Fe(2)-N(4)	75.4 (9)	N(7)-Fe(4)-N(8)	75.4 (9)
Fe(1)-O(1)-C(1)	130 (2)	Fe(3)-O(5)-C(25)	135 (2)
Fe(2)-O(2)-C(22)	127 (2)	Fe(4)-O(6)-C(46)	126 (2)
Fe(1)-O(3)-C(23)	127 (2)	Fe(3)-O(7)-C(47)	126 (2)
Fe(2)-O(3)-C(23)	127 (2)	Fe(4)-O(7)-C(47)	126 (2)
Fe(1)-O(3)-Fe(2)	103 (1)	Fe(3)-O(7)-Fe(4)	102 (1)
Fe(1)-O(4)-C(24)	129 (2)	Fe(3)-O(8)-C(48)	128 (2)
Fe(2)-O(4)-C(24)	123 (2)	Fe(4)-O(8)-C(48)	126 (2)
Fe(1)-O(4)-Fe(2)	102 (1)	Fe(3)-O(8)-Fe(4)	103 (1)
C(6)-C(7)-N(1)	129 (3)	C(30)-C(31)-N(5)	126 (3)
C(7)-N(1)-Fe(1)	123 (3)	C(31)-N(5)-Fe(3)	125 (2)
C(7)-N(1)-C(8)	119 (3)	C(31)-N(5)-C(32)	122 (3)
Fe(1)-N(1)-C(8)	118 (2)	Fe(3)-N(5)-C(32)	113 (2)
N(1)-C(8)-C(9)	104 (3)	N(5)-C(32)-C(33)	111 (3)
C(8)-C(9)-N(2)	113 (3)	C(32)-C(33)-N(6)	110 (3)
C(9)-N(2)-Fe(1)	96 (2)	C(33)-N(6)-Fe(3)	101 (2)
C(9)-N(2)-C(10)	113 (2)	C(33)-N(6)-C(34)	107 (2)
C(9)-N(2)-C(13)	109 (2)	C(33)-N(6)-C(37)	109 (2)
C(10)-N(2)-C(13)	110 (2)	C(34)-N(6)-C(37)	109 (2)
C(10)-N(2)-Fe(1)	113 (2)	C(34)-N(6)-Fe(3)	118 (2)
C(13)-N(2)-Fe(1)	115 (2)	C(37)-N(6)-Fe(3)	113 (2)
N(2)-C(10)-C(11)	113 (3)	N(6)-C(34)-C(35)	115 (3)
C(10)-C(11)-N(3)	110 (2)	C(34)-C(35)-N(7)	111 (3)
C(11)-N(3)-C(12)	111 (2)	C(35)-N(7)-C(36)	110 (2)
C(11)-N(3)-Fe(2)	115 (2)	C(35)-N(7)-Fe(4)	108 (2)
C(11)-N(3)-C(14)	115 (2)	C(35)-N(7)-C(38)	109 (2)
C(12)-N(3)-Fe(2)	109 (2)	C(36)-N(7)-Fe(4)	113 (2)
C(12)-N(3)-C(14)	107 (2)	C(36)-N(7)-C(38)	117 (2)
C(14)-N(3)-Fe(2)	109 (2)	C(38)-N(7)-Fe(2)	101 (2)
N(3)-C(12)-C(13)	109 (3)	N(7)-C(36)-C(37)	112 (3)
C(12)-C(13)-N(2)	112 (3)	C(36)-C(37)-N(6)	110 (3)
N(3)-C(14)-C(15)	108 (2)	N(7)-C(38)-C(39)	105 (2)
C(14)-C(15)-N(4)	106 (2)	C(38)-C(39)-N(8)	107 (2)
C(15)-N(4)-Fe(2)	118 (2)	C(39)-N(8)-Fe(4)	118 (2)
C(15)-N(4)-C(16)	116 (2)	C(39)-N(8)-C(40)	113 (3)
Fe(2)-N(4)-C(16)	123 (2)	Fe(4)-N(8)-C(40)	125 (2)
N(4)-C(16)-C(17)	124 (3)	N(8)-C(40)-C(41)	120 (3)

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Table V. Electronic Spectra of the Iron(III) Complexes and the Parent LH_2 Ligand[a]

compd	medium					
LH_2	CH_3OH			25.00 (3.51)	31.75 (3.73)	>33
	Nujol			23.2^b	31.10	>33
$Fe_2L(OCH_3)_2Cl_2$	CH_2Cl_2		19.61 (3.57)	22.5 $(\sim 3.4)^b$	30.77 (4.23)	>33
	Nujol	$\sim 17.0^b$	18.69	22.5^b	29.41	>33
Fe_2LCl_4	Nujol	$\sim 16.7^b$	17.86	22.5^b	29.41	>33

[a] Energies in 10^3 cm^{-1} (log ϵ in parentheses). [b] Shoulder.

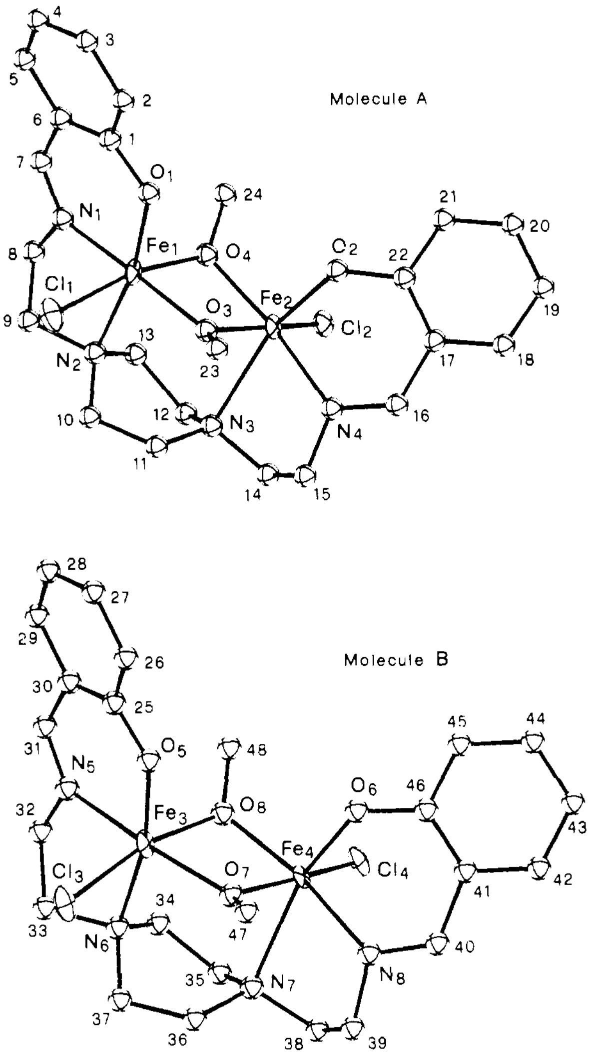

Figure 1. View of the two independent $Fe_2L(OCH_3)_2Cl_2$ molecules forming the asymmetric unit. Hydrogen atoms have been omitted for clarity.

(3) Å, as compared with Fe(1)···Fe(2) (3.097 (7) Å) and O(1)···O(2) (4.15 (3) Å)), result in severe distortions in the angles in the coordination sphere from ideal octahedral geometry; e.g., the O(1)Fe(1)N(2) and N(2)Fe(1)N(1) angles are 165.6 (9) and 76.3 (10)°, respectively.

The LH_2 ligand barely changes its conformation on complex formation. The change involves mainly the conformation of the piperazine ring, which is "chair" shaped in free LH_2[38] and "boat" shaped in the complex. Differences in distances and angles are largely masked by the inaccuracy of the present structural determination; however, the C–N(azomethinic) (1.25 (3)–1.33 (3) Å) and O–C(phenolic) (1.27 (2)–1.35 (2) Å) bond lengths in the complex seem to be longer and shorter, respectively, than the corresponding values for LH_2: 1.265 (4) Å and 1.350 (4) Å, respectively.

Infrared Spectra. The most significant effect of coordination on the vibrational spectrum of LH_2 is observed between ~1500 and ~1650 cm^{-1}. In this spectral region the free ligand exhibits two strong bands, at 1642 and 1505 cm^{-1}, that, in agreement with previously reported assignments for other salicylaldimines,[39–41] are attributed to the azomethinic ν(C–N) and phenolic ν(C–O) stretching modes, respectively. On complex formation, the energy of ν(C–N) decreases, and that of ν(C–O) increases: to 1623 and 1540 cm^{-1}, respectively, for $Fe_2L(OCH_3)_2Cl_2$, and 1619 and 1540 cm^{-1} for Fe_2LCl_4.

These findings are in agreement with the seemingly longer C–N(azomethinic) and shorter C–O(phenolic) bond lengths in $Fe_2L(OCH_3)_2Cl_2$ than in LH_2.

It has been suggested that bands at ~1550 cm^{-1} in the spectra of dimeric complexes with salicylaldimines can be taken as evidence for the presence of bridging phenolic oxygen.[40,42–44] The presence of similar bands in the spectra of $Fe_2L(OCH_3)_2Cl_2$, whose X-ray structure shows only terminal phenolic oxygens, Fe_2LCl_4, in which the metal atoms are unlikely to be bridged in light of the normal magnetic moment (vide infra), and also species[26a] containing the $(Fe(Sal)_2trien)^+$ unit, known to be mononuclear from the recent X-ray structural determination[45] of $(Fe(Sal)_2trien)Cl{\cdot}2H_2O$, introduces a word of caution in the diagnostic use of the ν(C–O) frequencies.

Magnetic Susceptibility Measurements. The effective magnetic moment of Fe_2LCl_4 is essentially constant, 5.8 ± 0.2 μ_B/iron ion, in the temperature range 93–293 K, and closely corresponds to the spin-only value of 5.9 μ_B expected for a magnetically noninteracting high-spin system. Antiferromagnetic exchange interactions are evident in the data for $Fe_2L(OCH_3)_2Cl_2$. With decreasing temperature, the μ_{eff} decreases from a value of 4.73 μ_B/iron ion at room temperature to a value of 1.35 μ_B at 7.2 K. The usual dipolar coupling approach of Van Vleck with a perturbing Hamiltonian $-2J(\hat{S}_1{\cdot}\hat{S}_2)$ and $S_1 = S_2 = {}^5/_2$ was used to fit the experimental data. An isotropic g value of 2.00 was assumed, and temperature-independent paramagnetism was neglected. A least-squares fitting was carried out including a term representing the paramagnetic susceptibility of a possible magnetically dilute ferric impurity.[1b,24] An adequate fit to the data was obtained with $J = -16.3$ cm^{-1} and 6.5% by weight of a noncoupled iron(III) impurity. This fit is illustrated in Figure 2. No attempt was made to improve the agreement between observed and calculated moments by using an additional parameter j' corresponding to a higher order exchange term in the Hamiltonian $[j'(\hat{S}_1{\cdot}\hat{S}_2)^2]$.[1b,46] In the present context the physical significance of such a treatment is not clear.

ESR Spectra. The room-temperature X-band ESR spectra of powdered samples of $Fe_2L(OCH_3)_2Cl_2$ show a very broad

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signal (peak to peak separation ~2000 G) centered at about $g \approx 2$. Superimposed on this signal there is a distinct, although weak, signal at $g = 2.13$. Decreasing the temperature of the sample to 100 K leads to a loss of the broad signal to give a sharper and more intense $g = 2.13$ signal, with a shouldering feature at $g = 2.3$. For the present system, ESR signals would be expected to arise from electronic states with a total spin S' of 5, 4, 3, 2, and 1. The energies of these states decrease with S'. It would appear, on this basis, that the $g = 2.13$ signal arises from one of the lower states that becomes perferentially thermally populated at 100 K. The ESR spectral features of $Fe_2L(OCH_3)_2Cl_2$ appear to be somewhat different from those of other exchange-interacting salicylaldimine complexes of iron(III) having less negative J.[24]

X-Band spectra at 100 K were also obtained for 60:40 toluene–dichloromethane glasses of $Fe_2L(OCH_3)_2Cl_2$. These are very similar to the powder spectra at the same temperature, notwithstanding the molecular association occurring in solution. In both the powder and frozen-solution spectra a weak signal at $g \approx 4.2$ is indicative of magnetically noninteracting iron(III) impurity,[24] in agreement with the analysis of the susceptibility data. No well-defined signal could be observed, for X-band frequencies at 300 or 100 K, for solid Fe_2LCl_4. Solution spectra for this compound could not be measured due to the low solubility.

Electronic Spectra. Electronic spectral data for the LH_2 ligand and its iron(III) derivatives are summarized in Table V. In agreement with the ESR results, there are no significant differences between the solid-state and solution spectra of $Fe_2L(OCH_3)_2Cl_2$. The absorptions of the two complexes are quite similar and are of rather high intensities. Since, for both species, all d–d transitions are expected to be spin forbidden, and hence weak, on the basis of the magnetic properties that are compatible only with an orbital singlet ground state, the observed absorptions are most likely to arise from charge-transfer and/or intraligand transitions. This assignment is also in accord with the spectral similarity of the two species, in spite of the presumably different ligand fields for the metal ions. The relatively weak spin–spin interaction in the methoxy compound is not expected to have any influence on the electronic transitions.[5,17,18,47]

Bands with similar energies and intensities to those of our compounds, between ~18 000 and ~28 000 cm^{-1}, have been reported for other iron(III) salicylaldimine complexes and have been assigned to d–d transitions intensified by borrowing intensity from the low-lying charge-transfer bands in the imine ligands.[18] The present data suggest a different assignment; e.g., the transition at ~22 500 cm^{-1} in $Fe_2L(OCH_3)_2Cl_2$, corresponding to the first transition (at 25 000 cm^{-1}) in LH_2, is discernible only as a shoulder on the more intense band at 19 610 cm^{-1} that is completely lacking for free LH_2. The tail into the low-energy region from the absorption envelopes of the ~19 000-cm^{-1} bands in the L^{2-} derivatives prevented any d–d band from being identified with certainty. However, in agreement with previous spectral results[17,18] for dialkoxo-bridged iron(III) dimers, there is no evidence for either substantial intensity enhancement of the spin-forbidden d–d bands or simultaneous pair excitations such as found in certain oxo-bridged iron(III) dimers.[47]

Discussion

As mentioned in the Introduction, magnetostructural results have shown that the MOM bridging angle, ϕ,[6,7] and the electron density at bridging oxygens[8,9] are crucial determinants of the magnetic properties of dihydroxo- and dialkoxo-bridged complexes of copper(II) or chromium(III), the antiferro-

Table VI. Structural and Magnetic Properties of Iron(III) Complexes Containing Four-Membered Iron–Oxygen Rings

compd	bridging groups	Fe coordination	Fe–Fe, Å	O–O, Å	Fe–O,[h] Å	FeOFe, deg	δ,[i] Å	C,[j] Å	J, cm^{-1} (ΔT)[k]	ref
$Fe_2L(OCH_3)_2Cl_2$	CH_3O^-	FeO_3N_2Cl[f]	3.106 (7)[h]	2.46[h]	1.99 (2)	103 (1)[h]	0.09	0.70	−16.3 (7.2–300 K)	this work
$[Dipic(H_2O)Fe(OH)]_2$[a]	OH^-	FeO_5N[f]	3.089 (2)	2.431	1.966 (5)	103.6 (2)	0.00	. . .	−11.4 (85–300 K)	15
$[Chel(H_2O)Fe(OH)]_2$[b]	OH^-	FeO_5N[f]	3.078 (2)	2.440	1.964 (5)	103.2 (2)	0.00	. . .	−7.3 (85–300 K)	15
$[A(H_2O)Fe(OH)]_2$[c]	OH^-	FeO_5N[f]	3.118 (3)	2.380	1.962 (9)	105.3 (4)	0.00	. . .	−11.7 (78–301 K)	16
$[Fe(SALPA)Cl]_2$[d]	$C_3H_7O^-$	FeO_3NCl[g]	3.12	2.23	1.92	109.0	0.00	0.08	−17 (20–300 K)	20
$[Fe(SALPA)Cl]_2 \cdot C_6H_5CH_3$[d]	$C_3H_7O^-$	FeO_3NCl[g]	3.089 (6)	2.40	1.96 (1)	104.1 (6)	0.00	0.28	−17 (77–300 K)	19
$Fe_2(SALPA)_2(SALPA\text{-}H)_2$[e]	$C_3H_7O^-$	FeO_4N_2[f]	3.217 (7)	2.278	1.97 (2)	109.4 (9)[h]	0.05	0.58	−17[l] (77–300 K)	18
$(FeSalenCl)_2$[e]	$C_6H_5O^-$	FeO_3N_2Cl[f]	3.291	2.54	2.078 (7)	105	0.00		−7.5 (20–300 K)	22–23

[a] Dipic = 2,6-pyridinedicarboxylate. [b] Chel = 4-hydroxo-2,6-pyridinedicarboxylate. [c] A = 4-(dimethylamino)-2,6-pyridinedicarboxylate. [d] SALPA = dianion of Schiff's base from salicylaldehyde and 3-aminopropanol. [e] Salen = *N,N'*-bis(salicylidene)ethylenediamine. [f] Distorted octahedral geometry. [g] Intermediate to a square-pyramidal and a trigonal-bipyramidal arrangement. [h] Mean value. [i] δ = maximum deviation from the plane of the four-membered iron–oxygen ring. [j] C = distance of the carbon atom attached to the bridging oxygen from the plane of the iron–oxygen ring. [k] ΔT = temperature range of the magnetic susceptibility measurements. [l] J value calculated in ref 15.

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(47) Schugar, H. J.; Rossman, G. R.; Thibeault, J.; Gray, H. B. *Chem. Phys. Lett.* **1970**, *6*, 26.

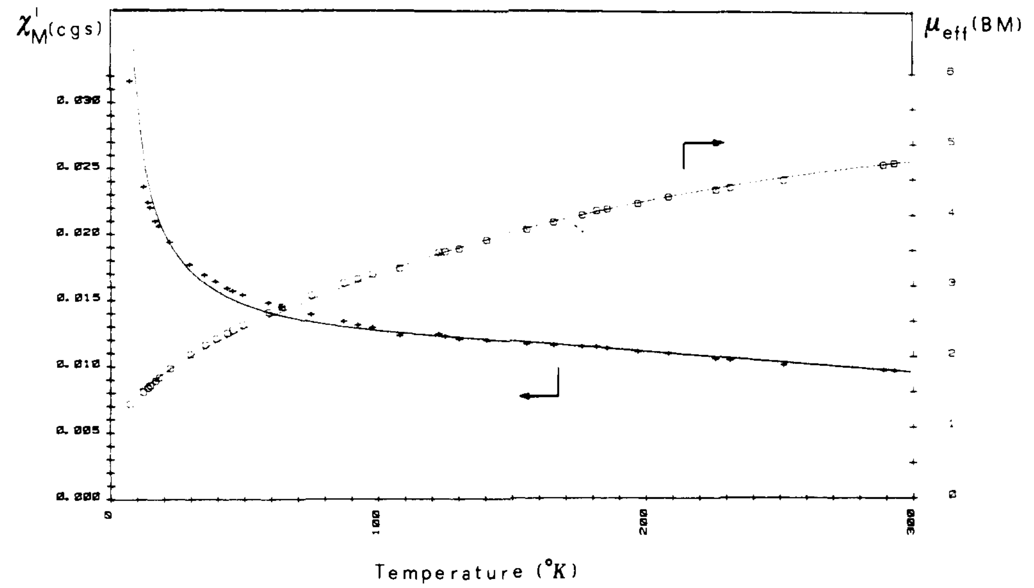

Figure 2. Molar paramagnetic susceptibility, in cgsu, and effective magnetic moment per ion, in μ_B, vs. temperature curves for $Fe_2L(OCH_3)_2Cl_2$. The solid lines result from least-squares fitting of the data to the $S_1 = S_2 = {}^5/_2$ dimer equation including a paramagnetic impurity ($g = 2.0$, no TIP included).

magnetic interaction being stronger for larger ϕ and/or increasing electron density. These (and other) effects have been accounted for in terms of changes in one-electron orbital splittings and overlaps with structure and substituents. Theoretical treatments of this type,[10-14] which can be generalized to any case of exchange interaction between transition ions, would suggest that some correlation between J and ϕ or the electron density at the bridging atoms should also exist for iron(III) compounds containing four-membered Fe_2O_2 rings. Few such systems have been investigated by X-ray methods. The magnetic and structural properties of $Fe_2L(OCH_3)_2Cl_2$ are compared to those of the related completely characterized compounds in Table VI.[48]

The mean Fe–O(bridging) distances are substantially equivalent in the hydroxo- and alkoxo-bridged systems and are only slightly shorter than the corresponding value for $(FeSalenCl)_2$, where a phenolic oxygen serves as the bridging group. In comparison to $Fe_2L(OCH_3)_2Cl_2$, two hydroxy compounds show approximately the same ϕ value of ~103° but weaker antiferromagnetic exchange; $(FeSalenCl)_2$ and $[A(H_2O)Fe(OH)]_2$ yield less negative J values with a larger bridging angle of ~105°, and the compounds containing the $Fe_2(propoxide)_2^{4+}$ units yield an almost unaltered J although ϕ increases up to ~109° in $Fe_2(SALPA)_2(SALPA\text{-}H)_2$.

The data are strongly indicative that variations in one-electron orbital overlaps and splittings with the bridging angle do not play a dominant role in determining the degree of antiferromagnetic exchange in these compounds.

The more negative J values obtained for the alkoxo- than for the hydroxo- or phenoxo-bridged systems in Table VI would seem to indicate that the electron density at the bridging oxygen atom has a greater effect than the bridging angle on the magnetic exchange. However, the substantially smaller extent of antiferromagnetic interaction, relative to that in $Fe_2L(OCH_3)_2Cl_2$, observed[17] for methoxy-bridged $[(DPM)_2Fe(OCH_3)]_2$ and $[(N\text{-}picO)_2Fe(OCH_3)]_2$, $J = -8.5$ cm^{-1}, and also $[(DPM)_2Fe(OC_2H_5)]_2$, $[(acac)_2Fe(OC_2H_5)]_2$, and $[(DPM)_2Fe(O\text{-}n\text{-}C_3H_7)]_2$, $J = -11$ cm^{-1}, does not lend credence to such a view. Apparently, in contrast with previous assumptions,[17,23] differences in the nature of the nonbridging ligands might have some influence on the magnetic properties of these systems.

A final comment concerns the interesting possibility, first suggested by Bertrand et al.,[20] that the extent of spin–spin exchange in oxygen-bridged iron(III) compounds may be related directly to the availability of π orbitals on the bridging oxygen. The present data argue against a π pathway for spin exchange between the iron atoms. The coordination of the bridging oxygen atoms in $Fe_2L(OCH_3)_2Cl_2$ is farther from a planar arrangement than those in the structures of the SALPA derivatives, as shown (Table VI) by the deviations of the carbon atoms linked to the bridging oxygens from the plane of the four-membered iron–oxygen rings. The seemingly more favorable oxygen coordination in the SALPA derivatives (having also larger bridging angles and more electron density at the bridge) than in the title compound does not appear to have any significant consequence on the extent of exchange interaction.

Acknowledgment. The authors express their appreciation to Dr. D. Fiorani for his very valuable assistance in the securing of magnetic measurements at liquid-helium temperatures.

Registry No. $Fe_2L(OCH_3)_2Cl_2$, 80409-99-0; Fe_2LCl_4, 80410-00-0; LH_2, 78186-31-9; 1-amino-2-bromoethane hydrobromide, 2576-47-8; salicylaldehyde, 90-02-8; piperazine, 110-85-0; trien, 112-24-3.

Supplementary Material Available: Listings of hydrogen atom coordinates and the observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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(48) As can be seen from Figure 1, a piperazine unit, besides the methoxy groups, bridges the iron atoms of $Fe_2L(OCH_3)_2Cl_2$. However, the piperazine bridge is not expected to influence the magnetic properties of this complex to any appreciable extent. In fact, the Fe–N directions, when viewed along an N–C bond, form an angle of ~93° with the C–C bonds. With this conformation, there should be not through-bond coupling of the piperazine N lone pairs[49] and, therefore, no pathway for magnetic exchange between the metal centers.[10]

(49) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.