Linear Chain Organometallic Electron-Transfer Complexes. Synthesis, Crystal Structures, and Magnetic Properties of 1:1 and 2:1 Decamethylferrocenium Salts of Tris[bis(trifluoromethyl)ethylene-1,2-dithiolato]molybdate Anions

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The synthesis and crystal structures of two organometallic electron-transfer salts, $[Fe(C_5Me_5)_2]_x\{Mo[S_2C_2(CF_3)_2]_3\}$ (x = 1, 2), are reported. For x = 1 the structure consists of discrete linear stacks of alternating $S = {}^1/_2$ $[Fe(C_5Me_5)_2]^{\bullet+}$ cations and $S = {}^1/_2$ $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ anions with the anions adopting a nearly perfect trigonal prismatic geometry. Crystal data: monoclinic, space group $C2/m$, a = 22.551 (3) Å, b = 12.997 (2) Å, c = 14.236 (4) Å, β = 91.23 (2)°, V = 4171.4 Å^3, Z = 4, R = 7.3%, and R_w = 8.3% at 25 °C. The high-temperature magnetic susceptibilities for polycrystalline samples of $[M(C_5Me_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ (M = Cr, Fe) and $[Fe(C_5H_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ can be fit to the Curie–Weiss law $\chi = C/(T - \theta)$, with θ = +1.0, +8.4, and +1.8 K and μ_{eff} = 4.32, 3.85, and 3.37 μ_B, respectively. The positive θ are characteristic of weak ferromagnetic interactions, and the μ_{eff} are consistent with independent spins contributing to the magnetic susceptibility. For x = 2, the structure contains interpenetrating linear arrays of alternating $S = {}^1/_2$ $[Fe(C_5Me_5)_2]^{\bullet+}$ cations and S = 0 $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ anions; the anion geometry is significantly distorted from the trigonal prismatic limit, apparently owing to crystal packing forces. Crystal data: triclinic, space group $P\bar{1}$, a = 11.426 (3) Å, b = 11.799 (4) Å, c = 23.375 (3) Å, α = 94.78 (2)°, β = 94.62 (2)°, γ = 103.77 (2)°, V = 3033.6 Å^3, Z = 2, R = 6.3%, and R_w = 7.4% at 25 °C. The magnetic susceptibility for polycrystalline samples of $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ can be fit to the Curie–Weiss law with θ = −3.2 K and μ_{eff} = 3.55 μ_B, indicating that weak intermolecular antiferromagnetic interactions exist between the $S = {}^1/_2$ $[Fe(C_5Me_5)_2]^{\bullet+}$ cations and that the $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ dianion is diamagnetic. The susceptibility of $\{[Fe(C_5H_5)_2]^{\bullet+}\}_2\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ obeys the Curie–Weiss law with θ = 2.53 K and μ_{eff} = 4.37 μ_B, whereas $[Ni^{IV}(C_5Me_5)_2]^{2+}\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ is diamagnetic.

Introduction

The preparation and characterization of molecular solids that exhibit ferromagnetic properties are of considerable current interest.[2,3] Linear-chain organometallic electron-transfer salts based on the donor (D) decamethylferrocene and a variety of planar organic electron acceptors[3] (A) comprise the only well-characterized class of molecular solids exhibiting ferromagnetic behavior. In particular, the low-temperature magnetic properties of $[Fe(C_5Me_5)_2][TCNE]$ (TCNE = tetracyanoethylene)[4] have been interpreted.[3,5] in terms of dominant bulk ferromagnetic interactions in the solid. For these compounds exhibiting linear chains of alternating radical anions and cations, stabilization of the ferromagnetic ground state is thought to result from configurational mixing of the ground state with the lowest charge-transfer excited state.[6] Subsequent work suggests that ferromagnetic coupling via such a mechanism is critically dependent upon both the stacking architecture of the ···DADA··· chains and the degeneracies of the frontier orbitals of the donor and acceptor species.[7,8]

An important issue is the competitive roles of interchain donor–acceptor ($D^{\bullet+}/A^{\bullet-}$), donor–donor ($D^{\bullet+}/D^{\bullet+}$), and acceptor–acceptor ($A^{\bullet-}/A^{\bullet-}$) interactions in determining bulk magnetic properties of the solid. The structures of ferromagnetic $[Fe(C_5Me_5)_2]^{\bullet+}[A]^{\bullet-}$ salts containing planar cyanocarbon[3,8] or bis(dithiolato)metalate[9,10] radical anion acceptors feature all three types of interchain interactions. Interchain $D^{\bullet+}/D^{\bullet+}$ and $D^{\bullet+}/A^{\bullet-}$ interactions are expected to promote bulk ferromagnetic behavior, while $A^{\bullet-}/A^{\bullet-}$ interactions should give rise to antiferromagnetic coupling. The ferromagnetic behavior of $[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ [9a] is consistent with this, and the crossover from ferromagnetic to antiferromagnetic behavior in the low temperature susceptibility of $[Fe(C_5Me_5)_2]^{\bullet+}[Ni(dmit)_2]^{\bullet-}$ was attributed[9b] to dominant antiferromagnetic interactions between $[Ni(dmit)_2]^{\bullet-}$ ions in neighboring ···DADA··· chains within the solid.

In an effort to minimize unfavorable interchain interactions, rock-salt-like structures with each $S = {}^1/_2$ ion being completely surrounded by six $S = {}^1/_2$ counterions in an out-of-registry fashion were sought. Thus, radical anions with size and shape similar to that of decamethylferrocene were deemed necessary, and the $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ anion was targeted for preparation as its $[Fe(C_5Me_5)_2]^{\bullet+}$ salt. The

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(4) Abbreviations: TCNE, tetracyanoethylene; tfd, bis(trifluoromethyl)ethylenedithiolato; dbdt, dimethyl-2-butenedioate-2,3-dithiolato; mnt, maleonitriledithiolato; bdt, benzene-1,2-dithiolato; qdt, quinoxaline-2,3-dithiolato; dmit, 2-thioxo-1,3-dithiole-4,5-dithiolato.

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unpaired electron in this complex anion resides in a nondegenerate molecular orbital of primarily metal d_z^2 character.[11] While this should favor strong ferromagnetic coupling within the chains, it may also weaken the interchain $D^{\bullet+}/A^{\bullet-}$ interactions important for stabilizing bulk ferromagnetic behavior.

In this paper, we describe the synthesis, structures, and magnetic properties of electron-transfer salts prepared by solution redox reactions between $M(C_5Me_5)_2$ (M = Fe, Ni, Cr) and ferrocene with $Mo\{S_2C_2(CF_3)_2\}_3$.

Experimental Section

All synthetic procedures were carried out under an atmosphere of dry nitrogen using standard Schlenk methods or in an inert atmosphere drybox. Tetrahydrofuran was dried by refluxing over Na/K with added benzophenone and then distilled under N_2. Dichloromethane was dried by refluxing over P_2O_5 and distilled under N_2. Elemental analyses were performed in house at the Inorganic Chemistry Laboratory, University of Oxford, or Oneida Research Services, Inc. (Whitesboro, NY).

$S_2C_2(CF_3)_2$ was prepared by the reaction of hexafluoro-2-butyne (PCR Chemicals) with refluxing sulfur as described in the literature.[12a] $Mo[S_2C_2(CF_3)_2]_3$ was prepared by reaction of $Mo(CO)_6$ with $S_2C_2(CF_3)_2$ according to literature methods[12b] and purified by vacuum sublimation. $M(C_5Me_5)_2$ (M = Fe, Ni, Cr) were obtained from Strem Chemical Co. and used as received. Infrared spectra were obtained as KBr mulls by using a Mattson Polaris FT-IR spectrometer. Magnetic susceptibility measurements were performed in the range 2.2–320 K by the Faraday method.[13] The susceptibilities have been corrected for the sample holder, the core diamagnetism of $M(C_5Me_5)_2$ (M = Fe, -230×10^{-6}; Ni, -230×10^{-6}; Cr, -232×10^{-6} emu mol^{-1}), $Fe(C_5H_5)_2$ (-120×10^{-6} emu mol^{-1}) and $Mo[S_2C_2(CF_3)_2]_3$ (-301×10^{-6} emu mol^{-1}) and when appropriate iron impurities (<100 ppm).

$[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$ was prepared by rapid mixing of a solution containing 200 mg (0.26 mmol) of $Mo[S_2C_2(CF_3)_2]_3$ in ca. 60 mL of THF with a solution containing 84 mg (0.26 mmol) of decamethylferrocene in 60 mL of THF. The mixture was taken to dryness under vacuum, and the residual solids were resuspended in a minimum volume of warm CH_2Cl_2. The resulting solution was filtered, cooled to room temperature, and then progressively cooled to 0, −20, and finally −80 °C. Large black rodlike crystals were isolated by filtration and dried in vacuo. Anal. Calcd for $C_{32}H_{30}F_{18}FeMoS_6$ (found): C, 34.92 (35.17); H, 2.75 (2.78); Fe, 5.05 (5.05). IR (rel intensity) 2963 (w), 2925 (w), C–H str; 1507 (w), anion C=C str; 1474 (w), 1385 (w), 1379 (w), 1370 (w), 1258 (m); 1223 (s), 1177 (s), 1163 (s), C–F str; 1100 (m, br), 1022 (m), 847 (w), 803 (m, br), 722 (m), 694 (w) cm^{-1}.

$[Cr(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$ was prepared by the above method using $Cr(C_5Me_5)_2$ as the donor (95 mg, 65%). The unit cell was determined to be c-centered monoclinic [a = 22.25 (6) Å, b = 12.896 (5), c = 14.24 (3), β = 91.38 (8)°, and V = 4083.5 Å^3] and is isomorphic to the Fe^{III} analogue (vide infra). Anal. Calcd for $C_{32}H_{30}CrF_{18}MoS_6$ (found): C, 34.04 (34.81); H, 2.76 (2.67).

$[Ni(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}\cdot MeCN$ was prepared by the above method using $Ni(C_5Me_5)_2$ as the donor (74 mg, 52%). IR (Nujol and Fluorolube) 1537 (w) cm^{-1} C=C str. Anal. Calcd for $C_{34}H_{33}F_{18}MoNNiS_6$ (found): C, 35.68 (35.80); H, 2.91 (2.36); N, 1.22 (1.41).

$[Fe(C_5H_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$ was prepared by the above method using ferrocene as the donor and toluene as the solvent (118 mg, 64%). IR (Nujol and Fluorolube) 1506 (w) cm^{-1} C=C str. Anal. Calcd for $C_{22}H_{10}F_{18}MoFeS_6$ (found): C, 27.51 (27.67); H, 1.05 (0.90).

$[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ was prepared by rapid mixing of a solution containing 179 mg (0.23 mmol) of $Mo[S_2C_2(CF_3)_2]_3$ in ca. 60 mL of THF to a stirred solution containing 150 mg (0.46 mmol) of decamethylferrocene in 30 mL of THF. Crystals began to form before addition was complete. The resulting suspension was warmed gently to dissolve the solids and then filtered. The filtrate was cooled to room temperature and then successively to 0, −20, and finally −80 °C. A mixture of green powder and elongated, platelike crystals was isolated by filtration and recrystallized from THF. Anal. Calcd for $C_{52}H_{60}F_{18}FeMoS_6$ (found): C, 43.76 (43.74); H, 4.20 (4.26); Fe, 7.83 (8.08). IR (rel intensity) 2980 (w, sh), 2963 (w), 2919 (w), 2870 (w, br), C–H str; 1530 (m), anion C=C str; 1477 (w), 1453 (w), 1426 (w), 1386 (w); 1250 (s), 1228 (s), 1158 (s), 1122 (s), C–F str; 1021 (m), 893 (w), 841 (w), 800 (w, br), 715 (m), 691 (w) cm^{-1}.

Crystals suitable for X-ray work were grown by diffusion of a THF solution of $Mo[S_2C_2(CF_3)_2]_3$ through a frit into a THF solution containing a large molar excess of decamethylferrocene.

$[Fe(C_5H_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ was prepared by the above method using ferrocene as the donor (98 mg, 53%). Large black rodlike crystals were isolated by filtration and dried in vacuo. IR (Nujol) 1537 (w) cm^{-1} C=C str. Anal. Calcd for $C_{32}H_{20}F_{18}Fe_2MoS_6$ (found): C, 33.52 (33.06); H, 1.76 (1.52).

X-ray Data Collection. Crystals of $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$ or $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ were sealed under nitrogen in Lindemann glass capillaries and were mounted on an Enraf-Nonius CAD4F diffractometer. Cell dimensions and orientation matrix were obtained by least-squares methods from the positions of 25 carefully centered reflections. During data collection three intensity-control reflections were measured every hour, and three orientation controls checked after every 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout data collection.

Lorentz and polarization corrections were applied together with an empirical absorption correction based on azimuthal scan data.[14] Equivalent reflections were merged, and only those for which $I > 3\sigma(I)$ were included in the refinement [where $\sigma(I)$ is the standard deviation based on counting statistics]. Crystallographic details are presented in Table I; a listing of the atomic positional pa-

Table I. Summary of Crystal Data and Intensity Collection Parameters

formula	$C_{32}H_{30}S_6F_{18}MoFe$	$C_{52}H_{60}S_6F_{18}MoFe_2$
formula wt, daltons	1100.70	1427.01
radiation, Å	0.71069	0.71069
temp, °C	25	25
space group	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)
a, Å	22.551 (3)	11.426 (3)
b, Å	12.997 (2)	11.799 (4)
c, Å	14.236 (4)	23.375 (3)
α, °		94.78 (2)
β, °	91.23 (2)	94.62 (2)
γ, °		103.77 (2)
V, Å^3	4171.4	3033.6
Z	4	2
calcd density, g cm^{-3}	1.75	1.562
μ, cm^{-1}	10.33	9.562
R^a	0.0728	0.0628
R_w^b	0.0832	0.0739

$^a R = \sum[|F_o| - |F_c|]/\sum|F_o|$. $^b R_w = [\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$.

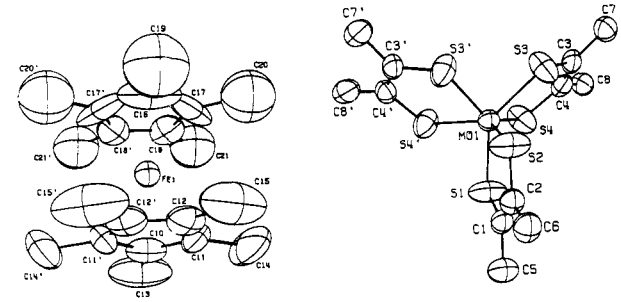

Figure 1. ORTEP plots of the cation and anion in $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$, showing the atom numbering scheme. Atoms are represented as 50% probability ellipsoids.

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Table II. Fractional Atomic Coordinates (×10⁴ Å) and Isotropic Thermal Parameters[a] (Å² × 10⁴) of All Non-Hydrogen Atoms for $[Fe(C_5Me_5)_2][Mo\{S_2C_2(CF_3)_2\}_3]$

atom	x/a	y/b	z/c	U_{iso}
Mo(1)	1640.2 (4)	0	2527.7 (6)	480
S(1)	2495 (1)	0	1598 (2)	756
S(2)	2370 (1)	0	3750 (2)	794
S(3)	1171 (1)	1178 (2)	3535 (2)	749
S(4)	1316 (1)	1212 (2)	1384 (2)	747
C(1)	3115 (4)	0	2310 (8)	547
C(2)	3055 (5)	0	3261 (8)	558
C(3)	872 (3)	2165 (5)	2879 (6)	552
C(4)	951 (3)	2198 (5)	1929 (6)	548
C(5)	3699 (5)	0	1809 (10)	763
C(6)	3569 (5)	0	3952 (9)	661
C(7)	539 (3)	2958 (7)	3421 (7)	688
C(8)	4269 (4)	1971 (7)	8696 (7)	721
Fe(1)	1690.0 (5)	0	7535.6 (9)	444
C(10)	1284 (4)	0	6212 (8)	681
C(11)	1643 (3)	876 (5)	6314 (5)	645
C(12)	2233 (3)	542 (3)	6461 (5)	677
C(13)	628 (6)	0	5991 (13)	1221
C(14)	1435 (8)	1972 (9)	6217 (9)	1226
C(15)	2749 (6)	1267 (15)	6581 (10)	1368
C(16)	2121 (7)	0	8860 (11)	1086
C(17)	1751 (3)	857 (7)	8757 (6)	863
C(18)	1163 (3)	539 (1)	8619 (6)	657
C(19)[b]	2781 (8)	0	9051 (26)	2531 (172)
C(20)[b]	2001 (8)	1922 (10)	8879 (14)	1937 (81)
C(21)[b]	618 (5)	1198 (12)	8523 (11)	1519 (58)
F(1)	4024 (3)	763 (7)	2005 (8)	1348
F(2)	3643 (4)	0	953 (7)	1377
F(3)	3913 (4)	739 (6)	3900 (8)	1388
F(4)	3415 (5)	0	4777 (8)	1743
F(5)	5 (3)	3032 (7)	3208 (7)	1178
F(6)	742 (4)	3867 (6)	3364 (9)	1408
F(7)	559 (6)	2797 (9)	4282 (6)	1501
F(8)	185 (3)	3226 (7)	1304 (7)	1236
F(9)	972 (4)	3881 (7)	1456 (10)	1512
F(10)	808 (8)	2857 (10)	458 (7)	1719

[a] For atoms refined anisotropically the isotropic equivalent thermal parameter is defined as $U_{iso} = (U_{11} + U_{22} + U_{33})/3$. [b] Refined isotropically.

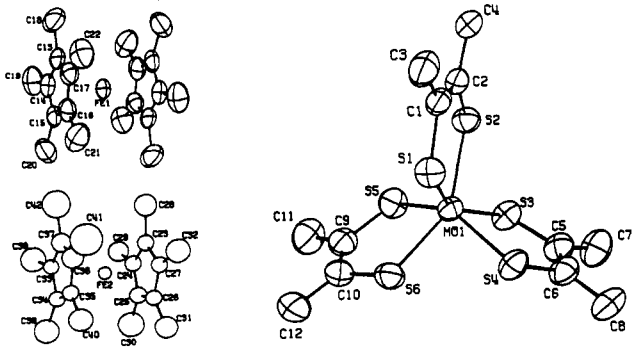

Figure 2. ORTEP plots of cations 1 and 2 and the anion for $[Fe(C_5Me_5)_2]_2[Mo[S_2C_2(CF_3)_2]_3]$, showing the atom numbering scheme. H and F atoms are omitted for clarity. The structure of cation 3 is essentially identical with that of cation 1. Atoms are represented by 50% probability ellipsoids except for cation 2, where isotropic equivalents are plotted at 20% probability.

rameters and selected interatomic distances and angles are given in Tables II and III, respectively, for the 1:1 salt and Tables IV and V, respectively, for the 2:1 salt. Atom labeling for the 1:1 and 2:1 salts is indicated in Figures 1 and 2, respectively.

Structure Solution and Refinement. For the 1:1 salt the position of the Mo atom was determined by using SHELX86.[15a]

(15) (a) Sheldrick, G. SHELX 86 System of Computing Programs; University of Cambridge, Cambridge, England. (b) For a discussion of crystallographic restraints see: Watkin, D. J. In *Crystallographic Computing 4: Techniques and New Techniques*; Isaacs, N. W., Taylor, M. R., Eds.; Oxford University Press: Oxford, 1988, and references therein.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[Fe(C_5Me_5)_2][Mo\{S_2C_2(CF_3)_2\}_3]$

Distances			
Mo(1)–S(1)	2.361 (3)	Fe(1)–C(11)	2.079 (7)
Mo(1)–S(2)	2.369 (3)	Fe(1)–C(12)	2.101 (7)
Mo(1)–S(3)	2.363 (2)	Fe(1)–C(16)	2.10 (1)
Mo(1)–S(4)	2.369 (2)	Fe(1)–C(17)	2.066 (8)
S(1)–C(1)	1.71 (1)	Fe(1)–C(18)	2.088 (7)
S(2)–C(2)	1.71 (1)	C(10)–C(11)	1.403 (7)
S(3)–C(3)	1.716 (8)	C(11)–C(12)	1.412 (7)
S(4)–C(4)	1.718 (8)	C(12)–C(12)′	1.409 (9)
C(1)–C(2)	1.36 (2)	C(16)–C(17)	1.398 (3)
C(3)–C(4)	1.37 (1)	C(17)–C(18)	1.398 (3)
Fe(1)–C(10)	2.08 (1)	C(18)–C(18)′	1.401 (3)
Angles			
S(1)–Mo(1)–S(2)	81.3 (1)	S(3)–C(3)–C(4)	120.2 (6)
S(3)–Mo(1)–S(4)	81.42 (8)	S(4)–C(4)–C(3)	119.7 (5)
Mo(1)–S(1)–C(1)	109.6 (4)	C(11)–C(10)–C(11)′	108.6 (9)
Mo(1)–S(2)–C(2)	108.7 (4)	C(10)–C(11)–C(12)	107.8 (6)
Mo(1)–S(3)–C(3)	109.3 (3)	C(11)–C(12)–C(12)′	107.9 (3)
Mo(1)–S(4)–C(4)	109.2 (3)	C(17)–C(16)–C(17)′	105.6 (12)
S(1)–C(1)–C(2)	119.4 (8)	C(16)–C(17)–C(18)	110.0 (10)
S(2)–C(2)–C(1)	121.0 (8)	C(17)–C(18)–C(18)′	107.2 (4)

Subsequent Fourier difference syntheses revealed the locations of the other non-hydrogen atoms. The methyl carbons on one of the pentamethylcyclopentadienyl (Cp*) rings [C(19) to C(21)] were refined isotropically; all other non-hydrogen atoms were refined anisotropically. The internal C–C and the ring–C–Me distances of the Cp* ring were restrained to their respective arithmetic means, with maximum permitted esd's of 0.01 and 0.02 Å, respectively.[15b] Hydrogen atoms were placed in calculated positions and refined riding on their attached carbon atoms.

For the 2:1 salt the positions of the Mo and Fe atoms were determined by using SHELX86. Subsequent Fourier difference syntheses revealed the locations of the other non-hydrogen atoms. The carbon atoms C(23) to C(32) and C(33) to C(42) of the Cp* rings were subject to soft restraints. The non-hydrogen atoms were refined anisotropically with the exception of Cp* ring carbons C(36) and C(37) and methyl carbon atoms C(28) to C(32) and C(38) to C(42). Hydrogen atoms were placed in calculated positions and refined riding on their attached carbon atoms.

For both structure determinations corrections for anomalous dispersion and isotropic extinction[16] were made in the final cycles of refinement; a Chebyshev weighting scheme[17] was used with the parameters as in Table SI (supplementary material; see the paragraph at the end of the paper). All calculations were performed on a VAX 11/750 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system.[18] Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[19]

Results and Discussion

Synthesis. Direct redox reaction between THF solutions containing donors decamethylferrocene or ferrocene and the strong acceptor complex $Mo[S_2C_2(CF_3)_2]_3$ results in the formation of two distinct salts (i.e., the 1:1 and 2:1 salts) depending upon the ratio in which the components are mixed.

The charges on the ions in these salts may be inferred from the solution redox potentials of the donor and acceptor species: in CH_3CN solution, $Fe(C_5Me_5)_2$ and $Fe(C_5H_5)_2$ each undergo one-electron reversible oxidations at $E_{1/2}(0/1+) = -0.12$ V and 0.40 V vs SCE, respectively,[20]

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Table IV. Fractional Coordinates (×10⁴ Å) and Isotropic Thermal Parameters[a] (Å² × 10⁴) of All Non-Hydrogen Atoms for $[(C_5Me_5)_2Fe]_2[Mo(tfd)_3]$

atom	x/a	y/b	z/c	U_{iso}	atom	x/a	y/b	z/c	U_{iso}
Mo(1)	7207.6 (4)	2654.4 (4)	2489.3 (2)	427	Fe(3)	5000	5000	0	430
S(1)	5178 (1)	2744 (1)	2210.4 (6)	519	C(13)	4209 (6)	5161 (6)	4187 (2)	532
S(2)	7355 (1)	4671 (1)	2781.6 (6)	526	C(14)	4874 (6)	6290 (5)	4453 (2)	551
S(3)	8839 (1)	2997 (1)	3237.2 (7)	574	C(15)	6102 (6)	6250 (6)	4562 (3)	555
S(4)	6378 (1)	1175 (1)	3069.2 (7)	561	C(16)	6197 (6)	5121 (6)	4364 (3)	586
S(5)	8772 (1)	3315 (1)	1905.2 (7)	607	C(17)	5030 (6)	4442 (5)	4128 (2)	558
S(6)	6694 (1)	1079 (1)	1729.9 (7)	583	C(18)	2885 (7)	4825 (9)	3983 (3)	821
F(1)	3804 (4)	5393 (4)	2017 (2)	785	C(19)	4369 (9)	7332 (7)	4566 (4)	892
F(2)	3048 (4)	4191 (5)	2605 (2)	821	C(20)	7134 (8)	7266 (7)	4816 (4)	883
F(3)	3206 (4)	3585 (4)	1746 (2)	821	C(21)	7341 (8)	4698 (9)	4382 (4)	845
F(4)	6102 (5)	6945 (3)	2417 (2)	792	C(22)	4731 (9)	3201 (7)	3856 (3)	845
F(5)	4906 (4)	6324 (4)	3044 (2)	810	C(23)	−547 (8)	8134 (8)	2042 (6)	956
F(6)	6812 (5)	6732 (3)	3261 (2)	834	C(24)	−683 (7)	8433 (8)	2618 (7)	982
F(7)	10134 (7)	3284 (8)	4328 (3)	1365	C(25)	−107 (10)	7805 (11)	2950 (5)	1098
F(8)	8793 (6)	2454 (7)	4789 (3)	1261	C(26)	421 (7)	7101 (7)	2610 (6)	936
F(9)	9819 (7)	1473 (7)	4392 (3)	1260	C(27)	136 (8)	7278 (7)	2034 (5)	916
F(10)	6368 (7)	−638 (5)	3844 (3)	1253	C(28)[b]	−1153 (16)	8634 (15)	1575 (8)	1795 (61)
F(11)	7687 (8)	107 (8)	4420 (4)	1412	C(29)[b]	−1442 (14)	9294 (13)	2841 (7)	1605 (52)
F(12)	6096 (11)	648 (8)	4387 (5)	1448	C(30)[b]	−69 (22)	7760 (21)	3604 (11)	2555 (105)
F(13)	10544 (6)	3373 (8)	1109 (3)	1307	C(31)[b]	1069 (15)	6227 (15)	2775 (8)	1813 (63)
F(14)	9789 (7)	1965 (8)	568 (4)	1417	C(32)[b]	395 (17)	6709 (17)	1491 (8)	1955 (70)
F(15)	9196 (8)	3478 (12)	537 (5)	1481	C(33)	1900 (7)	10580 (6)	2744 (5)	806
F(16)	6313 (8)	−169 (7)	635 (3)	1411	C(34)	2638 (7)	9876 (7)	2996 (4)	898
F(17)	8131 (8)	−25 (7)	558 (3)	1307	C(35)	3047 (6)	9305 (6)	2545 (5)	862
F(18)	7242 (8)	1084 (6)	182 (2)	1232	C(36)[b]	2636 (13)	9625 (12)	2035 (6)	1556 (52)
C(1)	5013 (5)	4158 (5)	2367 (2)	477	C(37)[b]	1983 (11)	10379 (10)	2148 (5)	1261 (36)
C(2)	5966 (5)	4999 (5)	2639 (2)	494	C(38)[b]	1381 (18)	11495 (13)	3042 (8)	2287 (89)
C(3)	3780 (6)	4327 (6)	2192 (3)	631	C(39)[b]	2989 (16)	9864 (17)	3622 (6)	2179 (83)
C(4)	5931 (7)	6232 (5)	2831 (3)	590	C(40)[b]	3847 (13)	8467 (15)	613 (8)	1911 (68)
C(5)	8419 (6)	2113 (6)	3776 (3)	612	C(41)[b]	2937 (22)	9206 (25)	1457 (9)	3311 (162)
C(6)	7354 (6)	1284 (6)	3701 (3)	600	C(42)[b]	1410 (21)	11049 (17)	1731 (9)	2663 (114)
C(7)	9302 (7)	2332 (8)	4309 (4)	838	C(43)	5146 (6)	4252 (5)	−819 (2)	533
C(8)	6884 (7)	410 (7)	4102 (4)	755	C(44)	4417 (6)	5056 (6)	−868 (2)	544
C(9)	8557 (6)	2381 (6)	1265 (3)	599	C(45)	5121 (6)	6180 (6)	−630 (3)	571
C(10)	7627 (6)	1416 (6)	1184 (3)	626	C(46)	6286 (6)	6075 (6)	−437 (2)	550
C(11)	9471 (8)	2796 (9)	860 (4)	852	C(47)	6320 (5)	4874 (6)	−551 (2)	516
C(12)	7292 (9)	575 (7)	650 (4)	845	C(48)	4771 (8)	2966 (7)	−1031 (3)	798
Fe(1)	5000	5000	5000	450	C(49)	3134 (7)	4782 (9)	−1138 (3)	796
Fe(2)	1146.9 (7)	8851.0 (7)	2484.6 (5)	585	C(5)	4721 (9)	7294 (8)	−604 (4)	850
					C(51)	7337 (8)	7065 (8)	−173 (4)	893
					C(52)	7388 (7)	4380 (9)	−435 (4)	842

[a] For atoms refined anisotropically, the equivalent isotropic thermal parameter is defined as $U_{iso} = (U_{11} + U_{22} + U_{33})/3$. [b] Refined isotropically.

while under the same conditions $Mo[S_2C_2(CF_3)_2]_3$ undergoes two reversible reductions at $E_{1/2}(0/1-) = +0.95$ and $E_{1/2}(1-/2-) = +0.36$ V, respectively.[10a] Thus, for a 1:1 donor/acceptor ratio, only the $[Mo\{S_2C_2(CF_3)_2\}_3]^{\bullet-}$ ion is produced, and $[Fe(C_5R_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ (R = H, Me) forms. However, in the presence of more than 1 equiv of decamethylferrocene further reduction of the acceptor occurs, yielding $\{[Fe(C_5R_5)_2]^{\bullet+}\}_2\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ (R = H, Me). Similarly, $Cr(C_5Me_5)_2$ undergoes a single reversible oxidation at $E_{1/2}(0/1+) = -1.04$ V vs SCE,[20] and the 1:1 electron-transfer salt can be prepared. Although $Ni(C_5Me_5)_2$ undergoes reversible oxidation at $E_{1/2}(0/1+) = -0.73$ V vs SCE[20] and the 1:1 electron-transfer salt can be prepared, $Ni(C_5Me_5)_2$ undergoes a second reversible oxidation at +0.37 V [$E_{1/2}(2+/1+)$] and thus the 1:1 salt is expected to be $S = 0$ $[Ni^{IV}(C_5Me_5)_2]^{2+}\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ and not $S_{total} = 1$ $[Ni^{III}(C_5Me_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$, as the solution driving force is 0.58 V for $[Ni^{IV}(C_5Me_5)_2]^{2+}\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ with respect to $[Ni^{III}(C_5Me_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$.

It has previously been observed[10] that the frequency of the C=C stretching mode of coordinated dithiolene ligands is sensitive to the overall charge on the complex. Thus, the proposed charge assignments may be confirmed by the IR spectra of the solid salts. The 1:1 $[Fe(C_5R_5)_2]^{\bullet+}$ (R = H, Me) salts show bands at 1506 and 1507 cm^{-1}, respectively, which are close to the value of 1508 cm^{-1} reported[21] for the C=C ligand vibration in the anion $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$. Similarly, the 2:1 Fe^{III} salts have absorptions at 1537 and 1530 cm^{-1}, close to the value of 1538 cm^{-1} reported[21] for $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$. Likewise, the 1:1 $[Ni(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$ salt exhibits an absorption at 1536 cm^{-1} that confirms the presence of the dianion. Further support for these charge assignments is provided by the crystal structures and analysis of the solid-state magnetic susceptibility data (vide infra).

Structure of $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$. Crystals of the 1:1 salt are monoclinic, space group $C2/m$. Since both the Fe and Mo atoms lie on a mirror plane, at $y = 0$, the asymmetric unit consists of half of a cation and half of an anion.

$[Fe(C_5Me_5)_2]^{\bullet+}$ Cation. The pentamethylcyclopentadienyl ligands of the cation adopt a staggered conformation, giving the ion approximate D_{5d} local symmetry, as previously observed both for decamethylferrocene[22] and for the decamethylferrocenium ion in the majority of its other crystallographically characterized salts.[5,9,23] The C_5 rings of both ligands are planar, the largest deviation of any carbon atom within either ring from the least-squares plane being 0.006 Å. The methyl groups are bent away

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Table V. Selected Interatomic Distances (Å) and Angles (deg) for $[Fe(C_5Me_5)_2]_2[Mo(tfd)_3]$

Distances			
Mo(1)-S(1)	2.387 (1)	Fe(2)-C(26)	2.089 (8)
Mo(1)-S(2)	2.383 (1)	Fe(2)-C(27)	2.084 (7)
Mo(1)-S(3)	2.386 (2)	Fe(2)-C(33)	2.036 (7)
Mo(1)-S(4)	2.365 (1)	Fe(2)-C(34)	2.060 (7)
Mo(1)-S(5)	2.361 (2)	Fe(2)-C(35)	2.098 (7)
Mo(1)-S(6)	2.391 (2)	Fe(2)-C(36)	2.13 (1)
S(1)-C(1)	1.735 (5)	Fe(2)-C(37)	2.08 (1)
S(2)-C(2)	1.734 (6)	C(23)-C(24)	1.39 (2)
S(3)-C(5)	1.727 (7)	C(23)-C(27)	1.42 (1)
S(4)-C(6)	1.754 (6)	C(24)-C(25)	1.35 (2)
S(5)-C(9)	1.747 (7)	C(25)-C(26)	1.38 (2)
S(6)-C(10)	1.739 (7)	C(26)-C(27)	1.40 (2)
C(1)-C(2)	1.358 (8)	C(33)-C(34)	1.44 (1)
C(5)-C(6)	1.356 (9)	C(33)-C(37)	1.41 (1)
C(9)-C(10)	1.35 (1)	C(34)-C(35)	1.38 (1)
Fe(1)-C(13)	2.081 (5)	C(35)-C(36)	1.36 (1)
Fe(1)-C(14)	2.091 (5)	C(36)-C(37)	1.31 (1)
Fe(1)-C(15)	2.094 (5)	Fe(3)-C(43)	2.076 (5)
Fe(1)-C(16)	2.091 (6)	Fe(3)-C(44)	2.095 (5)
Fe(1)-C(17)	2.095 (5)	Fe(3)-C(45)	2.099 (6)
C(13)-C(14)	1.429 (9)	Fe(3)-C(46)	2.093 (6)
C(13)-C(17)	1.414 (9)	Fe(3)-C(47)	2.083 (5)
C(14)-C(15)	1.418 (9)	C(43)-C(44)	1.410 (9)
C(15)-C(16)	1.405 (9)	C(43)-C(47)	1.431 (9)
C(16)-C(17)	1.422 (9)	C(44)-C(45)	1.419 (9)
Fe(2)-C(23)	2.069 (8)	C(45)-C(46)	1.408 (9)
Fe(2)-C(24)	2.086 (9)	C(46)-C(47)	1.429 (9)
Fe(2)-C(25)	2.09 (1)		

Angles			
S(1)-Mo(1)-S(2)	80.02 (5)	C(15)-C(16)-C(17)	108.6 (6)
S(3)-Mo(1)-S(4)	80.80 (5)	C(13)-C(17)-C(16)	107.6 (5)
S(5)-Mo(1)-S(6)	80.62 (6)	C(24)-C(23)-C(27)	107.0 (9)
Mo(1)-S(1)-C(1)	110.4 (2)	C(23)-C(24)-C(25)	108.5 (9)
Mo(1)-S(2)-C(2)	110.5 (2)	C(24)-C(25)-C(26)	110.2 (11)
Mo(1)-S(3)-C(5)	109.6 (2)	C(25)-C(26)-C(27)	107.1 (9)
Mo(1)-S(4)-C(6)	109.8 (2)	C(23)-C(27)-C(26)	107.2 (9)
Mo(1)-S(5)-C(9)	110.1 (2)	C(34)-C(33)-C(37)	103.5 (7)
Mo(1)-S(6)-C(10)	109.4 (2)	C(33)-C(34)-C(35)	106.6 (8)
S(1)-C(1)-C(2)	119.4 (4)	C(34)-C(35)-C(36)	109.9 (8)
S(2)-C(2)-C(1)	119.6 (4)	C(35)-C(36)-C(37)	108.2 (10)
S(3)-C(5)-C(6)	120.1 (5)	C(33)-C(37)-C(36)	111.8 (9)
S(4)-C(6)-C(5)	119.2 (5)	C(44)-C(43)-C(47)	108.4 (6)
S(5)-C(9)-C(10)	119.6 (5)	C(43)-C(44)-C(45)	108.0 (5)
S(6)-C(10)-C(9)	119.7 (5)	C(44)-C(45)-C(46)	108.3 (6)
C(14)-C(13)-C(17)	108.1 (5)	C(45)-C(46)-C(47)	108.3 (6)
C(13)-C(14)-C(15)	107.6 (6)	C(43)-C(47)-C(46)	106.9 (5)
C(14)-C(15)-C(16)	108.1 (6)		

from the metal in both ligands, displaced from the plane of the C_5 ring by an average of 0.04 and 0.06 Å, respectively. The average Fe–C distance of 2.085 (8) Å is typical of values previously reported[5,23,24] for the $[Fe(C_5Me_5)_2]^{\bullet+}$ ion and is significantly longer than the corresponding value of 2.050 (2) Å reported for decamethylferrocene.[22] The average C–C distances for the two Cp* rings [1.408 (7) and 1.399 (3) Å, respectively] fall within the range 1.382 (8)–1.447 (11) Å established by previously reported structures;[5,22-24] all C–C(Me) distances for both rings are equivalent with an average value of 1.504(10) Å.

The Cp* ligand containing C(16)–C(21) shows some evidence of enhanced thermal motion and/or partial disordering as reflected in the large thermal parameters of the methyl carbons C(19)–C(21) (Table II). This effect can be rationalized based on features of the solid-state structure as discussed below.

$\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ Anion. A view of the anion including the atom numbering scheme is shown in Figure 1. The molybdenum atom exhibits nearly perfect trigonal prismatic coordination by the chelating dithiolene ligands

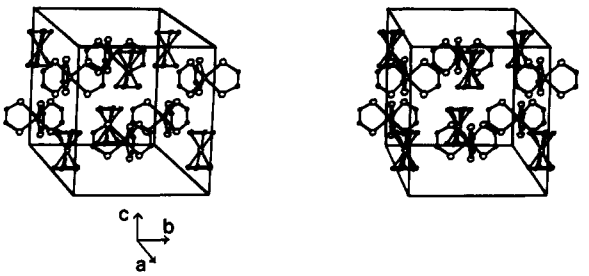

Figure 3. Stereoview of molecular packing including the unit cell for $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$. Peripheral CH_3 and CF_3 groups on the cations and anions have been omitted for clarity.

(vide infra). Both sulfur atoms and all four carbon atoms of one of the ligands lie on the mirror plane bisecting the molecule. The four independent Mo–S bond distances are equal within experimental error; the average Mo–S distance of 2.366 (2) Å falls within the range 2.33 (2)–2.39 (2) Å, found[25-27] in other crystallographically characterized molybdenum trisdithiolene complexes (Table VI). The average C–S distance within the metallocyclic MS_2C_2 rings [1.715 (9) Å] is considerably shorter than the sum of the covalent radii for these atoms (1.81 Å) given by Pauling,[28] reflecting the well-known delocalization of the π-electronic structure in chelating dithiolene ligands.[10] The large thermal parameters of the fluorine atoms are indicative of the substantial rotational freedom previously observed[9a,29] for the peripheral CF_3 groups on ligands of this type.

Solid-State Structure. A stereoview of the rock-salt-like molecular packing in $[Fe(C_5Me_5)_2][Mo\{S_2C_2(CF_3)_2\}_3]$ including the unit cell is shown in Figure 3. This structure contains discrete chains of alternating $S = {}^1/_2$ donor and $S = {}^1/_2$ acceptor molecules oriented along [001], Figure 4a. The Fe–Mo distances within a chain alternate, with values of 7.110 and 7.128 Å. There are no intermolecular contacts within or between chains that are shorter than the sum of the van der Waal's radii of the atoms involved. Unlike ferromagnetically coupled $[Fe(C_5Me_5)_2]^{\bullet+}$ salts of planar anions, e.g., $[Ni\{S_2C_2(CF_3)_2\}_2]^{\bullet-}$,[9a] there is essentially only one interchain (out-of-registry) interaction. The intrachain Fe···S separations of 5.635–6.024 Å are 0.2–0.9 Å shorter than observed for $[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$;[9a] however, due to the change in coordination geometry about Mo with respect to Ni the interchain Fe···S separations are longer.

The partial disordering of the $[Fe(C_5Me_5)_2]^{\bullet+}$ cation described above originates from the dissimilar interactions of the two Cp* ligands of the cation with neighboring complex anions within a chain (Figure 4b). The ring containing C(10)–C(15), which is ordered, adopts a staggered conformation with respect to the three dithiolene ligands of the neighboring anion, thereby minimizing steric interactions between its CH_3 groups and the CF_3 groups of the ligands. In contrast, one of the C–CH_3 bonds [C(16)–C(19)] of the second, apparently disordered Cp* ring is eclipsed with the plane of a dithiolene ligand of the adjacent anion. The partial disordering of this ring

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Table VI. Comparison of Mean Interatomic Distances and Angles for Seven Molybdenum Tris(dithiolene) Complexes[a]

complex[b]	$[Mo(bdt)_3]^0$	$[Mo(qdt)_3]^{\bullet-}$	$[Mo(tfd)_3]^{\bullet-}$	$[Mo(tfd)_3]^{2-}$	$[Mo(qdt)_3]^{2-}$	$[Mo(mnt)_3]^{2-}$	$[Mo(dbdt)_3]^{2-}$
			Distances				
Mo—S	2.367(6)	2.39(2)	2.366(4)	2.38(1)	2.39(1)	2.374(7)	2.393(5)
S—C	1.727(6)	1.745(4)	1.72(1)	1.74(1)	1.74(1)	1.74(2)	1.74(2)
C=C	1.41(1)	1.434(4)	1.367(4)	1.36(1)	1.442(7)	1.33(2)	1.34(5)
S—S (intra)[c]	3.110(8)	3.138(7)	3.085(3)	3.074(7)	3.126(6)	3.12(2)	3.09(2)
S—S (inter)[d]	3.09(2)	3.16(5)	3.11(4)	3.18(7)	3.14(2)	3.19(8)	3.18(6)
			Angles				
S—Mo—S (intra)[e]	82.1(4)	82.0(5)	81.38(7)	80.5(4)	81.6(3)	82.4(5)	80.5(5)
S—Mo—S ("trans")	136(1)	146(1)	135.5(7)	147(2)	138.7(5)	156(2)	143.9(3)[f]
			Reference				
	25	26	this work	this work	27c	27b	27a

[a] The standard deviations given are the larger of the individual standard deviations or the standard deviation of the mean. [b] Key to ligand abbreviations is given in footnote 3. [c] Intraligand. [d] Interligand, i.e., the side dimension of the trigonal face. [e] Ligand "bite" angle. [f] Value of largest trans angle in this structure.

therefore appears to arise from a slight rotation of the ring that relieves an unfavorable steric interaction between the CH_3 group and the CF_3 group of the adjacent anion, which occurs in the eclipsed conformation. Since the magnitudes of the U_{iso} values for the ring carbons C(16), C(17), and C(18) decrease in that order, it appears that the pivot for the ring rotation lies closer to the midpoint of the C(18)–C(18)′ bond than to the Cp* ring centroid. This is consistent with the hypothesis that the apparent disorder serves to relieve proximal nonbonded interactions.

Adjacent chains in the structure are out-of-registry with each other, with the result that each ion is completely surrounded by counterions. The shortest intermetallic distances between molecules in different chains are 10.184 Å (Fe···Fe), 10.209 Å (Mo···Mo), and 7.509 Å (Fe···Mo).

Structure of $[Fe(C_5Me_5)_2]_2[Mo[S_2C_2(CF_3)_2]_3]$. Crystals of the 2:1 salt are triclinic, space group $P\bar{1}$. The asymmetric unit consists of two half-cations [cation 1 containing Fe(1) and cation 3 containing Fe(3), centered on the special positions $^1/_2,^1/_2,^1/_2$, and $^1/_2,^1/_2,0$, respectively], one complete (cation 2), and one complete anion.

$[Fe(C_5Me_5)_2]^{\bullet+}$ Cations. The atom numbering scheme for the cations is shown in Figure 2. The structures of the two centrosymmetric cations (1 and 3) are essentially equivalent; in both cations the pentamethylcyclopentadienyl ligands adopt a crystallographically imposed staggered configuration, with the result that each ion has perfect D_{5d} local symmetry. The C_5 rings in both ions are planar, the largest deviation of any carbon atom within either ring from the least-squares plane being 0.008 Å. The methyl groups of the ligands are displaced from the C_5 plane away from the metal in both cations by an average of 0.05 and 0.07 Å, respectively. The metrical parameters of these ions are regular: the average Fe–C, C–C, and C–C(Me) distances for cation 1 [2.090 (5), 1.418 (9), and 1.50 (1) Å, respectively] and cation 3 [2.089 (5), 1.419 (9), and 1.50 (1) Å, respectively] are typical of those previously reported.[5,9,22-24]

The magnitudes of the equivalent isotropic thermal parameters (Table IV) for the ring and methyl carbon atoms of cations 1 and 3 indicate that they are not subject to disorder or undue thermal motion. In contrast, the structure of cation 2 shows evidence of disordering and/or substantial thermal motion of both pentamethylcyclopentadienyl ligands. The disorder could not be fit to a simple model, and thus the ring methyl carbons atoms of each ring [C(28) to C(32) and C(38) to C(42)] and two internal carbon atoms of one ring [C(36) and C(37)] could be refined only isotropically. The distances and angles within each Cp* ring were subject to soft restraints in order to achieve approximate D_{5h} symmetry for the ligand. There are no specific intermolecular interactions that can be held responsible for the structural disorder in cation 2; rather, it appears to result from generalized deficiencies in the molecular packing in this region of the structure.

$\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ Anion. A view of the anion including the atom numbering scheme is shown in Figure 2. The MoS_6 core of this anion is significantly distorted from the trigonal prismatic geometry found for the anion in the 1:1 salt; the nature of the distortion is discussed below. Four of the six Mo–S distances are equivalent within experimental error, their average being 2.387 (2) Å. The remaining two Mo–S bonds [S(3) and S(4)] are significantly shorter, with an average of 2.363 (2) Å. The six independent C–S distances within the chelate rings are essentially equivalent [average = 1.739 (6) Å], as are the three independent C–C distances [average = 1.36 (1) Å]. As in the 1:1 salt, the fluorine atoms of all six peripheral CF_3 groups of the anion have large thermal parameters, presumably the result of partial rotation about the C–CF_3 bond. In addition, the irregular geometries of the two CF_3 groups containing carbons C(7) and C(11), which lie in close proximity to the disordered Cp* ligand of cation 2, provide further evidence of packing deficiencies in this region of the structure.

Solid-State Structure. A stereoview of the molecular packing in $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ including the unit cell is shown in Figure 5. The structure can be described in terms of two sets of interpenetrating linear chains (extending along the [110] and [001] directions, respectively) containing alternating decamethylferrocenium cations and molybdenum tris(dithiolene) dianions. The chains extending along [110] are similar to those found in the structure of the 1:1 salt, except that each anion is displaced from the chain axis such that only one of its three chelating dithiolene ligands interacts directly with the neighboring cations within the chain (Figure 6a). The plane of this same dithiolene ligand is also interleaved between successive cations within the chain extending along [001] (Figure 6b) and thus acts as a bridge between the two distinct types of chains in the structure. The remaining two dithiolene ligands of each anion form a cleft that engages a decamethylferrocenium cation from a neighboring chain extending along [110].

The shortest intermolecular metal-metal distance is 7.072 Å between Mo and Fe(2); several other Mo···Fe distances range from 7.174 to 7.300 Å. The shortest Fe···Fe distance, 8.806 Å, occurs between cations 2 and 3; however, the relative orientation of these two cations would appear to preclude significant orbital overlap. Other Fe···Fe separations occur at 8.950 and 9.187 Å [both Fe(1)···Fe(2)], and 9.111 Å [Fe(2)···Fe(3)].

Magnetic Susceptibility. The 2.2–300 K Faraday balance magnetic susceptibility at 5.2, 15.8, and 19.5 kG

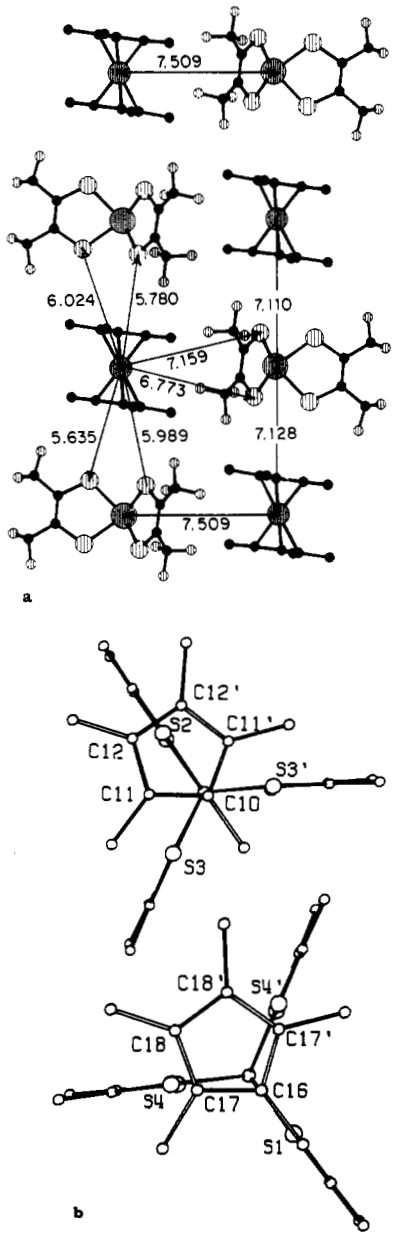

Figure 4. (a) Detail of ···$D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}$··· stacking in $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$. Atoms are represented by spheres of arbitrary size. Peripheral H and F atoms and a ligand have been omitted for clarity. (b) Views perpendicular to the planes of the two C_5Me_5 rings of the cation in $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$, showing interactions of each ring with the neighboring anion within the stack.

(Figure 7) shows that the 1:1 and 2:1 salts of $[Fe(C_5Me_5)_2]^{\bullet+}$ obeys the Curie–Weiss law, $\chi_M = C(T - \Theta)^{-1}$, with C = 1.85 emu K/mol, Θ = +8.4 K and C = 1.573 emu K/mol, Θ = −3.2 K, respectively. The effective moments, μ_{eff}, for polycrystalline samples of the 1:1 and 2:1 salts are 3.85 and 3.55 μ_B/mol, respectively. Comparable values were obtained for the $[Fe(C_5H_5)_2]^{\bullet+}$ salt: Θ = +1.8 K and μ_{eff} = 3.37 μ_B/mol. For the 1:1 Fe^{III} salts, the μ_{eff} is considerably larger than the sum of the spin-only values calculated for independent $S = {}^1/_2$ cations $\{g_\parallel = 4.0$ and $g_\perp = 1.3$,[30] yielding $\langle g\rangle^2 = {}^1/_3[4.0^2 + 2(1.3)^2] = 6.5\}$ and independent $S = {}^1/_2$ $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ anions $\{g_\parallel = 2.011$ and $g_\perp = 2.009$,[21] thus $\langle g\rangle^2 = 4.039\}$, i.e., $[6.46({}^3/_4) + 4.039({}^3/_4)]^{1/2} = 2.8\ \mu_B$. The large values of μ_{eff} most likely arises due to the extremely anisotropic nature of the Lande' g factors

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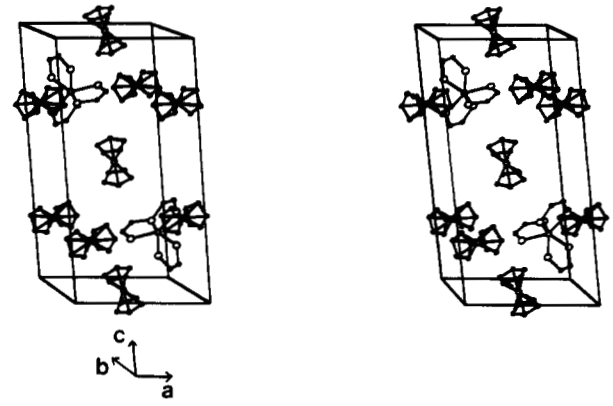

Figure 5. Molecular packing for $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$, showing the unit cell and the two distinct types of ···$D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}$··· chains. Peripherhal CH_3 and CF_3 groups on the cations and anions have been omitted for clarity.

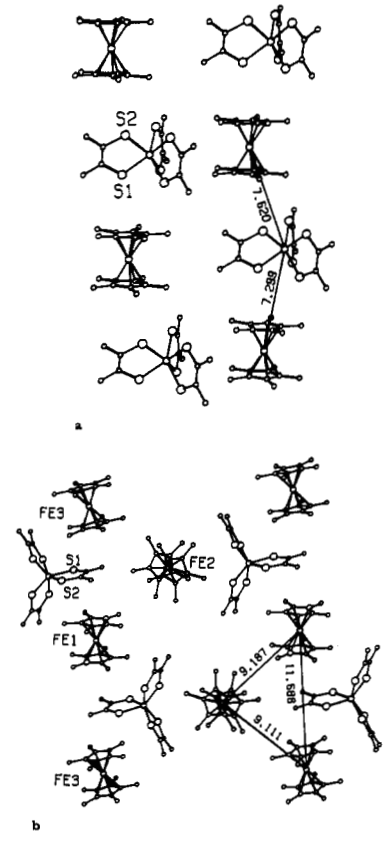

Figure 6. (a) Detail of the D–A–D–A stacking along the [110] crystal direction in $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$, showing the interaction between two adjacent stacks. Atoms are represented by spheres of arbitrary size, and peripheral H and F atoms have been omitted for clarity. (b) Stacking along the [001] direction showing the interaction between adjacent stacks.

for the ferrocenium ions[31] and the orientational variability of the polycrystalline sample.[32] Single crystals large enough for direct measurement of the magnetic anisotropy were not available for either Fe^{III} salt. The positive values of the Weiss constant, Θ = 1.8 and 8.4 K, are indicative of ferromagnetic interactions, which in view of the limited interchain contacts for the $[Fe(C_5Me_5)_2]^{\bullet+}$ salt are presumed to arise via coupling between spins localized on different molecules within the ···DADA··· chains. This

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(32) Balzer, P.; Hulliger, J. *Inorg. Chem.* **1984**, *23*, 4772.

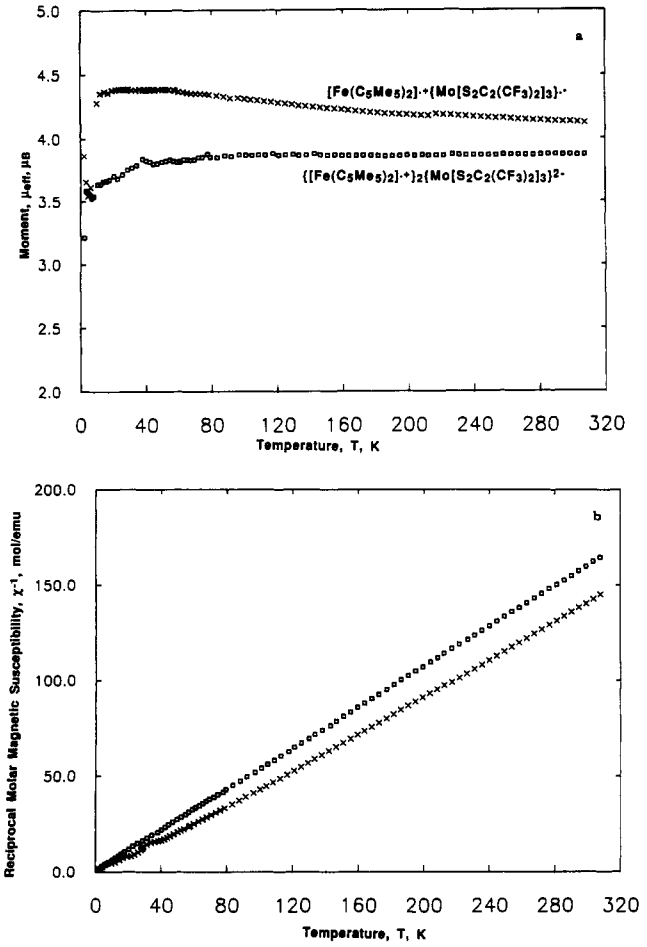

Figure 7. Magnetic susceptibility data taken at 5.2, 15.8, and 19.5 kG plotted as (a) μ_{eff} vs T and (b) χ^{-1} vs T for $[Fe(C_5Me_5)_2]\{Mo[S_2C_2(CF_3)_2]_3\}$ (×) and $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ (□).

value is smaller than $\Theta = +15$ K observed[9a] for the related salt $[Fe(C_5Me_5)_2]^{\bullet+}\{Ni[S_2C_2(CF_3)_2]_2\}^{\bullet-}$, which has substantially greater interchain interactions, suggesting that in the latter compound the ferromagnetic interchain $D^{\bullet+}/A^{\bullet-}$ interaction is stronger than the antiferromagnetic $A^{\bullet-}/A^{\bullet-}$ interaction.

The $[Cr^{III}(C_5Me_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ salt also obeys the Curie–Weiss law with $\Theta = +1.0$ K and $\mu_{eff} = 4.32\ \mu_B$. The μ_{eff} is essentially the sum of the spin-only values (4.24 μ_B) calculated for independent $\langle g \rangle = 2.0$,[20] $S = {}^3/_2$ $[Cr(C_5Me_5)_2]^{\bullet+}$ ions and independent $S = {}^1/_2$ $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ anions.

The electron-transfer salt with $Ni(C_5Me_5)_2$ is diamagnetic; thus, it is formulated as the two-electron-transfer salt $[Ni^{IV}(C_5Me_5)_2]^{2+}\{Mo[S_2C_2(CF_3)_2\}^{2-}$ as expected from consideration of the solution redox potentials and infrared spectra.

The effective moment for the 2:1 $[Fe^{III}(C_5Me_5)_2]^{\bullet+}$ and $[Fe^{III}(C_5H_5)_2]^{\bullet+}$ salts are $\mu_{eff} = 3.55$ and 4.37 μ_B, respectively, and are larger than the spin-only value of 3.11 μ_B calculated assuming an ideal polycrystalline sample containing two independent $S = {}^1/_2$ cations and a diamagnetic $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ dianion. The small Weiss constants $\Theta = -3.2$ K for the $[Fe^{III}(C_5Me_5)_2]^{\bullet+}$ and $\Theta = +2.53$ K for the $[Fe^{III}(C_5H_5)_2]^{\bullet+}$ salts suggest the presence of weak antiferromagnetic and weak ferromagnetic dipole–dipole interactions between radical cations within the respective solids. The cations are separated by anions, and thus the cation–cation interactions anticipated from the extended McConnell model[7] to be ferromagnetic are not present in the structure; only the antiferromagnetic cation–anion interactions are present. The structure of the $[Fe^{III}(C_5H_5)_2]^{\bullet+}$ salt is unknown; thus, a structure–function relationship cannot be determined.

Comparison with Other Tris(dithiolene) Complexes. It is of interest to compare the structures of the $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ and $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ anions with those of other crystallographically characterized molybdenum tris(dithiolene) complexes. Relevant structural parameters for seven complexes are summarized in Table VI. The mean Mo–S and S–C distances for the two complexes reported here fall within the ranges established by previous structures; the similarity of these values across the series indicates that the nature of the metal–ligand bonding in these complexes is qualitatively similar. Variation in the C=C distances and S–M–S "bite" angles across the series is a consequence of the incorporation of the C=C bonds into external aromatic rings in the bdt and qdt ligands.

The coordination geometries of metal tris(dithiolene) complexes are highly variable, ranging between the octahedral and trigonal prismatic limits.[27b] The values of the largest S–M–S ("trans") angle relating sulfur atoms diametrically opposed on the two trigonal faces of the prism have previously been used[27b] as a measure of the degree of distortion of a complex from idealized trigonal prismatic geometry. For an ideal trigonal prismatic trischelate complex with a fixed ligand "bite" of 82° (a typical value for metal dithiolene complexes), the values of the S–M–S "trans" angles are ca. 136°. As the prism distorts via a concerted twisting of the ligands, the "trans" angles expand, reaching a maximum value (determined by the ligand bite) of 174° in the limiting antiprismatic geometry. Furthermore, if the distortion is unsymmetrical, the variation in the values of the independent "trans" angles provides a useful measure of the deviation from idealized D_3 symmetry.

Mean values of the "trans" angles for structurally characterized molybdenum tris(dithiolene) complexes are summarized in Table VI. For the $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ ion, these angles range from 134.74 (8) to 136.20 (8)°, with a mean value of 135.5 (7)°, indicating that the MoS_6 core of this complex forms a nearly perfect trigonal prism. The neutral complex $Mo(bdt)_3$ possesses a comparable structure, with trans angles ranging from 134.43 (6) to 136.51 (7)°.[25] All Mo–S distances within both of these complexes are the same within experimental error, with mean values of 2.366 (4) and 2.367 (6) Å, respectively.

The three independent "trans" angles for the $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ ion values of 144.96 (6), 147.64 (6), and 147.71 (6)°, with a mean value of 147 (2)°, indicating that the MoS_6 core of this complex adopts a geometry midway between the trigonal prismatic and corrected octahedral limits. The magnitude of the distortion from idealized trigonal prismatic coordination is similar to those found[26,27a] for the $[Mo(qdt)_3]^{\bullet-}$ and $[Mo(dbdt)_3]^{2-}$ ions. In contrast, two other dianionic molybdenum tris(dithiolene complexes, $[Mo(mnt)_3]^{2-}$ and $[Mo(qdt)_3]^{2-}$, are found[27b,c] to approach more closely the trigonal prismatic and octahedral limits, respectively. The inequivalence of the three trans angles in $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ indicates that the MoS_6 core symmetry is lower than D_3. Consequently, the planes defined by the two triangular S_3 faces of the distorted prism are not parallel, but rather meet with a dihedral angle of ca. 9°. Although the corresponding planes of the other distorted complexes listed in Table VI also are not strictly parallel, the dihedral angles between the planes in those cases are considerably smaller (1–2°).

Consideration of the values of the interligand S···S distances shows that the distortion of the MoS_6 core results from the twisting of only *one* of the three chelating ligands [that containing S(1) and S(2)] toward the octahedral limit; the relative orientation of the other two ligands remains similar to that found in trigonal prismatic structures. A similar unsymmetrical distortion is found[33] in the $[Ta(bdt)_3]^-$ ion, which has trans angle values of 147.19 (8), 158.09 (8), and 158.69 (8)°, and a dihedral angle between the two S_3 faces of ca. 12°.

It has previously been proposed[11] that the trigonal prismatic structure observed for some metal tris(dithiolene) complexes is stabilized by π-bonding interactions between metal-based d orbitals (d_{xy} and $d_{x^2-y^2}$) and sulfur-based p orbitals of the ligands. According to this model, reduction of neutral, formally Mo(VI) complexes to yield charged anionic species populates the a_1 molecular orbital[11] of the complex, which has primarily metal d_{z^2} character. Since the π-interaction of the latter metal orbital with the ligands is antibonding in character, this model predicts that more highly reduced complexes should have structures that are more strongly distorted from the trigonal prismatic limit. The structures of the $[Mo(qdt)_3]^{\bullet-}$ and $[Mo(qdt)_3]^{2-}$ ions (Table VI) clearly contradict this model, suggesting that steric (crystal packing) effects might play the dominant role in determining the coordination geometry of the anions. In the present study, the $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ ion is found to be a nearly perfect trigonal prism, while the $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ ion is distorted, a result that would appear to be in accordance with the above MO description. However, the irregular nature of the distortion and its apparent relation to the crystal packing argues against electronic factors as an explanation. Specifically, it is found that the twisted ligand in the structure of the $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ ion is the only one involved in face-to-face stacking interactions with the decamethylferrocenium cations, while the remaining two ligands interact with a neighboring cation in a side-on manner that severely restricts their ability to twist relative to one another. Given the nature of these intermolecular interactions, we conclude that the distortion of the $\{Mo[S_2C_2(CF_3)_2]_3\}^{2-}$ anion results from crystal packing forces.

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Conclusions

Metal tris(dithiolene) complexes have been shown to be useful nonplanar building blocks for the preparation of magnetic electron-transfer salts. Magnetic measurements on $[Fe(C_5Me_5)_2]^{\bullet+}\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ provide evidence for weak ferromagnetic interactions, i.e., $\theta > 0$. This presumably arises from coupling between localized spins on adjacent anions and cations within the linear chains. On the basis of the field dependence of the magnetic susceptibility, however, bulk ferromagnetic behavior is not observed. The steric interactions between the peripheral CH_3 and CF_3 groups on adjacent molecules within the chains prevent good orbital mixing and therefore limit the strength of the intrachain coupling, while the peripheral substituents on the $\{Mo[S_2C_2(CF_3)_2]_3\}^{\bullet-}$ anion preclude the possibility of favorable $D^{\bullet+}/A^{\bullet-}$ interactions between chains. In light of these results, efforts are being directed toward preparation of analogous electron-transfer salts using radical anion complexes incorporating ligands with reduced steric demands and polarizable peripheral substituents.

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Supplementary Material Available: Summary of crystal data and collection parameters, interatomic distances and angles, least-squares planes, H-atom positions, and anisotropic thermal parameters for $[Fe(C_5Me_5)_2][Mo\{S_2C_2(CF_3)_2\}_3]$ and $Fe(C_5Me_5)_2]_2[Mo\{S_2C_2(CF_3)_2\}_3]$ (24 pages); tables of observed and calculated structure factors for $[Fe(C_5Me_5)_2][Mo\{S_2C_2(CF_3)_2\}_3]$ and $[Fe(C_5Me_5)_2]_2[Mo\{S_2C_2(CF_3)_2\}_3]$ (36 pages). Ordering information is given on any current masthead page.

Molecular Level Ceramic/Polymer Composites. 1. Synthesis of Polymer-Trapped Oxide Nanoclusters of Chromium and Iron

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$Cr(C_6H_6)_2$ or $Fe_3(CO)_{12}$ was added to polyamic acid solutions derived from 4,4'-oxydianiline and either 1,2,4,5-benzenetetracarboxylic acid dianhydride or 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride. Following thermal curing, polyimide films containing a homogeneous dispersion of nanoclusters (size <1–1.5 nm) of Cr_2O_3 or α-Fe(O)(OH) were obtained. Both scanning electron microscopy and secondary ion mass spectroscopy depth profile indicated that the usually observed migration of the dopant to the polymer surface had not occurred. The chemical composition of the dopants were established by X-ray photoelectron spectroscopy.

The demand for materials with novel combinations of properties has led to the recent efforts in modification of known polymers via the incorporation of a variety of additives. Ceramic nanoclusters with sizes ranging from <1

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