Table I. Chemical Shifts of $4\text{-}CH_3C_5H_4NBCl_3\text{-}AlCl_3$ Mixtures

$AlCl_3/4\text{-}CH_3\text{-}C_5H_4NBCl_3$	Chemical shift[a] 2,6-H	3,5-H	CH_3
0	543	458	158
1.02	552	480	169
2.04	554	487	174
∞[b]	559 ± 2	498 ± 4	179 ± 1

[a] In Hz, at 60 MHz, relative to CH_2Cl_2 320 Hz downfield from tetramethylsilane. [b] Extrapolated.

$$4\text{-}CH_3C_5H_4NBCl_3 + Al_2Cl_6 \rightleftarrows 4\text{-}CH_3C_5H_4NBCl_2^+ + Al_2Cl_7^- \quad (1)$$

The ^{11}B resonance spectrum at 19.3 MHz is in agreement with this proposition. A 1:2 mixture of $4\text{-}CH_3\text{-}C_5H_4NBCl_3$ and $AlCl_3$, which is a mobile liquid at room temperature, gives an exceedingly broad resonance 1090 ± 80 Hz wide, narrowing to 600 Hz at 57°, and centered at -29.0 ± 4 ppm relative to external $B(OCH_3)_3$. The ^1H or ^{11}B spectra are unchanged after heating and standing for 2 weeks. The position of the chemical shift in this mixture is important when compared to the ^{11}B shift of the neutral adduct (+10.1 ppm),[5] a tetrahedral cation $(4\text{-}CH_3\text{-}C_5H_4N)[(CH_5)_3N]BCl_2^+$ (+9.5 ppm),[6] or BCl_3 (−28.2 ppm).[7] Following the correlations of Nöth[7] a large downfield shift indicates a coordination number of three for boron and is caused by a lack of shielding of the boron nucleus in a trigonal-planar configuration which is not compensated fully by internal π bonding. A shift further downfield than in BCl_3 would be expected on the basis of the net positive charge on the species,[4] but our data are not sufficiently precise to allow this distinction to be made.

The existence of the cation is further supported by the results of conductance measurements carried out on mixtures of 4-methylpyridine–trichloroborane (0.010 *M*) with varying amounts of aluminum trichloride in CH_2Cl_2. The data are presented in Figure 1 and show the increase of conductance expected from the equilibrium in eq 1. The conductance at high $AlCl_3$ concentration approaches the value for 0.010 *M* $(4\text{-}CH_3\text{-}C_5H_4N)[(CH_3)_3N]BCl_2^+PF_6^-$ [6] in the same solvent, 1.493×10^{-3} ohm^{-1} cm^{-1}. In comparison the solvent or $4\text{-}CH_3C_5H_4NBCl_3$ is a nonconductor, whereas 0.010 *M* $AlCl_3$ gives a conductance of 0.08×10^{-3} ohm^{-1} cm^{-1} which steadily increases with time while the solution darkens. No such change is observed when excess $4\text{-}CH_3C_5H_4BCl_3$ is also present. Extrapolation of the nearly linear portion of Figure 1 to the composition $4\text{-}CH_3C_5H_4NBCl_2^+ \ Al_2Cl_7^-$ gives a specific conductance of 1.5×10^{-3} ohm^{-1} cm^{-1} for a hypothetical 0.01 *M* solution of the salt in which eq 1 is completely displaced to the right. From the smoothed conductance curve we estimate $K = 20 \pm 3$, for the equilibrium in eq 1 (uncorrected for nonideal behavior). Chemical shifts for the pure cation can also be extrapolated with the help of the conductance data and are listed in Table I.

The chemical behavior of the system is also in accord with our contention. Solid $(CH_3)_4N^+Cl^-$ added to a mixture of $4\text{-}CH_3C_5H_4NBCl_3$ and $AlCl_3$ completely restores the nmr multiplet pattern of the neutral borane. Passage of excess $(CH_3)_3N$ into the solution results in the formation of $(4\text{-}CH_3C_5H_4N)[(CH_3)_5N]BCl_2^+$ which can be isolated as the PF_6^- salt in 30% yield after extracting the reaction mixture with water and precipitating with NH_4PF_6. The neutral adduct does not react with $(CH_3)_3N$ in the absence of $AlCl_3$ under otherwise the same conditions. The trimethylamine adduct of boron trichloride appears to be considerably less reactive toward $AlCl_3$ since the mixture shows only a partial collapse of the long-range B–H coupling even with excess $AlCl_3$. This difference in behavior would be expected if the planar cation I were stabilized by the interaction of the π-electron system of the ring with an empty p orbital on boron.

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(5) S. R. Eaton and W. H. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, Inc., New York, N. Y., 1969, p 474.

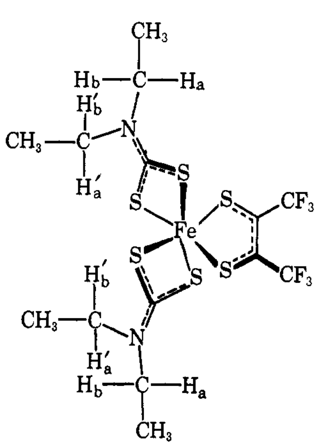
(6) W. J. Rademaker, Ph.D. Dissertation, University of Florida, 1969.

(7) H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966).

Complexes Containing the Fe–S_6 Core with Unusual Magnetic, Electrochemical, and Stereochemical Properties

Sir:

In the course of investigating oxidative addition reactions of iron(II) with ligating sulfur compounds we have observed that bis(N,N-diethyldithiocarbamato)iron(II),[1] $Fe(Et_2\text{-}dtc)_2$, and related complexes react smoothly with bis(perfluoromethyl)-1,2-dithietene[2] under anaerobic conditions in THF solution at 25° to afford a new series of Fe–S_6 complexes of general formulation $Fe(R_2\text{-}dtc)_2[(CF_3)_2C_2S_2]$. Those with R = Me, Et and R,R = $(CH_2)_{4,5}$ are representative and have been characterized by ^1H and ^{19}F nmr, infrared, and mass spectra, solution molecular weights, and elemental analyses. $Fe(Et_2\text{-}dtc)_2[(CF_3)_2C_2S_2]$ (**1**) has been examined in the greatest detail and manifests



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(1) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, **2**, 251 (1966).

(2) C. G. Krespan, *J. Amer. Chem. Soc.*, **83**, 3434 (1961).

Table I. Magnetic and Pmr Data for $Fe(R_2\text{-dtc})_2[(CF_3)_2C_2S_2]$

N substituent	μ_{eff} (BM) Solid,[a] 22°	μ_{eff} (BM) CH_2Cl_2,[b] 30°	^1H chemical shifts, ppm[c]
Me	1.27	1.27	−7.81 (50°); −7.46 (30°); −5.25, −5.68 (−75°)
Et[d] (**1**)	2.24	1.34	CH_2: −5.84, −7.60 (30°)
$CH_{2(\alpha)}(CH_2)_2CH_{2(\alpha)}$	1.13	1.50	$CH_{2(\alpha)}$: −12.70, −13.20 (30°)
$CH_{2(\alpha)}(CH_2)_3CH_{2(\alpha)}$	1.18	1.42	$CH_{2(\alpha)}$: −7.94, −9.81 (30°)

[a] Determined by the Faraday method. [b] Determined by the nmr method (D. F. Evans, *J. Chem. Soc.*, 2003 (1959)). [c] Measured at 100 MHz in CD_2Cl_2 solution, relative to TMS internal reference. [d] ^{19}F spectrum (30°): one signal at −16.83 ppm relative to $C_6H_5CF_3$ as an internal reference in toluene.

three properties not previously encountered in the *same* molecular species: (i) magnetic properties consistent with a spin-state equilibrium; (ii) reversible electrochemical reducibility; (iii) stereochemical mobility of a ligand structural portion and of the overall molecular configuration itself. Structure **1** has been confirmed by an X-ray study.[3]

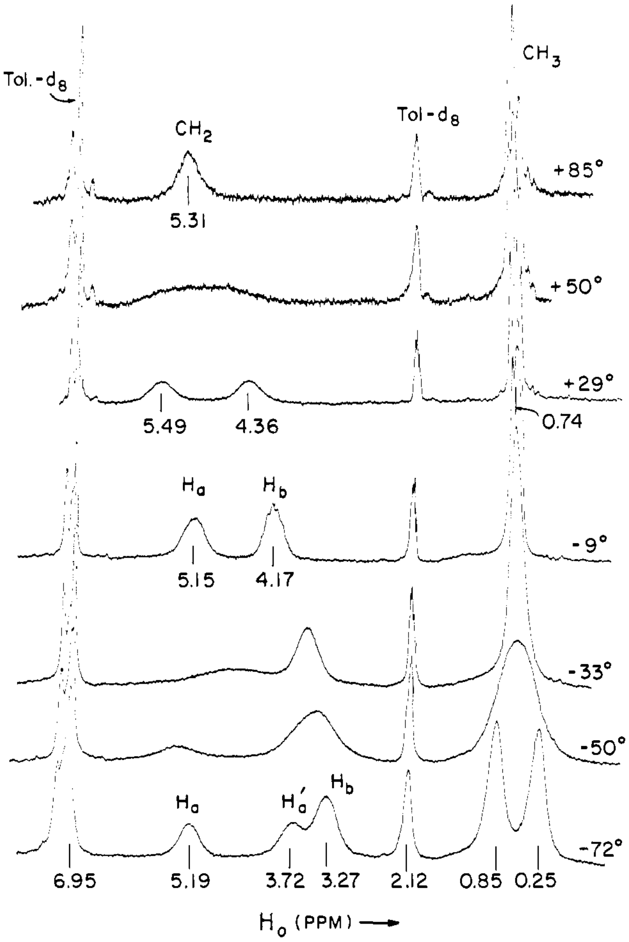

Figure 1. The 100-MHz pmr spectrum of $Fe(Et_2\text{-dtc})_2[(CF_3)_2C_2S_2]$ in toluene-d_8 at various temperatures. The designations H_a, H_a', and H_b are intended to convey only the diastereotopic nature of the methylene protons and not their positions in the frozen conformations as depicted in structure **1**.

The unusual magnetic properties characteristic of the series (Table I) reveal small but reproducible moments which are not due to paramagnetic iron(III) dithiocarbamate[4] or iron dithiolene[5] impurities. Spin equilibrium in solution is established by the following observations: reversible variation of the moment of **1** from 1.00 BM at −50° to 1.40 BM at +45° (dichloromethane); non-Curie chemical shift behavior superimposed upon chemical shift changes due to intramolecular rearrangements (*vide infra*). Shifts increase with increasing temperature in the slow- and fast-exchange regions (dichloromethane, toluene; *cf.* Figure 1) and at a given temperature those of comparable groups ($CH_{2(\alpha)}$) are consistent with measured magnetic moments (Table I). The X-band epr spectrum of powdered **1** (77°K, 100-kc modulation) is consistent with population of randomly oriented molecules in the triplet state; the half-field transition occurs at g = 4.315, and the center of the asymmetric high-field pattern is observed at $g \sim 2.130$.[6] These observations are in accord with a temperature-dependent population over a singlet ($S = 0$) ground state and a low-lying triplet ($S = 1$) excited state. Spin equilibria are well established for six-coordinate iron complexes,[7] *viz.*, $S = {}^1/_2 \rightleftharpoons {}^5/_2$ (Fe(III)[4,7]) and $S = 0 \rightleftharpoons 2$ (Fe(II)[7]), but the $S = 0 \rightleftharpoons S = 1$ equilibrium has not been previously observed with iron complexes of any type[8] and, among other complexes not undergoing simultaneous spin and structural changes, has been restricted to the dimeric Cu(II) alkanoates.[6b,9]

Polarographic studies of the complexes in acetonitrile solution reveal a reduction step near 0.0 V *vs.* sce, a second reduction at more negative potential, and a single oxidation. Complex **1** exhibits a one-electron reversible process at −0.048 V interpreted as reduction of the $FeS_2C_2(CF_3)_2$ portion and irreversible, apparently one-electron oxidation and reduction processes at +0.98 and −1.05 V, respectively.

The most thoroughly studied behavior of these complexes at the present time is their stereochemical mobility in solution. Complex **1** illustrates the types of behavior encountered; its pmr spectrum over the interval −72 to +85° in toluene-d_8 is shown in Figure 1. The indicated chemical shifts reveal the presence of isotropic (paramagnetic) contributions.[10] Structure **1**

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(3) W. D. Horrocks, Jr., and D. L. Johnston, unpublished results.

(4) A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).

(5) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

(6) (a) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964); (b) J. R. Wasson, C.-I. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968).

(7) R. L. Martin and A. H. White, *Transition Metal Chem.*, **4**, 113 (1968).

(8) Several six-coordinate iron complexes with an $S = 1$ ground state but not involved in a spin equilibrium have been characterized: E. König and K. Madeja, *J. Amer. Chem. Soc.*, **88**, 4529 (1966); J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *J. Chem. Soc.*, *A*, 816 (1968); E. J. Wharton and J. A. McCleverty, *ibid.*, 2258 (1969).

(9) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964); J. Lewis, F. E. Mabbs, L. K. Royston, and W. R. Smail, *J. Chem. Soc.*, *A*, 291 (1969), and references therein.

(10) These shifts may be compared with those of $Co(Et_2\text{-dtc})_3$ as a reasonable diamagnetic reference: CH_2, −3.74; CH_3, −1.28 ppm (30°) relative to TMS in $CDCl_3$.

conveys three key features: basically octahedral coordination about iron producing a chiral complex; partial double-bond character in the dithiocarbamate C–N bonds; the presence of methylene groups rendered diastereotopic by the chirality of the molecular configuration. At −9° the two diastereotopic methylene resonances H_a and H_b separated by 0.98 ppm are observed together with a single methyl triplet. With increasing temperature these signals undergo broadening and collapse to a single line, signifying increasingly rapid racemization of the complex. Indication that the averaging process is intramolecular follows from observations of the equilibrium

$$Fe(Et_2\text{-}dtc)_2[(CF_3)_2C_2S_2] + Fe(Me_2\text{-}dtc)_2[(CF_3)_2C_2S_2] \rightleftharpoons 2Fe(Et_2\text{-}dtc)(Me_2\text{-}dtc)[(CF_3)_2C_2S_2]$$

which is established immediately upon mixing. Ligand exchange is not observed under conditions where racemization of the R = Et complex is rapid. Decreasing the temperature below −9° results in broadening of both the methylene and methyl signals followed by a sharpening of these signals at −72°. At this temperature H_a has split into two signals (H_a and H_a') and the methyl resonance has separated into two well-defined peaks. These changes are entirely consistent with a slowing down and eventual freezing of rotation about the C–N bonds. Such frozen conformations will result in two nonequivalent methyl groups and four nonequivalent methylene protons; only three of the latter could be resolved. These stereochemical processes are reversible with temperature and are exhibited by the R,R = $(CH_2)_{4,5}$ complexes also. The ethyl and pentamethylene species show remarkable diastereotopic splittings of 1.76 and 1.87 ppm, respectively, in CD_2Cl_2 at 30°. The R = Me complex manifests only the restricted rotation process in its pmr spectrum since it lacks the diastereotopic protons required for detection of racemization. Approximate lifetimes for racemization and C–N bond rotation obtained from coalescence temperatures for **1** in CD_2Cl_2 solution are 1.3×10^{-3} (56°) and 3.9×10^{-3} sec (−60°).

The pmr work has produced two observations of some general importance. First, these results demonstrate the utility of diastereotopic groups in following racemization reactions of metal complexes, at least in those cases where isotropic interactions effect suitable chemical shift differences. Second, the direct observation of restricted rotation about C–N bonds of coordinated bidentate dithiocarbamates provides additional evidence for the contention founded on infrared data[11] and supported by structural determinations[3,11a,12] that such bonds generally have a multiplicity exceeding one, and proves that the activation energy for rotation is within convenient thermal range.

Further investigations of the structural and electronic properties of the group $M(R_2\text{-}dtc)_2[(CF_3)_2C_2S_2]^{0,-}$ and related complexes, and of restricted rotation about C–N bonds in dithiocarbamates are continuing, and the results will be reported in a subsequent publication.

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(11) (a) D. Coucouvanis, *Progr. Inorg. Chem.*, in press; (b) J. Chatt, L. A. Duncanson, and L. Venanzi, *Suomen Kemistilehti*, 75 (1956); F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 3, 1398 (1964).

(12) Tris(dithiocarbamato)metal(III) complexes: A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966); B. F. Hoskins and B. P. Kelly, *ibid.*, 1517 (1968); S. Merlino, *Acta Cryst.*, **B24**, 1441 (1968).

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(13) National Institutes of Health Postdoctoral Fellow, 1969–1970.

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Quenching of Alkyl Ketone Fluorescence by 1,3-Dienes

Sir:

A commonly used technique[1-8] for detecting the involvement of the triplet state in a photochemical reaction of a carbonyl compound is the quenching of the reaction by 1,3-dienes. In particular 1,3-pentadiene has been extensively used in this manner. The diolefin is presumed to accept energy from the triplet state of a given donor excited molecule but not from the donor's excited singlet state.[2] The reduction in the overall quantum yield (ϕ) for the reaction at high diolefin concentration (~10 *M*) is taken as a measure of the quantum yield from the triplet state, $\phi_T{}^0$, while the unaffected portion of ϕ is equated to the quantum yield from the singlet state, $\phi_S{}^0$; thus, if all the reaction is quenched at high diolefin concentration, the reaction is assumed to arise only from the donor's triplet state. In addition, Stern–Volmer plots of the quenching of a reaction by diolefins are used to evaluate the reaction rate constants from the triplet state. Slopes of these plots have been found to vary from rather large values to very small values, and, correspondingly, the lifetimes of the triplet state involved are concluded to be either long ($\sim 10^{-6}$ sec) or very short ($\sim 10^{-10}$ sec), as a result of the Stern–Volmer analysis.

If singlet energy transfer (or chemical reaction) between the molecule under study and the diolefin occurs, the conclusions of studies such as those described above are obviously open to question.

We wish to report that the fluorescence of 2-pentanone, norcamphor, *t*-butyl methyl ketone, and acetone is quenched by 1,3-pentadiene at high pentadiene concentrations, indicating that the singlet state of the carbonyl is affected by the diolefin. As a result, accurate measurements of the relative singlet–triplet quantum yields for reactions of alkyl ketones should not be made by the above-mentioned technique without corrections for singlet quenching. In addition, the quenching of a photoreaction of an alkyl ketone by high concentrations of diolefin should no longer be considered sufficient evidence to assign the reaction to an excited triplet state. This, unfortunately, makes the problem of distinguishing between very rapid triplet reactions and singlet reactions of alkyl ketones considerably more difficult. Furthermore, care must be taken in the use of triplet-sensitized *cis–trans* isomerization of diolefins,[9] such as

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(1) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, 83, 2396 (1961).

(2) P. J. Wagner and G. S. Hammond, *ibid.*, 87, 4009 (1965); (b) *ibid.*, 88, 1245 (1966).

(3) D. R. Coulson and N. C. Yang, *ibid.*, 88, 4511 (1966).

(4) N. C. Yang and E. D. Feit, *ibid.*, 90, 504 (1968).

(5) F. S. Wettack and W. A. Noyes, Jr., *ibid.*, 90, 3901 (1968).

(6) J. A. Barltrop and J. D. Coyle, *Tetrahedron Lett.*, 3235 (1968).

(7) C. H. Bibart, M. G. Rockley, and F. S. Wettack, *J. Amer. Chem. Soc.*, 91, 2802 (1969).

(8) P. J. Wagner, *ibid.*, 89, 2503 (1967).