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$\sim 3 \times 10^4$ s^{-1} in benzene, many times smaller than in water. Thus, the fraction of *tert*-butyloxy radicals undergoing β-scission would be $\sim$8% at the lowest concentration of *tert*-butyl hydroperoxide. The corresponding low yield of methylcobaloxime would have been below the detection limit. That this explanation is a reasonable one is demonstrated from known solvent effects. Polar solvents, particularly those capable of hydrogen bonding, accelerate greatly the rate of β-scission of *tert*-butyloxy radicals by stabilizing the transition state.[13,14] Polar solvents also decrease the rate of hydrogen atom abstraction because of the greater solvation of alkyloxy radicals.[14] Both effects favor β-scission over hydrogen atom abstraction in water but the reverse in benzene. The rate of β-scission of $(CH_3)_2CHC(CH_3)_2O\cdot$ (eq 3b) is so much higher[14b,15] that, even with this effect, β-scission remains the major pathway in benzene.

The final step in the mechanism is assigned to a rapid bimolecular reaction between $Co(dmgH)_2py$ and the alkylperoxy radical. Although no examples can be cited, the analogous coupling of $Co(dmgH)_2py$ and alkyl radicals occurs quite rapidly. In addition, eq 9 leads to the product actually isolated under the experimental conditions.

The situation where $Co(dmgH)_2py$ was in excess over $(CH_3)_3COOH$ is not as clearly defined. Secondary reactions were observed, however, and thus the expectation[13] of a substantial yield ($\sim$60%) of methylcobaloxime (<25% was detected) was based on estimates that were not able to allow for all the reactions occurring.

Conclusions

The change in products and stoichiometry between aqueous and benzene solution arises from the solvent effect on the rate constant for β-scission of the first radical intermediate, $(CH_3)_3CO\cdot$. In benzene, this is so slow that hydrogen atom abstraction occurs instead, leading to a second oxygen-centered radical, $(CH_3)_3COO\cdot$, and finally to the isolated product $(CH_3)_3COOCo(dmgH)_2py$.

Experimental Section

Flash photolytic measurements were made by photolyzing 2×10^{-4} M $(CH_3)_2CHCo(dmgH)_2py$ in benzene with visible light in a Xenon Corp. Model 710C system. Absorbance changes were monitored at 460 nm, where the molar absorptivity of the Co(II) complex, the principal absorbing species, is ca. 2.1×10^2 M^{-1} cm^{-1}. Stopped-flow measurements were made with a Canterbury SF-3A instrument at a wavelength of 520 nm. Samples spotted on TLC plates were eluted with a 2:2:1 mixture of ethyl acetate, chloroform, and methanol. Column chromatography was done similarly, with a second elution using a 7:7:1 mixture of the same solvents and a jacketed column held at 0 °C and wrapped with aluminum foil. Crystalline products were isolated by rotary evaporation.

tert-Butyl hydroperoxide was the commerical (90%) material, and 2,3-dimethyl-2-butyl hydroperoxide was prepared according to the literature method[16] as were the cobaloximes.[17]

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Registry No. $(CH_3)_3COOCo(dmgH)_2py$, 86561-35-5; $HOCo(dmgH)_2py$, 15688-61-6; $Co(dmgH)_2py$, 36451-60-2; $(CH_3)_3COOH$, 75-91-2; benzene, 71-43-2.

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(13) The ratio of rate constants for H atom abstraction from cyclohexane to that of β-scission is $k_H/k_\beta = 48.6$ M^{-1} in benzene at 298 K (Walling, C.; Wagner, P. J.; *J. Am. Chem. Soc.* **1964**, *86*, 3368). This ratio and the independently determined value $k_H = 1.6 \times 10^6$ M^{-1} s^{-1} in benzene (Scaiano, J. C., personal communication) afford the value cited for k_β.

(14) (a) Howard, J. A. *Adv. Free-Radical Chem.* **1972**, *4*, 49. (b) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

(15) Choo, K. Y.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 833.

(16) Hedaya, E.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1661.

(17) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.

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Exchange Interaction in Multinuclear Transition-Metal Complexes. 4.[1] Relative Magnetic Coupling in Hydroxo- and Methoxo-Bridged Dinuclear Complexes of Iron(III) with the Heptadentate Schiff Base Trisalicylidenetriethylenetetramine

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There is a continuing interest, from both an experimental[2] and theoretical[3,4] point of view, in determining whether the magnetic properties of exchange-coupled transition-metal compounds can be examined in terms of their geometrical and chemical features.

Combined magnetic and structural information is so far available for about 10 dinuclear iron(III) compounds having Fe_2O_2 bridging units, which have been briefly reviewed elsewhere.[5,6] As has been noted by us[5,6] and by others,[7] variations in weak antiferromagnetic coupling ($7 < |J| < 17$ cm^{-1}) within this series defy unified and comprehensive interpretation in terms of geometrical and chemical changes. Also, the behavior of these compounds seems to raise doubts about the proposed general applicability of the MO formalism that has been widely and successfully used to rationalize the magnetic properties of a number of copper(II)[4] or chromium(III)[8] coupled dimers. It must however be recognized that the analysis of the magnetic data for the Fe_2O_2 series is complicated by the fact that fully characterized compounds generally involve different ligands and coordination geometries.

Recently, we have described[6] the X-ray structure and magnetic properties of $Fe_2L(OCH_3)Cl_2$ (L^{3-} is the anion of the heptadentate Schiff base trisalicylidenetriethylenetetramine) having an Fe–OMe–Fe–OPh bridging unit.

Tasker et al.[9] have performed an X-ray analysis of the tetrahydrofuran solvate of the hydroxy analogue, $Fe_2L(OH)Cl_2\cdot C_4H_8O$, using crystals taken from ill-defined mixtures. The synthesis of the compound was not achieved.

In order to test the effect of changing the electron density at the bridging atom on the metal–metal coupling for a magnetically condensed iron(III) system, we have now completed the synthesis of $Fe_2L(OH)Cl_2\cdot C_4H_8O$, verified by X-ray methods that its X-ray structure is the same as that reported in the literature, and examined the magnetic behavior of the compound in the temperature range $\sim$4–200 K.

A comparison of X-ray data for the hydroxy and methoxy compounds shows that, except for the substituent linked to one bridging oxygen, the dinuclear molecules are virtually identical. Since, in addition, the electronic structures of the methoxy and hydroxy bridges are likely to be very similar, one has a situation where the relative J values for the two species should provide a reliable test of general expectations of MO theory regarding the effect on magnetic coupling of variations in electron density at the bridging atom.[4]

Experimental Section

Preparation. The LH_3 ligand has been prepared according to known procedures.[10]

$Fe_2L(OH)Cl_2\cdot C_4H_8O$. LH_3 (0.46 g, 1 mmol) was dissolved, at room temperature, in a 25-mL portion of a solution composed of 50 mL of tetrahydrofuran, 0.25 mL of triethylenetetramine, and 0.25 mL of water. The remaining portion of this solution was used to dissolve 0.54 g (2 mmol) of $FeCl_3\cdot 6H_2O$. The iron chloride and LH_3 solutions

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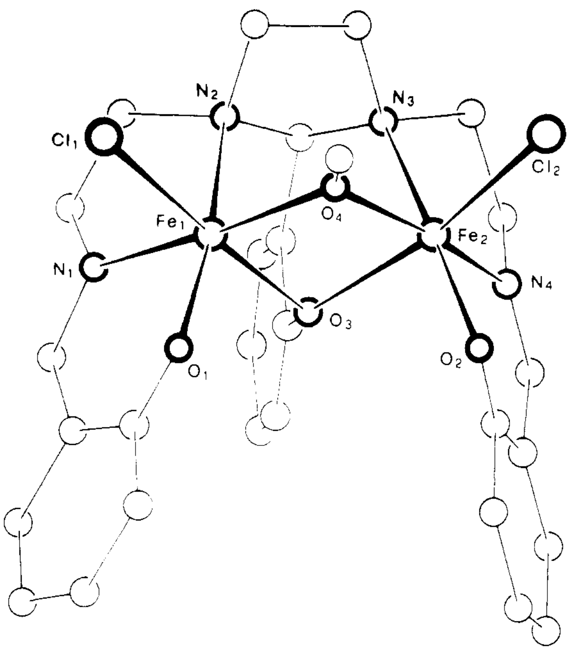

Figure 1. Schematic view of the molecular structure of the dinuclear units in $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ and $Fe_2L(OCH_3)Cl_2$.

were mixed at room temperature and then heated at ~70 °C for ~1 h. Dark needles separated, which were decanted and washed with tetrahydrofuran: yield 0.22 g (30%); mp >350 °C. Anal. Calcd for $C_{31}H_{36}N_4Cl_2O_5Fe_2$: C, 51.19; H, 5.00; N, 7.71; Cl, 9.75; O, 11.00; Fe, 15.36. Found: C, 50.09; H, 5.03; N, 7.84; Cl, 9.63; O, 10.50; Fe, 15.48.

X-ray Crystallography. As mentioned above, a preliminary account of the structure of $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ has been reported.[9] That the compound synthesized in this work has actually the same structure as that reported in the literature has been ascertained by subjecting data collected for our compound to several least-squares refinement cycles starting from the atomic coordinates pertaining to the previously determined structure. The atomic coordinates were supplied by Dr. P. A. Tasker. A dark, prismatic crystal with dimensions 0.08 × 0.09 × 0.35 mm was mounted on a Philips 1100 four-circle diffractometer equipped with Mo radiation and a graphite monochromator. The crystal was found to be orthorhombic, space group *Pbca* (from systematic extinctions). Cell dimensions, as determined by least-squares fitting of the angular ϑ, χ, and φ values of 25 reflections, were a = 15,380 (5), b = 21.583 (5), and c = 19.293 (5) Å. Crystal symmetry and lattice parameters closely agree with those (a = 15.375 (5), b = 21.533 (11), c = 19.346 (10) Å) reported by Tasker et al. Intensity data for 3371 independent reflections, in the range $2 < \vartheta < 20°$, were measured and treated with the procedures previously described for $Fe_2L(OCH_3)Cl_2$.[6] Due to the poor quality of our crystal, only 855 reflections had $I > 3[\sigma(I)]$, were considered as observed, and were used in the refinement. Several least-squares cycles led to an R value of 0.10. A Fourier difference map showed no significant residual maximum. Bond distances and angles were found to be very similar to those obtained in the previous analysis. There seems to be little doubt that the present compound has the same structure as that determined by Tasker et al. Since, owing to the poor quality of our crystals, there was no chance of improving the refinement carried out by these workers (R = 0.076 for 1797 observed reflections), further structural work was deemed useless, and structural details for $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ (only bond lengths in the first coordination sphere of iron were given in the preliminary communication) were deduced from the atomic coordinates obtained by Tasker et al.

Table I. Geometries of the Inner Coordination Sphere in $Fe_2L(OCH_3)Cl_2$ and $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$[a]

	$Fe_2L(OCH_3)Cl_2$[b]		$Fe_2L(OH)Cl_2{\cdot}C_4H_8O$[c]	
coordinating atoms[d]	Fe(1)	Fe(2)	Fe(1)	Fe(2)
	Bond Lengths, Å			
O(1)/(O(2)	1.90 (1)	1.91 (1)	1.87 (1)	1.89 (1)
O(3)	2.04 (2)	2.06 (2)	2.08 (1)	2.06 (2)
O(4)	2.00 (2)	1.95 (1)	1.98 (1)	1.95 (1)
N(1)/N(4)	2.13 (2)	2.11 (2)	2.13 (2)	2.10 (1)
N(2)/N(3)	2.29 (2)	2.26 (2)	2.28 (2)	2.32 (2)
Cl(1)/Cl(2)	2.304 (7)	2.330 (7)	2.311 (10)	2.295 (10)
	Bond Angles at Iron, deg			
O(3),N(1)/O(3),N(4)	90.6 (6)	90.5 (6)	90.2 (7)	91.9 (7)
N(1),Cl(1)/N(4),Cl(2)	95.2 (5)	94.7 (5)	94.8 (6)	95.1 (6)
Cl(1),O(4)/Cl(2),O(4)	97.2 (5)	96.8 (5)	99.0 (6)	95.3 (6)
O(3),O(4)	75.9 (5)	76.5 (5)	75.0 (7)	76.0 (7)
N(2),O(1)/N(3),O(2)	163.7 (6)	164.8 (6)	162.4 (7)	164.7 (7)
O(3),Cl(1)/O(3),Cl(2)	171.4 (4)	170.4 (5)	168.9 (6)	168.0 (6)
O(4),N(1)/O(4),N(4)	163.3 (6)	163.7 (6)	161.4 (7)	164.2 (7)
O(1),N(1)/O(2),N(4)	88.1 (6)	88.5 (6)	86.9 (7)	89.0 (7)
O(1),Cl(1)/O(2),Cl(2)	97.4 (5)	95.1 (5)	96.4 (6)	97.1 (6)
O(1),O(4)/O(2),O(4)	101.3 (5)	101.9 (5)	104.1 (7)	101.5 (7)
O(1),O(3)/O(2),O(3)	89.2 (5)	93.1 (5)	90.1 (7)	92.9 (7)
N(2),N(1)/N(3),N(4)	77.4 (6)	76.7 (6)	76.7 (7)	76.9 (7)
N(2),Cl(1)/N(3),Cl(2)	91.3 (5)	89.9 (5)	92.5 (6)	89.9 (6)
N(2),O(4)/N(3),O(4)	91.2 (6)	91.8 (6)	90.3 (7)	91.3 (7)
N(2),O(3)/N(3),O(3)	83.7 (6)	83.5 (6)	83.7 (7)	82.1 (7)

[a] Atomic numbering refers to Figure 1. [b] Data from ref 6. [c] Data from ref 9 and present work. [d] Atoms on the left of the slant are coordinated to Fe(1); those on the right of the slant are coordinated to Fe(2).

Table II. Structural Parameters for the Fe_2O_2 Bridging Units in $Fe_2L(OCH_3)Cl_2$ and $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$

	$Fe_2L(OCH_3Cl_2$	$Fe_2L(OH)Cl_2{\cdot}C_4H_8O$
Fe(1)···Fe(2), Å	3.139 (5)	3.162 (7)
O(3)···O(4), Å	2.48 (2)	2.47 (2)
Fe–O(3),[a] Å	2.05 (2)	2.07 (2)
Fe–O(4),[a] Å	1.98 (1)	1.97 (1)
Fe(1)O(3)Fe(2), deg	100 (1)	100 (1)
Fe(1)O(4)Fe(2), deg	105 (1)	107 (1)
D,[b] deg	166	166
δ,[c] Å	0.10	0.10

[a] Mean value. [b] D = dihedral angle between FeO_2 planes. [c] δ = deviation of the iron atoms from the best plane of the four-membered iron–oxygen ring.

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibility studies between 4.2 and ~200 K were performed, on solid polycrystalline samples, in the laboratory of Professor William E. Hatfield, with a Princeton Applied Research Model 155 vibrating-sample magnetometer operating at 10 kOe. The apparatus and techniques used to collect the data have been described elsewhere.[11]

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(1) Part 3: Chiari, B.; Hatfield, W. E.; Piovesana, O.; Tarantelli, T.; Ter Haar, L. W.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 1468.

(2) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173. Hatfield, W. E. *ACS Symp. Ser.* **1974**, *No. 5*, 108. Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105. Roundhill, D. M.; Bloomquist, D. R. Landee, C.; Willet, R. D.; Dooley, D. M.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 831. Boyd, P. D. W.; Mitra, S.; Raston, C. L.; Rowbottom, G. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 13. Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1982**, *21*, 2679.

(3) Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111 and references therein. de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *Ibid.* **1981**, *103*, 4007. Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 268. Kahn, O.; Briat, B. *Ibid.* **1976**, *72*, 1441. Bencini, A.; Gatteschi, D. *Inorg. Chim. Acta* **1978**, *31*, 11. Van Kalkeren, G.; Schmidt, W. W.; Block, R. *Physica. B+C (Amsterdam)* **1979**, *97B+C*, 315.

(4) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(5) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 1396.

(6) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 2444.

(7) Thich, J. A.; Chih Ou, C.; Powers, D.; Vasiliou, B.; Mastropaolo, D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1976**, *98*, 1425.

(8) Scaringe, R. P.; Hodgson, D. J.; Hatfield, W. E. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 340.

(9) Bailey, N. A.; Mc Kenzie, E. D.; Worthington, J. M.; Mc Partlin, M.; Tasker, P. A. *Inorg. Chim. Acta* **1977**, *25*, L137.

(10) Das Sarma, B.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 5476.

(11) Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033 and references therein.

A diamagnetic correction of 180 × 10^{-6} cgsu/Fe was calculated from Pascal constants.

ESR Spectra. These were obtained with a Varian E-109 spectrometer operating at X-band frequencies. The DPPH free radical was used as a field marker. Data were collected at room temperature and liquid-nitrogen temperatures maintained with use of an insertion Dewar made by Varian.

Infrared Spectra. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer. KBr pellets were used.

Chemical Analyses. These were performed by Microanalytisches Laboratorium, Elbach, West Germany.

Results and Discussion

The molecular structure of $Fe_2L(OH)Cl_2$ and $Fe_2L(OCH_3)Cl_2$ is schematically shown in Figure 1. The two molecules have $Fe_2(OH)(OPh)$ and $Fe_2(OCH_3)(OPh)$ bridging units, respectively, but are otherwise very similar Examination of Table I reveals that virtually all of the inner coordination sphere bond lengths and angles for one complex are within 3 esd's of the comparable bond lengths and angles for the other complex. Bond lengths and angles of the L^{3-} ligand in the two compounds, not reported in Table I, are also found to agree closely. Table II shows that structural parameters for the two bridging units are strictly similar. From the intermolecular contacts between dinuclear units, which are always longer than the sum of van der Waals radii, it appears that the individual molecules are magnetically dilute in both compounds.

In the structure of $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$, there is an O···O contact of 2.85 Å between the bridging hydroxide and a neighboring tetrahydrofuran molecule. This value is less than twice the van der Waals radius of oxygen as given by Bondi (3.02 Å)[12] but slightly greater than the corresponding value given by Pauling (2.80 Å).[13] Our inability to locate the hydrogen atom on the hydroxo oxygen prevents us from using hydrogen–oxygen distances to infer[14] the presence (or absence) of hydrogen bonding.

However, it has been shown,[7] through a combination of isotopic and metal ion substitutions, that, for dihydroxo-bridged $[Dipic(H_2O)Fe(OH)]_2$, the stretching mode of the bridging OH, which is not involved in any hydrogen bonding, appears as a strong, broad absorption at 3410 cm^{-1}. For our compound, the corresponding mode, whose identification is facilitated by the absence of ligand/lattice water, appears as a similar absorption at 3430 cm^{-1}. Therefore, there is no evidence for any shift of electronic charge toward the hydroxo oxygen in $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$. Such an effect (which is generally accounted for, in a valence-bond formalism, by considering[15] the resonance structure $O^-{\cdots}H{-}O^+$) would involve a weaker (and hence longer) O–H covalent bond and a lower OH stretching frequency. It is reasonable to conclude that the magnetic coupling in $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ is not influenced by the presence of the solvent molecules.

As was the case for $Fe_2L(OCH_3)Cl_2$,[6] X-band ESR spectra of powdered samples of the hydroxy compound, both at room temperature and at liquid-nitrogen temperatures, show only a broad, unresolved signal (peak to peak separation: ~2000 G at room temperature, ~1000 G at 77 K) at roughly $g \sim 2$. Signals at $g \sim 4.2$, indicative of the presence of magnetically noninteracting ferric impurities, were not observed.

Magnetic susceptibility data for $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ were analyzed with the spin–spin interaction model based on the exchange Hamiltonian $-2J\hat{S}_A{\cdot}\hat{S}_B$. The equation for the molar paramagnetic susceptibility of an $S_A = S_B = {}^5/_2$ exchange coupled dimer is

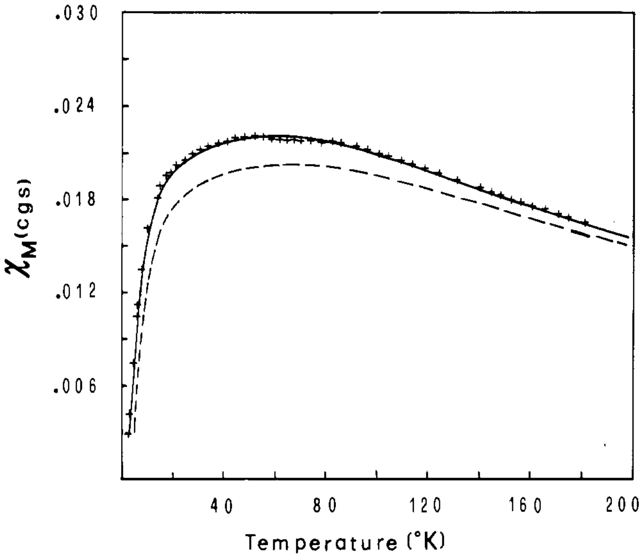

Figure 2. Magnetic susceptibility data for $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ between 4.2 and 200 K. The solid line through the data was generated by the $S_A = S_B = {}^5/_2$ dimer equation with an exchange coupling constant of $-7.40\ cm^{-1}$ ($g = 2.00$, TIP = 0, 0% paramagnetic impurities). The theoretical curve (---) calculated for $J = -8.0\ cm^{-1}$ ($g = 2.00$, TIP = 0, 0% paramagnetic impurities), which gave the best fitting for $Fe_2L(OCH_3)Cl_2$, is also shown.

$$\chi_M \text{ (per iron)} = (N\beta^2 g^2/kT)\{[55 + 30\exp(10x) + 14\exp(18x) + 5\exp(24x) + \exp(28x)]/[11 + 9\exp(10x) + 7\exp(18x) + 5\exp(24x) + 3\exp(28x) + \exp(30x)]\}$$

where $x = -J/kT$. A nonlinear fitting routine was used to fit the corrected experimental data to the above equation. The function minimized was $F = \sum_i w_i(\chi_i^{obsd} - \chi_i^{calcd})^2$ with the weights being assigned $w_i = (\chi_i^{obsd})^{-1}$. An isotropic g value of 2.0 was assumed, and temperature-independent paramagnetism was neglected. In agreement with the ESR results, the analysis of the susceptibility data did not indicate the presence of any significant amount of magnetically dilute ferric impurities. The best fit to the data is displayed in Figure 2, where the final value was $J = -7.40\ cm^{-1}$. The agreement factor was 4×10^{-4}, for 50 observations, and the estimated standard deviation of the J parameter from the last cycle of least squares was 0.15 cm^{-1}. Figure 2 also shows the theoretical curve calculated for $J = -8.0\ cm^{-1}$, $g = 2.0$, TIP = 0, and no noncoupled impurities, which gave the best fitting for $Fe_2L(OCH_3)Cl_2$. The good fit to the data obtained for both the hydroxy and methoxy compounds gives confidence that the difference in the J values between the two compounds, although small, is significant.

Hoffmann and co-workers[4] have suggested, on the basis of semiquantitative MO arguments, that, all other things being kept constant, the strength of antiferromagnetic interaction should increase as the electron density at the bridging atoms is enhanced. Since the methyl group is more electron donating than hydrogen, the more negative J value observed for $Fe_2L(OCH_3)Cl_2$ than for $Fe_2L(OH)Cl_2{\cdot}C_4H_8O$ conforms to the theoretical expectation, which seems to encourage the use of MO models in facing exchange problems presented by magnetically condensed iron(III) systems.

To our knowledge, the only previous direct evidence regarding the correlation between substituent electron-withdrawing power and metal–metal coupling is represented by the much larger extent of interaction ($J = -8.94\ cm^{-1}$) observed for $[Cr(3\text{-}Br\text{-}acac)_2(OC_2H_5)]_2$, relative to that ($J =$

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(12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(13) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(14) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; p 16.
(15) Coulson, C. A. In "Hydrogen Bonding"; Hadži D., Ed.; Pergamon Press: New York, 1959; p 339.

-3.55 cm^{-1}) for the methoxy analogue, with the two compounds having identical structures except for the bridging groups.[16] It has also been shown that benzyloxo-bridged $[Cu(Tmhd)(OCH_2Ph)]_2$, where Tmhd is 2,2,6,6-tetramethylheptane-3,5-dionate, has a much more negative J value, -324 cm^{-1}, than the value of -170 cm^{-1} predicted from the linear relationship between J and CuOCu angles observed for analogous Cu(II) dihydroxo-bridged dimers.[17] Apparently, a similar pattern may be inferred from the magnetic properties of other alkoxide-bridged Cu(II) dimers.[18,19] In terms of total exchange interaction energies ($E_{ex} = |4J_{AB}S_AS_B|$),[20] the changes due to substituent variation are found to be 152% for the chromium (–OMe → –OEt), 90% for the copper (–OH → –OCH_2Ph), and 8% for the iron system (–OH → OMe). Further work is in progress to ascertain whether the much smaller variation in E_{ex} observed for the iron compounds might involve (besides factors such as the asymmetry in the bridges) the d^5 configuration of the coupled metal centers.

Acknowledgment. The authors are indebted to Dr. P. A. Tasker, of the Polytechnic of North London, for providing the atomic coordinates of $Fe_2L(OH)Cl_2 \cdot C_4H_8O$. Magnetic measurements were made in the laboratory of Professor William E. Hatfield, at The University of North Carolina at Chapel Hill. O.P. thanks Professor Hatfield for his hospitality.

Registry No. $Fe_2L(OH)Cl_2 \cdot C_4H_8O$, 65732-88-9.

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(16) Estes, E. D.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1977**, *16*, 1605.

(17) Le May, H. E., Jr.; Hodgson, D. J.; Pruettiangkura, P.; Theriot, L. J. *J. Chem. Soc., Dalton Trans.* **1979**, 781.

(18) Mikuriya, M.; Ōkawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1086.

(19) Banci, L.; Bencini, A.; Dapporto, P.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1980**, *19*, 3395.

(20) Nesbet, R. K. *Ann. Phys. (Leipzig)* **1958**, *4*, 87. Bell, P. W.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1974**, 852.