opened by two Hg_2^{2+} binuclear cations. The asymmetrical unit contains two such moieties facing each other, the mercury atoms making a distorted cube.

Acknowledgment. We are indebted to Dr. C. Knobler for valuable advice and helpful discussions.

Registry No. $K_5Cs_5[As_2W_{19}Hg_4O_{67}(H_2O)]\cdot 3H_2O$, 92014-65-8; Hg, 7439-97-6.

Supplementary Material Available: Table II (anisotropic thermal parameters of Hg and W atoms), Table IV (selected bond distances and angles), and a listing of structure factor amplitudes (44 pages). Ordering information is given on any current masthead page.

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Exchange Interaction in Multinuclear Transition-Metal Complexes. 6.[1] Nature of Metal-Metal Coupling in Dinuclear Iron(III) Systems Containing Fe-O-Fe-O Bridging Units

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The crystal structures of the new complex bis(μ-ethoxy)dichloro[1,4-piperazinediylbis(*N*-ethylenesalicylaldiminato)]diiron(III), $Fe_2L(OC_2H_5)_2Cl_2$, $C_{26}H_{36}N_4O_4Cl_2Fe_2$, and of the already known bis(μ-ethoxy)bis[bis(2,4-pentanedionato)iron(III)], $Fe_2(acac)_4(OC_2H_5)_2$, $C_{24}H_{50}O_{10}Fe_2$, have been determined by X-ray methods. The L^{2-} derivative crystallizes in the orthorhombic space group *Pccn* with 4 molecules in a cell of dimensions $a = 10.840$ (3) Å, $b = 13.414$ (3) Å, and $c = 19.850$ (4) Å. Least-squares refinement of 1066 observed reflections and 173 parameters has led to a final *R* factor of 0.035. $Fe_2(acac)_4(OC_2H_5)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$. Lattice constants are $a = 9.761$ (3) Å, $b = 14.627$ (3) Å, $c = 10.485$ (3) Å, and $\beta = 105.83$ (2)°. The least-squares refinement converged to an *R* value of 0.052 for 1526 observed reflections and 161 parameters. Both complexes consist of two iron(III) ions that are symmetrically bridged by two ethoxide groups. The coordination around each iron center is roughly octahedral. In $Fe_2L(OC_2H_5)_2Cl_2$, three coordination sites are occupied by one oxygen and two nitrogens (cis) of hexadentate L^{2-} and the remaining three by the two bridging ethoxy groups and a terminal chloride atom. The average Fe-O (bridging) bond length is 1.991 Å, the Fe-Fe separation is 3.144 (1) Å, and the FeOFe angle is 104.3 (1)°. The Fe_2O_2 ring is buckled, the dihedral angle between FeO_2 planes being 169°. In $Fe_2(acac)_4(OC_2H_5)_2$, the coordination sites are occupied by the two bridging alkoxide groups and the oxygen atoms of two cis bidentate $acac^-$ ligands. The Fe_2O_4 bridging unit is perfectly planar, owing to inversion symmetry. The average Fe-O (bridging) bond length is 1.982 Å, the Fe-Fe separation is 3.116 (1) Å, and the FeOFe angle is 103.6 (3°). The magnetic susceptibility of powdered samples of $Fe_2L(OC_2H_5)_2Cl_2$ has been examined in the temperature range 4-300 K. The compound exhibits an antiferromagnetic exchange interaction, with the best fit to the Van Vleck equation yielding $J = -15.40$ cm^{-1}, with $g = 2.00$ and TIP = 0. The data for the L^{2-} derivative are compared to those for the previously characterized $Fe_2L(OCH_3)_2Cl_2$, $J = -16.30$ cm^{-1}, and to those for $Fe_2(acac)_4(OC_2H_5)_2$, $J = -11.0$ cm^{-1}. Attempts to describe the relative magnetic properties of these compounds in terms of structural parameters or qualitative molecular orbital theory have been made.

Introduction

How the exchange coupling constants for dinuclear iron(III) compounds containing the Fe_2O_2 bridging system are influenced by variations in the geometrical and chemical features of the bridging and nonbridging ligands is not yet understood.[2-5]

In a recent paper[2] we have shown that, in qualitative agreement with predictions of MO theory[6] regarding the effect on *J* of variations in the electron density at the bridging atoms, a change in the bridging unit from Fe-OMe-Fe-OPh to Fe-OH-Fe-OPh, with no other structural change, brings about a decrease in the magnitude of the antiferromagnetic interaction. This datum seems to represent the strongest evidence so far available in support of the view[6] that exchange coupling problems presented by iron(III) systems can be analyzed with the same MO formalism as that which has been widely and successfully used to rationalize structure-magnetism correlations observed for exchange-coupled copper(II)[6] or chromium(III)[7,8] systems.

Continuing our efforts[2-4] to clarify the mechanism of spin-spin interaction in iron(III) compounds of the aforementioned type, we have now synthesized the bis(ethoxy)-bridged compound $Fe_2L(OC_2H_5)_2Cl_2$, where L^{2-} is the anion of the hexadentate Schiff base 1,4-piperazinediylbis(*N*-ethylenesalicylaldimine), and investigated its X-ray structure as well its magnetic properties down to 4.2 K.

In addition, we have determined the X-ray structure of $Fe_2(acac)_4(OC_2H_5)_2$ ($acac^-$ = 2,4-pentanedionato), also diethoxy-bridged, whose synthesis and magnetic behavior, between ca. 10 and 300 K, have been previously reported by other workers.[9]

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The present structural and magnetic data, together with those previously obtained[3] in these laboratories for $Fe_2L(OCH_3)_2Cl_2$, provide a useful experimental basis for discussing the applicability of current MO models to exchange problems presented by exchange-coupled iron(III) dimers.

Experimental Section

Preparation. The LH_2 ligand has been obtained as previously described.[3]

$Fe_2L(OC_2H_5)_2Cl_2$. LH_2 (1 mmol) was dissolved in a 40-mL portion of a 9.4×10^{-2} M solution of sodium ethoxide in anhydrous ethanol. The resulting solution was added, at room temperature, to a solution of anhydrous $FeCl_3$ (2 mmol) in anhydrous ethanol (75 mL). The reaction mixture was heated under reflux for ca. 1 h, in a dry nitrogen atmosphere. A brown, microcrystalline product separated from the hot solution, which was decanted, washed with anhydrous ethanol, and dried under vacuum: yield 0.4 g (61%); mp 350 °C. Anal. Calcd for $C_{26}H_{36}N_4O_4Cl_2Fe_2$: C, 47.95; H, 5.57; N, 8.60. Found: C, 47.66; H, 5.38; N, 8.63. Completely insoluble in ethanol, the compound is soluble in dichloromethane. A molecular weight of 700 ± 15 (calculated 651) was measured in this solvent (0.3%).

Crystals of larger size, more suitable for X-ray analysis, were obtained in the following way. The reaction mixture, prepared as above, was put in a Pyrex vessel. This was hermetically sealed and then placed in a big metallic container. The whole system was kept at ca. 100 °C for ca. 3 h in a thermostatic stove. Then, the stove was turned off. The thermal inertness of the metallic container allowed a very slow cooling (~30 h) of the solution to room temperature. Crystals formed on the walls of the Pyrex vessel that were collected manually, washed with anhydrous ethanol, and dried under vacuum. Although this method allows the formation of crystals of more suitable size for crystallographic studies, it has the disadvantage that, besides the brown $Fe_2L(OC_2H_5)_2Cl_2$, another yellow, crystalline species is formed. However, it is easy to mechanically separate one species from the other. That this method of preparation actually affords the same brown product as that previously obtained has been ascertained with X-ray methods, by verifying that crystals from the two preparations belong to the same space group and have the same cell constants (vide infra). The yellow crystals appear to have similar composition (C, 47.82; H, 5.62; N, 8.55) to that of $Fe_2L(OC_2H_5)_2Cl_2$. They crystallize in the monoclinic space group $P2_1/n$, with cell constants a = 13.262 Å, b = 23.278 Å, c = 10.982 Å, and β = 105.98°. Due to a rather rapid decomposition under the X-radiation, the yellow species was not furhter investigated.

$Fe_2(acac)_4(OC_2H_5)_2$. This compound was prepared by the procedure of Gray et al., starting from $Fe(acac)_3$ and sodium ethoxide.[9] Orange crystals (mp 159 °C), suitable for X-ray analysis, were obtained upon recrystallization of the crude product from anhydrous ethanol, in a dry nitrogen atmosphere.

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

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

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibility studies of $Fe_2L(OC_2H_5)_2Cl_2$, between 4.2 and ~300 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.[10] A diamagnetic correction of 162×10^{-6} cgsu/Fe was calculated from Pascal constants.

X-ray Data and Structure Solution. $Fe_2L(OC_2H_5)_2Cl_2$. A well-formed prismatic crystal of the compound, with dimensions 0.30 × 0.25 × 0.15 mm, was mounted on the goniometer of a Philips PW1100 automated diffractometer equipped with graphite-monochromatized Mo Kα radiation. Routine work to find a set of 25 centering reflections allowed the determination of the orientation matrix **UB** and also of the lattice parameters. The crystal is orthorhombic with a = 10.840 (3) Å, b = 13.414 (3) Å, and c = 19.850 (4) Å. The $Pccn$ space group was assigned from systematic extinctions. On the assumption of 4 molecules in the unit cell, the calculated density is 1.493 g·cm^{-3}. A total of 3052 hkl and $hk\bar{l}$ intensity data were measured, at room temperature, in the range $2 \le 2\vartheta \le 40°$, with the ω–2ϑ technique. The scan speed was 0.06° s^{-1}; the scan width was 1.2° in ω. Three standard reflections were remeasured every 3 h and showed no significant variation during the data collection. The intensities were corrected for Lorentz–polarization factors. A semiempirical correction[11] for absorption was applied (absorption coefficient μ = 11.9 cm^{-1} for Mo Kα; transmission factors ranged between 0.69 and 0.98). Then, symmetry-related reflections were averaged.[12] A set of 1357 unique reflections was obtained, of which 291 had $I \le 3\sigma(I)$ (where $\sigma(I)$ is the esd of the intensity calculated from counting statistics) and were considered as unobserved.

Table I. Fractional Atomic Coordinates for Non-Hydrogen Atoms of $Fe_2L(OC_2H_5)_2Cl_2$

atom	x/a	y/b	z/c
Fe	−0.14355 (6)	0.17042 (5)	0.69474 (3)
Cl	−0.1521 (1)	−0.0015 (1)	0.7189 (1)
O(1)	−0.0946 (3)	0.1538 (2)	0.6037 (2)
O(2)	−0.3247 (3)	0.1828 (2)	0.6868 (2)
N(1)	0.0484 (4)	0.1779 (3)	0.7186 (2)
N(2)	−0.1390 (4)	0.2008 (3)	0.8139 (2)
C(1)	0.0115 (5)	0.1388 (4)	0.5724 (2)
C(2)	0.0118 (6)	0.1237 (5)	0.5031 (3)
C(3)	0.1223 (6)	0.1104 (5)	0.4686 (3)
C(4)	0.2337 (7)	0.1069 (5)	0.5031 (4)
C(5)	0.2341 (5)	0.1201 (4)	0.5702 (3)
C(6)	0.1265 (5)	0.1371 (4)	0.6075 (3)
C(7)	0.1341 (5)	0.1547 (4)	0.6780 (3)
C(8)	0.0833 (5)	0.1944 (4)	0.7899 (3)
C(9)	−0.0199 (5)	0.1552 (4)	0.8332 (3)
C(10)	−0.1343 (5)	0.3098 (4)	0.8330 (3)
C(11)	−0.2624 (5)	0.3497 (4)	0.8523 (2)
C(12)	−0.4107 (5)	0.1107 (4)	0.6619 (3)
C(13)	−0.4015 (6)	0.0966 (5)	0.5878 (3)

The structure was solved by means of direct methods using SHELX-76.[13] The molecule lies on the crystallographic twofold axis, and, therefore, the asymmetric unit is half of the dinuclear molecule, i.e. $C_{13}H_{18}O_2N_2ClFe$. The atomic parameters were refined by full-matrix least-squares methods. Anisotropic thermal parameters were used for the non-hydrogen atoms. The H atoms were included at their calculated positions. The C–H bond length was held constant at 1.08 Å. An overall isotropic thermal parameter, that refined to U = 0.07 Å^2, was assigned to all the H atoms. The final values of R and R_w[14] were 0.035 and 0.042, respectively, for 1066 observed reflections and 173 parameters.

$Fe_2(acac)_4(OC_2H_5)_2$. Short, prismatic crystals of the compound were monoclinic, with lattice constants a = 9.761 (3) Å, b = 14.627 (3) Å, c = 10.485 (3) Å, and β = 105.83 (2)°. From the systematic extinctions the space group was uniquely assigned as $P2_1/n$. On the assumption of 2 molecules in the unit cell (i.e., the molecules lie at the inversion centers), the calculated density is 1.388 g·cm^{-3}.

The intensity data were measured with the procedure described for $Fe_2L(OC_2H_5)_2Cl_2$. A crystal of dimensions 0.20 × 0.20 × 0.15 mm was used. Data collection parameters were as follows: scan speed 0.06° s^{-1}; scan width 1.8°. A total of 2641 unique reflections were scanned in the ϑ range 2–25°. The intensity data were corrected for Lorentz–polarization effects and for absorption[11] (μ = 10.2 cm^{-1} for Mo Kα; transmission factors in the range 0.92–1.00). A set of 1526 reflections having $I \ge 3\sigma(I)$ was considered as observed and used in the analysis.

The structure was solved and refined as in the case of $Fe_2L(OC_2H_5)_2Cl_2$. All non-hydrogen atoms were refined anisotropically. The H atoms were included at their calculated positions. The C–H distance

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(12) An internal consistency index based on the deviations of $|F_{h,i}|$ of equivalent reflections from their mean values $|\bar{F}_h|$ was calculated as $R_F = \sum_h\sum_i w_h(|\bar{F}_h| - |F_{h,i}|)^2/\sum_h\sum_i w_h F_{h,i}^2$, where $w_h = \sigma(F_h)^{-1}$. The resulting value was 0.03.

(13) Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.

(14) The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The agreement factor R is defined as $\sum(|F_o| - |F_c|)/\sum F_o$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 1/(\sigma(F_o)^2 + aF_o^2)$; a is 0.0022 for $Fe_2L(OC_2H_5)_2Cl_2$ and 0.0068 for $Fe_2(acac)_4(OC_2H_5)_2$.

Table II. Fractional Atomic Coordinates for Non-Hydrogen Atoms of $Fe_2(acac)_4(OC_2H_5)_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe	0.5500 (1)	0.0559 (1)	0.6310 (1)
O(1)	0.4116 (4)	−0.0392 (2)	0.5439 (3)
O(2)	0.6882 (4)	−0.0408 (3)	0.7270 (4)
O(3)	0.7081 (4)	0.1459 (3)	0.6919 (4)
O(4)	0.4181 (4)	0.1628 (3)	0.5633 (4)
O(5)	0.4833 (4)	0.0614 (3)	0.7949 (4)
C(1)	0.3316 (6)	−0.0975 (4)	0.6060 (6)
C(2)	0.1838 (7)	−0.0592 (5)	0.5921 (3)
C(3)	0.8210 (6)	−0.0344 (4)	0.7783 (5)
C(4)	0.8992 (7)	−0.1215 (5)	0.8271 (7)
C(5)	0.8959 (7)	0.0474 (4)	0.7926 (7)
C(6)	0.8399 (6)	0.1322 (4)	0.7491 (6)
C(7)	0.9328 (7)	0.2140 (5)	0.7689 (8)
C(8)	0.3338 (6)	0.2026 (4)	0.6167 (6)
C(9)	0.2382 (7)	0.2739 (5)	0.5336 (7)
C(10)	0.3221 (7)	0.1858 (4)	0.7442 (7)
C(11)	0.3957 (6)	0.1157 (4)	0.8256 (6)
C(12)	0.3671 (8)	0.0979 (6)	0.9576 (7)

Table III. Bond Distances (Å) in Complexes of the Type $Fe_2L(OR)_2Cl_2$

	R			R	
	C_2H_5[a]	CH_3[b]		C_2H_5[a]	CH_3[b]
Fe–O(1)	1.897 (3)	1.92	C(6)–C(1)	1.428 (7)	*d*
Fe–O(2)	1.977 (3)	1.99	C(6)–C(7)	1.423 (8)	1.46
Fe–O(2)[c]	2.005 (3)	1.99	C(7)–N(1)	1.269 (7)	1.29
Fe–Cl	2.357 (1)	2.32	N(1)–C(8)	1.482 (7)	1.48
Fe–N(1)	2.136 (4)	2.11	C(8)–C(9)	1.506 (8)	1.49
Fe–N(2)	2.401 (4)	2.43	C(9)–N(2)	1.479 (6)	1.49
O(1)–C(1)	1.322 (6)	1.32	N(2)–C(10)	1.512 (7)	1.49
C(1)–C(2)	1.391 (7)	*d*	N(2)–C(11)[c]	1.476 (7)	1.50
C(2)–C(3)	1.391 (8)	*d*	C(10)–C(11)	1.537 (8)	1.53
C(3)–C(4)	1.389 (9)	*d*	O(2)–C(12)	1.432 (6)	1.39
C(4)–C(5)	1.344 (7)	*d*	C(12)–C(13)	1.486 (8)	
C(5)–C(6)	1.400 (8)	*d*			

[a] This work. [b] Reference 3; mean values. [c] Symmetry code: $-{}^1/_2 - x,\ {}^1/_2 - y,\ z$. [d] Imposed value of 1.395 Å.

was held constant at 1.08 Å. The H atoms of the methyl groups were refined as rigid groups, starting from the staggered positions. An overall isotropic thermal parameter was assigned to the H atoms: this refined to a value of $U = 0.12$ Å^2. The refinement converged to an R value of 0.052 ($R_w = 0.056$) for 1526 reflections and 161 parameters.

Atomic scattering factors were taken from ref 15 for Fe and from the SHELX system of programs for Cl, O, N, C, and H. An anomalous dispersion correction was applied. The final atomic coordinates for the non-hydrogen atoms of $Fe_2L(OC_2H_5)_2Cl_2$ and $Fe_2(acac)_4(OC_2H_5)_2$ are listed in Tables I and II, respectively. Thermal parameters, observed and calculated structure factors, as well as the calculated H positions for both compounds are available as supplementary material.

Results

Description of the Structures. The crystal structure of $Fe_2L(OC_2H_5)_2Cl_2$ is built of discrete dinuclear molecules. The molecule and labeling scheme are shown in Figure 1. Bond distances and angles are listed in Tables III and IV, respectively. The present complex is structurally very similar to the previously characterized[3] methoxy-bridged complex $Fe_2L(OCH_3)_2Cl_2$. In the dinuclear unit the Fe(III) ions are symmetrically bridged by two ethoxy groups. The crystallographic twofold rotation axis is perpendicular to the plane of the four-membered iron–oxygen ring. The geometry around the iron atoms is approximately octahedral. Three coordination sites are occupied by one oxygen and two nitrogens (cis) of the hexadentate L^{2-} ligand; the remaining three are occupied by the two bridging ethoxy groups and a terminal chlorine atom. The two iron atoms and the oxygen atoms of the two ethoxy groups roughly lie on a plane. The deviation of the iron atoms from the best bridging plane is 0.08 Å. The α-carbon atoms of the ethoxy groups are displaced from the bridging plane by 0.57 Å, on the opposite side of the iron atoms. The Fe_2O_2 ring is buckled, with a dihedral angle between the FeO(2)O(2)^a and Fe^{a}O(2)O(2)^a planes of 169°. Angles at oxygen and iron are 104.3 (1) and 75.0 (1)°, respectively. The Fe···Fe separation is 3.144 (1) Å. The average Fe–O(bridging) bond length is 1.991 Å. The conformation of the L^{2-} ligand is very similar to that observed in $Fe_2L(OCH_3)_2Cl_2$. The present more accurate determination of bond lengths and angles allows some comparisons to the structure of free LH_2.[16] Upon complex formation, apart from the change in conformation of the piperazine ring from the "chair" form in free LH_2 to the "boat" form in the complex, there is a shortening of the O–C(phenolic) bond distance (from 1.350 (4) to 1.322 (6) Å), while the C–N(azomethinic) bond length remains virtually unchanged (from 1.265 (4) to 1.269 (7) Å).

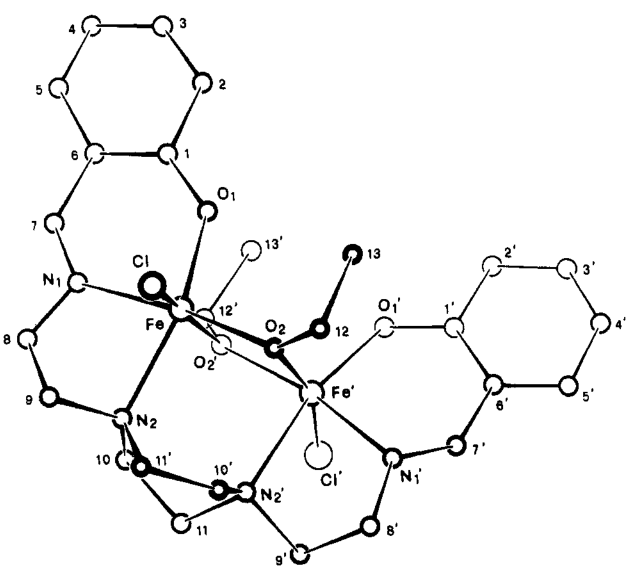

Figure 1. View of the dinuclear $Fe_2L(OC_2H_5)_2Cl_2$ molecule. Hydrogen atoms have been omitted for clarity.

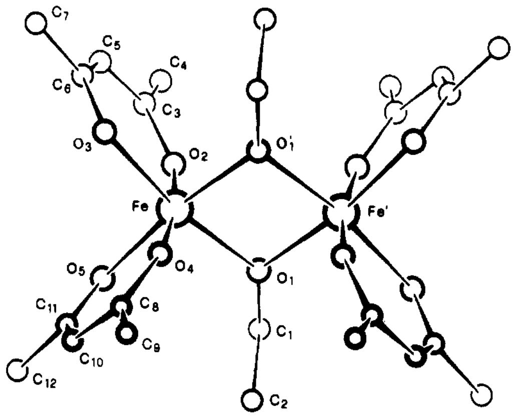

Figure 2. View of $Fe_2(acac)_4(OC_2H_5)_2$. Unlabeled atoms are related to labeled atoms by the inversion center.

The structure of $Fe_2(acac)_4(OC_2H_5)_2$ consists of bis(ethoxy)-bridged dimeric units that are well separated from one another. Structural information about this compound is reported in Figure 2 and Tables V and VI. The geometry about the iron atoms is approximately octahedral, the six coordination sites being occupied by two cis ethoxy groups and two cis,

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(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *38*, 331.

Table IV. Bond Angles (deg) in Complexes of the Type $Fe_2L(OR)_2Cl_2$

	R			R	
	C_2H_5[a]	CH_3[b]		C_2H_5	CH_3
O(1)-Fe-O(2)	102.2 (1)	98.4	C(6)-C(1)-C(2)	118.5 (5)	*d*
O(1)-Fe-O(2)[c]	95.1 (1)	96.8	C(1)-C(2)-C(3)	120.5 (6)	*d*
O(1)-Fe-Cl	95.2 (1)	95.8	C(2)-C(3)-C(4)	120.7 (6)	*d*
O(1)-Fe-N(1)	86.8 (2)	87.4	C(3)-C(4)-C(5)	119.2 (6)	*d*
O(1)-Fe-N(2)	162.4 (1)	163.5	C(4)-C(5)-C(6)	122.8 (6)	*d*
O(2)-Fe-O(2)[c]	75.0 (1)	76.6	C(5)-C(6)-C(1)	118.3 (5)	*d*
O(2)-Fe-Cl	93.4 (1)	96.1	C(5)-C(6)-C(7)	119.8 (5)	*d*
O(2)-Fe-N(1)	168.9 (2)	168.8	C(1)-C(6)-C(7)	121.9 (5)	*d*
O(2)-Fe-N(2)	94.9 (1)	96.7	C(6)-C(7)-N(1)	128.5 (5)	125
O(2)[c]-Fe-Cl	165.9 (1)	166.0	C(7)-N(1)-Fe	124.2 (4)	124
O(2)[c]-Fe-N(1)	98.0 (2)	93.9	C(7)-N(1)-C(8)	117.1 (5)	118
O(2)[c]-Fe-N(2)	85.1 (1)	82.8	C(8)-N(1)-Fe	117.9 (4)	120
Cl-Fe-N(1)	92.2 (1)	94.0	N(1)-C(8)-C(9)	107.6 (5)	107
Cl-Fe-N(2)	88.1 (1)	87.9	C(8)-C(9)-N(2)	110.9 (5)	109
N(1)-Fe-N(2)	75.8 (2)	76.3	C(9)-N(2)-Fe	101.7 (5)	102
Fe-O(2)-Fe[c]	104.3 (1)	103	C(10)-N(2)-C(11)[c]	109.8 (5)	110
Fe-O(2)-C(12)	128.1 (1)	126	C(10)-N(2)-Fe	114.3 (3)	113
Fe[c]-O(2)-C(12)	125.4 (1)	128	C(11)[c]-N(2)-Fe	114.6 (4)	113
O(2)-C(12)-C(13)	112.6 (2)		N(2)-C(10)-C(11)	111.6 (5)	112
Fe-O(1)-C(1)	135.1 (1)	130	N(2)-C(11)[c]-C(10)[c]	111.5 (5)	111
O(1)-C(1)-C(2)	119.3 (5)				
O(1)-C(1)-C(6)	122.2 (5)				

[a] This work. [b] Reference 3; mean values. [c] Symmetry code as in Table III. [d] Imposed value of 120°.

Table V. Bond Distances (Å) in $Fe_2(acac)_4(OC_2H_5)_2$

Fe-O(1)	1.979 (4)	C(3)-C(5)	1.389 (9)
Fe-O(2)	2.023 (4)	C(5)-C(6)	1.383 (8)
Fe-O(3)	1.996 (4)	C(6)-C(7)	1.481 (8)
Fe-O(4)	2.027 (4)	C(6)-O(3)	1.278 (7)
Fe-O(5)	1.998 (4)	O(4)-C(8)	1.257 (7)
Fe-O(1)[a]	1.985 (4)	C(8)-C(9)	1.508 (8)
O(1)-C(1)	1.427 (6)	C(8)-C(10)	1.395 (8)
C(1)-C(2)	1.517 (8)	C(10)-C(11)	1.400 (8)
O(2)-C(3)	1.264 (7)	C(11)-C(12)	1.508 (8)
C(3)-C(4)	1.501 (8)	C(11)-O(5)	1.271 (7)

[a] Symmetry code: $1 - x, -y, 1 - z$.

Table VI. Bond Angles (deg) in $Fe_2(acac)_4(OC_2H_5)_2$

O(1)-Fe-O(1)[a]	76.4 (2)	O(1)-C(1)-C(2)	111.1 (5)
O(1)-Fe-O(2)	91.0 (1)	Fe-O(2)-C(3)	128.9 (4)
O(1)-Fe-O(3)	168.9 (1)	O(2)-C(3)-C(4)	116.7 (5)
O(1)-Fe-O(4)	95.3 (2)	O(2)-C(3)-C(5)	123.9 (5)
O(1)-Fe-O(5)	94.8 (2)	C(4)-C(3)-C(5)	119.4 (6)
O(1)[a]-Fe-O(2)	96.0 (2)	C(3)-C(5)-C(6)	126.0 (6)
O(1)-Fe-O(3)	93.0 (2)	C(5)-C(6)-C(7)	120.4 (6)
O(1)-Fe-O(4)	91.9 (2)	C(5)-C(6)-O(3)	123.5 (5)
O(1)[a]-Fe-O(5)	171.0 (2)	C(7)-C(6)-O(3)	115.0 (6)
O(2)-Fe-O(3)	87.1 (2)	C(6)-O(3)-Fe	129.7 (4)
O(2)-Fe-O(4)	170.9 (2)	Fe-O(4)-C(8)	129.2 (4)
O(2)-Fe-O(5)	86.0 (2)	O(4)-C(8)-C(9)	116.1 (6)
O(3)-Fe-O(4)	88.0 (2)	O(4)-C(8)-C(10)	125.4 (5)
O(3)-Fe-O(5)	95.9 (2)	C(9)-C(8)-C(10)	118.4 (5)
O(4)-Fe-O(5)	86.9 (2)	C(8)-C(10)-C(11)	123.4 (5)
Fe-O(1)-Fe[a]	103.6 (3)	C(10)-C(11)-C(12)	119.6 (5)
Fe-O(1)-C(1)	126.8 (3)	C(10)-C(11)-O(5)	124.9 (5)
Fe[a]-O(1)-C(1)	127.8 (3)	C(12)-C(11)-O(5)	115.5 (5)

[a] Symmetry code as in Table V.

bidentate acac⁻ ligands. The average Fe–O(bridging) bond distance is 1.982 Å. The Fe···Fe separation is 3.116 (1) Å. Since the dimer lies on a crystallographic inversion center, the bridging Fe_2O_2 ring is perfectly planar. The FeOFe and OFeO bridging angles are 103.6 (3) and 76.4 (2)°, respectively. the α-carbon atoms of the ethoxy groups are displaced on opposite sides of the bridging plane by 0.29 Å. The two crystallographically independent acac⁻ ligands are virtually planar. The average C–O bond length is 1.268 Å (in the range 1.257 (7)–1.278 (4) Å); the mean C–C(methyl) distance is 1.500 Å (between 1.481 (8) and 1.508 (8) Å); the other C–C distances are in the range 1.383 (8)–1.400 (8) Å, averaging 1.392 Å.

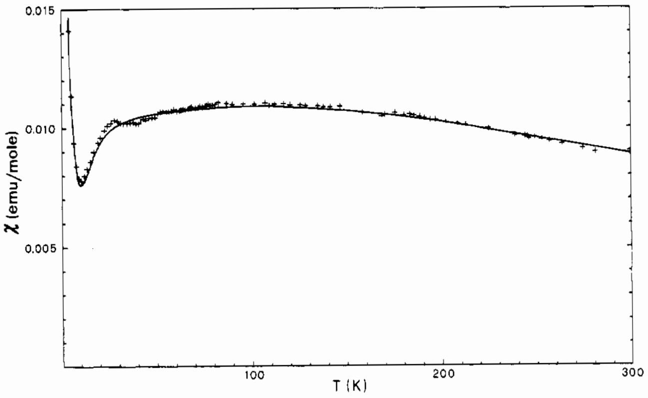

Figure 3. Temperature dependence of the magnetic susceptibility of $Fe_2L(OC_2H_5)_2Cl_2$. Experimental points are shown as crosses; the best fit is shown as the full line.

Magnetic Properties. Variable-temperature susceptibility data for $Fe_2L(OC_2H_5)_2Cl_2$ are given in Figure 3. With decreasing temperature, the μ_{eff} decreases from a value of 4.49 μ_B/iron at 281 K to a value of 0.62 μ_B/iron at 4.2 K. The dipolar coupling approach of Van Vleck with a perturbing Hamiltonian $-2J(\hat{S}_A \cdot \hat{S}_B)$ and $S_A = S_B = {}^5/_2$ was used to analyze the experimental susceptibility data. The magnetic susceptibility expression was

$$\chi_M \text{ (per iron)} = (N\beta^2 g^2/kT)\{[55 + 30 \exp(10x) + 14 \exp(18x) + 5 \exp(24x) + \exp(28x)]/[11 + 9 \exp(10x) + 7 \exp(18x) + 5 \exp(24x) + 3 \exp(28x) + \exp(30x)]\}(1 - p) + (35N\beta^2 g^2/12kT)p$$

where $x = -J/kT$. The parameter p gauges the amount of a possible magnetically dilute ferric impurity. Other symbols have their usual meaning. 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. The best fit to the data yielded $J = -15.40$ cm^{-1} and $p = 0.013$. The agreement factor F was 1.48 × 10^{-4} for 102 observations, and the estimated standard deviation of the J parameter from the last cycle of least squares was 0.10 cm^{-1}. The fit is illustrated in Figure 3.

Discussion

The exchange effect, purely orbital in nature, bears only a formal resemblance to a dipolar coupling between electron spins.[17] Although the exchange interaction in a multinuclear system can be represented by the Hamiltonian $H_{ex} = -2J(\hat{S}_A \cdot \hat{S}_B)$, it is conceivable that advances in our understanding of the mechanism by which the metal atoms interact in a cluster compound, and the factors that govern the magnitude and sign of the interaction, strongly depend on the development of orbital models appropriate to the exchange process and continued research efforts to obtain a greater number of experimental examples designed to verify these theoretical models.

Several discussions of aspects of orbital interactions in cluster compounds have recently appeared in the literature.[6,18-25] The MO formalism that, owing to simplicity and general applicability, appears to be more widely and successfully used for exchange-coupled transition-metal dimers is that developed by Hoffmann et al.[6]

It is of some interest to discuss the present experimental results in the framework of this theoretical model.

In Hoffmann's scheme, the exchange coupling constant of the Hamiltonian $H_{ex} = -2J(\hat{S}_A \cdot \hat{S}_B)$ is expressed as the sum of an antiferromagnetic term, J_{AF} (<0) and a ferromagnetic contribution J_F (>0):

$$J = J_F + J_{AF}$$

For a dinuclear Fe(III) complex with local octahedral environment about the metal ions and high-spin ($S_A = S_B = {}^5/_2$) ground states $(t_2)^3(e)^2$, one can write four (ϕ_1–ϕ_4) e-like MO's and six (ϕ_5–ϕ_{10}) t_2-like MO's; viz. from

$$\phi_1 \sim (xy)_A + (xy)_B \qquad \phi_2 \sim (xy)_A - (xy)_B$$

to

$$\phi_9 \sim (yz)_A + (yz)_B \qquad \phi_{10} \sim (yz)_A - (yz)_B$$

We assume a C_2 molecular symmetry (with the C_2 axis as the z axis and the x and y axes bisecting the OFeO and FeOFe angles, respectively), so that the two functions of a pair have different parity with respect to rotation. From these 10 orbitals one then forms orthogonalized localized orbitals on each center A and B; viz. from

$$(1/2^{1/2})(\phi_1 + \phi_2) = \phi_{a1} \sim (xy)_A$$
$$(1/2^{1/2})(\phi_1 - \phi_2) = \phi_{b1} \sim (xy)_B$$

to

$$(1/2^{1/2})(\phi_9 + \phi_{10}) = \phi_{a5} \sim (yz)_A$$
$$(1/2^{1/2})(\phi_9 - \phi_{10}) = \phi_{b5} \sim (yz)_B$$

Table VII. Structural Parameters for the Fe_2O_2 Bridging Units in $Fe_2L(OR)_2Cl_2$ ($R = CH_3, C_2H_5$) and $Fe_2(acac)_4(OC_2H_5)_2$

	Fe_2L-$(OCH_3)_2Cl_2$[a]	Fe_2L-$(OC_2H_5)_2Cl_2$[b]	$Fe_2(acac)_4$-$(OC_2H_5)_2$[b]
Fe···Fe, Å	3.106 (7)	3.144 (1)	3.116 (1)
O···O, Å	2.46 (2)	2.424 (6)	2.451 (6)
Fe–O, Å	1.98 (2)	1.977 (3)	1.979 (4)
	2.01 (2)	2.005 (3)	1.985 (4)
FeOFe, deg	103 (1)	104.3 (1)	103.6 (3)
OFeO, deg	76.6 (8)	75.0 (1)	76.4 (1)
D,[c] deg	168	168.5	180.0
δ,[d] Å	0.09	0.079	0.000
C,[e] Å	0.59[g]	0.57	0.29
θ,[b] deg	25.30	23.60	11.60
J, cm^{-1}	−16.30	−15.40	−11.0

[a] Data from ref 3. [b] This work. [c] Dihedral angle between the two FeO_2 planes. [d] δ = maximum deviation from the plane of the four-membered iron–oxygen ring. [e] C = distance of the carbon atom attached to the bridging oxygen from the plane of the iron–oxygen ring. [f] θ = dihedral angle between the bridging plane and the O–C vector of the bridging group. [g] The value of 0.70 originally given in ref 3 is slightly in error.

ϕ_{ai} contains both metal and ligand character but is largely a d orbital situated on metal A, and ϕ_{bi} is largely a d orbital on metal B. An analysis of the various terms in the exchange-coupling process leads to the following expressions for J_F and J_{AF}:

$$J_F = {}^1/_{25} \sum_{i \in A} \sum_{i \in B} K_{ij}$$

$$J_{AF} \sim -{}^1/_{25} \sum_{i=1}^{5} {}^1/_2 (2h_{ai,bi})^2 / (J_{ai,ai} - J_{ai,bi})$$
$$= -{}^1/_{25} \sum_{i=1}^{5} {}^1/_2 (\Delta_i)^2 / (J_{ai,ai} - J_{ai,bi}) \qquad (1)$$

where K_{ij} are exchange integrals, $J_{ai,ai}$ and $J_{ai,bi}$ are Coulomb integrals, h is the core operator, and Δ_i is the difference in energy between the symmetric and antisymmetric MO's of a distinct pair (ϕ_1,ϕ_2), (ϕ_3,ϕ_4), ... It is suggested that the K_{ij}, $J_{ai,ai}$, and $J_{ai,bi}$ terms are virtually constant in a series of chemically related compounds and that, therefore, changes in J with structure and substituents can be analyzed in terms of pairwise interactions of dimeric MO's. If it is assumed that the energies of the orbitals are proportional to overlap,[18] then a qualitative discussion of the effects of chemical and structural variations on J can be based on an examination of the effect of chemical and structural features on orbital overlap. Essentially, the overlap of the symmetric and antisymmetric combinations of the metal-based orbitals with those of the ligand bridge must be examined, where it may be expected that the oxygen 2p orbitals are the major participants in the interaction since they lie much higher in energy (−15.6 eV) than the 2s (−32.2 eV).[6]

Within this formalism, it has been shown for copper(II) systems,[6] but the argument can be easily extended to pairs of interacting chromium(III)[8] or iron(III) ions, that an increase in electron density at the bridging atoms should enhance the antiferromagnetic interaction. In agreement with this concept, magnetic–structural studies on alkoxide-bridged chromium(III) dimers have shown that a change from methoxide to ethoxide bridges, with no other structural change, brings about an increase in the magnitude of $2J$ from −8.53 to −17.88 cm^{-1}.[26] Also, a slightly larger extent of antiferromagnetic interaction ($J = -8.00$ cm^{-1}) was observed for $Fe_2L'(OCH_3)Cl_2$ (L^{3-} = anion of the heptadentate Schiff base trisalicylidenetriethylenetetramine) relative to that (−7.40 cm^{-1}) for the hydroxy analogue, with the two compounds

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(17) See, for example: Martin, R. L. In "New Pathways in Inorganic Chemistry"; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: New York, 1968; Chapter 9.

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having identical structures except for one bridging group.[2] It has also been pointed out that alkoxide-bridged copper(II) compounds usually exhibit more negative J values than those observed for analogous hydroxide-bridged compounds.[27,28]

The relative magnetic coupling observed for $Fe_2L(OC_2H_5)_2Cl_2$, $J = -15.40$ cm^{-1}, and $Fe_2L(OCH_3)_2Cl_2$, $J = -16.30$ cm^{-1},[3] does not conform to these patterns. The structures of both compounds consist of discrete and magnetically dilute dinuclear units. Examination of Tables III and IV reveals that the geometries of the inner coordination sphere and the L^{2-} ligand in both compounds are virtually identical in all respects. Structural parameters for the $Fe_2(OCH_3)_2$ and $Fe_2(OC_2H_5)_2$ bridging units are compared in Table VII. The only significant structural difference between the two bridging units appears to be the slightly larger Fe···Fe separation in the ethoxy (3.144 (1) Å) than in the methoxy compound (3.106 (7) Å). Both separations, however, are large enough to effectively preclude significant "direct" overlap of metal ion orbitals, on the basis of the ionic radius (0.65–0.79 Å) of high-spin, six-coordinate iron(III).[29] Even making allowance for the relative inaccuracy of the structural parameters pertaining to the methoxy compound, it appears reasonable to assume that the slightly less negative J value deduced for the ethoxy than for the methoxy compound reflects the different electron density at the bridge caused by the greater donating ability of ethyl relative to methyl, in contrast with the theoretical expectation.

A comparison of the structural and magnetic properties of $Fe_2L(OC_2H_5)_2Cl_2$ and $Fe_2(acac)_4(OC_2H_5)_2$ ($J = -11.0$ cm^{-1}),[9] both having $Fe_2(OC_2H_5)_2$ bridging units, is also of interest in regard to the question of the general applicability of Hoffmann's scheme. As can be seen from Table VII, the bridging unit in the acac$^-$ derivative differs from that in $Fe_2L(OC_2H_5)_2Cl_2$ in having (i) two shorter Fe–O bond distances, (ii) a strictly planar Fe_2O_2 ring, and (iii) a smaller angle between the O–C vector of the bridging group and the bridging plane. Let use consider each of these differences in turn. (i) Since the two compounds have the same bridging angle at oxygen, a decrease in the Fe–O bond distance is obviously expected to increase orbital overlap in all cases in which there is overlap. This should cause larger Δ_i in eq 1 and a stronger antiferromagnetic interaction, as actually found for pairs of interacting Cr(III)[7,8] or Cu(II)[30] ions. (ii) Charlot et al.[31] have shown for planar, bis(hydroxo)-bridged copper(II) dimers that, in agreement with simple overlap considerations, a decrease from 180° of the dihedral angle between CuO_2 planes in the bridge reduces the singlet–triplet splitting. A computer calculation of overlap integrals, with use of the atomic functions specified in ref 32 (iron) and 33 (oxygen), indicates that such a geometrical distorsion reduces the difference in orbital overlap between symmetric and antisymmetric combinations of the metal-based orbitals with those of the ligand bridge for each orbital pair in the d^5 case. (iii) To a first approximation, only metal-based molecular orbitals involving interactions with the out of plane p_z oxygen orbitals can be considered to examine the effect of the difference in the angle, θ, between the O–C vector of the bridging group and the bridging plane.[25,34,35] It has to be noted that, in the present case, θ is not an independent geometrical variable. Since the coordination of the bridging oxygens is equivalent in the two compounds (FeOFe angles of 104°, and angles of 127° between the Fe–O vectors and the O–C vectors), the value of the θ angle is related directly to the value of the dihedral angle, D, between the FeO_2 planes. When D decreases from 180°, θ increases and the overlap (antibonding in character) between the symmetric combination of d_{xz} and the antisymmetric combination of d_{yz} orbitals with the corresponding combinations of the oxygen p_z decrease, while the antisymmetric combination of d_{xz} and the symmetric combination of d_{yz} are essentially unaffected by variations in θ since they have no p_z character. An alternative, although strictly equivalent point of view, is in terms of hybrid orbitals. The larger θ value implies a larger angle between the oxygen lone pair orbital (with the assumption that three orthogonal 2s–2p hybrids pointing toward the two metal atoms and the ethyl group, the oxygen lone pair is described by an orthogonal hybrid forming an angle of 95° with the O–C direction, in the molecular yz plane) and the C_2 (z) axis and, hence, a less effective interaction with the d_{xz} and d_{yz} metal orbitals. It is concluded that J_{AF} should decrease as θ increases. Such a correlation has been actually noted for chromium(III) dimers[25,34-36] and has also been suggested for iron(III) dimers.[37] In the present case, the compound with larger θ has the more negative J value.

In summary, if it is assumed that J values are dominated by the bridging units (as is the case for oxygen-bridged copper(II)[30] or chromium(III)[7,8,25] dimers), all the observed structural differences between the $Fe_2(OC_2H_5)_2$ units of the acac$^-$ and L^{2-} derivatives lead to the expectation of a stronger antiferromagnetic coupling in the former compound, in contrast with the experimental findings.

The nature of the nonbridging ligands remains to be considered, and this factor is difficult to analyze with regard to the magnitude of the exchange coupling. On purely chemical grounds, since on going from the L^{2-} to the acac$^-$ derivative the inner coordination sphere changes from FeN_2ClO_3 to FeO_6 (without strong changes in the valence angles around the iron atoms) and oxygen is more electronegative than nitrogen and chlorine, one might guess a smaller electron density at the iron atoms of the acac$^-$ derivative, with a consequent smaller interelectronic repulsion, lower energy of the d orbitals, and more effective interaction with the bridging oxygens. The effect on magnetic coupling should be similar in nature to that caused by an increased electron density at the bridging atoms. Again, this might be expected to increase the antiferromagnetic interaction.

Conclusion

The data analysis for the present compounds illustrates the problem in attempting to describe the magnetic properties of Fe_2O_2 compounds in terms of qualitative molecular orbital theory. The problem is rendered difficult also by the rather small range of values of the exchange constant exhibited by these compounds (typical J values are -10 to -17 cm^{-1}).

A tentative explanation of the apparent inadequacy of the Hoffmann's formalism to account for the changes in small antiferromagnetic coupling observed for the compounds proposed herein brings into question the general validity of the assumption[6] that the ferromagnetic contribution to J, J_F (which is of positive sign), is small and not affected a great deal by structural distortions or substituent effects in a series of chemically related compounds. Actually, recent experimental and theoretical results[20,21,23,38] on d^1 bimetallic systems suggest

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that this contribution is geometry dependent and, in addition, may be important. Since the changes in J for the present compounds appear to be in the opposite direction of what would be expected upon consideration of the antiferromagnetic term only, it is possible that a description of the relative magnetic properties of Fe_2O_2 compounds requires an explicit consideration of both J_{AF} and J_F. Further work on additional members of this series of oxygen-bridged iron(III) compounds is in progress in order to elucidate this point.

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Registry No. $Fe_2L(OC_2H_5)_2Cl_2$, 91711-61-4; $Fe_2(acac)_4(OC_2H_5)_2$, 36107-36-5.

Supplementary Material Available: Listings of hydrogen atom coordinates, thermal parameters, and the observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Substituted Cysteamine Ligands and Their Complexes with Molybdenum(VI)

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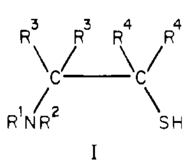
New bidentate cysteamine-based ligands containing CH_3-substituted carbon and nitrogen atoms have been synthesized. Together with known ligands the following complete set has now been prepared: $NH_2CH_2CH_2SH$, $CH_3NHCH_2CH_2SH$, $(CH_3)_2NCH_2CH_2SH$, $NH_2C(CH_3)_2CH_2SH$, $CH_3NHC(CH_3)_2CH_2SH$, $(CH_3)_2NC(CH_3)_2CH_2SH$, $NH_2CH_2C(CH_3)_2SH$, $CH_3NHCH_2C(CH_3)_2SH$, $(CH_3)_2NCH_2C(CH_3)_2SH$, $NH_2C(CH_3)_2C(CH_3)_2SH$, $CH_3NHC(CH_3)_2C(CH_3)_2SH$, and $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH$. Five of the ligands in this series are new, and their syntheses are reported in detail. Also $RNHCH_2C(CH_3)_2SH$ ligands with R = i-C_3H_7 and i-C_4H_9 are reported for the first time. These ligands, LH, were reacted in CH_3OH with $MoO_2(acac)_2$. In most cases the complex MoO_2L_2 resulted. However, in some cases this complex appears to be unstable. The syntheses and spectroscopic properties of the complexes are reported. The low values of ν(Mo–O) for some of the complexes are correlated either with H bonding or with the presence of a skew-trapezoidal-bipyramidal structure. Likewise electronic absorption spectra differ for complexes with octahedral as opposed to skew-trapezoidal-bipyramidal structures. For a given complex, ^{17}O and ^1H NMR spectroscopies are consistent with adoption in solution of the same octahedral or skew-trapezoidal-bipyramidal structure that is found in the solid state. Further, the skew-trapezoidal-bipyramidal complexes display temperature-dependent NMR spectra that are interpreted in terms of configurational averaging probably caused by Mo–N bond cleavage.

Introduction

Hexavalent molybdenum has been identified in several molybdoenzymes.[2-5] In sulfite oxidase,[6,7] xanthine oxidase,[8,9] and xanthine dehydrogenase,[10] structures containing oxo groups have been identified by EXAFS on the molybdenum absorption edge.[10] In addition to oxo, sulfur donors have been found[6-10] at distances commensurate with the presence of thiolate donors. Previous papers in this series[11-15] have reported Mo(VI) complexes of tri-[15] and tetradentate N,S donor ligands and have delineated attempts to structurally mimic the enzymic Mo site. Some of the complexes with tetradentate ligands show octahedrally based structures, with Mo–S and Mo–O distances quite similar to those found in sulfite oxidase.[11,13,14] However, in a preliminary paper[16] we reported that, with certain bidentate cysteamine-based ligands, unusual nonoctahedral complexes are obtained that have similar Mo–S and Mo–O distances. The accompanying paper[17] describes detailed structural studies of complexes in this class. This paper presents details of the preparation and spectroscopic characterization of a series of cysteamine-based ligands (I) and their Mo(VI) complexes.



I

Ligands based on cysteamine (I, $R^1 = R^2 = R^3 = R^4 = H$) have been well studied.[18,19] Kay and Mitchell[20] reported that

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