at a rate ($k = 1.6 \times 10^9$ sec^{-1} at 60°)[22] comparable with that of diffusion from the solvent cage. Our preliminary results support the existence of a noncage acyloxy or acetoxy radical.[5,23-27] Directly analogous to our findings, Janzen[5] showed that an acetoxy radical has a sufficient lifetime to undergo spin trapping *via* addition to α-phenyl-*N*-*tert*-butylnitrone. Our results indicate that the acetoxy radical survives long enough to abstract the phenolic hydrogen from I.

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Preparation, Electronic Properties, and Structure of a Binuclear Iron(III) Complex Containing a Four-Membered Iron–Oxygen Ring

Sir:

Recently there has been a considerable amount of interest in oxygen-bridged complexes of iron(III) because of the spin exchange that is possible in such systems. Structures have been reported for complexes which have a triangular arrangement of three metal ions around a central oxide ion,[1] a linear M–O–M arrangement,[2] and a four-membered iron–oxygen ring;[3] evidence for a four-membered iron–oxygen ring in a hydroxide complex has also been presented.[4] Recent studies[5-7] of complexes of the type CuL (where H_2L represents imines I and II) have prompted the authors to investigate similar complexes of other metal ions. The

Ia, $n = 2$
b, $n = 3$

IIa, $n = 2$
b, $n = 3$
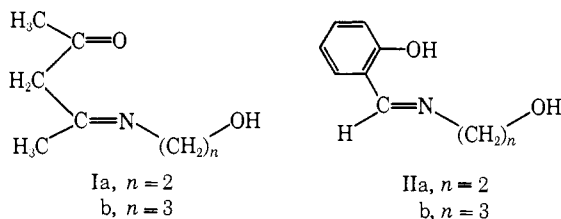
preparation of the iron(III) complex of IIa, FeLCl, was reported recently.[8]

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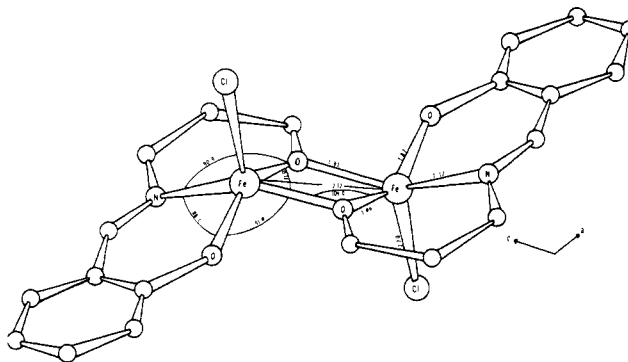(7) J. A. Bertrand, J. A. Kelley, and J. L. Breece, *ibid.*, **4**, 247 (1970).

Figure 1. Perspective drawing of the dimer with all atoms except carbons labeled. Bond distances and bond angles about iron are shown; estimated standard deviations are about 0.04 Å for bond lengths and about 1° for bond angles.

Herein, the preparation, structure, and properties of the iron(III) complex of IIb are described. This complex was prepared by mixing iron(III) chloride and the Schiff's base in methanol; the compound was recrystallized from tetrahydrofuran. The crystals are monoclinic [$a = 9.85$ (2),[9] $b = 14.86$ (2), $c = 9.39$ (2) Å, and $\beta = 124.25$ (10)°] of space group $P2_1/c$ (conditions for nonextinction: $0k0$, $k = 2n$; $h0l$, $l = 2n$) with two dimers per unit cell (density obsd, using carbon tetrachloride, 1.59 (2); calcd, 1.57).

Three-dimensional X-ray data were collected with a precession camera using Mo Kα radiation. A total of 418 unique, nonzero reflections from the hkl ($k = 0$–3) and hkl ($l = 0$–2) levels were obtained. Coordinates of the iron and chlorine atoms were obtained from successive calculations of the structure factors and electron density. With isotropic temperature factors (the largest temperature factor after refinement was 10.8) and with all reflections weighted at unity, the structure refined to a conventional R value of 0.12. Initially, only very small crystals were available for data collection; larger crystals have now been obtained and a more complete set of data will be collected for final refinement. However, the main features of the structure are apparent from the present refinement.

The dimer, which occupies a site of inversion symmetry, is shown in Figure 1. As in the copper complex of Ib,[5] the four-membered M–O ring is planar, the coordination of the bridging oxygen is planar (C_9 is only 0.08 Å out of the plane of the four-membered ring), and a delocalized π system is possible. The coordination of the iron can be described as square pyramidal—the three oxygens and the nitrogen form a planar base and the iron is 0.55 Å above this base.

The Mössbauer spectrum of this complex was measured at room and liquid nitrogen temperatures. The spectrum at each temperature, as the result of quadrupole splitting, consisted of two distinct lines. Table I presents the Mössbauer spectral parameters. The values for the quadrupole splitting, ΔE_Q, and the isomer shift, δ, are consistent with the formulation of the complex as one containing Fe(III) in the $S = \frac{5}{2}$ spin state and are similar to the Mössbauer parameters reported[10]

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Table I. Mössbauer Data

Temp, °K	ΔE_Q, mm/sec	δ,[a] mm/sec	Γ_1,[b] mm/sec	Γ_2,[b] mm/sec	Area[c] ratio	Peak height[c] ratio
RT[d]	1.00	0.33	0.311 ± 0.010	0.263 ± 0.009	1.13	1.34
78	1.03	0.44	0.266 ± 0.005	0.264 ± 0.005	1.03	1.04

[a] Relative to natural iron foil. [b] The error limits are the standard deviations as calculated from the variance of the line width. [c] Ratio of line with least shift to line with largest shift from zero velocity. [d] RT = room temperature.

for a five-coordinate mononuclear complex of iron with N,N'-ethylenebis(salicylideneiminate).[11] The most striking features of the Mössbauer spectrum are the distinct asymmetry exhibited by the two lines split by the quadrupole interaction at room temperature and the decrease in this asymmetry with decreasing temperature. It is apparent from Table I that although the temperature dependence is consistent with the Karyagin[12] asymmetry the line-width considerations are not. The line width for each line at 78°K is essentially the same, but at room temperature the line of most positive velocity is distinctly broadened. Thus, it would appear that the Karyagin effect cannot account for the asymmetry in the line widths at room temperature but may be responsible for the small asymmetry observed at 78°K. The observed asymmetry at room temperature could result from spin–spin relaxation effects.[13]

The magnetic susceptibility of the dimer was studied as a function of temperature; in Figure 2 the measured values of μ_{eff} are compared with values calculated[14]

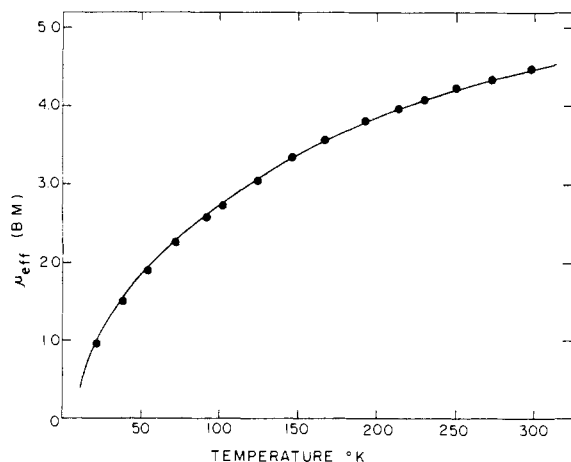Figure 2. Plot of μ_{eff} vs. temperature (●, experimental points; calculated for $J = -17$ cm^{-1}, $g = 2.00$, $N\alpha = 0$, and $S = {}^5/_2, {}^5/_2$).

assuming antiferromagnetic spin–spin exchange between two high-spin iron(III) ions. The experimental results are best fit with $g = 2.00$, $J = -17.0 \pm 0.6$ cm^{-1}, $N(\alpha) = 0$, and $S = {}^5/_2, {}^5/_2$; the experimental results are not consistent with the spin–spin interaction between two iron(III) ions of lower spin multiplicity.

For the oxygen-bridged iron(III) complexes for which magnetic data and X-ray data are available there appears to be a correlation between the extent of spin–spin interaction and the coordination of the bridging oxygen: for a complex with a linear two-coordinate

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oxygen[2], $J = -100$ cm^{-1};[10] for a complex with planar three-coordinate oxygens, $J = -17$ cm^{-1} for the complex reported in this paper; and $J = -7$ cm^{-1} [10] for a complex with pyramidal three-coordinate oxygens.[3] Hence, it would appear that the extent of spin–spin exchange can be related directly to the availability of π orbitals on the bridging oxygen.

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Catalysis of Aromatic Hydrogen–Deuterium Exchange by Metal Hydrides

Sir:

The exchange of hydrogen between water and aromatic hydrocarbons is catalyzed by strong acid,[1] by heterogeneous catalysts, and by a homogeneous system based on the $PtCl_4{}^{2-}$ ion.[2] In contrast, homogeneous catalytic exchange between gaseous hydrogen and a free aromatic hydrocarbon is unknown even though activation of o-H in aromatic phosphorus ligands is well established[3] for a number of transition metals. We now wish to report that the hydrides I–IV catalyze exchange between D_2 and benzene, probably by oxidative addition of the C–H bond to a coordinatively unsaturated intermediate.

$(\pi\text{-}C_5H_5)_2TaH_3$ L_2IrH_5
I   II, L = PhPEt$_2$
             III, L = Et$_3$P
             IV, L = Me$_3$P

Dicyclopentadienyltantalum trihydride (I),[4] like $(Ph_3P)_2ReH_7$, as reported earlier by Chatt and Coffey,[5]

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