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Synthesis and Stereochemistry of Bis(*N*,*N*-disubstituted-dithiocarbamato)maleonitriledithioleneiron Complexes

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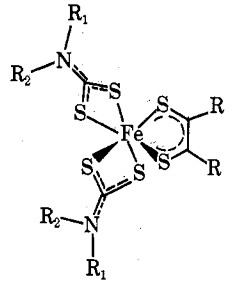
Synthesis of the title complexes $Fe(R_1,R_2dtc)_2mnt$ (dtc = *N*,*N*-disubstituted-dithiocarbamate where R_1,R_2 = Et,Et or Me,Ph and mnt = maleonitriledithiolene) was achieved by reaction of $Fe(R_1R_2dtc)_2$ with disodium maleonitriledithiolate followed by successive oxidation of the resultant dianions with air and copper(II) in acetonitrile. The magnetic moments of both complexes in the solid and solution phases are indicative of a singlet–triplet spin equilibrium with a higher population of the triplet state than previously found for analogous tfd species (tfd = trifluoromethyldithiolene). In dichloromethane solutions below *ca.* −80° both complexes exhibit maximum multiplicity of methylene and/or methyl pmr signals required by a chiral molecular configuration and slow carbon–nitrogen bond rotation. Both complexes are stereochemically nonrigid and display two distinct kinetic processes in their variable-temperature pmr spectra. That occurring at lower temperatures has been identified as inversion, the likely mechanism of which is a twist about the pseudo-threefold axis of the complex. The higher temperature process has been assigned to C–N bond rotation. The kinetic behavior of these complexes is quite similar to that of corresponding tfd complexes studied earlier. The higher triplet-state population found with $Fe(Et_2dtc)_2$-mnt appears to produce a small increase in inversion rate at −50° compared to that of $Fe(Et_2dtc)_2tfd$. Thermodynamic activation parameters for inversion of the two complexes do not differ within experimental uncertainty.

Introduction

Recently we reported the synthesis and stereochemical investigation[3,4] of the unusual complexes bis(*N*,*N*-disubstituted-dithiocarbamato)-1,2-bis(perfluoromethyldithiolene)iron, $Fe(R_1R_2dtc)_2tfd$ (**1**, R = CF_3).



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Compounds with R_1,R_2 = Me,Me; Et,Et; Me,Ph; $(CH_2)_4$; $(CH_2)_5$ display three properties not previously encountered in the same molecular species: (i) magnetic behavior consistent with a singlet–triplet spin equilibrium in the solid and solution phases; (ii) redox properties indicative of a three-membered electron transfer series; (iii) stereochemical nonrigidity of a ligand structural portion (restricted rotation about S_2C–N bonds) and of the overall molecular configuration itself (inversion). The detection of the latter two processes by nmr is facilitated by large chemical shifts due to isotropic magnetic interactions[5] arising in the triplet state. The primary mechanism of inversion below *ca.* −10° in the Me,Ph complex was deduced from variable-temperature nmr studies to be, in effect, a twist motion about the pseudo-threefold rotation axis (p-C_3) presumably involving a (distorted) trigonal-prismatic (TP) transition state.[4] A possible rationale for this mechanism derives from the structure of the crystalline diethyl analog. X-Ray results have shown that the Fe–S_6 coordination unit assumes a stereochemistry intermediate between idealized octahedral and TP geometry.[6]

In the present work the synthesis and dynamic stereochemistry of several bis(*N*,*N*-disubstituted-dithiocarbamato)maleonitriledithioleneiron complexes, $Fe(R_1R_2dtc)_2mnt$ (**1**, R = CN; R_1,R_2 = Et,Et, Me,Ph) are reported. This investigation was undertaken in order to assess the effect of replacing the tfd ligand with mnt on properties (i)–(iii). The comparative chemistry of bis- and tris-chelate complexes of these two ligands[7] indicates that the latter has a somewhat higher electron affinity and might be expected to confer measurable differences on certain electronic properties relative to those of its tfd analogs. A future report[8] will describe the magnetic, redox, and associated properties of the tfd and mnt groups of complexes.

Experimental Section

Preparation of Compounds. (a) $(Et_4N)[Fe(Et_2dtc)_2mnt]$. —All operations were performed under a nitrogen atmosphere. A suspension of freshly prepared bis(*N*,*N*-diethyldithiocarbamato)iron(II)[4,9] (2.80 g, 10 mmol) was prepared in a thoroughly degassed solution of methanol (200 ml) and 2,2′-dimethoxypropane (20 ml). This suspension was treated with a degassed solution of disodium maleonitriledithiolate[10] (1.86 g, 10 mmol) and 2,2′-dimethoxypropane (2 ml) in methanol (50 ml), resulting in a brown solution. The reaction mixture was briefly exposed to air, causing a change to a blood red color, and filtered into a solution of 6.3 g (30 mmol) of tetraethylammonium bromide and 2 ml of 2,2′-dimethoxypropane in 30 ml of methanol. The crystalline product which formed was collected by filtration and recrystallized from dry dichloromethane–methanol (1:5 v/v). The red-black crystals which separated upon slow evaporation under reduced pressure were filtered, washed with cold methanol, and dried *in vacuo*. A total of 3.3 g (53%) of pure product was obtained; mp 128–130°. *Anal.* Calcd for $C_{22}H_{40}N_5S_6Fe$: C, 42.43; H, 6.47; N, 11.24. Found: C, 42.23; H, 6.48; N, 10.90. Principal infrared bands (mull): 2175 (m, C≡N), 1490 (s, C—N), 1450 (m),

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TABLE I

SPIN-STATE POPULATIONS AND KINETIC DATA FOR REARRANGEMENT REACTIONS OF $\mathrm{Fe(R_1R_2dtc)_2(S_2C_2R_2)}$ COMPLEXES IN $\mathrm{CD_2Cl_2}$ SOLUTION

R[a]	R_1,R_2	N_t[b]	Process[c]	k^T, sec^{-1} (°C)	$\Delta F^{\ddagger}{}_T$,[d] kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
CF_3	Me,Me	0.16	I	1.89×10^2 (−50)	10.6 ± 0.2	9.2 ± 0.9	-6.1 ± 3.9
CF_3	Et,Et	0.22	I	7.85×10^2 (−50)	10.0 ± 0.2	8.3 ± 0.6	-7.5 ± 3.7
CN	Et,Et	0.75	I	3.11×10^3 (−50)	9.4 ± 0.2	8.6 ± 1.5	-3.4 ± 5.0
CF_3	Me,Ph	~0.10	R	1.29×10^2 (25)	14.9 ± 0.2	14.0 ± 2.1	-3.0 ± 7.8
CF_3	Et,Et	0.22	R	4.11×10^1 (25)	15.2 ± 0.2	16.4 ± 1.5	4.1 ± 4.5
CF_3	$(CH_2)_5$	0.25	R	4.38×10^1 (25)	15.2 ± 0.2	16.6 ± 2.4	4.7 ± 7.5
CN	Et,Et	0.75	R	2.30×10^1 (25)	14.1 ± 0.2	12.5 ± 2.0	-5.5 ± 6.0

[a] Kinetic parameters for CF_3 complexes from ref 4. [b] Estimated values (see text) in CH_2Cl_2 solution at ~30°. [c] I = inversion, R = $N-CS_2$ bond rotation. [d] Calculated from k^T at T°C using the relation $k^T = (k_BT/h)\exp(-\Delta F^{\ddagger}/RT)$.

1430 (m), 1275 (s), 1215 (m), 1075 (m), 995 (m), 855 (m), 780 cm^{-1} (m). μ_{eff}(solid, 24°) = 2.07 BM.

An alternative synthesis of $[\mathrm{Fe(Et_2dtc)_2mnt}]^-$, involving reaction of $\mathrm{Fe(Et_2dtc)_2Cl}$ and $\mathrm{Na_2mnt}$, appeared during the course of this work. The ion was isolated as its tetraphenylphosphonium salt.[11]

(b) **$\mathrm{Fe(Et_2dtc)_2mnt}$.**—A solution of 1.81 g (5.53 mmol) of tetrakis(acetonitrile)copper(II) tetrafluoroborate[12] in 30 ml of acetonitrile was added to a solution of $(\mathrm{Et_4N})[\mathrm{Fe(Et_2dtc)_2mnt}]$ (3.44 g, 5.53 mmol) in 50 ml of acetonitrile at 0°. The volume was reduced by one-half under reduced pressure, 40 ml of toluene added, and the solution filtered. This procedure was repeated with the filtrate, until a clear brown solution resulted. Upon addition of 40 ml of *n*-heptane and cooling, shiny black crystals separated. These were collected by filtration and recrystallized from a dichloromethane–toluene–heptane mixture (3:5:5 v/v), affording 830 mg (30%) of black needles, mp 148–149°. *Anal.* Calcd for $\mathrm{C_{14}H_{20}N_4S_6Fe}$: C, 34.14; H, 4.09; N, 11.37; S, 39.05. Found: C, 34.14; H, 4.10; N, 11.23; S, 39.18. Principal infrared bands (mull): 2200 (m, C≡N), 1510 (s, C—N), 1450 (m), 1435 (m), 1285 (s), 1205 (m), 1155 (m), 1080 (m), 495 cm^{-1} (m). Electronic spectrum ($\mathrm{CHCl_3}$) ($\lambda_{\max}$, cm^{-1} (ϵ)): 11,600 (610); 16,200 (sh, 750); 21,300 (sh, 2800); 27,600 (12,200); 38,200 (32,200). μ_{eff} (24°): 2.43 BM (solid), 2.46 BM ($\mathrm{CH_2Cl_2}$ solution).

(c) **Fe(Me,Phdtc)$_2$mnt.**—A methanol suspension of bis(*N*-methyl-*N*-phenyldithiocarbamato)iron(II) was treated as in preparation (a) and the crude tetraphenylarsonium salt isolated as a brown microcrystalline powder, mp 133–140°. This material was not purified and was oxidized as in preparation (b) to the analogous neutral complex. Purification was effected by crystallization from a slowly evaporating dichloromethane–heptane solution to yield a black crystalline product, mp 137–140°. *Anal.* Calcd for $\mathrm{C_{20}H_{16}N_4S_6Fe}$: C, 42.85; H, 2.88; N, 9.46. Found: C, 42.69; H, 2.77; N, 9.03. μ_{eff}($\mathrm{CH_2Cl_2}$ solution, 24°) = 1.80 BM.

Nmr Measurements.—Spectra were recorded on a Varian XL-100 or A-60-D spectrometer equipped with a variable-temperature probe. Chemical shifts were measured relative to TMS internal standard and temperatures were monitored by a thermocouple mounted in an nmr tube. The XL-100 spectrometer was operated in the ^{2}H locked mode using $\mathrm{CD_2Cl_2}$ as the internal lock signal. All spectra were recorded using $\mathrm{CD_2Cl_2}$ as solvent with complex concentrations of *ca.* 0.1 *M*.

Magnetic Measurements.—Solution moments were determined by the usual nmr method using dichloromethane solutions 5% v/v in TMS. Susceptibilities were obtained using the TMS shifts. Magnetic moments in the solid state were measured by the Faraday method.

Kinetic Analysis.—As is evident from Figure 1 $\mathrm{Fe(Et_2dtc)_2mnt}$ exhibits two distinct kinetic processes in its nmr spectrum, a low-temperature process (LTP) and a high-temperature process (HTP). Based on considerations described in the text, the LTP and HTP are assigned as inversion of the molecular configuration and rotation about the $\mathrm{N-CS_2}$ bond, respectively. In the LTP exchange broadening of the resonances of the nonequivalent methyl groups was monitored between −80 and −20°. In the HTP exchange broadening of the two methylene resonances was followed from 30 to 80°. Both processes involve two-site exchange and their kinetic parameters, given in Table I, were determined by a total line shape analysis. A computer simulation of line shapes was employed based on the Gutowsky–Holm equation[13] for two-site exchange. Calculated and experimental spectra were compared and best fits selected visually. The calculation for two-site exchange requires chemical shift differences between exchanging environments A and B, $\Delta\nu$, and the peak width at half-height for A or B, $H_{1/2}$. These parameters were determined in the exchange-broadened region by linear extrapolations of least-squares plots of $\Delta\nu$ *vs.* $1/T$ and $\ln H_{1/2}$ *vs.* $1/T$ using data measured under conditions of slow exchange. Shift differences and line widths[14] used in the kinetic analysis are summarized by the following slopes and intercepts for the indicated plots: $\Delta\nu$ (ppm) *vs.* $1/T$ (°K^{-1}): 7.65×10^2, −0.99 (LTP); 2.48×10^2, 1.52 (HTP); $\ln H_{1/2}$ (ln Hz) *vs.* $1/T$: 1.83×10^2, 0.14 (LTP); 43.4, 1.4 (HTP). The methyl signals (LTP) are partially resolved triplets (J = 7.1 Hz) and the exchange problem was treated as three two-site exchanges superimposed in one spectrum. Illustrated in Figures 1 and 2 are representative spectra used in the kinetic analysis.[15]

The lifetime of a proton in environment A or B is defined as τ (sec) (τ as defined here is equal to 2τ as used in the Gutowsky–Holm equation), so the rate constant for exchange (sec^{-1}) is $1/\tau = k$. Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined by least-squares fits to $\ln k/T$ *vs.* $1/T$ plots (Figure 3). Errors were assessed from error limits on τ, temperature, and standard deviation in least-squares fits. Rate constants and $\Delta F^{\ddagger}$ values are reported in the temperature region of exchange broadening and therefore manifest significantly smaller errors.[16]

Results and Discussion

Synthesis and Magnetic Properties.—The two $\mathrm{Fe(R_1R_2dtc)_2mnt}$ neutral complexes prepared in this work were obtained by the following reaction sequence. The initially formed dianions were not isolated but were

$$\begin{tikzcd}
\mathrm{Fe(R_1R_2dtc)_2} + \mathrm{mnt}^{2-} \arrow[r] & {[\mathrm{Fe(R_1R_2dtc)_2mnt}]^{2-}} \arrow[d, "\mathrm{O_2}"] \\
\mathrm{Fe(R_1R_2dtc)_2mnt} & {[\mathrm{Fe(R_1R_2dtc)_2mnt}]^{-}} \arrow[l, "\mathrm{Cu(II)-CH_3CN}"']
\end{tikzcd}$$

directly converted by aerial oxidation[17] to the monoanions. In the case of R_1,R_2 = Et,Et this spin-doublet species was isolated as a crystalline tetraethylammonium salt. The monoanions were oxidized to the neutral complexes by reaction with copper(II) in acetonitrile, which has previously been shown to be a strong one-electron oxidant.[18]

Both $\mathrm{Fe(Et_2dtc)_2mnt}$ and Fe(Me,Phdtc)$_2$mnt possess solution magnetic moments consistent with a singlet–triplet spin equilibrium. However, the magnetic behavior of the diethyl complex is not strictly comparable

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[11] J. A. McCleverty, D. G. Orchard, and K. Smith, *J. Chem. Soc. A*, 707 (1971).

[12] B. J. Hathaway, D. G. Holah, and A. E. Underhill, *ibid.*, 2444 (1962).

[13] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[14] Fast-exchange $H_{1/2}$ values were also used.

[15] Original data and more complete details on the kinetic analysis may be obtained from L. H. P.

[16] G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

[17] The ease of oxidation of dianion to monoanion is indicated by the half-wave potential of −0.70 V in acetonitrile *vs.* sce.

[18] B. Kratochvil, D. A. Zatko, and R. Markuszewski, *Anal. Chem.*, **38**, 770 (1966), and references therein.

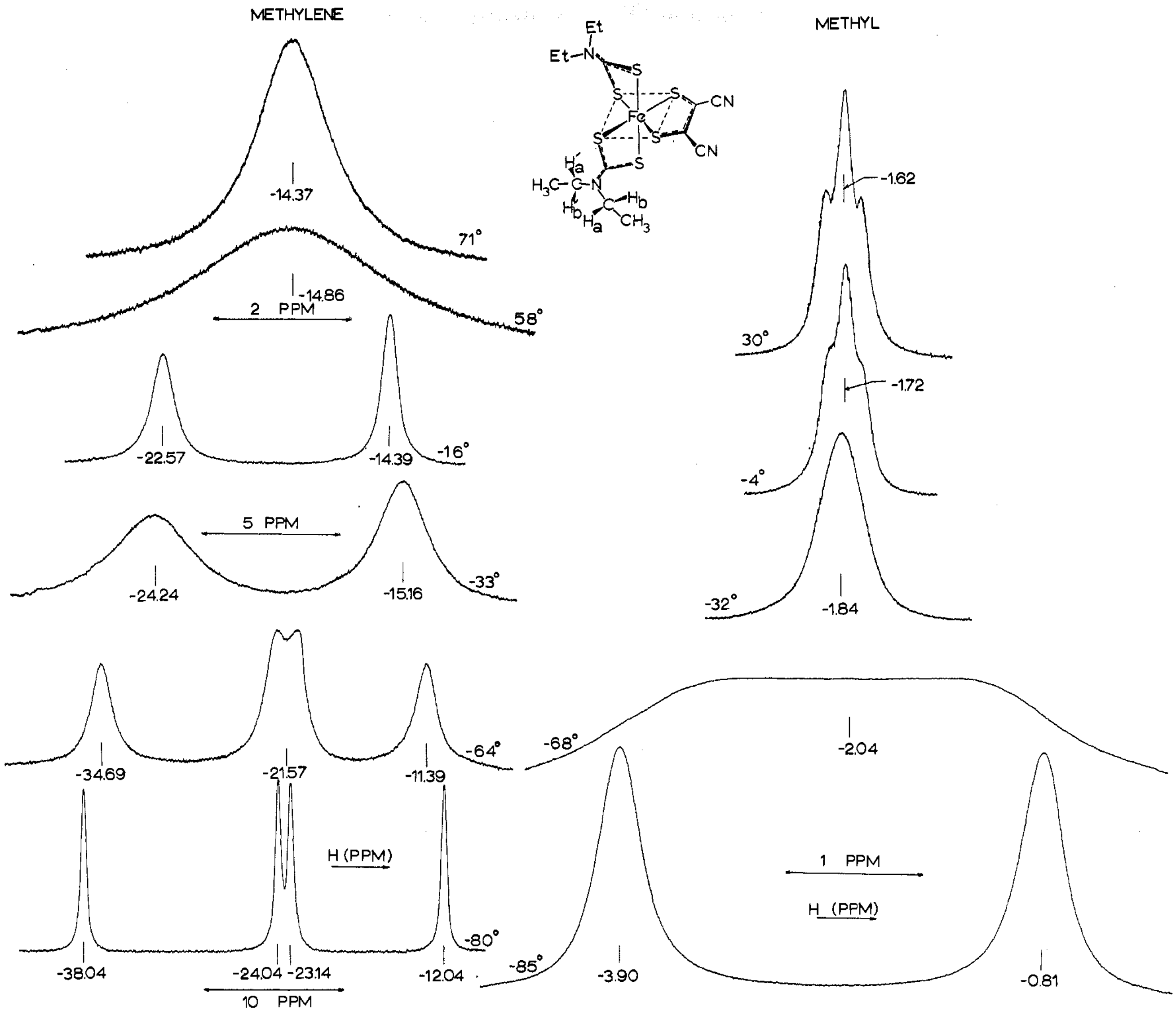

Figure 1.—Temperature dependence of the 100-MHz pmr spectrum of $Fe(Et_2dtc)_2mnt$ in CD_2Cl_2 solution. Sweep widths vary and are indicated below each series of spectra. Chemical shifts are downfield of TMS reference.

to that of its tfd analog.[4] Its magnetic moment is not sensitive to phase, being essentially the same in dichloromethane solution (2.46 BM) and in the solid state (2.43 BM) at ambient temperature. Further, the moment in solution shows a Curie behavior over the temperature interval of −50 to +40° with a least-squares intercept of $(-50 \pm 60) \times 10^{-6}$ cgsu/mol from a χ_M^{cor} *vs.* T^{-1} plot. In contrast, the tfd analog exhibits an increase of 1.0 to 1.4 BM from −50 to +45° in the same solvent. The behavior of the mnt complex follows only if its singlet–triplet separation is small compared to kT, requiring a mole fraction of triplet molecules (N_t) of *ca.* 0.75[19] in the temperature range of observation. Using this value a moment of 2.85 BM[20] at 25° is calculated for the triplet state of mnt complexes. Given in Table I are estimated values of N_t for mnt and tfd complexes assuming μ_t = 2.85 BM. By the same procedure N_t for $Fe(Me,Phdtc)_2mnt$ is estimated as 0.36. It is observed that the mnt ligand effects a greater stabilization of the triplet state. The presence of the spin-state equilibrium for tfd and mnt complexes indicates that their gross molecular geometries are similar. An X-ray study[6] of $Fe(Et_2dtc)_2tfd$ has shown that the molecule is chiral (crystallographic C_2 symmetry) and that the C–N bonds of the dithiocarbamato groups possess a significant degree of double-bond character. The latter property is quite general in dithiocarbamato complexes[22] and gives rise to restricted bond rotation observed by nmr in such species[23] as well as in dithiocarbamate esters.[24] The two structural features provide plausible sources of the two sorts of stereochemical nonrigidity manifested in the

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[19] This situation is approached with $Fe(Et_2dtc)_2tfd$ in the solid state above about 50°, under which conditions the magnetic moment approximates Curie behavior with a value of ~2.3 BM. Magnetic properties of tfd and mnt complexes will be described in detail in a subsequent report.[8]

[20] This result is close to the spin-only moment of 2.83 BM and is comparable to the moments of the only other spin-triplet $Fe-S_6$ complexes reported ($[Fe(mnt)_3]^{2-}$, 2.99 BM;[21] $[Fe(S_2C{=}C(CN)_2)(mnt)_2]^{2-}$, 2.85 BM[11]).

[21] J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *J. Chem. Soc. A*, 816 (1968).

[22] D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970); R. H. Holm and M. J. O'Connor, *ibid.*, **14**, 241 (1971).

[23] B. F. G. Johnson and K. H. Al-Obaidi, *Chem. Commun.*, 876 (1968); B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc. A*, 1668 (1969); D. C. Pantaleo and R. C. Johnson, *Inorg. Chem.*, **9**, 1248 (1970); H. C. Brinkhoff, A. M. Grotens, and J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, **89**, 11 (1970).

[24] C. E. Holloway and C. H. Gitlitz, *Can. J. Chem.*, **45**, 2659 (1967).

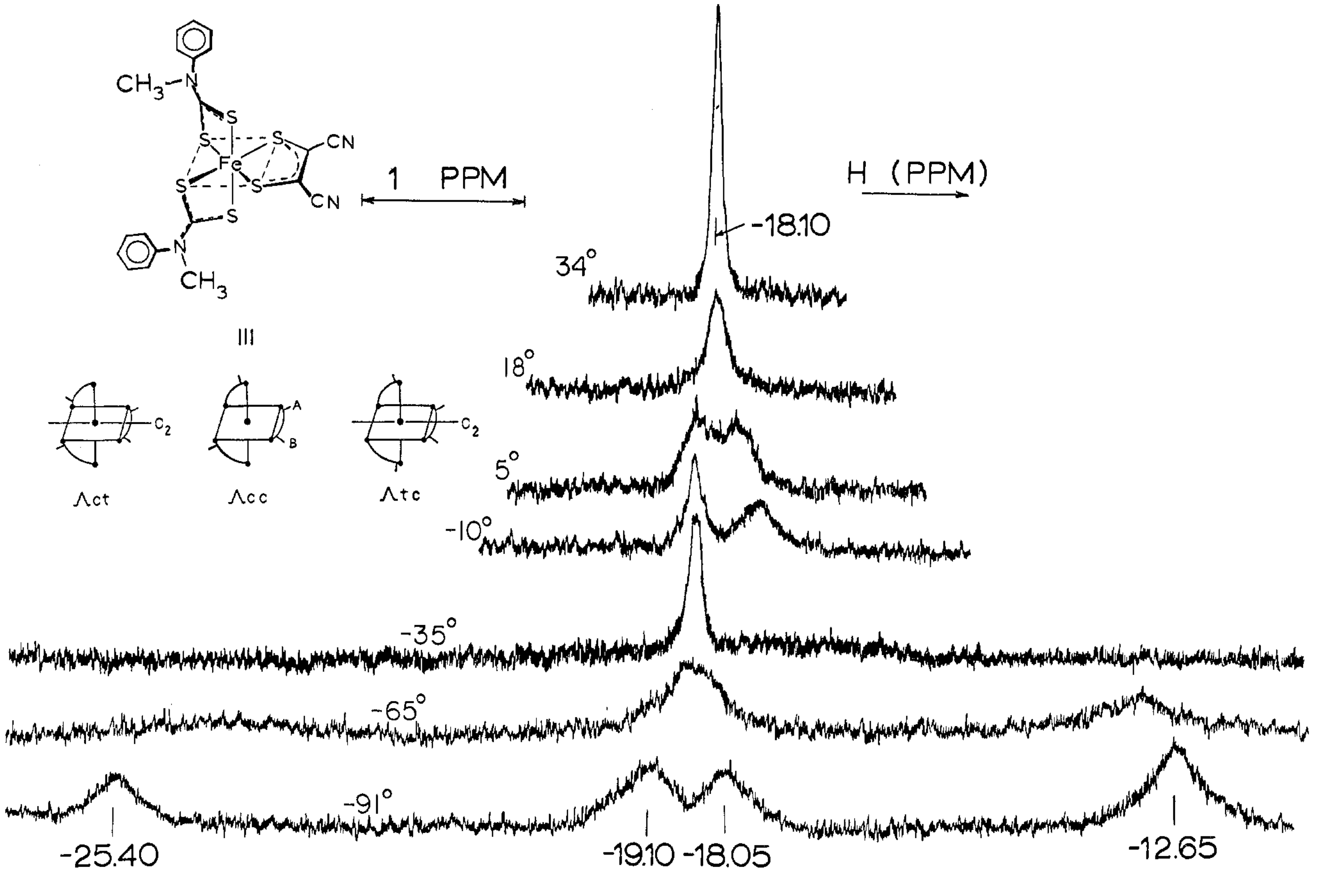

Figure 2.—Temperature dependence of the methyl 60-MHz pmr spectrum of Fe(Me,Phdtc)$_2$mnt in CD$_2$Cl$_2$ solution. Chemical shifts are downfield of TMS reference. The possible geometrical isomers (Λ absolute configuration) are illustrated with the same structural representative used previously for the analogous tfd complex.[4]

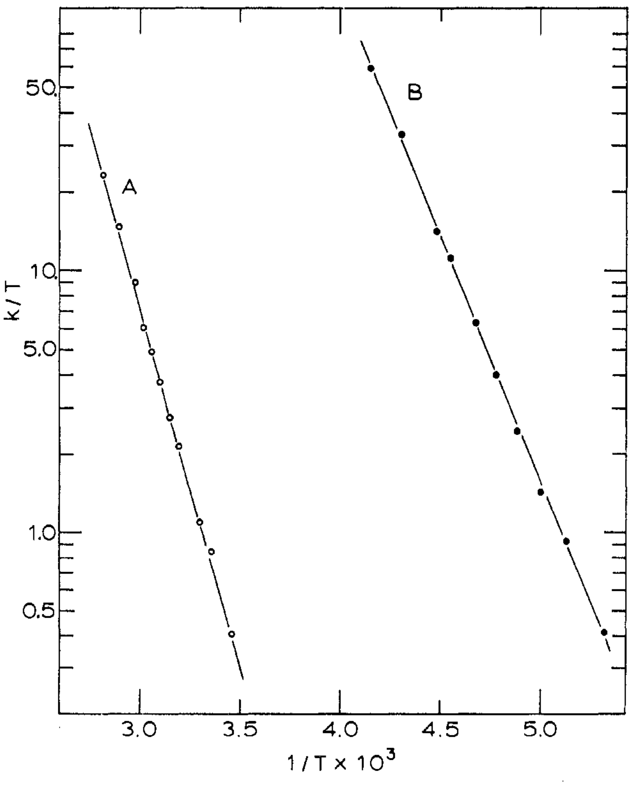

Figure 3.—Eyring plots for the intramolecular rearrangement reactions of Fe(Et$_2$dtc)$_2$mnt in CD$_2$Cl$_2$ solution: A, HTP (S$_2$C–N bond rotation); B, LTP (inversion).

variable-temperature nmr spectra of complexes of type 1. On the basis of arguments detailed earlier in a study of tfd complexes[4] the LTP, occurring in the range of *ca.* −80 to −5°, was identified as inversion, and the HTP, observable above *ca.* 0°, was assigned to C–N bond rotation.

Pmr Results.—Variable-temperature pmr spectra of Fe(Et$_2$dtc)$_2$mnt and Fe(Me,Phdtc)$_2$mnt encompassing the slow- and fast-exchange limits of methylene and methyl protons are shown in Figures 1 and 2. A plot of the isotropic shifts[5] (negative shifts downfield) *vs.* T^{-1} for the average of the methylene resonances of the diethyl complex from −40 to +80° yields a straight line with a least-squares intercept of -0.9 ± 1.0 ppm.[25] This result is consistent with the Curie dependence of the magnetic moment. The Me,Ph complex exhibits a nonlinear dependence of average methyl shifts with T^{-1}. Examination of Figures 1 and 2 reveals the operation of two distinct kinetic processes (LTP, HTP) for each complex.

At temperatures below −70° Fe(Et$_2$dtc)$_2$mnt displays four equally intense methylene signals ranging over 26 ppm and two equally intense methyl features separated by about 3 ppm. This multiplicity of signals can arise only if *both* inversion and N–CS$_2$ bond rotation are slow at these temperatures. Under these circumstances the four methylene and two methyl groups in a dithiocarbamato ligand are nonequivalent, with

[25] Isotropic shifts of the methylene protons were calculated using a reference value of −3.62 ppm from TMS, the shift observed in diamagnetic Ru(Et$_2$dtc)$_2$tfd.[4]

the two ligands related by symmetry (*cf.* structure **1**). The low-temperature spectrum of the tfd analog was explained similarly.[4] However, in that case the ranges of methylene and methyl shifts were only about 2.6 and 0.6 ppm, respectively, due to the smaller population of the triplet state. In addition, only three of the four methylene resonances could be resolved. During the LTP coalescence of two pairs of methylene resonances (those at −12.04, −23.14 and −24.04, −38.04 ppm at −80°) into two equally intense features and both methyl signals into a nearly resolved triplet occurs (*cf.* Figure 1). In the HTP the two methylene signals average to a single feature. The pmr spectrum of $Fe(Me,Phdtc)_2mnt$, illustrated in Figure 2, reveals four resolved methyl signals at slow exchange ranging over 13 ppm. Signal separation in the tfd analog at slow exchange is only 0.3 ppm. During the LTP the central pair of signals and that comprised of the extreme upfield and downfield resonance average to two signals. The HTP coalesces these two features.

The intramolecular nature of the processes responsible for the spectral behavior just described has been demonstrated by examination of solutions containing the mixtures $Fe(Et_2dtc)_2mnt$ + $Fe(Me,Phdtc)_2mnt$ and $Fe(Et_2dtc)_2mnt$ + $Fe(Et_2dtc)_2tfd$ in dichloromethane. Signals due to mixed-ligand species were observed immediately after mixing in the former. No indication of ligand exchange was evident in those temperature intervals where the HTP's of the pure complexes are fast. Rearrangement processes of tfd complexes have also been shown to be intramolecular by similar experiments.[4]

Kinetics of the LTP and HTP of $Fe(Et_2dtc)_2mnt$ have been evaluated by a total line shape analysis of the exchange-broadened spectra. Details are given in the Experimental Section. Rate constants were fit to the Eyring equation and kinetic plots are given in Figure 3. Activation parameters and rate constants are collected in Table I, together with related data for analogous tfd complexes.[4]

Stereochemistry and Rearrangement Mechanisms. (a) **Low-Temperature Process.**—The slow-exchange spectrum of $Fe(Et_2dtc)_2mnt$ is consistent with the molecular structure of the crystalline tfd analog. The averaging pattern of LTP is compatible with either inversion or bond rotation because either process will coalesce the methyl and pairs of methylene resonances.[4,26] The four methyl signals observed in the −91° spectrum of $Fe(Me,Phdtc)_2mnt$ must arise from restricted $N-CS_2$ bond rotation, which generates the three geometrical isomers represented schematically in Figure 2. The lack of symmetry of the cc (cis–cis) isomer renders the two methyls nonequivalent and allows assignment of their signals as the two equally intense central resonances. The ct (cis–trans) and tc (trans–cis) both possess twofold symmetry and their single methyl resonance cannot be uniquely identified. The cc:(ct + tc) isomer ratio estimated from intensities is 0.9 at −91°. In the LTP of this complex the ct + tc signals are averaged, as are the two methyl signals of cc. This result unambiguously assigns the LTP as inversion because bond rotation would simultaneously average all methyl environments and constrains ct + tc interconversion to a path not involving cc. Further, inasmuch as the three isomers are differentiated only because of the spatial distribution of groups well removed from the $Fe-S_6$ core, it is assumed that the same mechanism must apply to the ct–tc interconversion and to cc inversion.

Possible mechanisms for inversion reactions of tris chelates have been considered in detail in recent work.[4,27,28] These may be broadly classified as involving bond rupture (idealized trigonal-bipyramidal (TBP) or square-pyramidal (SP) transition states) or twisting motions (idealized TP transition states) around real or artificial threefold axes of the complex. Of the mechanisms appropriate to $Fe(Me,Phdtc)_2mnt$, which is of the general type $M(A-A')_2(B-B)$, only the TBP pathway can be eliminated on the basis of the constraint cited above and arguments developed previously.[4,29]

While the LTP of $Fe(Et_2dtc)_2mnt$ cannot be assigned uniquely from the spectral results in Figure 1, comparison of its kinetics with the coalescence lifetime of the Me,Ph complex strongly supports its assignment to an inversion process. The preexchange lifetime of the cc isomer of the latter at coalescence (−80°) due to inversion is 0.0070 sec.[30] This value compares closely with 0.0076 sec calculated for the diethyl complex at −80° from the activation parameters in Table I. The close similarity of the activation parameters for the LTP's of the diethyl mnt and tfd complexes clearly implies that both inversion reactions proceed by the same mechanism, which is considered to be the p-C_3 twist assigned previously to $Fe(Et_2dtc)_2tfd$.[4] The assumption of an identical mechanism for the interconversion of ct and tc isomers of Me,Ph complexes leads to the sequence $\mathbf{3} \rightleftharpoons \mathbf{4} \rightleftharpoons \mathbf{5}$, which results in simultaneous inversion and isomerization. The rearrangement mechanisms proposed are most simply visualized as twisting motions with respect to the p-C_3 axes. However, any motion, with or without bond rupture, which is operationally equivalent in the sense of effecting the same nmr averaging processes, obviously cannot be distinguished from the conceptually simple twist process.

(b) **High-Temperature Process.**—In the higher temperature region two kinetic processes are operative, but only one of them, designated as the HTP, is sufficiently slow to effect the spectral changes observed. If the p-C_3 twist is the only metal-centered rearrangement occurring in this region, the HTP of mnt complexes is assigned to $N-CS_2$ bond rotation. A similar assignment was made for tfd complexes.[4] This process will lead to averaging of the two methylene signals of

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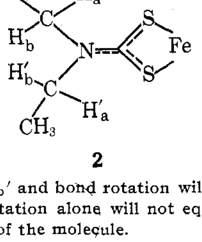
[26] With reference to the structural fragment **2**, inversion will average H_a with H_b and H_a' with H_b' and bond rotation will average H_a with H_a' and H_b with H_b'. Bond rotation alone will not equilibrate all methylene protons due to the chirality of the molecule.



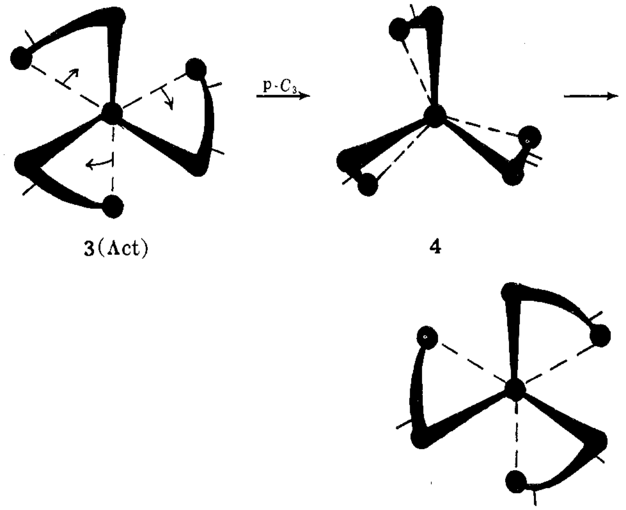
2

[27] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970), and references therein.

[28] J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

[29] See in particular the correlation diagrams for interconversion of $M(A-A')_2(B-B)$ isomers by bond rupture and twist mechanisms in ref 4. Only the TBP mechanism disallows direct ct–tc interconversion.

[30] Lifetimes determined by an approximate computer fit to experimental coalescence spectra.



3(Λct)

4

5(Δtc)

the diethyl complex and the two methyl signals of the Me,Ph complex observed above *ca.* −16 and −10°, respectively (*cf.* Figures 1 and 2). Kinetic parameters for bond rotation in Fe(Et$_2$dtc)$_2$mnt are given in Table I. $\Delta F^{\ddagger}$ values are identical within experimental error.

Because substitution of tfd by mnt increases the triplet state population the kinetic parameters for inversion of Fe(Et$_2$dtc)$_2$(S$_2$C$_2$R$_2$) can be examined in terms of N_t. The rate constant, k, and $\Delta F^{\ddagger}$, determined in the temperature region of exchange broadening, are the more accurate parameters from a total line shape analysis.[16] At −50° the rate of the mnt complex is faster than that of its tfd analog.[31] This rather small rate increase cannot, however, be interpreted in terms of experimentally different values of activation enthalpy or entropy changes. Interpretation of this effect will require additional measurements of inversion rates of other analogous tfd–mnt complexes and, possibly, a structural determination of an mnt complex if the conjecture that ground-state structures are related to the occurrence and rate of a p-C_3 twist is accepted.

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(31) N_t values for the two complexes at this temperature are estimated as 0.75 (mnt) and 0.12 (tfd[4]).

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Antiferromagnetic Exchange Interactions and Delocalization in Some Tetrahedral Binuclear Cobalt(II) Complexes of Phthalazine and Pyrazine Ligands

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Some new cobalt complexes of the ligand 1,4-di(2′-pyridyl)aminophthalazine are reported and characterized by vibrational and electronic spectroscopy and magnetism. The complexes contain tetrahedrally coordinated cobalt(II) and are binuclear. The magnetic behavior (from 78 to 375°K) of species of this type are reported for the first time and demonstrate the presence of antiferromagnetically coupled ions. Similar data are reported for some previously reported binuclear tetrahedral cobalt(II) complexes of methylpyrazine and 2,5-dimethylpyrazine. The data were fitted to the standard equation for two spin-coupled $S = {}^3/_2$ ions using J, the exchange integral, and k^2, the delocalization coefficient, as variables. By allowing the temperature-independent paramagnetism to vary and using, for this term, a value of $10Dq$ derived from the electronic spectrum, excellent agreement between theory and experiment, as illustrated by a least-squares analysis, was obtained. All the complexes exhibited very weak exchange with J of the order of −1 to −5 cm^{-1}. Trends in k^2 which varied from about 0.5 to 1.05 were discussed in the light of current theory. The variations in J, k^2, and B, the Racah parameter, were rationalized in terms of the electronegativity of the coordinating halogens.

While binuclear complexes of divalent copper in which the metal atoms are fairly close together have been extensively investigated[1] and very large numbers of such complexes are known, relatively few such binuclear divalent nickel or cobalt complexes have been characterized. Some dimeric cobalt complexes of methylpyrazines[2] represented the first examples of binuclear cobalt complexes of tetrahedral stereochemistry in which exchange coupling might be expected to occur. Since then some syntheses of other binuclear cobalt species have been reported[3–9] but without detailed magnetic data. Recently attempts have been made to design ligands which have a strong tendency to coordinate to two metal atoms simultaneously and to constrain these two metal atoms to be in close proximity. Such ligands are generally quadridentate amines in which the two central nitrogen atoms are adjacent and are based in concept upon 2-pyridinealdazine, the first ligand shown to have such a capability.[10] Quite a few ligands of this general type

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