Contribution No. 5046 from the Central Research and Development Department, Experimental Station E328,
E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19880-0328, and Contribution from
the Departments of Physics and Chemistry, The Ohio State University, Columbus, Ohio 43210-1106

Ferromagnetic Behavior of Linear-Chain Organometallic Complexes. Structural and Magnetic Properties of 1:1 Decamethylferrocenium Salts of Planar Radical Anion Bis(dithiolato)metalates

Joel S. Miller,*[1a] Joseph C. Calabrese,[1a] and Arthur J. Epstein[1b]

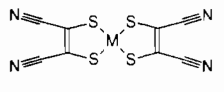
Received February 16, 1989

The reaction of decamethylferrocene and bis(maleonitriledithiolato)nickelate monoanion, $\{Ni[S_2C_2(CN)_2]_2\}^{\bullet-}$, or the platinum analogue results in the formation of purple reflecting 1:1 crystals of $[Fe(C_5Me_5)_2]\{M[S_2C_2(CN)_2]_2\}$ composition. The complex $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ was also prepared and characterized by X-ray diffraction. These salts possess $[Fe(C_5Me_5)_2]^{\bullet+}$ (D) cations and $[M(S_2C_2R_2)_2]^{\bullet-}$ (A) anions with molecular structures typical of these previously characterized radical ions. Crystals of $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$ belong to the centrosymmetric monoclinic $P2_1/c$ space group [a = 9.959 (1) Å, b = 12.338 (2) Å, c = 25.086 (6) Å, β = 99.54 (1)°, V = 3039.8 Å^3, Z = 4, R = 7.3%, and R_w = 6.6% at −100 °C]. The unit cell is comprised of isolated, centrosymmetric DAAD dimers with an essentially eclipsed $S = 0$ $[A_2]^{2-}$ (separated by 3.482 Å) and two $S = {}^1/_2$ cations. The cation lies essentially over the NiS_2C_2 chelate ring. The intradimer Fe⋯Fe separation is 14.64 Å whereas the interdimer Fe⋯Fe separations are 9.959, 9.971, and 12.66 Å. The Pt-containing salt exists in two polymorphs: α- and β-phases. The α-phase belongs to the centrosymmetric monoclinic $C2/m$ space group [a = 16.802 (5) Å, b = 21.095 (5) Å, c = 12.942 (4) Å, β= 94.52 (2)°, V = 4473 (2) Å^3, Z = 6, R = 2.8%, and R_w = 3.1% at 20 °C]. The unit cell is complex with ⋯DAADAA⋯ chains also containing an essentially eclipsed $S = 0$ $[A_2]^{2-}$ ion (separated by 3.537 Å) and an $S = {}^1/_2$ cation. Orthogonal to this chain is a layered motif comprised of alternating $[D^{\bullet+}]_2A^{\bullet-}$ moieties such that the D's and A's form extended edge-to-edge chains. The adjacent and intrachain Fe⋯Fe separations are 8.401 and 10.548 Å, respectively. The β-phase belongs to the centrosymmetric triclinic $P\bar{1}$ space group [a = 12.106 (2) Å, b = 14.152 (5) Å, c = 14.374 (6) Å, α = 108.94 (3)°, β = 96.37 (2)°, γ = 90.51 (2)°, V = 2312 (3) Å^3, Z = 3, R = 5.5%, and R_w = 5.8% at 23 °C]. The unit cell for this polymorph possesses parallel ⋯DADADA⋯ chains with intra- and interchain Fe⋯Fe separations of 12.11 and 16.58 Å, respectively. The cation lies essentially over the NiS_2C_2 chelate ring such that each chelate ring has only one cation C_5 ring canted to it by 3.73°. Additionally, the β-phase has isolated DAAD dimers containing an essentially eclipsed $S = 0$ $[A_2]^{2-}$ ion (separated by 3.55 Å) and two $S = {}^1/_2$ cations. The complex $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ belongs to the centrosymmetric monoclinic $C2/c$ space group [a = 14.417 (4) Å, b = 12.659 (2) Å, c = 18.454 (6) Å, β = 95.17 (3)°, V = 2354 (3) Å^3, Z = 4, R = 6.1% and R_w = 5.2% at −70 °C]. The unit cell possesses parallel $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chains. The $\{Ni[S_2C_2(CN)_2]_2\}^{\bullet-}$, α- and β-$\{Pt[S_2C_2(CN)_2]_2\}^{\bullet-}$, and $\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$ salts have Curie–Weiss parameters of Θ = 0, +6.6, +9.8, and +15 K and μ_{eff} = 2.83, 3.05, 3.10, and 3.73 μ_B, respectively. These results are consistent with the presence of an $S = 0$ $[A]_2{}^{2-}$ dimer with a thermally inaccessible triplet state. Field-dependent susceptibility characteristic of ferromagnetic coupling, not bulk ferromagnetic behavior, was observed for complexes with $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chains.

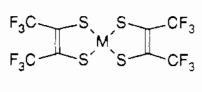
Introduction

Cooperative magnetic properties of linear-chain alternating donor/acceptor (D/A), ⋯DADADA⋯, complexes have been the focus of contemporary study. The spin–Peierls transition form an antiferromagnetic state to a diamagnetic state was established for $[TTF]^{\bullet+}\{Cu[S_2C_2(CF_3)_2]_2\}^{-2}$ (TTF = tetrathiafulvalene). Ferro-, meta-, and antiferromagnetic behaviors have been reported for decamethylmetallocenium, $[M(C_5Me_5)_2]^{\bullet+}$, salts of planar cyano radical anions.[3] The linear chain, 1-D, phase of the 1:1 electron-transfer complex $[Fe(C_5Me_5)_2]^{\bullet+}[TCNQ]^{\bullet-}$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) exhibits an antiferromagnetic ground state (T_{Neel} = 2.55 K) that in the presence of a 1.6-kG applied field exhibits a transition to a high-moment state characteristic of ferromagnetic behavior.[3,4] Since metamagnetic behavior is unprecedented for molecular materials, we have undertaken the systematic study of the structure–function relationship between salts primarily comprising metallocenium cations and planar polycyano anions with the goal of elucidating the electronic and steric requirements for the stabilization of the ferromagnetic state in a molecular material. Utilizing the tetracyanoethenide,[3,5] and hexacyanobutadienide[3,6] anions and the anion of and 2,5-diiodo-7,7,8,8-tetracyano-*p*-quinodimethane ($(TCNQ)I_2$)[7] as the $[Fe(C_5Me_5)_2]^{\bullet+}$ salts, we have demonstrated the occurrence of ferromagnetic exchange in an electron-transfer salt and, moreover, a 3-D ferromagnetic ground state. The former electron-transfer complex possesses a spontaneous magnetic moment at zero applied field.[3,8]

We specifically aimed to prepare complexes with higher transition temperatures, stable under ambient conditions, and large single crystals enabling the detailed study of the physical properties on oriented single-crystal samples. Thus, we sought to prepare 1:1 salts with stable planar radical anions enabling formation of the $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ structure type that has been shown to support ferromagnetic behavior[3] and have prepared materials based on planar bis(dithiolate) radical anions, **1** and **2**. Herein we report on the preparation, struture, and magnetic susceptibility of $[Fe(C_5Me_5)_2]^{\bullet+}\{M[S_2C_2(CN)_2]_2\}^{\bullet-}$ (M = Ni, Pt) and $[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$.



1



2

Experimental Section

$[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CN)_2]_2\}^{\bullet-}$ was prepared from $[Fe(C_5Me_5)_2]^{\bullet+}[BF_4]^{-}$[5b] and $[Bu_4N]^{+}\{Ni[S_2C_2(CN)_2]_2\}^{\bullet-}$[9a] in an inert-atmosphere glovebox. $[Fe(C_5Me_5)_2]^{\bullet+}[BF_4]^{-}$ (48 mg; 0.117 mmol) was

---

[1] (a) E. I. du Pont de Nemours and Co., Inc. (b) The Ohio State University.

[2] Bray, J. W.; Interrante, L. V.; Jacobs, I. S.; Bonner, J. C. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Publishing Corp.: New York, 1983; Vol. 3, pp 353–415.

[3] Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Isr. J. Chem.* **1987**, *27*, 363–373. Miller, J. S.; Epstein, A. J; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201–220. Miller, J. S.; Epstein, A. J. *NATO ASI Ser., Ser. B* **1988**, *168*, 159–174. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem Res.* **1988**, *21*, 114–120. Miller, J. S.; Epstein, A. J; Reiff, W. M. *Science* **1988**, *240*, 40–47.

[4] Candela, G. A.; Swarzendruber, L.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2755–2756.

[5] (a) Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Reiff, W. M.; Zhang, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1026–1027. (b) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Zhang, J. H.; Chittipeddi, S.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769–781.

[6] Miller, J. S.; Zhang, J. H.; Reiff, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 5484.

[7] Miller, J. S.; Calabrese, J. C.; Zhang, J. H.; Reiff, W. M.; Chittipeddi, S.; Selover, M. A.; Epstein, A. J. Submitted for publication.

[8] Chittipeddi, S.; Kromack, K. R.; Miller, J. S.; Epstein, A. J. *Phys. Rev. Lett.* **1987**, *58*, 2695.

[9] Davison, A.; Holm, R. H. *Inorg. Synth.* **1967**, *10*, 8–26. (b) A gift from S. Freilich (Du Pont).

0020-1669/89/1328-4230$01.50/0

Table I. Summary of Crystallographic Data

	$[Fe(C_5Me_5)_2]$-$\{Ni[S_2C_2(CN)_2]_2\}$	α-$[Fe(C_5Me_5)_2]$-$\{Pt[S_2C_2(CN)_2]_2\}$	β-$[Fe(C_5Me_5)_2]$-$\{Pt[S_2C_2(CN)_2]_2\}$	$[Fe(C_5Me_5)_2]$-$\{Ni[S_2C_2(CF_3)_2]_2\}$
formula	$C_{28}H_{30}FeN_4NiS_4$	$C_{28}H_{30}FeN_4PtS_4$	$C_{28}H_{30}FeN_4PtS_4$	$C_{28}H_{30}F_{12}FeNiS_4$
fw	665.39	801.75	801.75	837.36
radiation, Å	0.71069	0.71073	1.54184	0.71069
temp, °C	−100	+20 ± 1	+23 ± 1	−70
space group	$P2_1/c$ (No. 14)	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	9.959 (1)	16.802 (5)	12.106 (2)	14.417 (4)
b, Å	12.338 (2)	21.095 (5)	14.152 (5)	12.659 (2)
c, Å	25.086 (6)	12.942 (4)	14.394 (5)	18.454 (6)
α, deg	90.00	90.00	108.94 (3)	90.00
β, deg	99.54 (1)	94.52 (2)	96.37 (2)	95.17 (3)
γ, deg	90.00	90.00	90.51 (2)	90.00
V, Å^3	3039.8	4473 (2)	2312 (3)	2354 (3)
Z	4	6	3	4
d_{calcd}, g/cm^3	1.454	1.747	1.73	1.658
μ, cm^{-1}	13.88	0.54	149.4	13.2
$R(F_o^2)$	0.073	0.028	0.055	0.061
$R_w(F_o^2)$	0.066	0.031	0.065	0.052

dissolved in 0.5 mL of acetonitrile (distilled under argon from P_2O_5 and subsequently CaH_2). This solution was added to 68 mg (0.117 mmmol) of $[Bu_4N]^+\{Ni[S_2C_2(CN)_2]_2\}^{\bullet-}$ also dissolved in 0.2 mL of MeCN. When the mixture was allowed to stand, a dark solid precipitated and was collected via vacuum filtration (43 mg; 55%). Anal. Calcd for $C_{28}H_{30}FeN_4NiS_4$: C, 50.54; H, 4.54; N, 8.42. Found (Galbraith, Knoxville, TN): C, 50.77; H, 4.57; N, 8.58. Infrared spectral data (Nujol): $\nu(C{\equiv}N)$ = 2207 s and 2222 w cm^{-1}.

α-$[Fe(C_5Me_5)_2]^{\bullet+}\{Pt[S_2C_2(CN)_2]_2\}^{\bullet-}$ was prepared from $[Fe(C_5Me_5)_2]^{\bullet+}[BF_4]^-$ and $[Ph_3PMe]^+\{Pt[S_2C_2(CN)_2]_2\}^{\bullet-}$[9a] as described above (63%). Anal. Calcd for $C_{28}H_{30}FeN_4PtS_4$: C, 41.94; H, 3.77; N, 6.99. Found: C, 41.94; H, 3.90; N, 6.93. Infrared spectral data (Nujol): $\nu(C{\equiv}N)$ = 2210 s and 2224 w cm^{-1}.

β-$[Fe(C_5Me_5)_2]^{\bullet+}\{Pt[S_2C_2(CN)_2]_2\}^{\bullet-}$ was prepared from $[Fe(C_5Me_5)_2]^{\bullet+}[BF_4]^-$ and $[Bu_4N]^+\{Pt[S_2C_2(CN)_2]_2\}^{\bullet-}$[9a] as described above (86%). Infrared spectral data (Nujol): $\nu(C{\equiv}N)$ = 2207 s and 2223 s cm^{-1}.

$[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$ was prepared from $Fe(C_5Me_5)_2$ (64 mg; 0.197 mmol) (Strem) and $Ni[S_2C_2(CF_3)_2]_2$[9] (100 mg; 0.197 mmol) in dichloromethane. One-milliliter solutions of each of the above were mixed, and when the mixture was allowed to stand at room temperature, a black crystalline precipitate formed (130 mg; 87%). Anal. Calcd for $C_{32}H_{30}F_{12}FeNiS_4$: C, 40.16; H, 3.61; F, 27.23. Found: C, 40.28; H, 3.54; F, 28.31.

$[Fe(C_5Me_5)_2]^{\bullet+}[Ni(S_2C_6H_3Me)_2]^{\bullet-}$ was prepared from $[Fe(C_5Me_5)_2]^{\bullet+}[BF_4]^-$ (470 mg; 1.15 mmol; in 5 mL of acetonitrile) and $[NBu_4][Ni(S_2C_6H_3Me)_2]^-$[9a] (700 mg; 1.15 mmol; in 10 mL of acetonitrile). One-milliliter solutions of each of the above were mixed, and when the mixture was allowed to stand at room temperature, a dark brown precipitate formed (624 mg; 78%). Anal. Calcd for $C_{34}H_{42}FeNiS_4$: C, 58.88; H, 6.10. Found: C, 58.88, 58.77; H, 6.00, 6.10. Several attempts to determine the single-crystal X-ray structure failed as the crystals did not diffract.

X-ray Data Collection, Reduction, Solution, and Refinement. Crystals of $[Fe(C_5Me_5)_2]\{M[S_2C_2(CN)_2]_2\}$ and $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ were used to solve the single-crystal X-ray structures in the usual fashion. The key parameters for the data collection, data reduction, solution, and refinement are summarized in Table I and described in detail in Table SI.

Results and Discussion

Crystal Structure. The structures of $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$, the α- and β-phases of $[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$, and $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ possess C_5 radical cations and D_{2h} anions with the expected structures. The atomic coordinates can be found in Tables II–V, respectively. A summary of the average bond distances is located in Table VI and except for disorder in the C_5 rings of the Ni-containing salt the molecular structures are essentially equivalent to those previously reported for the individual cations[5b] and anions.[10–14] Thus, discussion of

Table II. Fractional Coordinates (Å × 10^4) for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$

atom	x	y	z	B_{iso}, Å^2
Ni(1)	9012.2 (12)	5993.8 (13)	259.9 (5)	2.9 (0)[a]
Fe(1)	6313 (1)	8201 (1)	1744 (1)	2.9 (0)[a]
S(1)	8295 (3)	6810 (3)	−486 (1)	4.3 (1)[a]
S(2)	10894 (3)	6873 (3)	385 (1)	4.2 (1)[a]
S(3)	9750 (2)	5202 (3)	1006 (1)	3.6 (1)[a]
S(4)	7118 (2)	5119 (3)	148 (1)	3.3 (1)[a]
N(1)	9220 (12)	9079 (12)	−1349 (5)	8.2 (5)[a]
N(2)	12725 (12)	9089 (12)	−172 (6)	9.2 (5)[a]
N(3)	8666 (11)	3211 (14)	1958 (5)	10.9 (6)[a]
N(4)	5250 (11)	3100 (10)	856 (4)	6.6 (4)[a]
C(1)	9586 (11)	7729 (9)	−530 (5)	4.0 (4)[a]
C(2)	9391 (13)	8451 (13)	−994 (6)	6.5 (5)[a]
C(3)	10736 (11)	7726 (10)	−150 (5)	4.5 (4)[a]
C(4)	11823 (13)	8488 (13)	−177 (6)	6.6 (5)[a]
C(11)	8405 (10)	4361 (9)	1086 (4)	3.3 (3)[a]
C(12)	8547 (11)	3710 (14)	1573 (5)	6.5 (5)[a]
C(13)	7282 (9)	4345 (9)	708 (3)	2.9 (3)[a]
C(14)	6146 (12)	3630 (11)	792 (5)	4.6 (4)[a]
C(20)	5257 (12)	8551 (10)	2369 (4)	4.3 (4)[a]
C(21)	4525 (9)	8956 (9)	1888 (4)	3.3 (3)[a]
C(22)	5259 (15)	9703 (13)	1661 (5)	6.2 (3)
C(23)	6444 (17)	9762 (14)	1981 (8)	8.3 (6)[a]
C(24)	6540 (12)	9163 (16)	2440 (6)	8.0 (6)[a]
C(25′)	4366 (25)	7530 (24)	2602 (10)	4.9 (5)
C(25″)	5066 (25)	7868 (22)	2843 (9)	4.8 (5)
C(26′)	3160 (22)	8791 (22)	1513 (9)	4.4 (5)
C(26″)	3012 (19)	8503 (19)	1751 (8)	2.9 (4)
C(27′)	4480 (20)	10294 (19)	1095 (7)	3.1 (4)
C(27″)	5448 (35)	10468 (29)	1220 (13)	8.7 (9)
C(28′)	7444 (18)	10783 (19)	1811 (7)	3.1 (4)
C(28″)	8121 (35)	10203 (32)	2251 (13)	9.9 (10)
C(29′)	7776 (19)	9295 (19)	2871 (8)	3.4 (4)
C(29″)	7350 (27)	8436 (25)	3073 (11)	6.6 (7)
C(30)	7645 (19)	7837 (11)	1218 (9)	7.1 (6)[a]
C(31)	7980 (16)	7240 (16)	1705 (7)	7.4 (6)[a]
C(32)	6786 (26)	6614 (13)	1736 (7)	8.3 (7)[a]
C(33)	5961 (13)	6783 (17)	1318 (8)	7.7 (6)[a]
C(34)	6319 (20)	7491 (17)	991 (5)	7.6 (6)[a]
C(35)	8182 (30)	8715 (27)	833 (12)	2.6 (6)
C(35′)	8966 (28)	8547 (26)	1203 (11)	3.0 (6)
C(35″)	7543 (47)	8750 (41)	636 (18)	6.5 (11)
C(36)	9259 (30)	7091 (29)	2166 (11)	3.8 (7)
C(36′)	9623 (25)	7881 (25)	1819 (10)	2.5 (5)
C(37)	5969 (37)	5781 (34)	2079 (14)	4.9 (8)
C(37′)	8154 (49)	6278 (42)	2332 (18)	8.3 (12)
C(37″)	7155 (43)	5680 (37)	2257 (16)	6.0 (9)
C(38)	4653 (31)	5977 (33)	1288 (14)	3.8 (6)
C(38′)	4430 (33)	6622 (33)	902 (14)	4.7 (8)
C(38″)	5186 (57)	5667 (47)	1610 (23)	9.4 (14)
C(39)	5430 (32)	7804 (30)	446 (11)	2.7 (6)
C(39′)	6191 (38)	8386 (34)	430 (13)	4.8 (8)
C(39″)	4966 (32)	7413 (31)	524 (12)	3.0 (7)

[a] Four-thirds of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

---

(10) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295.

(11) Kuppusamy, P.; Monoharan, P. T. *Proc.—Indian Acad. Sci., Chem. Sci.* **1987**, *98*, 115–129. Ramakrishna, B. L. *Inorg. Chim. Acta* **1986**, *114*, 31–34.

(12) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253–6277.

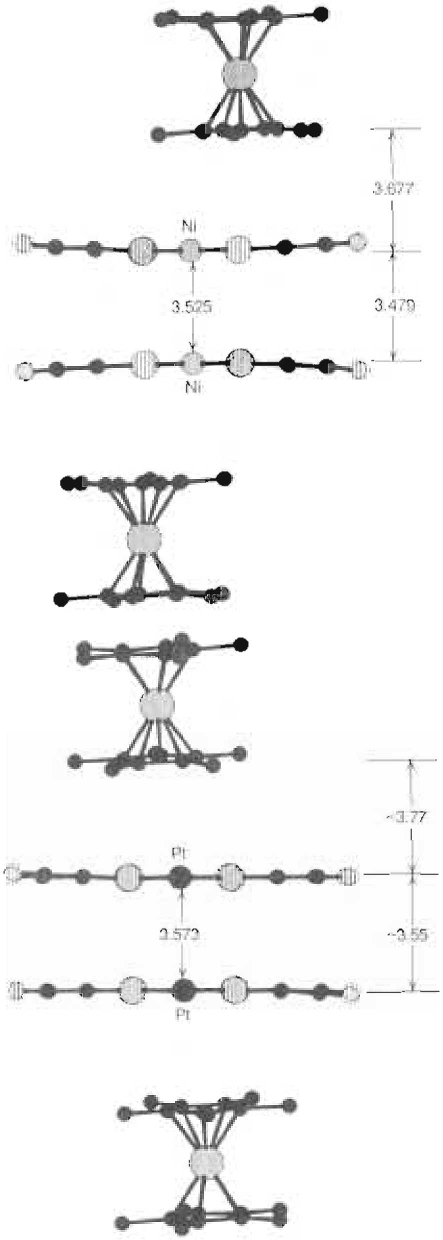


Figure 1. Centrosymmetric DAAD dimer repeating units of [Fe(C_5Me_5)$_2$]{Ni[$S_2C_2(CN)_2$]$_2$} (a, top) and β-[Fe(C_5Me_5)$_2$]{Pt[$S_2C_2(CN)_2$]$_2$} (b, bottom).

the structures is limited to the solid-state packing motifs and their consequences on their physical properties.

The anisotropic thermal parameters, intra- and intermolecular distances, and intramolecular angles, as well as weighted least squares planes and atom-labeling diagrams and stereoviews for [Fe(C_5Me_5)$_2$]{Ni[$S_2C_2(CN)_2$]$_2$}, α- and β-[Fe(C_5Me_5)$_2$]{Pt[$S_2C_2(CN)_2$]$_2$}, and [Fe(C_5Me_5)$_2$]{Ni[$S_2C_2(CF_3)_2$]$_2$} are located in the supplementary material.

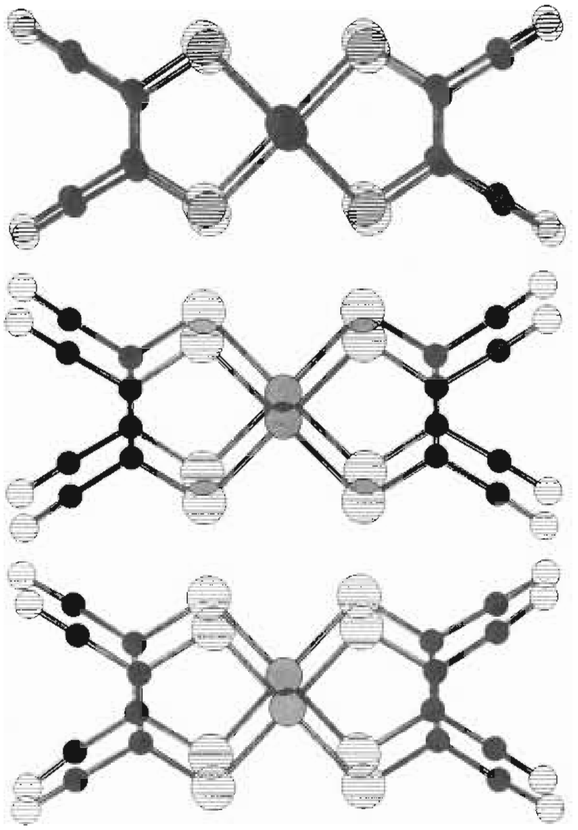


Figure 2. Centrosymmetric S = 0 {M[$S_2C_2(CN)_2$]$_2$}$_2^{2-}$ dimers in [Fe(C_5Me_5)$_2$]{Ni[$S_2C_2(CN)_2$]$_2$} (a, top) α-[Fe(C_5Me_5)$_2$]{Pt[$S_2C_2(CN)_2$]$_2$} (b, middle) and β-[Fe(C_5Me_5)$_2$]{Pt[$S_2C_2(CN)_2$]$_2$} (c, bottom).

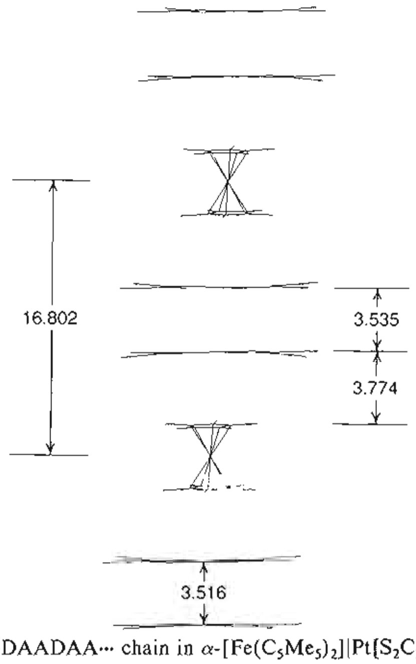


Figure 3. ···DAADAA··· chain in α-[Fe(C_5Me_5)$_2$]{Pt[$S_2C_2(CN)_2$]$_2$}.

Solid-State Structures. [Fe(C_5Me_5)$_2$]{Ni[$S_2C_2(CN)_2$]$_2$}. The solid is composed of centrosymmetric DAAD dimers (Figure 1a). The {Ni[$S_2C_2(CN)_2$]$_2$}$^-$ dimer (Figure 2a) is essentially eclipsed with the parallel S_4 planes being separated by 3.482 Å and a short Ni···Ni distances of 3.525 Å.[11,13,14c] The anion is not planar, with the CN groups being bent away from the S_4 plane. The CN carbons deviate from the plane by 0.11–0.17 Å and the average

---

(13) Kuppusamy, P.; Manoharan, P. T.; Mahadevan, C.; Seshasayee, M. *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 359. Kobayashi, A.; Sasaki, Y.; Mahadevan, C. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2650–2656. Seshasayee, M.; Murthy, B. V. R.; Kuppusamy, P.; Manoharan, P. T. *Acta Crystallogr.* **1983**, *C39*, 1335. Ramakrishna, B. L.; Manoharan, P. T. *Inorg. Chem.* **1983**, *22*, 2113. Fritchie, C. J., Jr. *Acta Crystallogr.* **1966**, *20*, 107–118. Kisch, H. Fernandez, A.; Wakatsuki, Y.; Yamazaki, H. *Z. Naturforsch.* **1985**, *40B*, 292–297. Harris, N. J.; Underhill, A. E. *J. Chem. Soc., Dalton Trans.* **1987**, 1683–1685.

(14) (a) Ahmad, M. M.; Turner, D. J.; Underhill, A. E.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H. *J. Chem. Soc.* **1984**, *1759*–1762. (b) Shibaeva, R. P.; Kaminskii, V. F.; Simonov, M. A.; Yagubskii, E. B.; Kostyuchenko, E. E. *Sov. Phys.—Crystallogr.* (*Engl. Transl.*) **1985**, *30*, 283–285. (c) Bunn, K.; Endres, H.; Weiss, J. *Z. Naturforsch.* **1987**, *42B*, 1222–1226. (d) Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Underhill, A. E.; Ahmad, M. M. *Chem. Lett.* **1984**, 305–308. Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Underhill, A. E.; Ahmad, M. M. *J. Chem. Soc.* **1982**, 390. Kobayashi, A.; Takehiko, M.; Yukiyoshi, S.; Kobayashi, H.; Ahmad, M. M.; Underhill, A. E. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3262.

Table III. Fractional Coordinates[a] (×10^4) for α-Fe[(C$_5$Me$_5$)$_2$]{Pt[S$_2$C$_2$(CN)$_2$]$_2$}

atom type[b]	fractional coord x	y	z	equiv isotropic thermal param B,[d] Å^2	atom type[b]	fractional coord x	y	z	equiv isotropic thermal param B,[d] Å^2
Anion I									
Pt(1)	0^e	0^e	5000^e	38 (1)	C(1)	2350 (9)	0^e	3497 (10)	54 (4)
S(11)	745 (2)	0^e	3620 (2)	46 (1)	C(2)	2668 (8)	0^e	5674 (9)	45 (4)
S(12)	1134 (2)	0^e	6078 (2)	44 (1)	N(1)	2861 (7)	0^e	2973 (9)	79 (4)
C(11)	1727 (7)	0^e	4193 (8)	39 (3)	N(2)	3324 (6)	0^e	6043 (8)	62 (3)
C(12)	1886 (6)	0^e	5226 (8)	41 (3)					
Anion II									
Pt(2)	982 (1)	0^e	−440 (1)	36 (1)	C(3)	563 (5)	−2033 (4)	−1398 (5)	47 (2)
S(21)	480 (1)	−767 (1)	−1533 (1)	42 (1)	C(4)	1517 (5)	−2017 (4)	522 (5)	52 (3)
S(22)	1495 (1)	−751 (1)	667 (2)	48 (1)	N(3)	370 (4)	−2492 (3)	−1814 (5)	62 (2)
C(21)	797 (4)	−1446 (3)	−906 (5)	37 (2)	N(4)	1753 (6)	−2455 (4)	930 (6)	79 (3)
C(22)	1240 (5)	−1438 (4)	29 (5)	43 (2)					
Cation I									
Fe(3)	5000^e	0^e	0^e	30 (1)	H(31b)	2948 (43)	401 (34)	−1119 (59)	81 (23)
C(31)	3753 (6)	0^e	−124 (8)	36 (3)	H(32a)	3594	1264	−545	*c*
C(32)	4035 (4)	539 (4)	433 (6)	45 (2)	H(32b)	4266	1533	247	
C(33)	4501 (4)	333 (3)	1338 (5)	41 (2)	H(32c)	3460	1290	642	
M(31)[e]	3222 (8)	0^e	−1095 (10)	51 (4)	H(33a)	4861	1187	1996	
M(32)[e]	3848 (6)	1223 (4)	144 (8)	69 (3)	H(33b)	5464	634	2284	
M(33)[e]	4909 (5)	743 (5)	2156 (7)	62 (3)	H(33c)	4634	652	2764	
H(31a)	3266 (60)	0^e	−1619 (76)	67 (28)					
Cation II									
Fe(4)	7500^e	2500^e	5000^e	28 (1)	H(41c)	9302	3313	4711	
C(41)	8096 (4)	3377 (3)	5066 (6)	40 (2)	H(42a)	7847	2973	2589	
C(42)	7657 (4)	3301 (3)	4077 (5)	36 (2)	H(42b)	8565	3267	3279	
C(43)	6843 (4)	3237 (3)	4252 (5)	33 (2)	H(42c)	7938	3713	2678	
C(44)	6763 (4)	3264 (3)	5334 (5)	32 (2)	H(43a)	5692	3385	3633	
C(45)	7542 (4)	3351 (3)	5842 (5)	36 (2)	H(43b)	6016	2741	3225	
M(41)	8990 (4)	3485 (4)	5237 (9)	64 (3)	H(43c)	6361	3386	2850	
M(42)	8011 (5)	3317 (4)	3044 (7)	57 (3)	H(44a)	6081	3302	6581	
M(43)	6157 (5)	3168 (4)	3426 (6)	55 (3)	H(44b)	5683	2853	5720	
M(44)	5996 (4)	3231 (4)	5846 (6)	49 (2)	H(44c)	5717	3580	5527	
M(45)	7718 (6)	3442 (4)	6993 (6)	63 (3)	H(45a)	8222	3240	7181	
H(41a)	9149	3289	5892	*c*	H(45b)	7318	3273	7408	
H(41b)	9077	3935	5288		H(45c)	7767	3891	7109	

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] The letter M is used to designate methyl carbon atoms. Each methyl hydrogen atom carries the same number as the methyl carbon to which it is covalently bonded as well as a letter, a, b, or c, to distinguish between hydrogens bonded to the same carbon. Positions for hydrogen atoms H(31a) and H(31b) were located from a difference Fourier map and were refined as independent isotropic atoms. The remaining methyl carbons and their hydrogens were refined as rigid rotors assuming sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each methyl group was determined by three rotational parameters. [c] With the exception of hydrogen atoms H(31a) and H(31b), which were refined as independent isotropic atoms, the isotropic thermal parameter of each remaining hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. [d] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [e] This is a symmetry-required value and is therefore listed without an estimated standard deviation.

displacement is 0.15 Å.[15] Likewise, the N's have a greater deviation from the mean S$_4$ plane with the distances ranging from 0.18 to 0.30 Å, and the average displacement is 0.22 Å away from the plane. The intradimer S···S distances are 3.531 and 3.553 Å and average 3.542 Å. This suggests that a strong [A]$_2^{2-}$ dimer, not two A$^{\bullet-}$'s, is present.[15] The average C$_5$ ring carbon–S$_4$ plane distance is 3.694 Å, and the intradimer Fe···Fe spacing is 14.64 Å. The cation is located essentially above the NiS$_2$C$_2$ ring. These dimers pack in a herringbone motif with adjacent dimers being orthogonal to each other. The interdimer Fe···Fe spacings are 7.909, 9.774, 12.66, and 18.71 Å. The Fe···Ni distances are 5.642, 10.47, and 16.96 Å. There are no interion distances less than the sum of the van der Waals radii. The essentially eclipsed {Ni[S$_2$C$_2$(CN)$_2$]$_2$}$_2^{2-}$ dimer has a geometry not previously reported for {Ni[S$_2$C$_2$(CN)$_2$]$_2$}$^-$.[10-13] Thus, the overall composition is D$^{\bullet+}$A$_2^{2-}$D$^{\bullet+}$, and the repeating unit is composed of an $S = {}^1/_2$ cation and an $S = 0$ anion. Thus, the repeating unit has only a D$^{\bullet+}$.

α-[Fe(C$_5$Me$_5$)$_2$]{Pt[S$_2$C$_2$(CN)$_2$]$_2$} possesses a complex unit cell with two distinct nonintersecting chains. The simplest chain has a ···DAADAA··· motif (Figure 3) where the dimeric anions are essentially eclipsed as noted above (Figure 2b). The Pt···Pt separation is 3.576 Å, and the parallel S$_4$ planes are separated by 3.537 Å. The latter is slightly larger than the 3.440 and 3.49 Å observed for Rb{Pt[S$_2$C$_2$(CN)$_2$]$_2$}·2H$_2$O[14a] and (perylene){Pt[S$_2$C$_2$(CN)$_2$]$_2$}·2H$_2$O,[14b] respectively. However, due to slippage of the plane, the Pt···Pt separation is intermediate between the values (3.335 and 5.22 Å, respectively) reported for these two compounds. The anion is not planar, with the CN groups being bent away from the mean S$_4$ plane. The CN carbons deviate from the plane by 0.03–0.13 Å, and the average displacement is 0.08 Å away from the plane. Likewise, the N's have a greater deviation from the mean S$_4$ plane with the distances ranging from 0.03 to 0.20 Å, and the average displacement is 0.12 Å away from the plane. The shortest intradimer S···S separation is 3.586 Å. As for the above structure, this suggests that a strong [A]$_2^{2-}$ dimer, not two A$^{\bullet-}$'s, is present. The intrachain Fe···Fe distance is 16.802 Å and the C$_5$ ring carbon–S$_4$ plane distances range from 3.907 to 4.016 Å and average 3.965 Å. As noted above, the anion forms a strong dimer with a $S = 0$ ground state (vide infra).

Perpendicular to the parallel ···DAADAA··· chain motif is an unusual extended layer motif composed of alternating D's and A's such that the D's and A's form extended edge to edge chains

---

(15) The cyano groups bending away from the mean plane is also observed for many $S = 0$ [TCNQ]$_2^{2-}$ dimers; see, for example, ref 16.

Table IV. Fractional Coordinates for β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$

atom	*x*	*y*	*z*	*B*,[a] Å²
Pt(1)	0.06403 (5)	0.89877 (5)	0.41704 (5)	3.74 (1)
Pt(2)	0.000	0.000	0.000	4.59 (2)
Fe(1)	0.2557 (2)	0.5227 (2)	0.2589 (2)	3.56 (5)
Fe(2)	0.500	0.000	0.000	3.02 (7)
S(1)	−0.0230 (3)	0.7931 (3)	0.4779 (3)	4.57 (9)
S(2)	−0.0787 (3)	0.8733 (3)	0.2937 (3)	4.59 (9)
S(3)	0.2061 (3)	0.9239 (3)	0.5403 (3)	4.42 (9)
S(4)	0.1504 (3)	1.0069 (3)	0.3584 (3)	4.7 (1)
S(5)	−0.0789 (4)	0.1322 (3)	−0.0332 (3)	5.4 (1)
S(6)	−0.0312 (4)	0.0653 (3)	0.1599 (3)	5.7 (1)
N(1)	−0.271 (1)	0.627 (1)	0.427 (1)	7.9 (5)
N(2)	−0.338 (1)	0.722 (1)	0.191 (1)	7.3 (5)
N(3)	0.473 (1)	1.064 (1)	0.638 (1)	6.3 (4)
N(4)	0.406 (1)	1.168 (1)	0.407 (1)	7.2 (4)
N(5)	−0.209 (2)	0.364 (1)	0.085 (1)	8.3 (5)
N(6)	−0.153 (2)	0.281 (2)	0.330 (1)	12.7 (8)
C(1)	−0.140 (1)	0.755 (1)	0.396 (1)	4.7 (4)
C(1A)	−0.215 (1)	0.683 (1)	0.413 (1)	5.6 (5)
C(2)	−0.163 (1)	0.788 (1)	0.318 (1)	4.6 (4)
C(2A)	−0.262 (1)	0.753 (1)	0.247 (1)	5.2 (4)
C(3)	0.293 (1)	1.008 (1)	0.517 (1)	4.2 (4)
C(3A)	0.394 (1)	1.039 (1)	0.584 (1)	4.7 (4)
C(4)	0.269 (1)	1.043 (1)	0.437 (1)	4.3 (4)
C(4A)	0.346 (1)	1.113 (1)	0.422 (1)	5.1 (4)
C(5)	−0.117 (1)	0.200 (1)	0.079 (1)	5.0 (4)
C(5A)	−0.168 (2)	0.292 (1)	0.084 (1)	6.1 (5)
C(6)	−0.094 (1)	0.171 (1)	0.162 (1)	6.3 (5)
C(6A)	−0.129 (2)	0.236 (1)	0.259 (1)	6.9 (5)
C(10)	0.360 (1)	−0.042 (1)	−0.107 (1)	4.5 (4)
C(10M)	0.345 (2)	−0.027 (2)	−0.208 (1)	7.9 (6)
C(11)	0.356 (1)	−0.020 (1)	0.057 (1)	5.3 (4)
C(11M)	0.281 (2)	0.126 (1)	−0.007 (2)	9.1 (7)
C(12)	0.331 (1)	0.024 (1)	−0.018 (1)	4.7 (4)
C(12M)	0.334 (2)	0.027 (2)	0.168 (1)	9.8 (8)
C(13)	0.399 (1)	−0.112 (1)	0.017 (1)	5.4 (4)
C(13M)	0.442 (2)	−0.221 (2)	−0.161 (2)	9.4 (7)
C(14)	0.404 (1)	−0.127 (1)	−0.085 (1)	4.4 (4)
C(14M)	0.435 (2)	−0.187 (2)	0.071 (2)	10.7 (6)
C(20M)	0.523 (2)	0.520 (2)	0.241 (2)	9.3 (8)
C(20)	0.407 (1)	0.465 (1)	0.216 (1)	5.0 (4)
C(21M)	0.348 (2)	0.497 (2)	0.047 (1)	9.9 (6)
C(21)	0.330 (1)	0.453 (1)	0.131 (1)	5.1 (4)
C(22M)	0.138 (2)	0.360 (2)	0.057 (2)	10.4 (7)
C(22)	0.237 (1)	0.393 (1)	0.135 (1)	5.9 (5)
C(23M)	0.185 (2)	0.300 (1)	0.253 (2)	10.6 (7)
C(23)	0.260 (1)	0.367 (1)	0.222 (1)	5.3 (4)
C(24M)	0.417 (2)	0.398 (2)	0.368 (2)	9.9 (7)
C(24)	0.362 (1)	0.410 (1)	0.271 (1)	4.7 (4)
C(25M)	0.138 (3)	0.679 (2)	0.156 (2)	17 (1)
C(25)	0.178 (2)	0.647 (1)	0.256 (1)	10.3 (6)
C(26M)	0.357 (3)	0.746 (2)	0.309 (3)	25 (1)
C(26)	0.268 (2)	0.679 (1)	0.322 (1)	7.3 (6)
C(27M)	0.342 (2)	0.656 (2)	0.486 (2)	12.3 (9)
C(27)	0.258 (2)	0.636 (1)	0.398 (1)	6.0 (5)
C(28M)	0.114 (2)	0.528 (2)	0.439 (2)	13.1 (7)
C(28)	0.158 (1)	0.582 (1)	0.374 (1)	5.1 (4)
C(29M)	−0.014 (2)	0.537 (2)	0.236 (3)	18 (1)
C(29)	0.104 (1)	0.589 (1)	0.281 (2)	8.2 (6)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

with the $[D^{\bullet+}]_2A^{\bullet-}$ repeating unit. This is best observed in Figure 4. In this arrangement the C_5 rings are canted 7.41° with respect to the rigorously parallel anions. Adjacent cations have an 8.401-Å separation between the Fe's, whereas the Fe···Fe separation in a $D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}$ segment is 10.548 Å. Thus, the overall composition is $D^{\bullet+}[A]_2^{2-}[D^{\bullet+}]_2A^{\bullet-}$, and the repeating unit is composed of three $S = {}^1/_2$ cations, an $S = 0$ $[A]_2^{2-}$ anion, and an $S = {}^1/_2$ $A^{\bullet-}$ radical anion. Thus the repeating unit is $D^{\bullet+} + {}^1/_3\ A^{\bullet-}$.

Table V. Fractional Coordinates (Å × 10⁴) for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$

atom	*x*	*y*	*z*	B_{iso}, Å²
Ni(1)	2500	2500	5000	2.4 (1)[a]
Fe(1)	5000	5685 (2)	2500	1.8 (1)[a]
S(1)	1560 (2)	2890 (2)	5781 (2)	3.2 (1)[a]
S(2)	2663 (2)	4137 (3)	4733 (2)	3.3 (1)[a]
F(1)	1873 (12)	6478 (9)	5794 (7)	5.5 (5)[a]
F(1′)	2459 (26)	6447 (29)	5613 (24)	6.2 (10)
F(2)	2728 (9)	6352 (8)	4927 (9)	4.6 (5)[a]
F(2′)	2240 (26)	6273 (21)	4561 (15)	3.5 (7)
F(3)	1253 (19)	6324 (12)	4740 (12)	10.1 (8)[a]
F(3′)	1142 (32)	6373 (33)	5179 (22)	5.4 (10)
F(4)	170 (6)	5364 (8)	5914 (5)	7.7 (4)[a]
F(5)	340 (7)	4026 (8)	6564 (5)	9.2 (4)[a]
F(6)	1235 (7)	5319 (9)	6748 (5)	9.1 (4)[a]
C(1)	1441 (8)	4260 (10)	5728 (6)	2.8 (4)[a]
C(2)	1940 (9)	4800 (9)	5267 (6)	2.9 (4)[a]
C(3)	809 (12)	4738 (13)	6252 (10)	5.1 (6)[a]
C(4)	1970 (13)	5985 (12)	5159 (10)	4.2 (5)[a]
C(10)	3820 (9)	4854 (10)	2094 (6)	2.7 (4)[a]
C(11)	4415 (8)	5037 (10)	1537 (6)	2.5 (4)[a]
C(12)	4504 (8)	6142 (10)	1439 (6)	2.7 (4)[a]
C(13)	3987 (8)	6645 (10)	1951 (7)	2.7 (4)[a]
C(14)	3550 (7)	5842 (11)	2355 (5)	2.5 (4)[a]
C(15)	4825 (10)	4213 (12)	1079 (7)	5.3 (5)[a]
C(16)	5048 (10)	6713 (12)	893 (6)	4.9 (5)[a]
C(17)	3861 (11)	7801 (11)	2032 (8)	5.8 (5)[a]
C(18)	2906 (9)	6067 (13)	2935 (7)	5.5 (5)[a]
C(19)	3518 (10)	3801 (12)	2348 (8)	5.9 (5)[a]
H(15)	5461	4380	1034	4.5
H(15′)	4497	4203	607	4.5
H(15″)	4787	3536	1297	4.5
H(16)	5487	6243	705	4.5
H(16′)	5368	7297	1115	4.5
H(16″)	4628	6954	496	4.5
H(17)	3254	7949	2164	4.5
H(17′)	3948	8142	1583	4.5
H(17″)	4309	8062	2399	4.5
H(18)	3238	6257	3370	4.5
H(18′)	2536	5445	3008	4.5
H(18″)	2483	6622	2771	4.5
H(19)	3909	3265	2180	4.5
H(19′)	2893	3674	2156	4.5
H(19″)	3556	3792	2862	4.5

[a] Four-thirds of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

Table VI. Summary of Average Bond Distances (Å) for $[Fe(C_5Me_5)_2]\{M[S_2C_2R_2]_2\}$

	Intramolecular Distances			
M	Ni	Pt α phase	Pt β phase	Ni
R	C≡N	C≡N	C≡N	CF_3
Fe—C	2.07	2.098	2.085	2.087
C—C	1.37	1.420	1.403	1.417
C—Me	*a*	1.506	1.537	1.499
Fe—C_5 ring centroid	1.706	1.716	1.706	1.704
M—S	2.141	2.265	2.265	2.135
S—C	1.710	1.728	1.702	1.730
C—C	1.353	1.355	1.383	1.348
C—CN	1.456	1.42	1.450	1.514
C≡N	1.152	1.14	1.123	
	Intramolecular Dimer Distances			
M—M	3.525	3.576	3.573	
S_4—S_4 plane	3.482	3.537	3.55	
S_4—S distance	3.531	3.586	3.534	

[a] Disordered.

β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ possesses a complex unit cell comprising an extended $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chain (Figure 5) and orthogonal $D^{\bullet+}A_2^{2-}D^{\bullet+}$ dimers (Figure 1b). The $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chain possesses cations essentially over the PtS_2C_2 rings. The C_5 ring carbon–S_4 plane distances range from 3.49 to 4.06 Å, and the average is 3.56 Å. The intra- and interchain Fe···Pt separations are 12.11 and 18.23 Å, respectively. The interchain Fe···Fe and Pt···Pt distances are 16.58 Å. The dimer contains dimer anions that are essentially eclipsed as noted above (Figure 2c). The anion is not planar, with the CN groups being bent away from the mean S_4 plane. The CN carbons deviate from the plane by 0.0–0.11

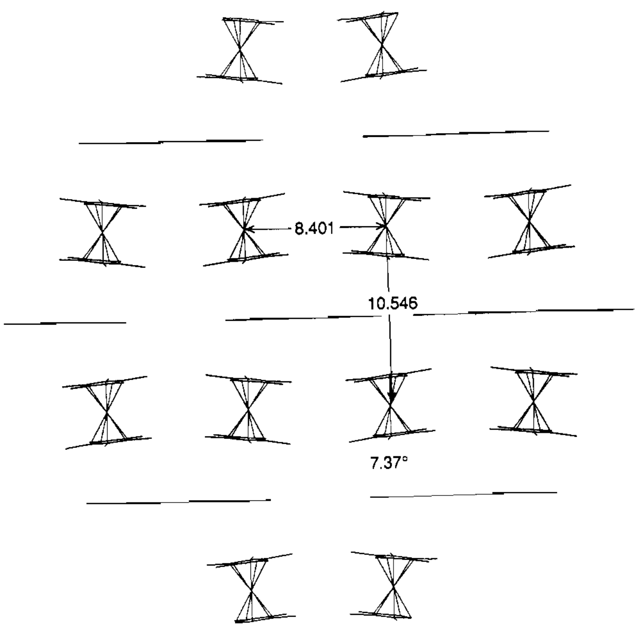


Figure 4. "X" chain motif in α-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$.

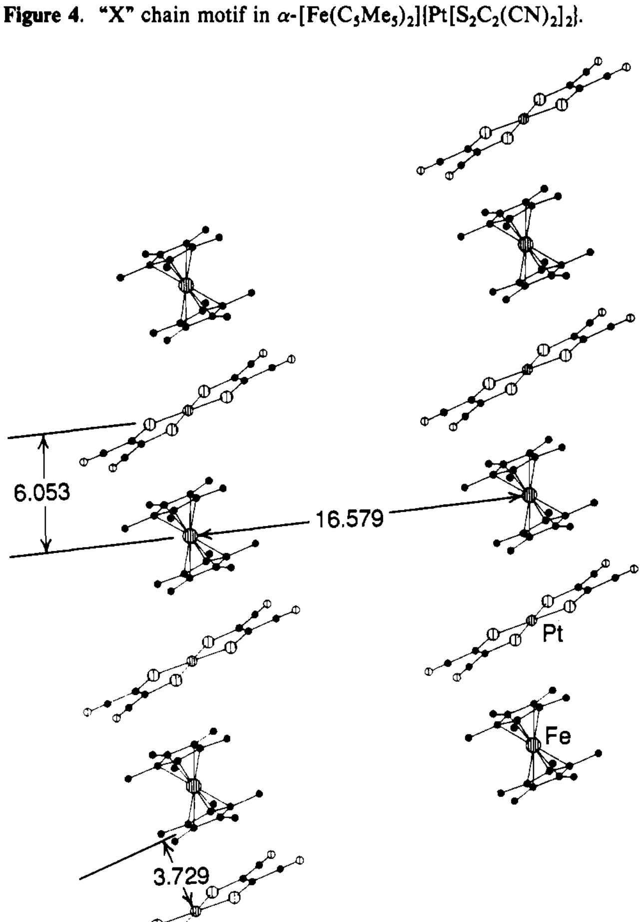


Figure 5. 1-D ⋯DADA⋯ chain in β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$.

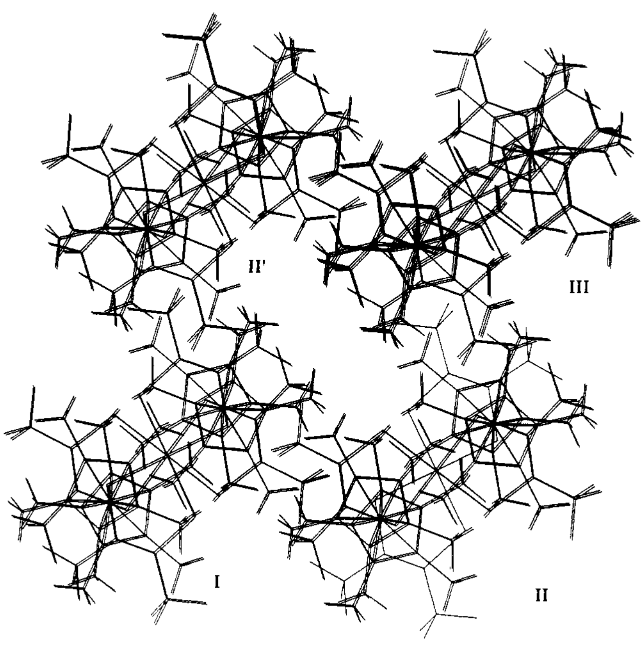


Figure 6. View normal to chains showing the four unique chains I, II, II', and III for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$.

Å, and the average displacement is 0.01 Å away from the plane. Likewise, the N's have a greater deviation from the mean S_4 plane with the distances ranging from 0.00 to 0.21 Å, and the average displacement is 0.07 Å away from the plane. The intradimer Pt⋯Pt and Fe⋯Fe separations are 3.573 and 14.80 Å, respectively. The parallel S_4 planes are separated by ~3.55 Å. The shortest interdimer S⋯S separation is 3.534 Å; the C_5 ring carbon–S_4 plane distances range from 3.676 to 3.876 Å, and the average is 3.774 Å. As for the above structures this suggests that a strong $[A_2]^{2-}$ dimer, not two $A^{\bullet-}$'s, is present. Thus the overall composition is $D^{\bullet+}A_2^{2-}D^{\bullet+}[D^{\bullet+}A^{\bullet-}]$. Like the α-phase this corresponds to three $S = {}^1/_2$ cations and $S = {}^1/_2$ and $S = 0$ anion dimers per repeating unit. Thus the repeating unit is $D^{\bullet+} + {}^1/_3A^{\bullet-}$.

$[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ is comprised of centrosymmetric extended $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chains. The cation sits essentially above a S_2C_2 fragment, and the C_5 ring–S separation is ~3.53 Å. The unit cell has three unique pairwise interchain interactions I–II, I–III, and II–II' (Figure 6) that are shown in Figure 7. The intrachain Fe⋯Fe and Fe–Ni spacings are 12.097, and 6.049 Å, respectively. The interchain Fe⋯Fe distances are 9.389, 9.605, 12.349, 12.695, 13.051, 13.802, and 14.417 Å, whereas the interchain Fe⋯Ni distances are 7.323, 10.589, 11.80, and 12.349 Å. The Ni⋯Ni distance for the in-registry interaction is 12.695 Å. There are no intraion distances less than the sum of the van der Waals radii. Thus, the overall composition is $D^{\bullet+}A^{\bullet-}$. This corresponds to a $S = {}^1/_2$ cation and $S = {}^1/_2$ anion per repeat unit.

Magnetic Susceptibility. The magnetic susceptibility, χ, was measured between 2 and 320 K by the Faraday method.[17,18] The salt $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$ obeys the Curie–Weiss expression $\chi = C/(T - \Theta)$, with $\Theta = 0 \pm 1.8$ K (Figure 8a). The effective moments, μ_{eff}, for four samples were 2.66, 2.71, 2.80, and 3.14 μ_B and the average was 2.83 μ_B. Assuming $\langle g \rangle = 2$ for both the cation and anion, a μ_{eff} of 2.45 μ_B is expected. The g values for $[Fe(C_5Me_5)_2]^{\bullet+}$, however, are very anisotropic; i.e., $g_{\parallel}$ is 4.4, $g_{\perp}$ is 1.3, and $\langle g \rangle$ is 2.8.[5b,19] Thus, for two independent spins and random orientation a μ_{eff} of 3 μ_B is predicted. The relatively short contact of $\{Ni[S_2C_2(CN)_2]_2\}^-$ to form $S = 0$ $\{Ni[S_2C_2(CN)_2]_2\}_2^{2-}$ akin to $\{[Fe(C_5Me_5)_2]^{\bullet+}\}_2[TCNQ]_2^{2-}$[16] seems likely. In this circumstance, only the cation spin contributes to the susceptibility. Alternatively, the lower observed moment can arise from preferential orientation of the samples with the C_5 molecular axis perpendicular to the magnetic field. Previously, the magnetic susceptibilities of $\{Ni[S_2C_2(CN)_2]_2\}_2^{2-}$ dimers have been interpreted by a singlet ground state with a thermally excited

---

(16) Miller, J. S.; Reiff, W. M.; Zhang, J. H.; Preston, L. D.; Reis, A. H., Jr.; Gebert, E.; Extine, M.; Troup, J.; Dixon, D. A.; Epstein, A. J.; Ward, M. D. *J. Phys. Chem.* **1987**, *91*, 4344–4360.

(17) Miller, J. S.; Dixon, D. A.; Calabrese, J. C.; Vazquez, C.; Krusic, P. J.; Ward, M. D.; Wasserman, E.; Harlow, R. L. *J. Am. Chem. Soc.*, in press.

(18) Diamagnetic corrections: $Fe(C_5Me_5)_2$, -230×10^{-6} emu/mol; $Ni[S_2C_2(CN)_2]_2$, -137×10^{-6} emu/mol; $Pt[S_2C_2(CN)_2]_2$, -158×10^{-6} emu/mol; $Ni[S_2C_6(CH_3)]_2$, -191×10^{-6} emu/mol; $Ni[S_2C_2(CF_3)_2]_2$, -192×10^{-6} emu/mol.

(19) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955–970.

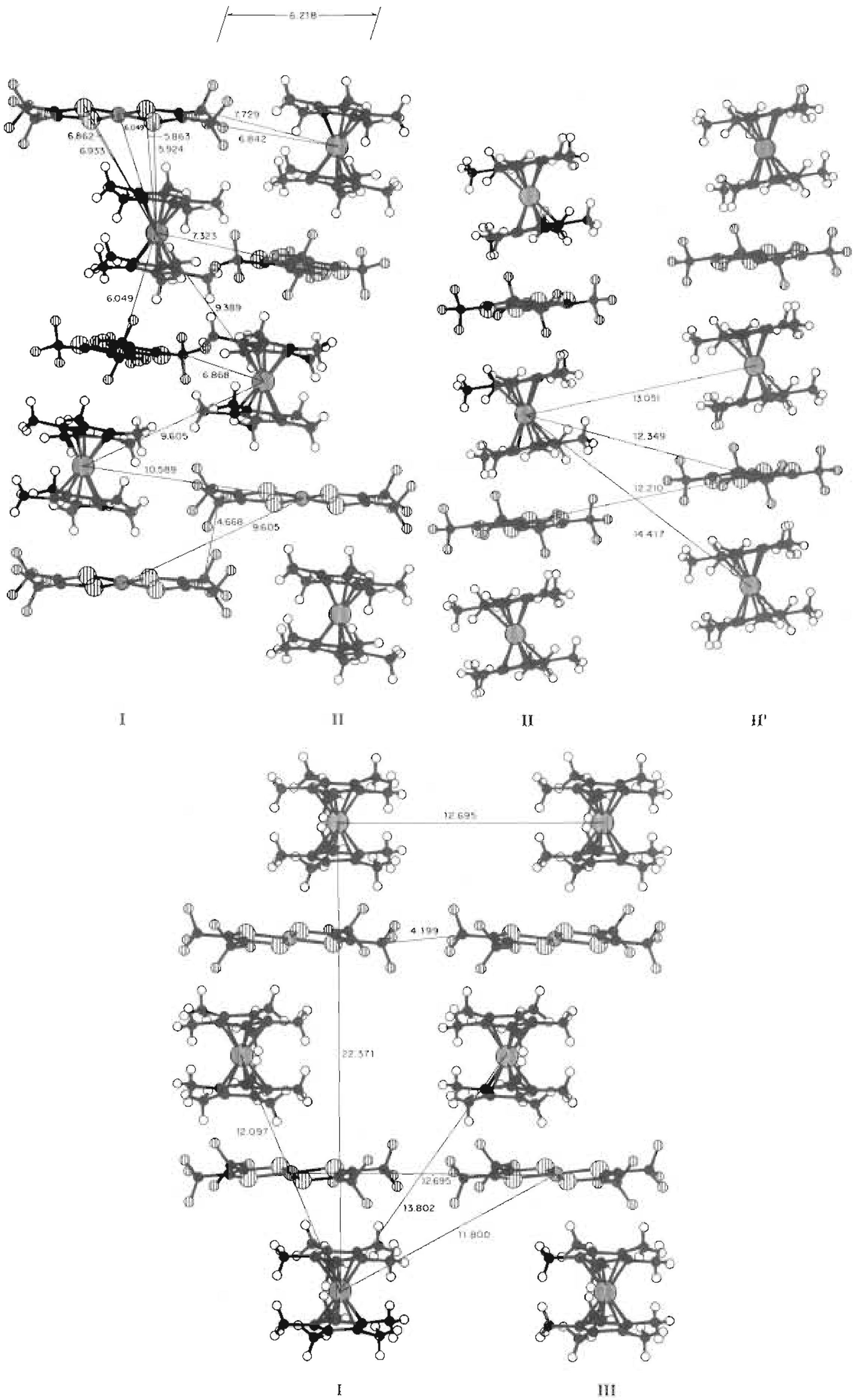


Figure 7. Out-of-chain interactions between chains I and II (top left) and between II and II′ (top right) and in-registry interactions between chains I and III (bottom) for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$.

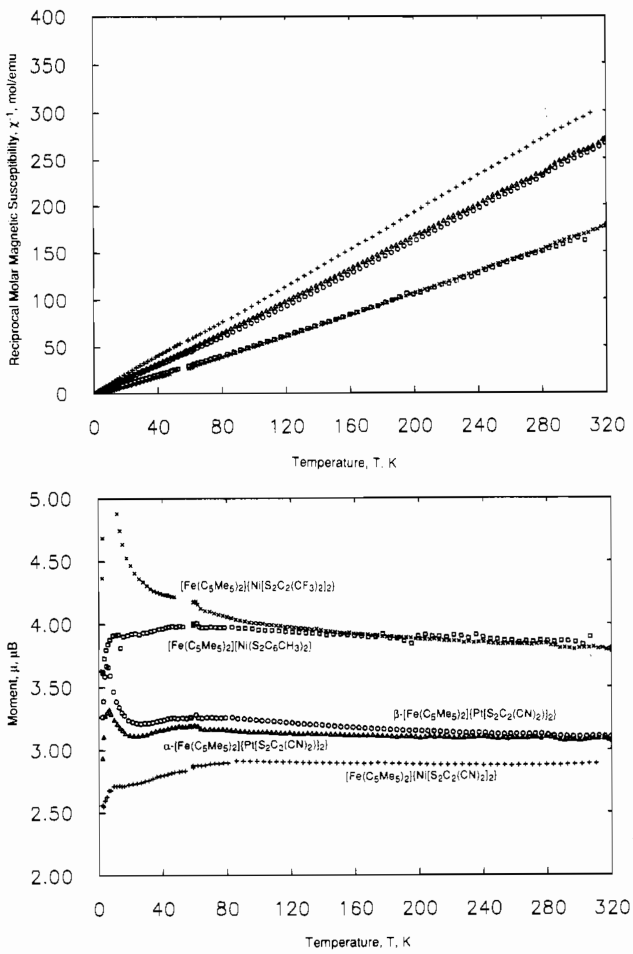


Figure 8. Reciprocal molar magnetic susceptibility (a, top) and moment (b, bottom) as a function of temperature for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$ (+), α-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ (△), β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ (○), $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ (×), and $[Fe(C_5Me_5)_2]\{Ni[S_2C_6Me]_2\}$ (□).

state with an exchange constant of <620 cm^{-1}.[11,20] The observed reciprocal susceptibility for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$ is linear over the entire range of the experiment (2–320 K) and suggests that triplet state is much greater in energy ($J > 1200$ cm^{-1}) and thus does not significantly contribute to the observed susceptibility. This is consistent with the observed dimer, which has a short intradimer separation and has more Ni···Ni overlap than the Ni···S overlap ascribed as the superexchange pathway for the $[PPh_3Me]\{Ni[S_2C_2(CN)_2]_2\}$.[20] Larger single crystals enabling the study of the anisotropy magnetic properties are required to resolve this point.

The susceptibilities of α- and β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ obey the Curie–Weiss operation with $\Theta = +6.6$ K and $\mu_{eff} = 3.05\ \mu_B$ for the α-phase and $\Theta = +9.8$ K (the average of 9.3 and 10.4 K) and $\mu_{eff} = 3.10\ \mu_B$ (the average of 3.06 and 3.13 μ_B) for the β-phase. The moment, as discussed above, is suggestive of independent paramagnetic spins with a random orientation of the anisotropic cation. The observed data are consistent with random orientation of the cation's spins and a spin from the anion. For both phases from the structural data the anions exist as isolated $S = {}^1/_2$ $A^{\bullet-}$ and $S = 0$ $[A_2]_2^{2-}$; i.e., two-thirds exist in a diamagnetic ground state. Thus, the observed susceptibility should be reduced, but this can be masked by orientation effects that would give the cation a greater effective moment. These susceptibilities could also have a contribution from a thermally populated triplet. However, like the Ni analogue, the observed reciprocal susceptibility is linear over the entire range of the experiment (2–320 K), suggesting that the triplet state is much

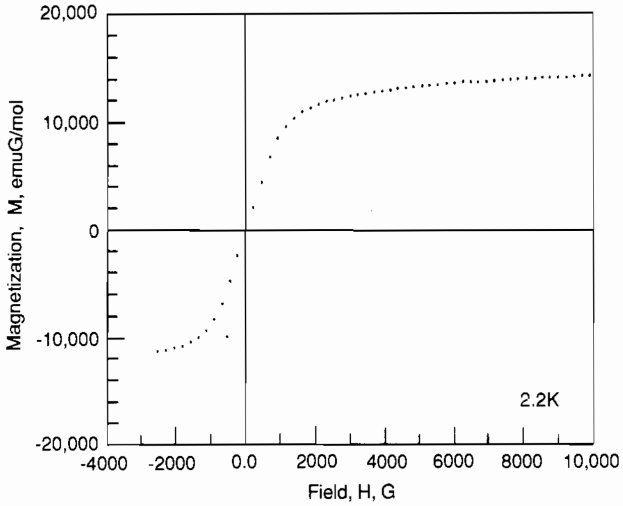


Figure 9. Magnetization, M, as a function of field, H, at 4.2 K for $[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$.

higher in energy and thus does not significantly contribute to the observed susceptibility. It should be noted that $[NEt_4]\{Pt[S_2C_2(CN)_2]_2\}$ has a thermally accessible triplet with an exchange constant of 350 cm^{-1}; however, the structure is unknown.[20]

The β-phase exhibits a field-dependent susceptibility below 7 K. This is consistent with ferromagnetic coupling within the observed $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chains[20] as noted for the TCNE,[3,5] $C_4(CN)_6$,[3,6] TCNQ,[3,4] and $(TCNQ)I_2$[7] electron-transfer salts of $Fe(C_5Me_5)_2$. Larger single crystals enabling the study of the anisotropic magnetic properties are required to resolve these points.

In contrast, the susceptibility of $[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$ has a larger effective moment (3.64, 3.65, 3.72, and 3.91 μ_B; average = 3.73 μ_B) at room temperature. The susceptibility varies approximately as expected for a Curie–Weiss mean-field behavior; i.e., $\chi = C/(T - \Theta)$ with $C = \Sigma g^2\mu_B{}^2J(J + 1)/3k_B$ where the sum is over all the radicals of the unit cell and Θ is a constant. Detailed inspection of the data shows that the small curvature in the plots of χ^{-1} vs T (Figure 8a) leads to estimates of $\Theta = 15$ K (using data for $T > 100$ K) and $\Theta = 5$ K ($10 \leq T \leq 100$ K). Like $[Fe(C_5Me_4H)_2]^{\bullet+}[TCNE]^{\bullet-}$[21] and $[Cr(C_6Me_3H_3)_2]^{\bullet+}[TCNE]^{\bullet-}$[22] the effective moment rises with decreasing temperature up to 4.2 K, suggesting that the primary interaction along the chain is ferromagnetic. The effective moment at room temperature suggests partial orientation of the sample in a magnetic field, with the degree of orientation varying with the samples. Below ~8 K, the molar susceptibility exhibits a marked field dependence. Magnetization data were obtained as a function of applied field at 2.15 and 4.2 K (Figure 9). The magnetization as a function of the applied field rises faster than the Brillouin function at both 2.15 and 4.2 K, indicating ferromagnetic interactions. Neither hysteresis at zero magnetic field nor remnant magnetization was observed. This indicates that, at the lowest temperature attained, 2.15 K, long-range three-dimensional (bulk ferromagnetic) magnetic order (bulk ferromagnetism) had not yet occurred. The measured saturation moment, 12 300 emu G/mol, is within the range expected for a polycrystalline sample containing a radical of isotropic ($\langle g \rangle = 2$) and an anisotropic g ($g_\parallel = 4.4$, $g_\perp = 1.4$ for $[Fe(C_5Me_5)_2]^{\bullet+}$).

The susceptibility of $[Fe(C_5Me_5)_2]^{\bullet+}[Ni(S_2C_6H_3Me)_2]^{\bullet-}$ obeys the Curie–Weiss expression with $\Theta = +5.5$ K. The effective moment is 3.83 μ_B; thus, isolated $[Ni(S_2C_6H_3Me)_2]^{\bullet-}$'s are expected to exist in the solid state. Like β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ a field dependence was observed at low temperature. However, since the single-crystal structure could not be determined and the moment drops off at low temperature in a manner typical of antiferromagnetic coupling, further study of

---

(20) Weiler, J. F.; Melby, L. F.; Benson, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 4329–4333.

(21) Miller, J. S.; Glatzhofer, D. T.; O'Hare, D. M.; Reiff, W. M.; Chackraborty, A.; Epstein, A. J. *Inorg. Chem.* **1989**, *28*, 2930–2939.

(22) Miller, J. S.; O'Hare, D. M.; Chackraborty, A.; Epstein, A. J. *J. Am. Chem. Soc.*, in press.

this material was not undertaken at this time.

Conclusion

Ferromagnetic coupling, as evidenced by the positive Θ, is observed for those structures possessing $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chains. This has also been observed for other systems.[3] Of the compounds studied, $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ solely has an 1-D chain structure. It also has the greatest Weiss constant, Θ, largest effective moment, and most pronounced field dependence of the susceptibility. $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$ possesses isolated $D^{\bullet+}A_2{}^{2-}D^{\bullet+}$ dimers and has the lowest μ_{eff}; Θ is zero, and there is no field dependence of the susceptibility. This is consistent with one highly anisotropic moment per repeating unit. The α- and β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ phases possess 1-D $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ strands in one direction and $\cdots$DAAD$\cdots$ units in another direction and its Θ, μ_{eff}, and $M(H)$ are intermediate in value. This is consistent with the presence of one-third of the anions having a singlet ground state.

These results support the necessity of a 1-D $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chain structure for achieving ferromagnetic coupling and ultimately bulk ferromagnetic behavior as observed for $[Fe(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$.[2] With the wide variation of bis- and tris(dithiolates) available[10-12,23] other salts may exhibit stronger ferromagnetic coupling and possibly bulk ferromagnetic behavior. Furthermore, many polymorphs with differing physical properties can easily, albeit sometimes irreproducibly,[22,24] be prepared, and the specific design of structure types, e.g., 1-D $\cdots$DADADA$\cdots$ chains, continues to be an art.[25]

Acknowledgment. A.J.E. and J.S.M. gratefully acknowledge support from the U.S. Department of Energy, Division of Materials Science (Grant No. DE-FG02-86ER45271.A000). We also appreciate the gift of $Ni[S_2C_2(CF_3)_2]_2$ by Dr. S. Freilich and the synthetic assistance supplied by C. Vazquez and D. Wipf as well as the Faraday susceptibility data taken by R. S. McLean (Du Pont CR&DD) and magnetization data taken by K. S. Narayan (Ohio State).

Registry No. **1**·$[Fe(C_5Me_5)_2]^+$ (M = Ni), 122799-70-6; **1**·$[Fe(C_5Me_5)_2]^+$ (M = Pt), 122762-60-1; **1**·$[Bu_4N]^+$ (M = Ni), 55401-12-2; **1**·$[Ph_3PMe]^+$ (M = Pt), 69990-22-3; **2** (M = Ni), 18820-78-5; **2**·$[Fe(C_5Me_5)_2]^+$ (M = Ni), 122722-21-8; $[Fe(C_5Me_5)_2]^+[BF_4]^-$, 100021-51-0; $Fe(C_5Me_5)_2$, 12126-50-0; $[Fe(C_5Me_5)_2]^+[Ni(S_2C_6H_3Me)_2]^-$, 122762-61-2; $[NBu_4][Ni(S_2C_6H_3Me)_2]$, 15492-42-9.

Supplementary Material Available: A summary of the crystallographic data (Table SI), tables of bond angles, least-squares planes, anisotropic thermal parameters, general temperature factors, and bond angles, and stereoviews and labeling diagrams for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$, the α- and β-phases of $[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$, and $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ (40 pages); tables of calculated and observed structure factors (44 pages). Ordering information is given on any current masthead page.

---

(23) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. Hoyer, E.; Dietzsch, W.; Schroth, W. *Z. Chem.* **1971**, *2*, 41–53. Burnes, R. P.; McAulliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303–348.

(24) O'Hare, D. M.; Ward, M. D.; Miller, J. S. Submitted for publication.

(25) Miller, J. S.; Glatzhofer, D. T. Submitted for publication.

Contribution from Fachbereich Chemie Anorganische Chemie,
Universität Dortmund, Postfach 50 05 00, D-4600 Dortmund 50, FRG

Preparation and Spectroscopic Characterization of Difluorophosphorane, PH_3F_2. ^{31}P NMR Spectrum of Protonated Diphosphine, $P_2H_5{}^+$

Rolf Minkwitz* and Andreas Liedtke

Received August 15, 1988

The preparation of difluorophosphorane, PH_3F_2, from the reaction of diphosphine and hydrogen fluoride is reinvestigated; it has been characterized by multinuclear (^1H, ^{19}F, ^{31}P) NMR spectroscopy. Complete infrared and Raman low-temperature spectra of difluorophosphorane are reported. It reacts with alkali-metal fluorides to give phosphine and hexafluorophosphates(V). On the basis of ^{31}P NMR spectroscopic results, a reaction mechanism for the formation of PH_3F_2 is proposed. The byproducts of the reaction were PH_2F_3, $(PH)_n$, and $P_2H_5{}^+$; the last was observed for the first time. In carbon disulfide solution, diphosphine neither reacts with hydrogen halides to yield protonated diphosphine nor interacts with hydrogen fluoride to form difluorophosphorane.

From its position in the periodic table of the elements phosphorus is an element predestined to form compounds of trigonal-bipyramidal (tbp) structure that are stable and neutral and therefore volatile and isolable. The nonequivalence of axial and equatorial ligands gives rise to interesting preparative aspects[1-3] and offers sensitive tests of bonding theories.[4,5] A basic demand of MO theory is that the axial ligands must be able to take up considerable amounts of negative charge.[6,7] Thus, the electronegativity rule, which was established[8] by experiment, is theoretically verified.

Following the MO concept, in the series of fluorophosphoranes, $PH_{5-n}F_n$ (n = 1–5), difluorophosphorane, PH_3F_2, should lie at the limit of preparatively accessible tbp compounds. Indeed, ab initio calculations[9-13] show that phosphoranes containing less fluorine should be thermodynamically unstable with respect to decomposition to phosphine.

---

(1) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper & Row: London, 1976.

(2) Holmes, R. R. *Pentacoordinated Phosphorus-I and II*; ACS Monographs 175 and 176; American Chemical Society: Washington, DC, 1980.

(3) Corbridge, D. E. C. *Phosphorus*; Elsevier: Amsterdam, New York, 1985.

(4) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

(5) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262 and literature cited therein.

(6) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

(7) Pitzer, K. S. *Science* **1969**, *139*, 414.

(8) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613.

(9) Kutzelnigg, W.; Wasilewski, J. *J. Am. Chem. Soc.* **1982**, *104*, 953.

(10) Trinquier, G.; Daudey, J.-P.; Caruana, G.; Madaule, Y. *J. Am. Chem. Soc.* **1984**, *106*, 4794.

(11) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849.

(12) Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1987**, *133*, 553.

(13) Breidung, J.; Thiel, W.; Komornicki, A. Private communication.

0020-1669/89/1328-4238$01.50/0