advantage over the outer-sphere pathway.

Conclusions

This study has demonstrated the following: (1) For all reactions for which the critical parameters are known, outer-sphere reductions of $Co(OH_2)_6^{3+}$ exhibit a classical Marcus dependence on the reaction free energy change.

(2) The $Co(OH_2)_6^{3+,2+}$ self-exchange parameter required to correlate these outer-sphere cross reactions is ~12 orders of magnitude smaller than the experimental value found for the $Co(OH_2)_6^{3+,2+}$ self-exchange.

(3) The calculated Franck–Condon factors imply a self-exchange rate ~7 orders of magnitude smaller than the experimental value found for $Co(OH_2)_6^{3+,2+}$.

(4) The outer-sphere cross reactions of $Co(OH_2)_6^{3+}$ and the $Co(OH_2)_6^{3+,2+}$ self-exchange reactions differ in mechanism, with the latter most likely proceeding through a "water-bridged" pathway.

(5) Franck–Condon factors alone do not account for the outer-sphere behavior of the $Co(OH_2)_6^{3+,2+}$ couple; a significant contribution of electronic terms is likely.

Registry No. $Co(OH_2)_6^{3+}$, 15275-05-5; $Co(Me_2[14]4,7\text{-diene}N_4\text{-6-one})(OH_2)_2^{2+}$, 61025-63-6; $Co(Me_2pyo[14]trieneN_4)(OH_2)_2^{2+}$, 73704-78-6; $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$, 38337-82-5; $Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+}$, 38331-68-9; $Co([14]aneN_4)(OH_2)_2^{2+}$, 65554-13-4; $Co([15]aneN_4)(OH_2)_2^{2+}$, 74093-13-3; $Co(sep)^{2+}$, 63218-22-4; $Ru(NH_3)_4(phen)^{2+}$, 69799-59-3; $Ni(Me_6[14]\text{-}4,11\text{-diene}N_4)^{2+}$, 18444-38-7; $Ni([14]aneN_4)^{2+}$, 46365-93-9.

Supplementary Material Available: Table of the pH-dependent rate constants for several reductions of $Co(OH_2)_6^{3+}$ (3 pages). Ordering information is given on any current masthead page.

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Exchange Interaction in Multinuclear Transition-Metal Complexes. 2.[1] Synthesis and Structural and Magnetic Studies of a Dinuclear Iron(III) Derivative of the Heptadentate Schiff Base Trisalicylidenetriethylenetetramine

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In an attempt to experimentally determine magnetostructural relationships for magnetically condensed iron(III) dinuclear systems, we have synthesized the compound $Fe_2L(OCH_3)Cl_2$ (L^{3-} is the heptadentate trianion of the Schiff base trisalicylidenetriethylenetetramine) and investigated its X-ray structure as well as its temperature dependence on magnetic susceptibility. $Fe_2L(OCH_3)Cl_2$ crystallizes in the tetragonal space group $P4_2/n$. The structure consists of dinuclear units. The two iron atoms are asymmetrically bridged by a phenolic oxygen and a methoxy group. The metal coordination geometry is distorted octahedral, the six coordination sites being occupied by two cis oxygens and two cis nitrogens of L^{3-}, a terminal chlorine atom, and a bridging methoxy group. The magnetic susceptibility of powdered samples of the compound has been examined in the temperature range 5–290 K. The best fit to the Van Vleck equation yielded $J = -8.0\ cm^{-1}$.

Introduction

The correlation between the structural and magnetic properties of dinuclear copper(II) and chromium(III) compounds involving four-membered M–O–M–O rings is becoming increasingly well documented. It has been found for these systems that the magnitude and sign of the exchange coupling, as reflected by the interaction constant, J, are principally determined by the geometry of the bridging unit,[2,3] the electron density at the oxygen bridge,[4,5] and in the case of copper(II), distortions from planar ligand environments at the metal center.[6] Molecular orbital[7] and angular overlap[8] approaches have been used to discuss magnetostructural relationships in copper(II) dimers.

How the exchange interaction in iron(III) systems of the aforementioned type is affected by structural changes remains to be established.[1,9] In the previous paper[1] we have suppemented the few iron(III) systems[9,10] for which both structural and magnetic properties have been examined with the first example of a completely characterized dimethoxo-bridged complex, this being di-μ-methoxy-dichloro[1,4-piperazinebis(N-ethylenesalicylaldiminato)]diiron(III), $Fe_2L'(OCH_3)_2Cl_2$. Here we report the synthesis and X-ray structural and magnetic characterization of a derivative of the closely related ligand trisalicylidenetriethylenetetramine (called LH_3 hereafter), $Fe_2L(OCH_3)Cl_2$, containing a Fe–OMe–Fe–OPh bridging unit.

Experimental Section

Measurements. There were performed as described previously.[1]

Syntheses. LH_3. This ligand has been prepared according to known procedures.[11]

$Fe_2L(OCH_3)Cl_2$. A 15-mL quantity of a 0.1 M solution of CH_3ONa in methanol was added to a solution of $FeCl_3{\cdot}6H_2O$ in the same solvent (0.54 g, 2 mmol, in 15 mL). To the resulting solution, heated at 70 °C, was added with stirring LH_3 dissolved in methanol (0.46 g, 1 mmol). The reaction mixture was kept at 70 °C for 15 min and then allowed to cool to ~15 °C. Crystallization was allowed to continue for ~24 h before brown prismatic crystals were collected by filtration,

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Table I. Fractional Atomic Coordinates and Thermal Parameters for Nonhydrogen Atoms of $Fe_2L(OCH_3)Cl_2$[a]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.4746 (2)	0.1651 (1)	0.3527 (3)	0.047 (2)	0.028 (2)	0.042 (2)	0.003 (2)	0.001 (2)	−0.003 (2)
Fe(2)	0.5932 (1)	0.1651 (1)	0.4990 (3)	0.035 (2)	0.032 (2)	0.044 (2)	−0.003 (2)	0.003 (2)	−0.004 (2)
Cl(1)	0.4614 (3)	0.1442 (3)	0.1732 (5)	0.092 (6)	0.063 (5)	0.040 (5)	0.004 (4)	−0.008 (4)	−0.002 (4)
Cl(2)	0.6979 (3)	0.1475 (3)	0.4621 (6)	0.036 (4)	0.050 (4)	0.103 (7)	0.001 (3)	0.009 (4)	−0.009 (4)

atom	x/a	y/b	z/c	U, Å^2	atom	x/a	y/b	z/c	U, Å^2
O(1)	0.4262 (6)	0.0980 (6)	0.4065 (11)	0.034 (4)	C(11)	0.6211 (11)	0.2573 (12)	0.3125 (19)	0.061 (8)
O(2)	0.5849 (6)	0.0965 (6)	0.5949 (10)	0.032 (4)	C(12)	0.5410 (10)	0.2963 (11)	0.4082 (7)	0.042 (7)
O(3)	0.4999 (6)	0.1864 (6)	0.5058 (13)	0.038 (4)	C(13)	0.6450 (9)	0.2949 (10)	0.4963 (17)	0.045 (6)
O(4)	0.5605 (6)	0.1307 (7)	0.3662 (11)	0.040 (4)	C(14)	0.6301 (12)	0.2858 (11)	0.6108 (18)	0.056 (8)
N(1)	0.3942 (8)	0.2225 (8)	0.3665 (15)	0.041 (5)	C(15)	0.5912 (9)	0.2087 (10)	0.7274 (19)	0.038 (7)
N(2)	0.5131 (9)	0.2620 (8)	0.3152 (16)	0.047 (6)	C(16)	0.5662 (6)	0.1495 (5)	0.7625 (12)	0.030 (6)
N(3)	0.6010 (8)	0.2611 (8)	0.4261 (15)	0.043 (6)	C(17)	0.5466 (6)	0.1447 (5)	0.8685 (12)	0.047 (7)
N(4)	0.6104 (8)	0.2225 (8)	0.6323 (15)	0.038 (5)	C(18)	0.5256 (6)	0.0878 (5)	0.9080 (12)	0.057 (8)
C(1)	0.3719 (6)	0.0954 (5)	0.4524 (11)	0.020 (6)	C(19)	0.5242 (6)	0.0358 (5)	0.8415 (12)	0.052 (7)
C(2)	0.3545 (6)	0.0382 (5)	0.4958 (11)	0.042 (6)	C(20)	0.5438 (6)	0.0406 (5)	0.7354 (12)	0.032 (6)
C(3)	0.2962 (6)	0.0313 (5)	0.5430 (11)	0.060 (8)	C(21)	0.5649 (6)	0.0975 (5)	0.6959 (12)	0.033 (6)
C(4)	0.2552 (6)	0.0815 (5)	0.5469 (11)	0.070 (8)	C(22)	0.5009 (6)	0.2960 (7)	0.5071 (10)	0.041 (6)
C(5)	0.2726 (6)	0.1386 (5)	0.5035 (11)	0.049 (7)	C(23)	0.4808 (6)	0.3525 (7)	0.5494 (10)	0.054 (7)
C(6)	0.3310 (6)	0.1456 (5)	0.4563 (11)	0.033 (6)	C(24)	0.4399 (6)	0.3533 (7)	0.6360 (10)	0.050 (7)
C(7)	0.3460 (10)	0.2033 (11)	0.4140 (17)	0.042 (7)	C(25)	0.4191 (6)	0.2975 (7)	0.6802 (10)	0.049 (8)
C(8)	0.4022 (10)	0.2872 (10)	0.3292 (19)	0.049 (8)	C(26)	0.4392 (6)	0.2410 (7)	0.6378 (10)	0.036 (6)
C(9)	0.4598 (10)	0.2947 (10)	0.2682 (18)	0.041 (7)	C(27)	0.4801 (6)	0.2403 (7)	0.5513 (10)	0.036 (6)
C(10)	0.5651 (10)	0.2593 (11)	0.2391 (19)	0.048 (7)	C(28)	0.5805 (11)	0.0766 (11)	0.3059 (21)	0.053 (7)

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

washed with absolute ethanol, and dried by the usual methods: yield 0.5 g (70%); mp >340 °C. Anal. Calcd for $C_{28}H_{30}N_4Cl_2O_4Fe_2$: C, 50.27; H, 4.48; N, 8.37; Cl, 10.61; O, 9.57; Fe, 16.70. Found: C, 50.07; H, 4.95; N, 8.34; Cl, 10.35; O, 9.65; Fe, 16.63. The compound can also be obtained, with the procedure described above, by using 10 mL of a 0.25 M solution of triethylamine in methanol instead of 15 mL of a 0.1 M solution of CH_3ONa in methanol.

Properties. $Fe_2L(OCH_3)Cl_2$ is air stable and slightly soluble in common organic solvents, where it exhibits a strictly nonelectrolytic behavior. Molecular weight measurements in dichloromethane (0.5%) yielded a value of 763 (calculated 669). Infrared and electronic spectral features of the compound closely resemble those of $Fe_2L'(OCH_3)_2Cl_2$[1] and are similarly interpreted. The L^{3-} derivative exhibits the azomethinic ν(C–N) stretching mode at 1620 cm^{-1} and the phenolic ν(C–O) stretching mode at 1538 cm^{-1}. Corresponding values for free LH_3 are 1640 and 1502 cm^{-1}, respectively, and for $Fe_2L'(OCH_3)_2Cl_2$ are 1623 and 1540 cm^{-1}, respectively. No splitting of the ν(C–O) band was observed, although the structure of the present complex involves terminal as well as bridging phenolic oxygens (vide infra). This and the similar frequency found for $Fe_2L'(OCH_3)_2Cl_2$, having only terminal phenolic oxygens, further support the view[1] that ν(C–O) frequencies cannot be taken as evidence for the presence of bridging phenolic oxygens in multinuclear complexes with Schiff bases.

The electronic spectrum of LH_3 in methanol shows bands at 25 000 (log ϵ = 3.46), 31 600 (3.80), and ~36 400 cm^{-1} (shoulder). Absorption maxima for the iron(III) derivative in dichloromethane occur at 18 870 (log ϵ = 3.73), ~23 000 (shoulder), 30 770 (4.40), and 33 900 cm^{-1} (4.34). The visible Nujol mull spectrum shows the following bands: 16 700, 17 900, and 23 300 cm^{-1}. All the bands of the complex are attributable[1] to charge-transfer and/or intraligand transitions.

Very little information was obtained from X-band ESR spectra. Powdered samples of the complex at both room temperature and 100 K, as well as 60:40 toluene–dichloromethane glasses at 100 K, show only a very broad, unresolved signal, at roughly $g \approx 2$. Unlike the case of $Fe_2L'(OCH_3)_2Cl_2$, the effect of a decrease in temperature on the intensity of the signal is very small. In agreement with the magnetic susceptibility results (vide infra), signals, even weak, at $g \approx 4.2$, indicative of the presence of magnetically noninteracting ferric impurities,[1,12b] were not observed.

X-ray Data and Structural Solution. A well-formed prismatic crystal of $Fe_2L(OCH_3)Cl_2$ with dimensions 0.20 × 0.20 × 0.35 mm was mounted on a Philips PW1100 four-circle diffractometer equipped with Mo radiation and a graphite monochromator. The crystal was found to be tetragonal with Laue symmetry $4/m$. From systematic extinctions ($hK0$, $h + k = 2n$; $00l$, $l = 2n$) the space group $P4_2/n$ was uniquely assigned. Cell dimensions, as determined by least-squares fitting of the angular ϑ, χ, and φ values of 25 reflections, are as follows: a = 21.520 (4) Å, c = 12.494 (3) Å. For a cell content of eight formula units (mol wt = 668.5, corresponding to $C_{28}H_{30}O_4N_4Fe_2Cl_2$), the calculated density is 1.534 g cm^{-3}, in agreement with the measured value of 1.49 g cm^{-3}, obtained by the flotation method in a water solution of potassium iodomercurate. The intensity data were measured with the ϑ–2ϑ scan technique up to ϑ = 20°. The scan speed was 0.04° s^{-1} and the scan width 1.2°. As a general check on experimental conditions, the intensities of three reflections were monitored every 180 min. No significant variations during the period of data collection were detected. Intensities were corrected for Lorentz and polarization factors but not for absorption (μ = 11.9 cm^{-1} for Mo Kα). A total of 2336 independent reflections were measured, 1469 of which had $I \leq 3\sigma(I)$[13] and were considered to "unobserved".

The structure was solved by the direct multisolution method with MULTAN.[14] The E map for the best solution showed the positions of the Fe atoms and part of the coordination sphere around them. The structure was completed by successive Fourier syntheses. The refinement was carried out with the full-matrix least-squres method employing the SHELX system of programs.[15] The three phenyl rings of the L^{3-} ligand were constrained to perfect hexagons, with a C–C distance of 1.395 Å and CCC angles of 120°, and refined with their H atoms as rigid groups. The other H atoms, except for those of the methyl group, 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 = 0.08 Å^2. 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 shift/esd ratios were less than 0.1. The R value[16] converged to 0.055 for 867 observed reflections and 146 parameters. R_w was 0.058. The atomic scattering factors

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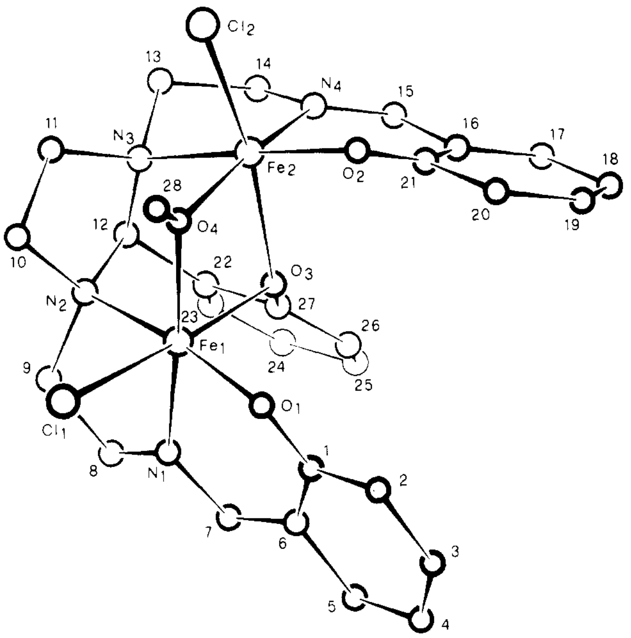

Figure 1. View and labeling scheme of the $Fe_2L(OCH_3)Cl_2$ molecule. Hydrogen atoms have been omitted for clarity.

Table II. Bond Lengths (Å) in $Fe_2L(OCH_3)Cl_2$

Fe(1)–Cl(1)	2.304 (7)	Fe(2)–O(3)	2.06 (1)
Fe(2)–Cl(2)	2.330 (7)	Fe(2)–O(4)	1.95 (1)
Fe(1)–O(1)	1.90 (1)	Fe(1)–N(1)	2.13 (2)
Fe(1)–O(3)	2.04 (2)	Fe(1)–N(2)	2.29 (2)
Fe(1)–O(4)	2.00 (1)	Fe(2)–N(3)	2.26 (2)
Fe(2)–O(2)	1.91 (1)	Fe(2)–N(4)	2.11 (2)
O(1)–C(1)	1.31 (2)	N(3)–C(12)	1.52 (2)
O(2)–C(21)	1.33 (2)	N(3)–C(13)	1.48 (2)
C(6)–C(7)	1.39 (2)	C(13)–C(14)	1.48 (3)
C(7)–N(1)	1.26 (2)	C(14)–N(4)	1.45 (3)
N(1)–C(8)	1.48 (2)	N(4)–C(15)	1.29 (2)
C(8)–C(9)	1.47 (3)	C(15)–C(16)	1.45 (2)
C(9)–N(2)	1.47 (2)	O(2)–C(2)	1.33 (2)
N(2)–C(10)	1.47 (2)	C(12)–C(22)	1.51 (2)
N(2)–C(12)	1.50 (2)	C(27)–O(3)	1.36 (2)
C(10)–C(11)	1.51 (3)	O(4)–C(28)	1.45 (3)
C(11)–N(3)	1.49 (3)		
Fe(1)–Fe(2)	3.139 (5)		

of neutral Cl, O, N, C, and H were those of the SHELX system of programs; Fe scattering factors were taken from ref 17. A correction for anomalous dispersion was applied.

Positional and thermal parameters of nonhydrogen atoms are listed in Table I.

Observed and calculated structure factors and hydrogen atom coordinates are available as supplementary material.

Results

Description of the Structure. The structure of $Fe_2L(OCH_3)Cl_2$ consists of dinuclear units that are well separated from one another. A preliminary report of the structures of two solvates of $Fe_2L(OH)Cl_2$, obtained as the major product of the hydrolysis of presumably monomeric species, has appeared.[18] The dinuclear units in these structures are very similar to those in our compound. The $Fe_2L(OCH_3)Cl_2$ molecule and labeling scheme are shown in Figure 1. Bond distances and angles are given in Tables II and III, respectively. The two iron atoms are bridged by phenoxy and methoxy oxygens to form a four-membered ring. The molecule has a nearly perfect C_s symmetry with the mirror plane perpendicular to the iron–oxygen ring. Bridging oxygens O(3) and O(4) and carbon atoms C(12), C(22)–C(27), and C(28) lie approximately on the mirror plane. Deviations of these atoms from the least-squares plane are given in Table IV. The metal coordination geometry is distorted octahedral, the six coordination sites being occupied by two cis oxygens (one bridging and one nonbridging) and two cis nitrogens of heptadentate

Table III. Bond Angles (Deg) in $Fe_2L(OCH_3)Cl_2$

Cl(1)–Fe(1)–O(1)	97.4 (5)	Cl(2)–Fe(2)–O(2)	95.1 (5)
Cl(1)–Fe(1)–O(3)	171.4 (4)	Cl(2)–Fe(2)–O(3)	170.4 (5)
Cl(1)–Fe(1)–O(4)	97.2 (5)	Cl(2)–Fe(2)–O(4)	96.8 (5)
Cl(1)–Fe(1)–N(1)	95.2 (5)	Cl(2)–Fe(2)–N(3)	89.9 (5)
Cl(1)–Fe(1)–N(2)	91.3 (5)	Cl(2)–Fe(2)–N(4)	94.7 (5)
O(1)–Fe(1)–O(3)	89.2 (5)	O(2)–Fe(2)–O(3)	93.1 (5)
O(1)–Fe(1)–O(4)	101.3 (5)	O(2)–Fe(2)–O(4)	101.9 (5)
O(1)–Fe(1)–N(1)	88.1 (6)	O(2)–Fe(2)–N(3)	164.8 (6)
O(1)–Fe(1)–N(2)	163.7 (6)	O(2)–Fe(2)–N(4)	88.5 (6)
O(3)–Fe(1)–O(4)	75.9 (5)	O(3)–Fe(2)–O(4)	76.5 (5)
O(3)–Fe(1)–N(1)	90.6 (6)	O(3)–Fe(2)–N(3)	83.5 (6)
O(3)–Fe(1)–N(2)	83.7 (6)	O(3)–Fe(2)–N(4)	90.5 (6)
O(4)–Fe(1)–N(1)	163.3 (6)	O(4)–Fe(2)–N(3)	91.8 (6)
O(4)–Fe(1)–N(2)	91.2 (6)	O(4)–Fe(2)–N(4)	163.7 (6)
N(1)–Fe(1)–N(2)	77.4 (6)	N(3)–Fe(2)–N(4)	76.7 (6)
Fe(1)–O(1)–C(1)	133 (1)	Fe(2)–O(2)–C(21)	128 (1)
Fe(1)–O(3)–C(27)	120 (1)	Fe(2)–O(3)–C(27)	121 (1)
Fe(1)–O(3)–Fe(2)	100 (1)	Fe(2)–O(4)–Fe(1)	105 (1)
Fe(1)–O(4)–C(28)	122 (1)	Fe(2)–O(4)–C(28)	130 (1)
C(6)–C(7)–N(1)	132 (2)	C(16)–C(15)–N(4)	127 (2)
C(7)–N(1)–Fe(1)	121 (2)	C(15)–N(4)–Fe(2)	123 (2)
C(7)–N(1)–C(8)	124 (2)	C(15)–N(4)–C(14)	119 (2)
Fe(1)–N(1)–C(8)	115 (1)	Fe(2)–N(4)–C(14)	117 (2)
N(1)–C(8)–C(9)	112 (2)	N(4)–C(14)–C(13)	112 (2)
C(8)–C(9)–N(2)	114 (2)	C(14)–C(13)–N(3)	112 (2)
C(9)–N(2)–C(10)	111 (2)	C(13)–N(3)–C(11)	114 (2)
C(9)–N(2)–C(12)	113 (2)	C(13)–N(3)–C(12)	113 (2)
C(9)–N(2)–Fe(1)	104 (1)	C(13)–N(3)–Fe(2)	105 (1)
C(10)–N(2)–C(12)	102 (2)	C(11)–N(3)–C(12)	98 (2)
C(10)–N(2)–Fe(1)	112 (1)	C(11)–N(3)–Fe(2)	111 (1)
C(12)–N(2)–Fe(1)	116 (1)	C(12)–N(3)–Fe(2)	117 (1)
C(11)–C(10)–N(2)	103 (2)	C(10)–C(11)–N(3)	110 (2)
N(2)–C(12)–C(22)	114 (2)	N(3)–C(12)–C(22)	111 (2)
N(2)–C(12)–N(3)	102 (2)		

Table IV. Least-Squares Pseudomirror Plane within the $Fe_2L(OCH_3)Cl_2$ Molecule

$$17.0826x - 0.2712y + 7.5276z = 12.285$$

atom	dev, Å	atom	dev, Å	atom	dev, Å
O(2)	0.04	C(23)	0.01	C(26)	−0.00
O(3)	0.05	C(24)	−0.04	C(27)	0.04
C(12)	−0.02	C(25)	−0.04	C(28)	−0.07
C(22)	0.04				

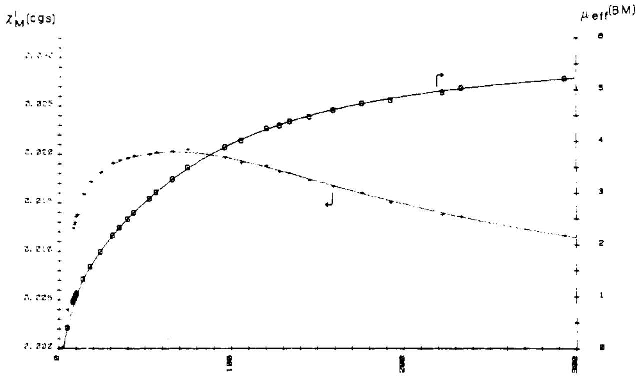

Figure 2. Molar paramagnetic susceptibility in cgsu and effective magnetic moment per iron in μ_B vs. temperature curves for $Fe_2L(OCH_3)Cl_2$. The solid lines result from least-squares fitting of the data to the dimer equation for $S_1 = S_2 = {}^5/_2$, $g = 2.0$, and TIP = 0.

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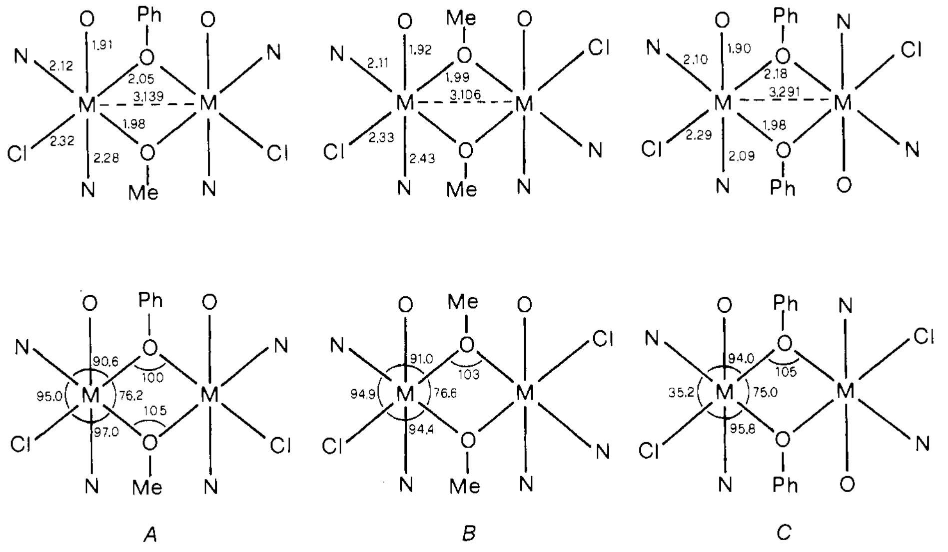

Figure 3. Bond lengths (Å) and angles (deg) in the inner coordination spheres of $Fe_2L(OCH_3)Cl_2$ (A), $Fe_2L'(OCH_3)_2Cl_2$ (B), and $(FeSalenCl)_2$ (C). Symmetry: A, C_s; B, C_2; C, C_i. Maximum deviation from the plane of the four-membered iron–oxygen ring: A, 0.10; B, 0.09; C, 0.00 Å. Dihedral angle between FeO_2 planes of the bridging unit: A, 166; B, 168; C, 180°. Distances of the carbon atoms attached to the bridging oxygens from the plane of the iron–oxygen ring: A, 0.71 (Me), 0.59 (Ph); B, 0.70; C, 0.62 Å.

L^{3-}, a terminal chlorine atom, and a bridging methoxy oxygen. The iron–oxygen ring is not planar. The dihedral angle between the Fe(1)O(3)O(4) and Fe(2)O(3)O(4) planes is 166°. The iron atoms are displaced from the best plane by 0.10 Å, on the same side of the plane, toward the nitrogens of the imidazole ring. Similar values were found for the dimethoxo-bridged $Fe_2L'(OCH_3)_2Cl_2$ (L′ = dianion of 1,4-piperazinebis(*N*-ethylenesalicylaldimine)):[1] 168° and 0.09 Å, respectively. The Fe⋯Fe and O(3)⋯O(4) separations are 3.139 (5) and 2.48 (2) Å, respectively. The bridging angle at the phenoxy oxygen, 100 (1)°, is smaller than that at the methoxy oxygen, 105 (1)°; O(3)FeO(4) angles average 76.2°. Bridging phenolic oxygen–iron bond lengths average 2.05 Å, to be compared with corresponding values of 1.978 (7) and 2.178 (7) Å for $(FeSalenCl)_2$.[19] The mean Fe–OCH_3 distance, 1.98 Å, is similar to that of 1.99 Å found for $Fe_2L'(OCH_3)_2Cl_2$.[1] The methoxy and phenoxy carbon atoms attached to the bridging oxygens are displaced on opposite sides of the bridging plane by 0.71 and 0.59 Å, respectively.

Magnetic Properties. The magnetic susceptibility of $Fe_2L(OCH_3)Cl_2$ was measured in the temperature range 5–290 K. A diamagnetic correction of 159 × 10^{-6} cgsu per iron ion, as calculated from Pascal's constants, was used. The usual spin–spin interaction model[12] based on the exchange Hamiltonian $H = 2J\hat{S}_a{\cdot}\hat{S}_b$ with $S_a = S_b = {}^5/_2$, $g = 2.00$, and TIP = 0 was used to analyze the experimental data. The fitting was carried out by least-squares techniques. The best fit to the data, displayed in Figure 2, yielded $J = -8.0\ \mathrm{cm}^{-1}$. The least-squares fitting did not indicate the presence of magnetically dilute ferric impurities.[12]

Discussion

Reactions between LH_3 and transition-metal ions generally afford $(Sal)_2trien^{2-}$ derivatives through the loss of a salicylaldehyde molecule and consequent opening of the imidazole ring.[11] The very few L^{3-} complexes so far reported have been described as consituents of ill-defined mixtures.[11,18,20] $Fe_2L(OCH_3)Cl_2$ appears to be the first L^{3-} derivative that has been prepared as a pure species and in a reasonably high yield.

In the complex, an imidazole molecule, besides the methoxy and phenoxy groups, bridges the metal centers. The imidazole bridge is not expected[7] to contribute to magnetic exchange in this compound, the Fe–N directions, when viewed along an N–C bond, forming angles of ca. 99° with the C–C(imidazole) bond. No significant through-bond coupling of the imidazole nitrogen lone pairs appears possible with this conformation.[21]

The extent of antiferromagnetism exhibited by $Fe_2L(OCH_3)Cl_2$ is in the range so far observed ($7 \leq |J| \leq 17\ \mathrm{cm}^{-1}$) for iron(III) complexes involving Fe_2O_2 bridging units.[1,9,10]

As mentioned before, the factors responsible for the variations in the *J* parameter through this series remain to be ascertained. Apparently, in contrast with previous assumptions,[22a,23] changes in the nature of nonbridging ligands and iron coordination number might also be of some importance.[1]

Of special interest, within this context, are the magnetic properties of $Fe_2L'(OCH_3)_2Cl_2$[1] and $(FeSalenCl)_2$,[22] which have $Fe_2(OMe)_2{}^{4+}$ and $Fe_2(OPh)_2{}^{4+}$ units, respectively, and the same iron coordination number and donor set as the title compound. As shown in Figure 3, with the exception of one Fe–N bond length in $(FeSalenCl)_2$,[19] 2.09 Å, that is significantly shorter than corresponding values involving piperazine or imidazole nitrogens in $Fe_2L'(OCH_3)_2Cl_2$, 2.43 Å, or $Fe_2L(OCH_3)Cl_2$, 2.28 Å, respectively, comparable nonbridging bond lengths and angles in the three complexes are reasonably similar.

In spite of this simplifying feature, the relative extent of exchange interaction for $Fe_2L(OCH_3)Cl_2$ ($J = -8.0\ \mathrm{cm}^{-1}$), $Fe_2L'(OCH_3)_2Cl_2$ ($J = -16.3\ \mathrm{cm}^{-1}$), and $(FeSalenCl)_2$ ($J = -7.5\ \mathrm{cm}^{-1}$) continues to defy unified and comprehensive interpretation. For instance, two reasons that, according to current views,[7,12a] $Fe_2L(OCH_3)Cl_2$ shows an antiferromagnetic interaction considerably smaller than that of $Fe_2L'(OCH_3)_2Cl_2$ should be the reduced electron density at the bridge brought about by the electron-withdrawing ability of the phenyl group being greater than that of the methyl group and the fact that the $Fe_2(OMe)(OPh)^{4+}$ unit has two Fe–O bridging bond distances, 2.05 Å, longer than those found for the $Fe_2(OMe)_2{}^{4+}$ unit, 1.98 Å. However, when one goes from the $Fe_2(OMe)(OPh)^{4+}$ to the $Fe_2(OPh)_2{}^{4+}$ compound, differences in

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electron density between methoxy and phenoxy oxygens and the lengthening of two Fe–O bridging bond distances from 2.05 to 2.18 Å are almost magnetically invisible since the methoxophenoxo- and the diphenoxo-bridged complexes show not significantly different *J* values.

Whether or not the effects of the two longer Fe–O bond distances and the reduced electron density in the Salen^{2-} derivative are counterbalanced by other factors such as the effect of one larger bridging angle at oxygen or the planarity of the bridging unit remains unknown.

In summation, when it is considered collectively, the evidence of the properties of the three complexes does not indicate any unequivocal magnetostructural relationship. This result, although rather disappointing, is not totally surprising. Although the effects on the ordering of spin states of geometrical distortions and of substituent changes for a variety of Cu(II) dimers could be accounted for[7,8] by analyzing, in terms of pairwise interactions of dimeric MO's, only the direct superexchange mechanism (coupling with ionic states), a very recent ab initio direct calculation[24] of the singlet-triplet separation in cupric acetate hydrate dimer has shown that at least other three essential contributions (whose dependence on structural changes in the system has still to be analyzed) must be considered in order to quantitatively understand the observed magnetic properties. The problem is easily predicted to be greatly complicated by the presence of five electrons per atom.

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Supplementary Material Available: Listings of the hydrogen atom coordinates and the observed and calculated structure factor amplitudes for $Fe_2L(OCH_3)Cl_2$ (6 pages). Ordering information is given on any current masthead page.

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On the Meaning of Spin-Pairing Energy in Transition-Metal Ions

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Conventional multiplet theory predicts a number of well-verified regularities for the spin-pairing energy in transition-metal ions. In the present work, these predictions are analyzed at the Hartree–Fock level. It is shown that many regularities persist in the SCF wavefunctions and energies but that the interpretation of the results is quite different. The implications for other parts of multiplet theory and ligand field theory are briefly discussed.

Introduction

In ligand field theory, the formation of high-spin vs. low-spin transition-metal complexes is considered to result from the interplay of two opposing tendencies. On the one hand, the ligand field induces one-electron energy differences between the metal d orbitals; the larger these differences, the more the lower lying orbitals will tend to be fully occupied. On the other hand, the complete occupation of these orbitals and the corresponding spin pairing is taken to be hindered by the larger repulsion, characterizing two electrons with opposite spins. The properties of the complex can be described by considering the balance of some typical one-electron ligand field parameter (10*Dq* in octahedral complexes) and the so-called spin-pairing energy. Within the framework of the conventional multiplet theory,[1] this spin-pairing energy is an interelectronic repulsion energy and can be expressed in terms of the Racah *B* and *C* parameters or alternatively in terms of the Slater–Condon integrals F^k.

The most general treatment of the spin-pairing energy has been given by Jørgensen[2] and Slater;[3] on the basis of first-order perturbation theory, they show that, for any nd^q configuration

$$E(S) = E(nd^q) + [\overline{S(S+1)} - S(S+1)]D$$

where $E(nd^q)$ is the weighted mean energy of the configuration, $E(S)$ is the weighted mean energy of the multiplets characterized by *S* spin quantum number, $\overline{S(S+1)}$ corresponds to the average value of the total spin angular momentum, and *D* is a typical metal parameter. Therefore

$$\Delta E = E(S-1) - E(S) = 2SD \qquad (1)$$

It is clear that ΔE provides the neatest way to describe the average effect of changing the spin of just one electron. For d^q systems, where more than two multiplicities are possible (q = 4–6) this means that

$$\frac{E(S-1) - E(S)}{E(S-2) - E(S-1)} = \frac{S}{S-1}$$

The relevant quantity is then $\Delta E/2S = D$, the spin-pairing parameter; it is a measure for the energy required to change just two electrons from unpaired (↑↑) to paired (↑↓). For all nd^q systems, *D* is given by one single parametric expression,[2,3] eq 2. It can also be shown that *D* is proportional to the

$$D = {}^7\!/_{12}(5B + 2C) = {}^5\!/_{84}[F^2(nd;nd) + F^4(nd;nd)] \qquad (2)$$

average exchange integral K_{av} of the d^q system: $D = {}^7\!/_6 K_{av}$.

Since the Racah repulsion parameters *B* and *C* are inherently positive, *D* and ΔE are also positive; therefore eq 1 goes some length toward the rationalization of Hund's first rule.

It is well-known that this first-order perturbation approach leads to very satisfactory results: nearly all the predictions of the classical multiplet theory are qualitatively and semiquantitatively verified by extensive spectral data for nearly all the elements of the periodic system.

Yet, for certain first-row atoms and ions, a detailed comparison of first-order perturbation theory and SCF calculations

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