The Characterization of Dimeric Dithiolene Complexes[1]

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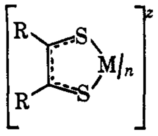
Abstract: Several series of bis(dithiolene)cobalt and -iron complexes have been prepared. Their spectral, magnetic, and electrochemical properties are best interpreted and systematized when the complexes are considered as members of the general series $[M\text{–}S_4]_2^0$, $[M\text{–}S_4]_2^-$, $[M\text{–}S_4]_2^{-2}$, $[M\text{–}S_4]^{-2}$. By utilizing the ligands toluene-3,4-dithiolate, maleonitriledithiolate, and bisperfluoromethyl-1,2-dithiene, partial or complete electron-transfer series of this type have been established by preparation and/or polarographic detection of some or all of the complexes in each. The complete series of dithietene complexes, $[MS_4C_4(CF_3)_4]_2^0$, $[MS_4C_4(CF_3)_4]_2^-$, $[MS_4C_4(CF_3)_4]_2^{-2}$, $[MS_4C_4(CF_3)_4]^{-2}$ (M = Fe, Co) has been demonstrated, and all four members of the cobalt series have now been isolated in this and previous work. The paramagnetic complexes usually do not obey the Curie law, and the temperature dependence of their magnetic moments is indicative of antiferromagnetic spin exchange. The results of this work, together with recent X-ray structural determinations, reveal that the bis-chelate dimer structure represents a third clear-cut stereochemical pattern in the chemistry of dithiolene complexes, and that, in particular, it resembles the other two (planar, trigonal prismatic-octahedral) by supporting well-defined electron-transfer series.

The chemistry of bis- and tris-chelate complexes formally derived from *cis*-1,2-disubstituted ethylene-1,2-dithiolates (**1**) and 1,2-dimercaptobenzene (**2**) and its ring-substituted variants, hereafter referred to as dithiolene complexes,[4,5] has progressed to a point such that two basic stereochemical patterns in particular are known to be of general significance. X-Ray structural studies have established the square-planar stereochemistry of $[NiS_4C_4Ph_4]$,[6] $[Ni(mnt)_2]^-$,[7] $[Ni(mnt)_2]^{-2}$,[8] $[Co(mnt)_2]^{-2}$,[9] $[Co(tdt)_2]^-$,[10] and $[Cu(mnt)_2]^-$.[11] Isomorphism relationships indicate planar structures for $[M(mnt)_2]^{-2}$ (M = Rh, Pt, Cu) as well.[12] On the basis of the current body of chemical and physical evidence, it appears quite likely that all $[Co\text{–}S_4]^{-2}$, $[Ni\text{–}S_4]^{-2,0}$, $[Pd\text{–}S_4]^{-2}$, $[Pt\text{–}S_4]^{-2}$, $[Au\text{–}S_4]^-$, and $[Cu\text{–}S_4]^{-2,-1}$ complexes of types **1** and **2** exist as planar monomeric species in crystalline and solution phases.



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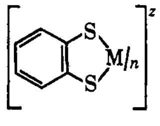

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The second stereochemical pattern of considerable importance is the trigonal prism which is found in the neutral tris complexes $[MS_6C_6R_6]$ and $[M(tdt)_3]$.[13,14] Thus far this structure has been definitely established for $[ReS_6C_6Ph_6]$,[14a] $[MoS_6C_6H_6]$,[14b] and $[VS_6C_6Ph_6]$,[14c] and may also extend to the general group of neutral complexes $[MS_6C_6(CF_3)_6]$[15] and to certain anionic complexes.[13,14c]

The occurrence of the more usual tetrahedral and octahedral coordination polyhedra and, more significantly, the generality of these structures as a function of metal and total charge *z* have not yet been established in detail. It is likely that $[Zn\text{–}S_4]^{-2}$ species, such as $[Zn(tdt)_2]^{-2}$ [16] and $[Zn(mnt)_2]^{-2}$,[12c] are tetrahedral. The only proven structures of these types are those of $[Fe(mnt)_3]^{-2}$, in which a nearly octahedral coordination of sulfurs around the iron was found,[17] and $[V(mnt)_3]^{-2}$, which has only C_2 symmetry and whose coordination polyhedron may be considered a very distorted octahedron.[18]

In this paper we present evidence bearing on the occurrence and generality of a third important stereochemical pattern in dithiolene chemistry, the *bis-chelate dimers* $[M\text{–}S_4]_2^z$. The first indication of interionic or

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(4) We subscribe to the term "dithiolene," coined by others,[5] as a generic name for ligands of the types $R_2C_2S_2$ and $1,2\text{-}C_6H_4S_2$ in complexes **1** and **2** of differing total charge *z*. By so doing formal oxidation states of the ligands and metal are not implied by the nomenclature. Classical oxidation states are for most purposes misleading when defined for $[M\text{–}S_4]^{0,-1}$ and related species; *cf.* F. Lalor, *et al.*, *J. Am. Chem. Soc.*, **89**, 2278 (1967), and R. H. Holm, *et al.*, *ibid.*, **89**, 2866 (1967). The standard abbreviations mnt for $(NC)_2C_2S_2$ and tdt for $4\text{-}CH_3C_6H_3S_2$ are used throughout the text.

(5) J. Locke, J. A. McCleverty, E. J. Wharton, and C. J. Winscom, *Chem. Commun.*, 677 (1966).

(6) D. Sartain and M. R. Truter, *J. Chem. Soc., Sect. A*, 1264 (1967). For preliminary X-ray data on $[NiS_4C_4H_4]$, *cf.* E. Höhne, P. Prokop, and E. Hoyer, *Z. Chem.*, **6**, 71 (1966).

(7) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966).

(8) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).

(9) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1500 (1964).

(10) R. Eisenberg, Z. Dori, H. B. Gray, and J. A. Ibers, submitted for publication.

(11) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1507 (1964).

(12) (a) E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 926 (1964); (b) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962); (c) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

(13) E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965); E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2956 (1966); G. N. Schrauzer and V. P. Mayweg, *ibid.*, **88**, 3235 (1966).

(14) (a) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966); (b) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965); (c) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966); R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 1844 (1967).

(15) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **86**, 2799 (1964).

(16) W. H. Mills and R. E. D. Clark, *J. Chem. Soc.*, 175 (1936).

(17) I. Bernal and A. Sequeira, Abstracts, American Crystallographers, Washington, D. C., Aug 1967; I. Bernal, private communication.

(18) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 3353 (1967).

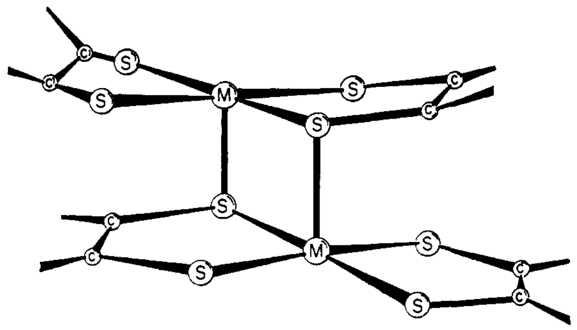

Figure 1. Idealized representation of the structures of dimeric dithiolene complexes, based on the structures of $[CoS_4C_4(CF_3)_4]_2$,[19] $(n\text{-}Bu_4N)_2[Fe(mnt)_2]_2$,[20] and $(n\text{-}Bu_4N)_2[Co(o\text{-}S_2C_6Cl_4)_2]_2$.[24]

intermolecular interaction of dithiolene complexes was found in the reduced magnetic moments of some crystalline $[M\text{–}S_4]^-$ salts (M = Ni, Pd, Pt), which in solution gave moments expected for a doublet ground state.[19] $[CoS_4C_4(CF_3)_4]$ was found to be a diamagnetic solid and dimeric in carbon tetrachloride solution.[20] Shortly thereafter, it was demonstrated that the magnetic susceptibilities of crystalline salts of $[M(mnt)_2]^-$ (M = Ni, Pd, Pt) could be interpreted in terms of pairwise interaction of doublet-state anions.[21] The $[Ni(mnt)_2]^-$ anions have been shown to be weakly dimerized in the triphenylmethylphosphonium salt.

Final proof of the existence of discrete dimers in the crystalline phase has been provided by the X-ray studies of $[CoS_4C_4(CF_3)_4]_2$,[22] $(n\text{-}Bu_4N)_2[Fe(mnt)_2]_2$,[23] and $(n\text{-}Bu_4N)_2[Co(C_6Cl_4S_2)_2]_2$.[24] The dimer of each of these species has the same essential structure, which is shown in Figure 1. Each dimer is formed by the lateral interaction of two bisdithiolene units such that the metal assumes square-pyramidal coordination by forming, in addition to the four basal M–S bonds in the monomeric unit, a somewhat longer apical M–S bond. The presently available detailed structural data, summarized in Table I, reveal the close similarity of the coordination polyhedra, supporting the assumption made in this work that the structure shown in Figure 1 may be taken as the prototype for all bisdithiolene dimers. The apical M–S distance in $[Ni(mnt)_2]^-$ is indicative of a nearly limiting case of weak yet discernible dimerization. Further supporting evidence for the generality of the dimer structure is found in the isomorphism of $[FeS_4C_4(CF_3)_4]_2$ and its cobalt analog[25,26] and the possible isostructural relationships of $[MS_4C_4(CF_3)_4]$ and $[MS_4C_4Ph_4]$ (M = Fe, Co).[26]

Table I. Brief Structural Comparison of Dimeric Dithiolenes

Distance, Å	$[CoS_4C_4(CF_3)_4]_2$[a]	$[Fe(mnt)_2]_2^{-2}$[b]	$[Co(o\text{-}S_2C_6Cl_4)_2]_2^{-2}$[c]	$[Ni(mnt)_2]^-$[d]
Basal M–S (av)	2.16	2.23	2.18	2.15
Apical M–S	2.38	2.46	2.40	3.59
M–S_4 plane[e]	0.37	0.36	0.26	...
M···M	2.78	...[f]	3.10	4.40

[a] Data from ref 22. [b] Bu_4N^+ salt; data from ref 23. [c] Bu_4N^+ salt; data from ref 24. [d] $(Ph_3PMe)^+$ salt; data from ref 7; the shortest set of interionic distances given. [e] Vertical distance of metal from S_4 plane. [f] Not reported.

In this work we show that the basic dimeric structure of Figure 1 resembles the planar and trigonal prismatic (or the latter in combination with octahedral) stereochemistries in that it supports electron-transfer reactions in which the essential stereochemistry is unchanged as the total charge on the complex is varied in the series $[MS_4C_4R_4]_2^z$ (M = Fe, Co) and $[Fe(tdt)_2]_2^z$. We have previously communicated sufficient information to demonstrate the existence of electron-transfer series of dimeric dithiolenes,[25] and more recently conductivity measurements have been published which support the presence in solution of certain $[Co\text{–}S_4]_2^{-2}$ species.[27] A more complete body of results is presented here which serves to define the electron-transfer series of dithiolene dimers and to characterize individual members of each series. More detailed interpretations of the magnetic properties of individual dimers and their solution equilibria will be presented subsequently.[28]

Experimental Section

Preparation of Compounds. $[FeS_4C_4(CF_3)_4]_2$. This preparation follows the previously reported procedure for "$[FeS_6C_6(CF_3)_6]$".[20] Iron pentacarbonyl (5.8 g, 30 mmoles) and 14 g (62 mmoles) of bisperfluoromethyl-1,2-dithietene[29] (freshly distilled, bp 96–98°) were refluxed in 600 ml of dry n-pentane under a nitrogen atmosphere. The reaction mixture became very dark red within several hours. Refluxing was continued until the solution color was blue-black (15–20 hr) The warm solution was filtered to remove a small quantity of insoluble material. The filtrate, protected from moist air, was cooled to −10°. The crystals which slowly deposited were collected and washed with pentane. A yield of about 25% results. The product was recrystallized several times from carbon tetrachloride to yield fine black crystals: mp 190–191° (sealed tube).

Anal. Calcd for $C_{12}F_{18}S_6Fe$: C, 19.65; H, 0.00; S, 26.20. Calcd for $C_8F_{12}S_4Fe$: C, 18.90; H, 0.00; S, 25.24. Found: C, 18.78; H, 0.03; S, 25.70.

$[(C_2H_5)_4N][FeS_4C_4(CF_3)_4]_2$. In 1 hr a solution of 1.597 g (3.125 mmoles) of $[NiS_4C_4(CF_3)_4]$[19] in 150 ml of dry dichloromethane was added to a slurry of 3.986 g (6.245 mmoles) of $[(C_2H_5)_4N]_2[FeS_4C_4(CF_3)_4]_2$[20] in 200 ml of dry dichloromethane. After this mixture was refluxed for 6 hr, it was filtered while still hot. The black crystalline material collected was washed with dichloromethane and vacuum dried. The yield of crude product was 3.32 g (93%). Purification was accomplished by Soxhlet extraction with dry dichloromethane, yielding black crystals, mp 259° dec.

Anal. Calcd for $C_{24}H_{20}F_{24}NS_8Fe_2$: C, 25.14; H, 1.76; F, 39.77; N, 1.22; S, 22.37. Found: C, 25.28; H, 1.52; F, 40.72; N, 0.99; S, 22.18.

This compound has also been prepared in an entirely analogous procedure but by use of $[FeS_4C_4(CF_3)_4]_2$ and $[(C_2H_5)_4N]_2[FeS_4C_4(CF_3)_4]_2$ in an exact 1:1 mole ratio. Black crystals were isolated, mp 261–262° dec.

$[(n\text{-}C_4H_9)_4N][Fe(S_2C_6H_3CH_3)_2]_2$. A solution of 0.1511 g (1.190 mg-atoms) of iodine in 70 ml of dichloromethane was added slowly with stirring to a solution of 1.356 g (2.234 mmoles) of $[(C_4H_9)_4N][Fe(S_2C_6H_3CH_3)_2]$[30] in 30 ml of dichloromethane. A steel blue color

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(19) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(20) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **3**, 814 (1964).

(21) J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Am. Chem. Soc.*, **86**, 4339 (1964).

(22) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

(23) W. C. Hamilton and I. Bernal, *ibid.*, **6**, 2003 (1967).

(24) M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, submitted for publication.

(25) A. L. Balch and R. H. Holm, *Chem. Commun.*, 552 (1966).

(26) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 4604 (1966).

(27) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(28) I. G. Dance and R. H. Holm, unpublished work.

(29) C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

(30) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

developed as the iodine was added. On completion of the addition the solution was rapidly filtered into 250 ml of 2-propanol. The product precipitated as a black microcrystalline powder which was collected, washed with 2-propanol and pentane, and vacuum dried. A yield of 0.83 g or 95% was obtained. In solution the complex decomposes to yield an oily yellow precipitate and a wine-colored solution.

Anal. Calcd for $C_{44}H_{60}NS_8Fe_2$: C, 54.41; H, 6.23; N, 1.44; S, 26.41. Found: C, 54.71; H, 6.26; N, 0.83; S, 26.79.

$[(n\text{-}C_4H_9)_4N]_2[FeS_4C_4(CF_3)_4]_2$. This compound was prepared in a manner similar to that for the tetraethylammonium salt.[20] The crude material separated as an oil. The aqueous reaction solution was decanted and the oil treated with a small volume of 2-propanol, which caused it to solidify. This solid was recrystallized from acetone–2-butanol. Black crystals were obtained, mp 182–183° (sealed tube).

Anal. Calcd for $C_{24}H_{36}F_{12}NS_4Fe$: C, 38.40; H, 4.83; F, 30.37; S, 17.09. Found: C, 37.96; H, 4 53; F, 30.39; S, 17.24.

$[(n\text{-}C_4H_9)_4N]_2[FeS_4C_4(CN)_4]_2$. Preparation of this compound was effected by the previously published procedure for the tetraethylammonium salt.[21] It was purified by careful recrystallization from acetone-*n*-heptane. Black crystals were obtained, mp 197–198° (sealed tube).

Anal. Calcd for $C_{24}H_{36}N_5S_4Fe$: C, 49.81; H, 6.27; N, 12.10; S, 22.16 Found: C, 50.14; H, 6.46; N, 12.01; S, 22.09.

$[(C_2H_5)_4N][CoS_4C_4(CF_3)_4]_2$. A filtered solution of 1.25 g (1.22 mmoles) of $[CoS_4C_4(CF_3)_4]_2$ in 400 ml of dry dichloromethane was added slowly with stirring to a slurry of 1.49 g (1.17 mmoles) of $[(C_2H_5)_4N]_2[CoS_4C_4(CF_3)_4]_2$ in 100 ml of dry dichloromethane. The mixture was refluxed for 6 hr, and then the volume was reduced to 250 ml. After cooling, the black crystalline complex was collected by filtration and washed with dichloromethane to yield 2.35 g (88%). Purification was achieved by Soxhlet extraction using dry dichloromethane.

Anal. Calcd for $C_{24}H_{20}F_{24}NS_8Co_2$: C, 25.00; H, 1.75; F, 39.55; N, 1.22; S, 22.25. Found: C, 24.96; H, 1.74; F, 42.09; N, 1.14; S, 22.25.

$[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CF_3)_4]_2$. The preparation follows that of the tetraethylammonium salt.[20] The crude product separated as an oil. Dichloromethane and water were added to the reaction mixture to produce two separate phases. The complex was extracted into the dichloromethane layer (green solution), which was separated, dried over sodium sulfate, and reduced in volume at room temperature until the product crystallized. This material was once recrystallized from acetone–2-propanol; black needles were obtained, mp 169–169.5°.

Anal. Calcd for $C_{24}H_{36}F_{12}NS_4Co$: C, 38.24; H, 4.81; S, 17.02. Found: C, 38.14; H, 4.78; S, 16.82.

Other complexes used in this study were available from earlier investigations or were prepared according to published procedure.[12c,19–21,26,27,30]

Physical Measurements. Polarographic measurements were obtained by use of the techniques and instrumentation previously described[31] except that for measurements in dichloromethane solution a modified reference electrode was employed. The modification involves replacing $(n\text{-}C_4H_9)_4NPF_6$ with $(n\text{-}C_4H_9)_4NClO_4$ (0.50 *M*) as supporting electrolyte in the reference electrode compartment and in the salt bridge connecting the reference electrode with the junction compartment (see Figure 1 of ref 31). This modification was made because it was observed that dichloromethane solutions of $(n\text{-}C_4H_9)_4NPF_6$ decompose slowly with production of acid. This decomposition, presumably abetted by traces of moisture, was not sufficient to affect any of our previous polarographic measurements.

Conductivities were measured using Spectrograde acetonitrile as solvent and a Serfass conductivity bridge. Mass spectra were recorded on a Picker MS-9 spectrometer by employing 70-ev ionizing electrons and direct insertion. Electronic spectra were obtained using a Cary Model 14 spectrophotometer. Magnetic measurements of solids and solutions were made by the Gouy method using $HgCo(NCS)_4$ and freshly boiled, distilled water as the calibrants, respectively. For measurements of solids below room temperature, a cryostat capable of continuous temperature regulation from 77 to 300°K was employed.

Results and Discussion

Mass Spectra. In view of the tight dimeric structures established in the crystalline solids, we sought to ascertain if dimers remained intact upon vaporization. Data from the mass spectra of the only two complexes suitable for such a study, $[CoS_4C_4(CF_3)_4]_2$ and $[FeS_4C_4(CF_3)_4]_2$, are given in Table II. The most striking feature of these spectra is the observation of ions which indicate that the dimeric structure of these complexes persists in the gas phase. Both complexes exhibit a parent ion,[32] and both appear to fragment similarly. Fragmentation of the parent ion *via* the process

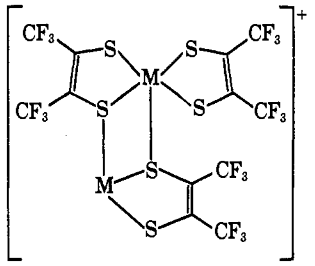
Table II. Principle Metal-Containing Ions with $m/e > 450$ in Mass Spectra of $[CoS_4C_4(CF_3)_4]_2$ and $[FeS_4C_4(CF_3)_4]_2$

Ion	*m/e* for ^{56}Fe	*m/e* for ^{59}Co
$[M_2S_8C_{16}F_{24}]^+$	1016	1022
$[M_2S_8C_{16}F_{23}]^+$	997	1003
$[M_2S_6C_{12}F_{18}]^+$	790	796
$[M_2S_6C_{12}F_{17}]^+$	771	777
$[MS_6C_{12}F_{15}]^+$	677	680
$[MS_6C_{12}F_{14}]^+$	658	661
$[M_2S_4C_8F_{12}]^+$	564	...
$[MS_4C_8F_{12}]^+$	508[a]	511[a]
$[MS_4C_8F_{11}]^+$	489	492
$[MS_4C_8F_{10}]^+$	470	473
$[MS_4C_8F_9]^+$	451	454

[a] Careful observation reveals no ions of half-integral mass in this region; thus the ions observed are not the doubly charged parent ions.

$$[MS_4C_4(CF_3)_4]_2^+ \longrightarrow [M_2S_6C_6(CF_3)_6]^+ + S_2C_2(CF_3)_2$$

is supported by observation of metastable peaks [for M = Co: calcd 620, found 620; for M = Fe: calcd 614, found 614]. Presumably this process results in the loss of one of the nonbridging ligands to produce a daughter ion with structure **3**. This is further evidence of the strength of the bridging metal–sulfur bonds but is



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a different decomposition pattern from that of $[FeS_4C_4Ph_4]_n$, which is thermally induced.[26] These results also confirm the stoichiometry of the iron complex, which was assigned a tris formulation in earlier work[20] but has since been corrected.[25,26]

The ions $[MS_6C_6(CF_3)_5C]^+$ and $[MS_6C_6(CF_3)_4CF_2C]^+$ could result from the presence of some $[MS_6C_6(CF_3)_6]$ as an impurity. However, we consider this to be unlikely because the mass spectra of the tris complexes of molybdenum and tungsten do not exhibit ions of this type but do show well-defined parent ions.[32] No $[MS_6C_6(CF_3)_6]^+$ ions are observed in the mass spectra

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[31] F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, 5, 1542 (1966).

[32] Mass spectra of the *monomeric* complexes $[NiS_4C_4(CF_3)_4]$ and $[PtS_4C_4(CF_3)_4]$ do not exhibit any ions with *m/e* greater than that expected for the (observed) parent ions: A. L. Balch, unpublished observations.

of the cobalt and iron compounds. We suggest that $[MS_6C_6(CF_3)_5C]^+$ might result from either of the processes

$$[M_2S_6C_6(CF_3)_6]^+ \longrightarrow [MS_6C_6(CF_3)_5C]^+ + MF_3$$

$$[M_2S_8C_8(CF_3)_8]^+ \longrightarrow [MS_6C_6(CF_3)_5C]^+ + F_3MS_2C_2(CF_3)_2$$

but metastable peaks which could substantiate these ideas have not been observed. The first proposed fragmentation is similar to that observed for $[Co(CO)S_2C_2(CF_3)_2]_3$,[33] *viz.*, $[Co_3S_6C_6(CF_3)_6]^+ \longrightarrow [Co_2S_6C_6(CF_3)_5CF]^+ + CoF_2$.

Ions related by successive loss of fluorine are a prominent feature of these spectra. In this regard the observed fragmentation patterns are similar to those observed for a series of π-cyclopentadienyl complexes derived from bisperfluoromethyl-1,2-dithietene.[34]

Spin–Spin Interactions in Crystalline Solids. Association of monomers to form dimers or higher aggregates can seriously perturb the magnetic properties of the monomers if exchange coupling is sufficiently strong. This is the situation found in salts of $[M(mnt)_2]^-$ whose temperature-dependent magnetic susceptibilities have been successfully interpreted in terms of a thermal population of singlet and triplet spin states arising from antiferromagnetic coupling of two spin-doublet metal atoms.[21] From their magnetic properties we have obtained evidence that a number of iron and cobalt dithiolenes are not monomeric in the crystalline state. On the basis of X-ray evidence already cited, it is assumed that the most likely mode of association in the solid phases is dimeric, in which case the possible spin multiplicities of the various species are as follows.

$$\begin{array}{ccc} [M\text{–}S_4]_{20} & [M\text{–}S_4]_2^- & [M\text{–}S_4]_2^{-2} \\ S = 0, 1, 2, \ldots & S = {}^1/_2, {}^3/_2, {}^5/_2, \ldots & S = 0, 1, 2, \ldots \end{array}$$

The magnetic susceptibilities of the paramagnetic, potentially dimeric or polymeric, dithiolene complexes have been measured over the temperature interval 80–300°K, and the full data and interpretations will be presented in a forthcoming publication.[28] The data given in Table III are adequate for the present purpose of detecting spin exchange, manifested by reduction of magnetic moments with decreasing temperature, and the attendant dimeric (or polymeric) structures of the complexes. Because of small spin–orbit coupling in the first transition series and the considerable covalency in the metal–ligand bonding, magnetic moments are not expected to decrease significantly below the spin-only values for the various spin states. Spin-doublet, -triplet, and -quartet dimers are then expected to have moments equal to or in excess of 1.73, 2.83, and 3.88 BM, or in terms of the monomeric units, 1.23, 2.00, and 2.74 BM, respectively. We find that the monomeric complex $(Bu_4N)[Co(tdt)_2]$ obeys the Curie–Weiss relation $\chi^M_{cor}(T + 14)$ = constant, and thus confirms the spin-triplet ground state[30] in the solid phase. In contrast, all complexes listed in Table III except $(Et_4N)[CoS_4C_4(CF_3)_4]_2$ *do not follow the Curie–Weiss law.* Their moments decrease with decreasing temperature, reflecting antiferromagnetic coupling of spins between adjacent $[M\text{–}S_4]$ coordination units.

The cobalt and iron dimers fall into five isoelectronic groups: $[Fe\text{–}S_4]_2{}^0$, $[Fe\text{–}S_4]_2^-$, $[Fe\text{–}S_4]_2^{-2}$ and $[Co\text{–}S_4]^0$, $[Co\text{–}S_4]_2^-$, and $[Co\text{–}S_4]_2^{-2}$. The detailed susceptibility data for the iron complexes of the first three groups reveal that excited electronic states of spin degeneracy greater than that of the ground state are thermally populated in the 80–300°K range. Except possibly for $[CoS_4C_4Ph_4]_n$, where the effect is very small, we have found no examples of cobalt dimers which exhibit populations of excited spin states. Both $[Co(mnt)_2]_2^{-2}$ and $[CoS_4C_4(CF_3)_4]_2^{-2}$ are diamagnetic in several different salts; this behavior does not, of course, prove their dimeric formulation for diamagnetic monomers $[Co\text{–}S_4]^-$ are in principle possible. The diamagnetism[35] of crystalline $(Bu_4N)_2[Co(o\text{-}S_2C_6Cl_4)_2]_2$, known to contain a dimeric dianion,[24] together with the frequent insensitivity of magnetic properties (spin-Hamiltonian parameters and magnetic moments) of dithiolene complexes to ligand structure suggests that $[Co\text{–}S_4]^-$ monomers would possess a spin-triplet ground state as does $[Co(tdt)_2]^-$. An X-ray study of the cobalt-mnt complex reported in progress[27] should further clarify the structure–magnetism relationship of these diamagnetic cobalt species.

Table III. Magnetic Moments of Crystalline Solids

Compound	μ_{eff}, BM[a] (T, °K)	Ground-state spin
$[CoS_4C_4Ph_4]_n$	0.73 (293)	0
$(Et_4N)[CoS_4C_4(CF_3)_4]_2$[b]	1.91 (300), 1.83 (91)	$^1/_2$
$[FeS_4C_4Ph_4]_n$	1.63 (292), 0.77 (82)	0
$[FeS_4C_4(CF_3)_4]_2$	1.59 (301), 1.13 (87)	0
$(Et_4N)[FeS_4C_4(CF_3)_4]_2$[b]	2.08 (300), 1.74 (80)	$^1/_2$
$(Et_4N)_2[FeS_4C_4(CF_3)_4]_2$	1.39 (299), 0.31 (87)	0
$(Bu_4N)_2[FeS_4C_4(CF_3)_4]_2$	1.42 (301), 0.37 (90)	0
$(Et_4N)_2[FeS_4C_4(CN)_4]_2$	1.67[c] (301) 0.48 (84)	0
$(Bu_4N)_2[FeS_4C_4(CN)_4]_2$	1.55 (299), 0.43 (81)	0
$(Bu_4N)[Fe(o\text{-}S_2C_6H_3CH_3)_2]$	1.99[d] (299), 0.96 (80)	0
$(Bu_4N)[Fe(o\text{-}S_2C_6H_3CH_3)_2]_2$[b]	3.6 (300), 2.8 (80)	$^1/_2$[e]

[a] Curie magnetic moment per metal atom, unless otherwise indicated, without inclusion of temperature independent paramagnetism and corrected for diamagnetism. [b] Moment per dimer unit. [c] 1.62 BM reported in ref 21. [d] 2.07 BM reported in ref 30. [e] Moments indicate high population of excited spin state(s).

Polarography. Establishment of Electron-Transfer Series. Polarographic measurements supplemented by synthesis and isolation of many of the complexes involved have clearly demonstrated that monomeric bis-dithiolene complexes may exhibit electron-transfer series of two or three members[16,17,21,24,27,36,37] represented generally by

$$[M\text{–}S_4]^{-2} \rightleftharpoons [M\text{–}S_4]^- \rightleftharpoons [M\text{–}S_4]^0$$

For $[MS_4C_4R_4]^z$ complexes the ease of oxidation is strongly dependent on the R group, the order of oxidative stability for a given metal being CN > CF_3 > Ph > H > alkyl.[37] $[M(tdt)_2]^z$ and $[MS_4C_4Ph_4]^z$ species appear to have comparable oxidative stabilities.[30] All three members have frequently been isolated or detected polarographically in Ni, Pd, and Pt series, whereas only the $-2 \rightleftharpoons -1$ step has been reported in published investigations of the Cu and Au series.

The polarographic data set out in Table IV present convincing evidence that dimeric complexes participate in electron-transfer reactions. Data are reported on all iron and cobalt complexes that have been isolated to

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(33) R. B. King and T. F. Korenowski, *Chem. Commun.*, 771 (1966).

(34) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

(35) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 4870 (1966).

(36) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 1483 (1965).

(37) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *ibid.*, **88**, 4876 (1966).

Table IV. Polarographic Data for Cobalt and Iron Dithiolene Complexes in Dichloromethane[a]

Complex	$2[MS_4]^{-2} \rightleftharpoons [MS_4]_2^{-2}$		$[MS_4]_2^{-2} \rightleftharpoons [MS_4]_2^-$		$[MS_4]_2^- \rightleftharpoons [MS_4]_2$	
	$E_{1/2}$, v	i_d/C,[g] μa/mM	$E_{1/2}$, v	i_d/C,[g] μa/mM	$E_{1/2}$, v	i_d/C,[g] μa/mM
$[CoS_4C_4(CF_3)_4]_2$	−0.14	+34	+0.52	+18	+1.19	+20
$(Et_4N)[CoS_4C_4(CF_3)_4]_2$	−0.11	+41	+0.54	+22	+1.23	−21
$(Bu_4N)_2[CoS_4C_4(CF_3)_4]_2$	−0.09	+40	+0.56	−17	+1.24	−20
$(Et_4N)_2[CoS_4C_4(CF_3)_4]$	−0.05	(−)[b]	+0.60	(−)[b]	+1.29	(−)[b]
$(Bu_4N)_2[CoS_4C_4(CN)_4]_2$	+0.17	+35	+1.03	−18	...[c]	
$(Bu_4N)_2[CoS_4C_4(CN)_4]$	+0.24	−17	+1.06	−9	...[c]	
$(Bu_4N)[Co(o\text{-}S_2C_6H_3CH_3)_2]$	−0.71	+17	...[c]		...[c]	
$[FeS_4C_4(CF_3)_4]_2$	...[d]		+0.67	−19	+1.24	−19
$(Et_4N)[FeS_4C_4(CF_3)_4]_2$	...[d]		+0.69	+19	+1.27	−18
$(Bu_4N)_2[FeS_4C_4(CF_3)_4]_2$	−0.60[e]	+9.5[e]	+0.71	−16	+1.27	−17
$(Bu_4N)_2[FeS_4C_4(CN)_4]_2$	...[d,f]		+1.06	−17	...[c]	
$(Bu_4N)[Fe(o\text{-}S_2C_6H_3CH_3)_2]_2$	...[d]		+0.16	+17	+0.48	−17
$(Bu_4N)[Fe(o\text{-}S_2C_6H_3CH_3)_2]$	−0.95[e]	+15[e]	+0.18	−7	+0.48	−7

[a] Using $(n\text{-}Bu_4N)ClO_4$ as supporting electrolyte, a rotating platinum working electrode unless otherwise specified, and the reference electrode described in the Experimental Section. [b] The oxidative instability of this compound precluded determination of the diffusion current. [c] No wave corresponding to this process has been observed. [d] Very drawn out waves which may correspond to this reduction are observed on a platinum electrode in both dichloromethane and acetonitrile. [e] Obtained in acetonitrile solution with a dropping Hg electrode, saturated calomel electrode, and 0.1 *M* Pr_4NClO_4 as supporting electrolyte. Under these conditions the reduction of $(Bu_4N)_2[CoS_4C_4(CF_3)_4]_2$ (to $[CoS_4C_4(CF_3)_4]^{-2}$) yields an i_d/C of 9.3 μa/m*M*. [f] Apparent reaction with Hg precludes measurement. [g] Concentrations calculated on the basis of the formulas given in column 1.

date with the ligand systems selected for study. In all cases where two or more complexes appear to be related by simple electron-transfer reactions, this relationship is confirmed by the observation of the appropriate polarographic waves which occur at quite similar potentials regardless of which member is investigated.[38] This behavior is illustrated in Figure 2, in which are shown the actual polarographic traces obtained from dichloromethane solutions of $(Bu_4N)_2[CoS_4C_4(CF_3)_4]_2$ and $(Et_4N)[CoS_4C_4(CF_3)_4]_2$.

It is convenient to consider the polarographic behavior in terms of complexes having a single negative charge per metal because these species are common to every series of dimers studied. The general features of the polarography of this group of complexes are exhibited by $(Bu_4N)_2[CoS_4C_4(CF_3)_4]_2$. The most striking feature is the appearance of a reduction wave with a diffusion current twice that of each of the *two* oxidative waves. This behavior is consistent with the occurrence of two oxidative processes *which leave the dimer intact* to produce, successively, $[CoS_4C_4(CF_3)_4]_2^-$ and $[CoS_4C_4(CF_3)_4]_2$. The reduction wave involves a two-electron transfer, yielding two $[CoS_4C_4(CF_3)_4]^{-2}$ ions. In the Co-mnt series the only isolable dimeric species, $[Co(mnt)_2]_2^{-2}$, was observed to undergo only a single oxidation, presumably producing $[Co(mnt)_2]_2^-$. The polarographic behavior of $[FeS_4C_4(CF_3)_4]_2^{-2}$ and $[Fe(mnt)_2]_2^{-2}$ closely parallels that of their respective cobalt analogs. However, on a rotating platinum electrode the reduction waves of these species, which should by analogy with the cobalt series produce $[Fe\text{-}S_4]^{-2}$, are very drawn out and irreversible in either dichloromethane or acetonitrile. The reason for this behavior is not understood. With a dme in acetonitrile this wave is well developed for $[FeS_4C_4(CF_3)_4]_2^{-2}$, but with $[Fe(mnt)_2]_2^{-2}$ an apparent reaction with mercury precludes measurement.

It is to be noted that diffusion currents given in Table IV for redox reactions measured in solutions prepared from $[M\text{-}S_4]_2^{-2,-1}$ salts or $[M\text{-}S_4]_2^0$ have been calculated using dimeric formula weights. These values in general compare favorably with diffusion currents for one-electron-transfer reactions of monomeric species in dichloromethane solution which are listed in Table V.

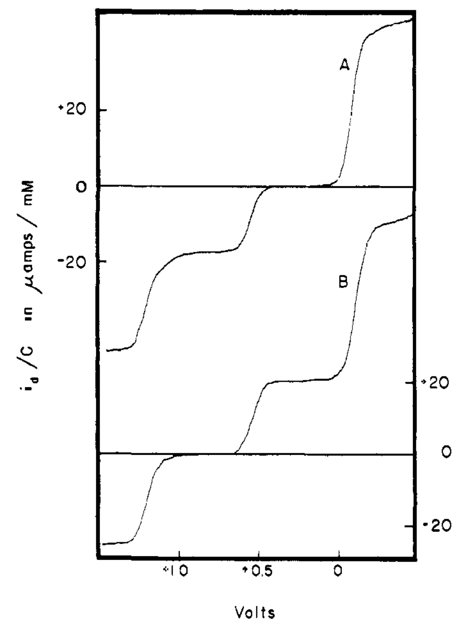

Figure 2. Polarograms in dichloromethane solution: (A) $(n\text{-}Bu_4N)_2[CoS_4C_4(CF_3)_4]_2$, (B) $(Et_4N)[CoS_4C_4(CF_3)_4]_2$. The voltage scale is common to both polarograms; the left i_d/C scale refers to A.

Further, diffusion currents for the process $[Co\text{-}S_4]_2^{-2} \rightleftharpoons 2[Co\text{-}S_4]^{-2}$ are roughly twice those for the single electron transfers. Because $[Co\text{-}S_4]^{-2}$ species are unquestionably monomeric,[9,27] the relative values of the diffusion currents are in agreement with the formation of dimeric species of charges −2, −1, 0 in the redox reactions.[39]

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[38] The small variations in $E_{1/2}$ observed are probably due to an incompletely compensated *iR* drop which results from working in a low dielectric solvent.

[39] Spectrophotomeric studies of the composition of solutions prepared from salts of the dimeric cobalt and iron dianions are currently in progress. Of the species thus far studied in detail, it is concluded from Beer's law deviations that in dichloromethane $[CoS_4C_4(CF_3)_4]_2^{-2}$ and $[Fe(mnt)_2]_2^{-2}$ are partially dissociated into monomeric monoanions. $[FeS_4C_4(CF_3)_4]_2^{-2}$ is only very slightly dissociated. These observations refer to a 10^{-2}–10^{-5} *M* concentration range of total metal

Table V. Polarographic Data for Monomeric Bisdithiolene Complexes in Dichloromethane[a,b]

Metal	Ligand	Step	$E_{1/2}$, v	i_d/C, μa/mM
Cu	$S_2C_2(CN)_2$	$-2 \rightleftharpoons -1$	+0.41	20
	$S_2C_2(CF_3)_2$	$-2 \rightleftharpoons -1$	0.00	24
		$-1 \rightleftharpoons 0$[d]	+1.37	24
Au	$S_2C_2(CF_3)_2$	$-2 \rightleftharpoons -1$	−0.97	26
		$-1 \rightleftharpoons 0$[d]	+1.32	25
Ni	$S_2C_2(CN)_2$	$-2 \rightleftharpoons -1$	+0.37	21
		$-1 \rightleftharpoons 0$[d]	+1.38	24
	$S_2C_2(CF_3)_2$	$-2 \rightleftharpoons -1$	−0.05	21
		$-1 \rightleftharpoons 0$	+1.01	23
	$S_2C_6H_3CH_3$	$-1 \rightleftharpoons 0$[c]	+0.52	22
	$S_2C_2(C_6H_5)_2$	$-1 \rightleftharpoons 0$[c]	+0.20	25
		$0 \rightleftharpoons +1$[d]	+1.45	21
	$S_2C_2H_2$	$-2 \rightleftharpoons -1$	−0.72	27
		$-1 \rightleftharpoons 0$	+0.28	28
Pd	$S_2C_2(CN)_2$	$-2 \rightleftharpoons -1$	+0.59	20
	$S_2C_2(CF_3)_2$	$-2 \rightleftharpoons -1$	+0.25	19
		$-1 \rightleftharpoons 0$	+1.08	24
Pt	$S_2C_2(CF_3)_2$	$-2 \rightleftharpoons -1$	+0.02	18
		$-1 \rightleftharpoons 0$	+0.93	23

[a] Using the exact method as described in ref 31. The potentials measured in this way differ by only ±0.02 v from potentials measured using the modified reference cell described in the Experimental Section of this paper. [b] The following complexes were also investigated and found to show no clean oxidative waves: $[Zn(mnt)_2]^{-2}$, $[Cu(tdt)_2]^-$,[c] $[Au(mnt)_2]^-$.[c] [c] No attempt was made to study the reduction of these complexes in dichloromethane although all show well-defined waves in other solvents for the reduction to complexes with −2 charge. [d] New waves which have not been observed in conventional polarographic solvents.

Table VI. Electron-Transfer Series Involving Dimeric Dithiolene Complexes[a]

$\underline{[CoS_4C_4(CF_3)_4]_2^0}$ [b]	$\rightleftharpoons$	$\underline{[CoS_4C_4(CF_3)_4]_2^-}$ [c]	$\rightleftharpoons$	$\underline{[CoS_4C_4(CF_3)_4]_2^{-2}}$ [b]	$\longrightarrow$	$\underline{2[CoS_4C_4(CF_3)_4]^{-2}}$ [b]
		$[CoS_4C_4(CN)_4]_2^-$ [h]	$\rightleftharpoons$	$\underline{[CoS_4C_4(CN)_4]_2^{-2}}$ [d,e]	$\rightleftharpoons$	$\underline{2[CoS_4C_4(CN)_4]^{-2}}$ [f]
$\underline{[FeS_4C_4(CF_3)_4]_2^0}$ [b,c]	$\rightleftharpoons$	$\underline{[FeS_4C_4(CF_3)_4]_2^-}$ [c]	$\rightleftharpoons$	$\underline{[FeS_4C_4(CF_3)_4]_2^{-2}}$ [b]	$\rightleftharpoons$	$2[FeS_4C_4(CF_3)_4]^{-2}$ [h]
		$[FeS_4C_4(CN)_4]_2^-$ [h]	$\rightleftharpoons$	$\underline{[FeS_4C_4(CN)_4]_2^{-2}}$ [c,e]		
$[Fe(tdt)_2]_2^0$ [h]	$\rightleftharpoons$	$\underline{[Fe(tdt)_2]_2^-}$ [c]	$\rightleftharpoons$	$\underline{2[Fe(tdt)_2]^-}$ [g,i]	$\rightleftharpoons$	$2[Fe(tdt)_2]^{-2}$ [h]

[a] Species underlined have been isolated; they were characterized in the indicated references. [b] Reference 20. [c] This work. [d] Reference 19. [e] Reference 21. [f] Reference 12b and A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 3049 (1963). [g] Reference 30. [h] Detected by polarography in dichloromethane but not isolated. [i] Correctness of the monomeric formulation is uncertain.

In the absence of any information to the contrary, $[Co(tdt)_2]^-$ and $[Fe(tdt)_2]^-$ are taken to be unassociated in dichloromethane; both are monomers in acetonitrile (*vide infra*). In this solvent $[Co(tdt)_2]^-$ does not exhibit any clean polarographic oxidation although reduction to $[Co(tdt)_2]^{-2}$ has been observed.[30] The iron analog undergoes two polarographic oxidations with diffusion currents consistent with the successive formation of $[Fe(tdt)_2]_2^-$ and $[Fe(tdt)_2]_2$. As has been found with the other iron complexes, a drawn-out reduction wave is observed on a platinum electrode, but this wave is considerably sharper in acetonitrile on a dme.

The foregoing polarographic evidence leads to the following general formulation of the electron-transfer series of dimeric dithiolene complexes in dichloromethane solution.

$$2[M\text{–}S_4]^{-2} \rightleftharpoons [M\text{–}S_4]_2^{-2} \rightleftharpoons [M\text{–}S_4]_2^{-} \rightleftharpoons [M\text{–}S_4]_2^{0}$$

The entire situation is summarized in Table VI, which sets out the various series, partial and complete, which have been established polarographically together with the members of each which have been isolated and definitely characterized. As with monomeric complexes, the half-wave potentials of a given reaction are strongly ligand-dependent with the usual order of oxidative stability, tdt < $S_2C_2(CF_3)_2$ < mnt, preserved for iron and cobalt. The large positive potentials required to form the neutral mnt dimers precludes their detection. The cobalt and iron dithietene series have been completely defined polarographically. The cobalt series is completely specified chemically as well because all four members have been isolated and characterized.

Previous polarographic studies of several of the complexes studied here in dichloromethane did not lead to the recognition of dimeric species in acetonitrile solution.[19,20] The polarographic behavior of the complexes formulated as $[M\text{–}S_4]_n^{-n}$ (M = Fe, Co; n = 1, 2) has been reexamined in acetonitrile. Although the potentials of reduction waves observed correlated with those measured in dichloromethane,[40] in only two cases were the anodic processes similar. Polarographic oxidation of $[Fe(tdt)_2]^-$ in acetonitrile shows waves corresponding to the oxidation to $[Fe(tdt)_2]_2^-$ and $[Fe(tdt)_2]_2$. The previously reported[20] oxidative wave at $E_{1/2}$ = 0.535 v for $[CoS_4C_4(CF_3)_4]_2^{-2}$ in acetonitrile has a diffusion current which is half the value of the diffusion current of the cathodic wave at $E_{1/2}$ = −0.398 v. The anodic wave results in the production of $[CoS_4C_4(CF_3)_4]_2^-$, not $[CoS_4C_4(CF_3)_4]$ as previously reported;[20] Oxidation to $[CoS_4C_4(CF_3)_4]_2$ is not detected in acetonitrile. The difference in polarographic behavior in dichloromethane from that in other solvents is probably due to two effects: (i) the ability of basic solvents to rupture the dimeric ions by coordinating with the metal;[41] (ii) the ability of basic solvents to reduce the oxidized member of couples with $E_{1/2}$ (in dichloromethane) greater than

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in all forms. The presence of monomers under conditions approaching those used in the polarographic studies does not invalidate the diffusion current values calculated on the basis of only dimers in solution, or the conclusions made above relative to the existence of dimeric electron-transfer series. A rapid monomer ⇄ dimer equilibrium can accommodate consumption of the dimer in the electrode reaction, allowing all of the solute access to the electrode in dimeric form at those potentials under which the dimer, but not the monomer, is electroactive. That the monomers are not electroactive within potential ranges required to span the dimeric electron transfer series is indicated by the following observations: (i) three polarographic waves for most systems whereas monomeric species generally produce only two (*cf.* Table V), (ii) a ratio of ~2:1:1 for diffusion currents of successive oxidative processes whereas an approximate 1:1 ratio is found for monomeric complexes, (iii) values of the diffusion currents for the two most positive oxidations which if calculated from monomeric formula weights are a factor of ~2 too small for a transfer of one electron per metal.

(40) For a large number of dithiolene complexes that exhibit similar behavior in the two solvents, the half-wave potentials are related by $E_{1/2}$ (in CH_3CN) ≅ $0.88E_{1/2}$ (in CH_2Cl_2) − 0.15.

(41) The polarography of five- or six-coordinate monomeric complexes is quite distinct from that of the dimers: A. L. Balch, *Inorg. Chem.*, 6, 2158 (1967).

+0.4 v.[20] In connection with the latter suggestion, it should be noted that the two complexes whose polarographic behavior is similar in acetonitrile and dichloromethane are the cases where the least positive half-wave potentials are involved.

In an effort to search for other examples of dimerization, the polarography of a number of other planar dithiolene complexes has been examined. The results are set out in Table V. Although no other dimeric species were found, several oxidative waves were observed which were undetected in other solvents. Dichloromethane appears to be an excellent, unreactive solvent for anodic polarography.

Conductivity Results. The degree of association n of an electrolyte A_nB_n may be determined from measurement of the equivalent conductivity as a function of concentration.[42] In this manner cobalt–mnt and -dithietene complexes were formulated as $[Co(mnt)_2]_2^{-2}$ and $[CoS_4C_4(CF_3)_4]_2^{-2}$, and $[Co(tdt)_2]^-$ was shown to be unassociated.[27,43] Spectral results[39] are consistent with this observation for the first complex, but for the second they reveal ~50% dimer dissociation in the lower concentration range employed in the conductivity study. Evidently the published data[27] are insufficiently accurate to detect the substantial degree of dissociation.

Results of similar studies of $[Fe\text{–}S_4]_n^{-n}$ ions in acetonitrile are given in Table VII and presented graphically in Figure 3. A plot of conductivity *vs.* $\sqrt{c}$ ($c = 10^{-2}$–10^{-3} M) for $(Bu_4N)_2[FeS_4C_4(CF_3)_4]_2$ (not shown) in acetonitrile is nonlinear, consistent with some dimer dissociation. With the adoption of $(Bu_4N)_2[Ni(mnt)_2]$ and $(Bu_4N)[Ni(mnt)_2]$ as standard 2:1 and 1:1 electrolytes and the established monomeric nature of $(Bu_4N)[Co(tdt)_2]$,[24,27] the most reasonable interpretation of the results in Figure 3 is that $(Bu_4N)[Fe(tdt)_2]$ and $(Bu_4N)_2[Fe(mnt)_2]_2$ yield monomeric anions in acetonitrile over the concentration range studied. The spectrum of the second compound in acetonitrile, when compared with those of a dichloromethane solution and the solid, is consistent with complete dimer dissociation. The spectrum of crystalline $(Bu_4N)[Fe(tdt)_2]$ also changes on dissolution in acetonitrile. However, the detailed state of association of $[Fe(tdt)_2]^-$ in the solid and in solution where its spectrum is markedly solvent dependent[30] is not yet clear and must await the results of further investigations in progress.

Table VII. Conductivity Measurements in Acetonitrile Solution[a]

Compound	Λ, ohm^{-1} cm^2 equiv^{-1} [b]	A
$[Bu_4N]_2[NiS_4C_4(CN)_4]$	172	760
$[Bu_4N][NiS_4C_4(CN)_4]$	132	315
$[Bu_4N][Co(S_2C_6H_3CH_3)_2]$	131	450
$[Bu_4N][FeS_4C_4(CN)_4]$	125	360
$[Bu_4N][Fe(o\text{-}S_2C_6H_3CH_3)_2]$	128	530

[a] *Cf.* ref 27 for additional results on the same and related complexes. [b] *Cf.* ref 43.

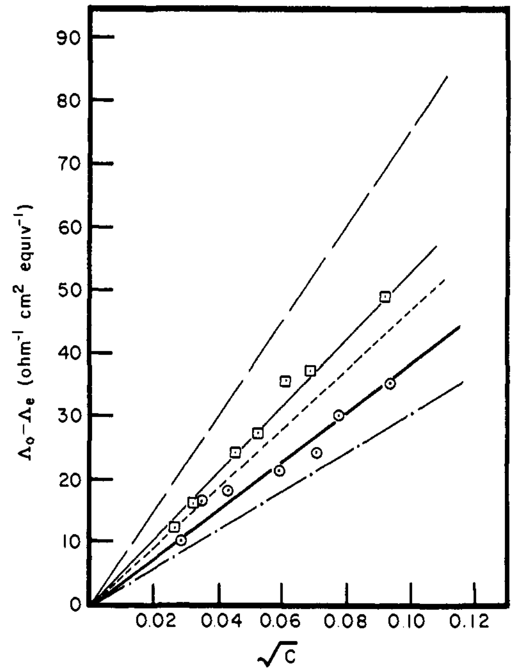

Figure 3. Conductivity results for electrolytes in acetonitrile solution: ⊙, $(n\text{-}Bu_4N)[Fe(mnt)_2]$; ⊡, $(n\text{-}Bu_4N)[Fe(tdt)_2]$; — · —, $(n\text{-}Bu_4N)[Ni(mnt)_2]$; - - - -, $(n\text{-}Bu_4N)[Co(tdt)_2]$; — — —, $(n\text{-}Bu_4N)_2[Ni(mnt)_2]$.

Other Sulfur-Bonded Dimers and Polymers. An exception to the dimer structure of Figure 1 may be $[Re(mnt)_2]_2^{-2}$,[44] in which the strong Re–Re bond prevalent in binuclear Re(III) species may be preserved. The low solubilities of $[MS_4C_4Ph_4]$[26] (M = Fe, Co) and $[Sn(tdt)_2]$[45] could be accounted for by six-coordinate polymeric structures formed by repetition of the dimeric unit. Salts containing, nominally, $[FeS_4C_4Ph_4]^-$ and $[CoS_4C_4Ph_4]^-$ have recently been prepared.[26,46] The reported[26] diamagnetism of the tetraethylammonium salt of each requires a dimeric or polymeric structure for the iron complex and is suggestive of the same for the cobalt complex. The dimer structure is not confined to dithiolene complexes. Extremely similar $M\text{–}S_5$ coordination polyhedra are found in crystalline bis-N-N-diethyl-[47] and bis-N,N-di-*n*-propyldithiocarbamatocopper(II),[48] which exist as centrosymmetric dimers. This same structure may extend to $M(S_2CNEt_2)_2$ complexes isomorphous with $Cu(S_2CNEt_2)_2$.[49]

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(42) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(43) We have studied several compounds that were also studied in ref 27. Our values of A agree with those obtained by Davison, *et al.*; however, our values of Λ_0 are uniformly lower. This discrepancy may result from errors in cell calibration which would affect Λ_0 but not A. Since the degree of association is determined from comparison of A values, the discrepancy does not effect any of the conclusions.

(44) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967).

(45) R. C. Poller and J. A. Spillman, *J. Chem. Soc., Sect. A*, 958 (1966).

(46) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Am. Chem. Soc.*, **89**, 6082 (1967).

(47) M. Bonamico, G. Dessy, A. Mugnoli, and A. Vaciago, *Acta Cryst.*, **19**, 886 (1965).

(48) A. Pignedoli and G. Peyronel, *Gazz. Chim. Ital.*, **92**, 745 (1962).

(49) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Letters*, 251 (1966). Note that the isomorphism of the Cu(II), Mn(II), and Fe(II) complexes with $Cu(S_2CNEt_2)_2$ does not certify that they all are isostructural; the Zn(II) complex is also claimed to be isomorphous but has a centrosymmetric dimeric structure which is markedly different from that of $Cu(S_2CNEt_2)_2$; *cf.* M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19**, 898 (1965).