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The Crystal and Molecular Structure of the Tetra-*n*-butylammonium Salt of Bis(maleonitriledithiolato)iron(III)-A Pyramidal Iron(III) Dimer[1,2]

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The room-temperature magnetic susceptibility reported for salts of the type $RFe(MNT)_2$, where R is a cation and MNT is 1,2-dicyano-1,2-ethylenedithiol, led us to investigate the temperature dependence of this quantity and also the crystal structure of the *n*-butylammonium derivative. $(n\text{-}C_4H_9)_4NFe(MNT)_2$ crystallizes in the monoclinic space group I2/a with cell dimensions $a = 27.53$ A ($\sigma = 0.08$), $b = 14.33$ A ($\sigma = 0.04$), $c = 15.10$ A ($\sigma = 0.04$), $\beta = 95° 5'$ ($\sigma = 5'$). The measured density (flotation in $ZnCl_2$) is 1.28 g/cc. The density calculated for $Z = 16$ molecules/cell is 1.295 g/cc. A four-circle diffractometer was used to measure the intensities of 1700 reflections by the θ–2θ scan technique. The structure was refined by least-squares techniques to a conventional R factor of 0.074 (based on F). The molecules crystallize in discrete, tightly bound dimers in which the iron atoms are bridged by MNT sulfurs thus conferring to each iron atom a square-pyramidal coordination. The basal plane of the pyramid contains four sulfur atoms above which (at 0.36 A) the Fe^{3+} ion is found. The four Fe–S distances ($\sigma = 0.01$) to the basal plane are: $Fe\text{–}S_1 = 2.25$ A, $Fe\text{–}S_2 = 2.20$ A, $Fe\text{–}S_3 = 2.28$ A, $Fe\text{–}S_4 = 2.20$ A. The fifth or bridging $Fe\text{–}S_{3'}$ bond length is 2.46 A. The dimeric nature of the anion readily accounts for the observed temperature dependence of the magnetic susceptibility. The *n*-butylammonium ions contain three normal alkyl chains. However, the fourth chain, which is close to that of a neighboring *n*-butylammonium ion, contains disordered terminal $-CH_2\text{–}CH_3$ groups.

Introduction

Since the initial report by Schrauzer and Mayweg[3] and Gray, *et al.*,[4] of the preparation of transition metal derivatives of the *cis*-dithiols, there has been much work directed toward the understanding of the behavior of these interesting substances. The reviews by Gray[4] and Schrauzer[5] summarize much of what is known about them up to this time. A brief discussion of the available structural data has been presented by Sartain and Truter[6] and by Forrester, Zalkin, and Templeton.[7]

Our interest in the $Fe(MNT)_2^-$ ion derives from the reported[8] spin $^3/_2$ for the Fe^{3+} in the triphenylmethylarsonium salt, when measured at room temperature in acetone solution, and the report of Weiher and associates[9] of a χ *vs.* T behavior for the tetraethylammonium salt which strongly suggests antiferromagnetic interactions between ions. We[10] have measured the temperature dependence of the tetra-*n*-butylammonium derivative from 60 to 393°K and also find antiferromagnetic behavior which can be fitted reasonably well to a system with two $S = {}^1/_2$ components.

In view of the disagreement between our measurements[10] and those of Weiher and associates[9] with those of Gray, *et al.*,[8] we decided to investigate the structure of our salt in order to avoid further speculation concerning the interpretation of the magnetic susceptibility data. A Mössbauer spectral study will be reported elsewhere.[11]

Experimental Section

Crystal Data.—The compound was synthesized by a procedure similar to that described by Weiher and associates[9] and recrystallized from ethanol. Well-formed green-black prisms which are easily cleaved into appropriate samples are obtained by evaporation of the solvent. The compound crystallizes in the monoclinic system with cell dimensions $a = 27.53$ A ($\sigma = 0.08$), $b = 14.33$ A ($\sigma = 0.04$), $c = 15.10$ A ($\sigma = 0.04$), $\beta = 95° 5'$ ($\sigma = 5'$), and $V = 5961.8$ A^3. By flotation in $ZnCl_2$, d(measd) = 1.28 g/cc, while d(X-ray) = 1.295 g/cc using $Z = 16$. Systematic extinctions (as observed on Weissenberg and precession films with Mo Kα radiation) are: hkl, for $h + k + l = 2n + 1$; $h0l$, for $h = 2n + 1$. The probable space groups, therefore, are Ia and I2/a. Our successful refinement of the structure using the latter space group indicates that our choice of the centrosymmetric space group was correct. For the origin chosen, the equivalent general positions are $\pm\{(x, y, z), (x, {}^1/_2 - y, {}^1/_2 + z)\} + \{(0, 0, 0), ({}^1/_2, {}^1/_2, {}^1/_2)\}$.

Intensities.—The crystal used to collect intensities had dimensions 0.2 × 0.3 × 0.4 mm and was mounted with the b axis parallel to the ϕ axis of the diffractometer. Mo Kα (λ 0.7107 A) radiation was used to obtain the intensity data which were measured using a θ–2θ scan technique and subtracting the background.

For Mo Kα radiation there are approximately 2400 allowed reflections in a hemisphere of reciprocal space for $0 \leqslant 2\theta \leqslant 30°$. Of these, approximately 1700 were scanned. We rejected 300 reflections as being too weak to give meaningful counting statistics with our crystal, and 400 recorded reflections were symmetry related to others. These latter reflections were compared and averaged. The deviation between equivalent pairs did not exceed 2%.

Absorption corrections were ignored since the crystal was small and nearly cubic and for Mo radiation $\mu = 8.1$, making the neglect of the absorption correction only a minor source of error. (The *maximum* effect on the intensities would be about 8%.)

Calculations were made using a number of BNL programs for

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[1] Research performed in part under the auspices of the United States Atomic Energy Commission.

[2] Presented at the 7th Congress of the International Union of Crystallography, Moscow, July 1966.

[3] G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

[4] (a) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962); (b) H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 240 (1965).

[5] G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 5174 (1966), and references therein.

[6] D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

[7] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500, 1507 (1964).

[8] H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).

[9] J. F. Weiher, L. R. Melby, and R. E. Benson, *ibid.*, **86**, 4329 (1964).

[10] R. Lalancette, N. E. Elliot, and I. Bernal, to be published.

[11] N. E. Erickson, to be published.

the IBM 7094 and CDC 6600 computers. Tabulated values[12] of the atomic scattering factors were used for neutral Fe, S, N, C, and H and for the real and imaginary parts of the anomalous scattering of Fe and S. Anomalous scattering was included correctly in the structure factor calculations.[13]

Determination of the Structure

The initial set of data was corrected for Lorentz and polarization effects and a sharpened, origin-removed Patterson function was calculated using 919 reflections with net intensities greater than 3 counts/sec. Since the number of molecules in the unit cell suggested that all atoms lie in general positions, no assistance could be obtained from arguments of space group symmetry requirements. After several false starts, the positions of the iron and sulfur atoms were derived from the Patterson function.

A three-dimensional electron density calculation, using signs calculated from the contributions of iron and sulfur ($R = 0.56$), indicated fairly clearly the positions of several other atoms of the MNT ligands. A series of Fourier and least-squares refinements led easily to the location of all of the nonhydrogen atoms in the structure with the exception of two carbon atoms at the end of one of the *n*-butyl chains. There is apparently some disorder or an unusually large amplitude of thermal motion in this region of the crystal (see Figure 1). Approximate mean positions for these two atoms were assigned and refined by least squares, but the high thermal parameters obtained indicate that the positions and hence the bond lengths involving these two carbon atoms (C_{6C} and C_{6D}) should not be taken seriously.

The weighting scheme used was based on the agreement between the observed intensities for pairs of equivalent reflections. The data were divided into intensity classes, and the mean value of the quantity

$$\sigma = 2^{-1/2}\left|F_1^2 - F_2^2\right|$$

was plotted as a function of

$$F_\mu^2 = \left\{\frac{F_1^2 + F_2^2}{2}\right\}$$

Based upon this plot, we assigned the following standard deviations to the observed F^2: $0 < F^2 < 225$, data omitted; $225 < F^2 < 500$, $\sigma = 0.069F^2$; $500 < F^2 < 1000$, $\sigma = 0.036F^2$; $1000 < F^2 < 5000$, $\sigma = 0.029F^2$; $5000 < F^2 < 15{,}000$, $\sigma = 0.027F^2$; $15{,}000 < F^2$, $\sigma = 0.020F^2$. The standard deviation of F was approximated by $\sigma(F) = \sigma(F^2)/2F$. At the conclusion of the refinement, the standard deviation of an observation of unit weight was 7.5, thus indicating that the chosen standard deviations were on the average too small by a factor of 7.5, thus suggesting that the model on which the refinement was based was inadequate—probably in description of the thermal parameters—or else that there were unknown sources of systematic error. A final analysis of variance of residuals using the program HANOVA (available on request from W. C. H.) suggested that the relative weights were correct, in that there were no significant correlations between the values of $|\Delta F|/\sigma$ and intensity.

TABLE I

FRACTIONAL COORDINATES OF THE ATOMS[a]

Atom	x	y	z
Fe	2610 (1)	3216 (2)	3251 (2)
S(1)	2541 (3)	4743 (5)	3555 (5)
S(2)	1990 (2)	2914 (4)	4005 (4)
S(3)	2758 (2)	1650 (5)	3299 (4)
S(4)	3377 (3)	3481 (5)	3042 (5)
N(1)	1643 (8)	−3499 (18)	4091 (14)
N(2)	0925 (11)	4080 (16)	4800 (16)
N(3)	3757 (8)	−0073 (19)	3219 (14)
N(4)	4509 (11)	2254 (18)	2710 (17)
N(5)	4107 (7)	−3427 (13)	3250 (12)
C(1A)	1979 (9)	4814 (19)	3954 (15)
C(1B)	1791 (10)	−4239 (23)	4070 (18)
C(2A)	1748 (10)	4005 (17)	4167 (15)
C(2B)	1298 (14)	4054 (17)	4528 (18)
C(3A)	3362 (10)	1574 (19)	3182 (15)
C(3B)	3591 (10)	0682 (23)	3180 (16)
C(4A)	3647 (11)	2357 (17)	3059 (15)
C(4B)	4132 (16)	2296 (20)	2897 (20)
C(6A)	4449 (9)	−2544 (16)	3454 (16)
C(6B)	4577 (10)	−2423 (19)	4458 (18)
C(6C)	4980 (18)	−1436 (34)	4451 (34)
C(6D)	5180 (24)	−1477 (49)	5086 (49)
C(7A)	4342 (9)	−4354 (16)	3673 (15)
C(7B)	4812 (9)	−4596 (17)	3283 (16)
C(7C)	4967 (10)	−5531 (17)	3739 (16)
C(7D)	5419 (11)	−5920 (20)	3354 (18)
C(8A)	0988 (9)	−1554 (16)	2764 (16)
C(8B)	1273 (8)	−0667 (16)	3081 (15)
C(8C)	1299 (9)	−0614 (18)	4110 (17)
C(8D)	1630 (10)	0240 (20)	4427 (18)
C(9A)	3630 (9)	−3337 (15)	3670 (14)
C(9B)	3374 (10)	−2368 (17)	3422 (18)
C(9C)	2878 (10)	−2404 (17)	3866 (17)
C(9D)	2603 (10)	−1447 (19)	3657 (18)

[a] Standard deviations are given in parentheses. The coordinates and their standard deviations have both been multiplied by 10^4.

In the final series of refinements, anisotropic thermal parameters were refined for Fe and S but not for the other atoms. The final parameters are presented in Tables I and II. The structure factors calculated for these parameters and the observed structure amplitudes are presented in Table III. The final R factors calculated using all of the observed reflections were

$$R = \frac{\sum\left||F_c| - |F_o|\right|}{\sum|F_o|} = 0.074$$

$$wR = \left[\frac{\sum w\left||F_c| - |F_o|\right|^2}{\sum w|F_o|^2}\right]^{1/2} = 0.100$$

At the conclusion of the isotropic refinements these values were 0.076 and 0.106.

Extinction appeared to be unimportant.

Description of the Structure

The anions are dimeric, so that the coordination around each iron atom is square pyramidal. The steric arrangement of the atoms in one of the $[Fe_2S_8C_{16}N_8]^{2-}$ dimers is shown in Figure 2. The stacking

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[12] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

[13] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

TABLE II

Mean-Square Anisotropic Thermal Amplitude Tensor Components in 10^{-3} A^2.
Standard Deviations in Parentheses. The Debye–Waller Factor is Given by $\exp[-2\pi^2\sum_{ij} U_{ij}h_ih_ja_i^*a_j^*]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	54.8 (3.4)	59.3 (3.2)	72.9 (3.5)	−2.6 (2.6)	6.1 (2.3)	−5.3 (2.3)
S(1)	61.2 (6.1)	64.2 (5.8)	88.5 (5.9)	−11.7 (4.6)	11.5 (4.8)	−10.6 (4.5)
S(2)	65.0 (6.1)	53.4 (5.6)	71.9 (5.3)	−7.8 (4.6)	8.2 (4.8)	7.9 (4.5)
S(3)	53.2 (6.5)	62.7 (5.7)	62.5 (6.0)	−8.2 (4.2)	8.0 (4.2)	3.2 (4.3)
S(4)	53.2 (6.1)	65.3 (5.7)	94.4 (6.4)	−17.3 (4.2)	8.4 (4.6)	−6.9 (4.4)

Isotropic Temperature Factors for Light Atoms. The Debye–Waller Factor is $\exp[-(B(\sin^2\theta)/\lambda^2]$
Standard Deviations (×10) are given in Parentheses

Atom	B	Atom	B	Atom	B	Atom	B
N(1)	7.9 (7)	C(2B)	6.1 (8)	C(6C)	16.0 (16)	C(8B)	5.1 (6)
N(2)	9.2 (8)	C(3A)	5.2 (6)	C(6D)	24.2 (28)	C(8C)	6.9 (7)
N(3)	8.0 (6)	C(3B)	6.8 (8)	C(7A)	5.3 (6)	C(8D)	9.0 (8)
N(4)	10.2 (9)	C(4A)	5.2 (6)	C(7B)	5.9 (7)	C(9A)	4.5 (6)
N(5)	5.5 (5)	C(4B)	8.7 (9)	C(7C)	6.4 (7)	C(9B)	6.5 (7)
C(1A)	5.4 (6)	C(6A)	5.3 (6)	C(7D)	8.5 (8)	C(9C)	6.8 (7)
C(1B)	7.0 (8)	C(6B)	7.8 (8)	C(8A)	5.4 (6)	C(9D)	7.5 (8)
C(2A)	5.1 (7)						

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS

of the dimers in the unit cell is shown in Figure 3 while the arrangement of the *n*-butylammonium groups is shown in Figure 4. The dimeric units are clearly isolated from each other in the *ab* plane by the bulky cations; columns of the dimers lie approximately along the *c* axis (Figure 5), but the separation between the Fe atoms in adjacent dimers (~6 A) makes it clear that the interaction is of a pairwise nature, as was found by Enemark and Lipscomb[14] for $Co_2S_8C_{16}F_{24}$ dimers. This is in contrast with the $Cu(MNT)_2^-$ studied by Forrester, *et al.*,[7] and the $Ni(MNT)_2^-$ studied by Fritchie[15] which consist of infinite chain stackings of planar molecules.

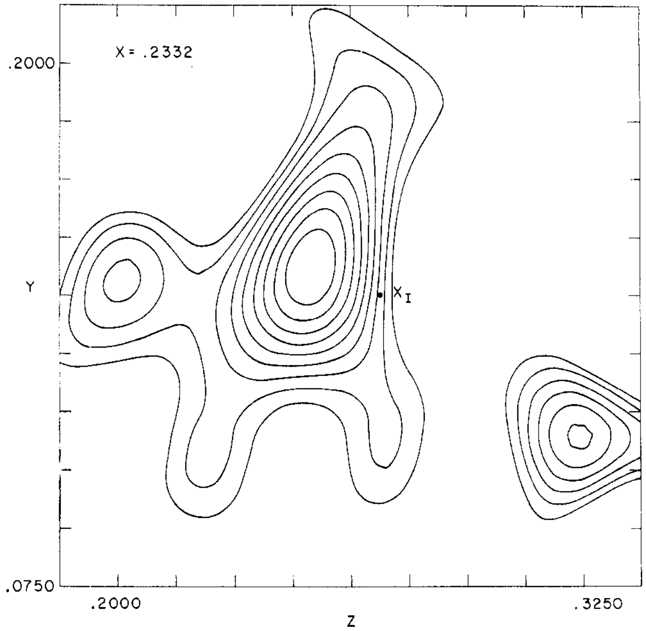

Figure 1.—Difference electron density synthesis in the plane where C_{6D} is expected to lie, assuming a bond length of 1.54 A and a tetrahedral C–C–C angle. The projection of the best position for C_{6C} is indicated by the point X_I. Either a large amplitude of thermal motion or disorder in the position of C_{6D} is indicated. The scale divisions are 0.4 A, and the contour interval is 0.08 e A^{-3}. The maximum peak height is about one-third that expected for a carbon atom.

The $[Fe(MNT)_2]^-$ Ion.—The dimensions of half of the

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

[15] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

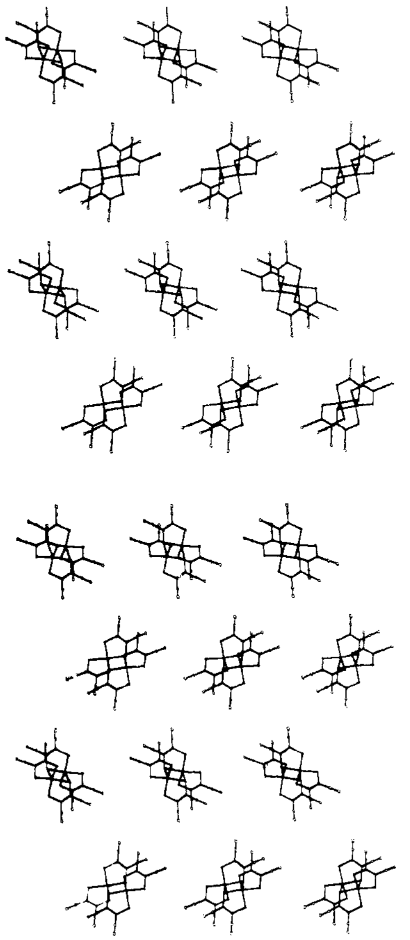

Figure 3.—Arrangement of the dimers in the *ab* plane (stereo pair). The spaces between the dimers are occupied by the tetrabutylammonium ions.

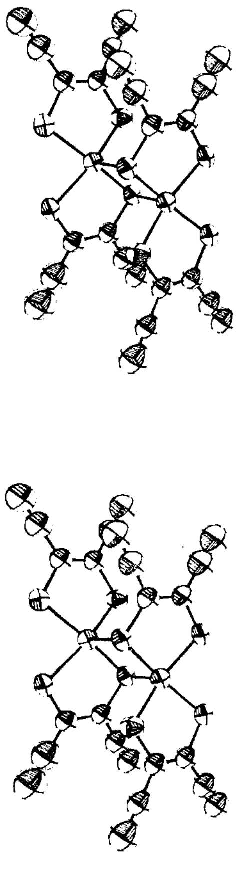

Figure 2.—Structure of the centrosymmetric $[Fe(MNT)_2]_2^{2-}$ ion. The ellipsoids indicate the magnitudes of thermal vibration; only the Fe and S atoms were subjected to an anisotropic refinement. This is a stereo pair and may be conveniently viewed with the aid of a hand-held stereo viewer.

dimeric unit $[Fe_2S_8C_{16}N_8]$ and of the Fe_2S_2 four-membered ring are given in Figure 6 where we show also our numbering system. The estimated standard deviations in the Fe–S distances are $\sigma = 0.007$ A, those in the light-atom bond distances 0.03 A. For the bond angles, $\sigma = 0.3°$ for S–Fe–S and $\sigma = 1.5°$ for angles involving only light atoms.

The Fe–S distances differ significantly. The Fe–S_1 bond between the halves of the dimer is 0.2 A longer than the Fe–S bonds in the dimer but may still be considered a strong bond. In the dimer, the Fe–S_2 and Fe–S_4 bonds, equal in length at 2.20 A, are significantly shorter than Fe–S_1 and Fe–S_3. The Fe–S_3 bond may be expected to be unusual since S_3 is bonded to two iron atoms. That the Fe–S_1 bond is also lengthened may possibly be attributed to the fact that this bond is coplanar with the Fe_2S_2 ring and that there may be some charge shift from this bond which aids in stabilizing the ring.

The ligands are nearly planar. For the ligand that includes S_1 and S_2, no atom is more than 0.05 A from the best least-squares plane through S_1, S_2, C_{1A}, C_{2A}, C_{1B}, C_{2B}, N_1, and N_2. (The standard deviations of the perpendicular distances to the plane are about 0.03 A.) The iron atom however lies 0.4 A out of this plane. In the ligand which includes S_3 and S_4, one of the nitrogen atoms lies 0.09 A out of the best plane, but the iron atom lies within 0.02 A of this plane—which was again fit to the light atoms only. The small distortions from planarity of the ligands and the departure of the $C—C{\equiv}N$ angles from 180° are indicative of the crowding which is associated with dimerization. The iron atom lies 0.36 A above the basal plane of the pyramid defined by the sulfur atoms.

In Table IV a comparison is made of the relevant bond distances with those of several related compounds. Although of a different series, we also list in Table IV the structural data for $Co_2S_8C_{16}F_{24}$ given by Enemark and Lipscomb.[14] This latter compound can, formally, be considered isoelectronic with $[Fe_2S_8C_{16}N_8]^{2-}$ if the perfluoro ligand is assumed to be dinegatively charged.

The Fe–S distances in the $Fe(MNT)_2^-$ dimer are in the same range as those of similar dithiols.[6,7,14–16] The nominally isoelectronic Co(IV) compound shows somewhat shorter M–S bonds (average for Co, 2.15 A; average for Fe, 2.23 A) as one would expect from an increase in the charge of the central metal ion for Co(IV). It is unfortunate that the presence of CF_3 groups in the cobalt compound renders this comparison less valid; however, the isoelectronic pair $Cu(MNT)_2^{2-}$ and $Ni(MNT)_2^-$ studied by Forrester, *et al.*,[7] and Fritchie,[15] respectively, show the same pattern described above.

The Fe–S bond (2.46 A) between the halves of the dimer must be nearly as strong as those within each half of the dimer (2.23 A, average). This strong interaction is probably responsible for the fact that the iron lies 0.36 A above the plane of its four nearest sulfur

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[16] R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964).

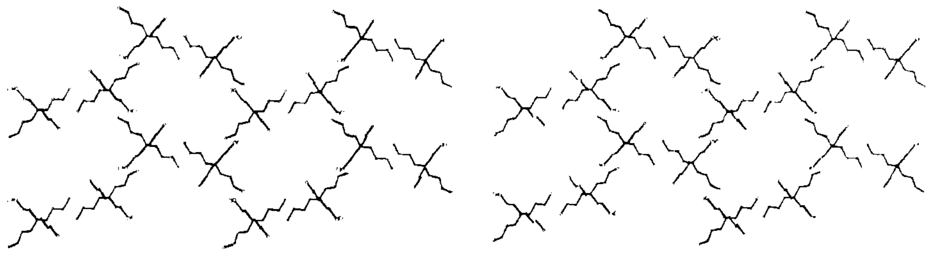

Figure 4.—Arrangement of the tetrabutylammonium ions in the *ab* plane (stereo pair). This is the same region of the structure shown in Figure 3.

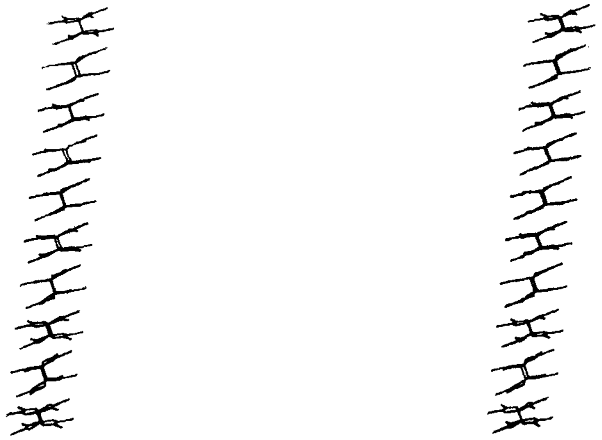

Figure 5.—Stacking of the dimeric ions in columns approximately parallel to *c* (stereo pair).

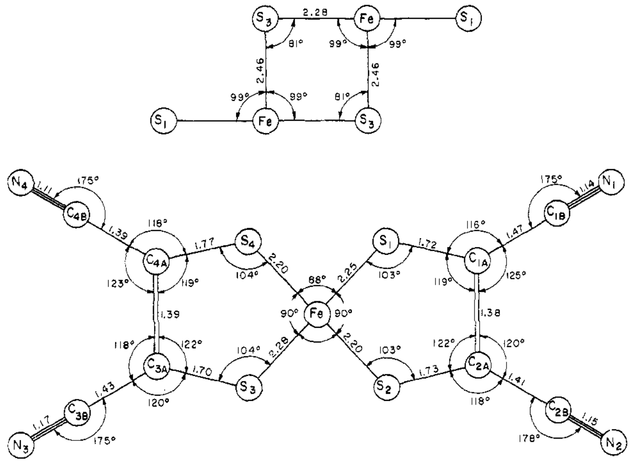

Figure 6.—Bond distances and angles in half of the [Fe-$(MNT)_2]_2^{2-}$ ion. S_3 is the sulfur atom which is bonded to the iron in the other half of the dimer. Also shown are the dimensions of the Fe–S–Fe–S ring. Standard deviations in the bond distances are 0.007 A for Fe–S and 0.03 A for other distances. For the angles, σ = 0.3° for Fe–S–S and about 1.5° for the others.

ligands. The coordination around the iron is clearly that of a tetragonal pyramid. The Co atom in $Co_2S_8C_{16}F_{24}$ has a virtually identical environment.

Comparison of the S–C distances between isoelectronic pairs again shows the same trends. The complex containing the metal with the larger formal charge shows shorter C–S bonds, as would be expected from extensive delocalization of the electron density from the

TABLE IV

	Metal ion					
	Fe^{3+}	Co^{4+}	Co^{2+}	Ni^{3+}	Ni^{2+}	Cu^{3+}
Total no. of electrons	23	23	25	25	26	26
No. of d electrons	5	5	7	7	8	8
Ligand	MNT	PDT[a]	MNT	MNT	MNT	MNT
M—S_1	2.20	2.14	2.16	2.15	2.16	2.17
M—S_2	2.20	2.14	2.16	2.15	2.16	2.17
M—S_3	2.25	2.16	2.16	2.15	2.16	2.18
M—S_4	2.28	2.18	2.16	2.15	2.16	2.16
M—S_5	2.46	2.38	...	3.59	...	4.43 4.03
S—C	1.73	1.694	1.723	1.714	1.750	1.72
C=C	1.39	1.393	1.34	1.356	1.30	1.32
C—C	1.43	1.506	1.40	1.430	1.43	1.45
C≡N	1.14	...	1.15	1.14	1.13	1.145
h[b]	0.36	0.37	Planar	Planar	Planar	Planar
Ref	This work	14	7	15	16	7

[a] PDT = perfluorodithiethene. [b] h = height of the metal above the plane of the four sulfur atoms.

ethylene bridge toward the metal as the central charge increases. At the same time, the ethylenic C–C bond length increases, as has already been noted in other cases by Sartain and Truter.[6]

The Tetra-*n*-butylammonium Ion.—The ion is shown in Figure 7. The coordination about the central nitrogen is normal, the average C–N–C angle being 109.7° while the average C–N bond length is 1.56 A (σ_μ = 0.02 A). This value is not significantly different from the average value of 1.525 A found by Forrester, *et al.*,[7] for the same ion in a closely related system. Both values are much larger than the commonly accepted C–N single bond length of 1.48 A. For example, McCullough[17] finds an average C–N bond length of 1.470 A (σ = 0.014 A) in tetramethylammonium perchlorate and Caron and Donohue[18] given 1.48 A (σ = 0.011 A) for the C–N bond length in $(CH_3)_3NO \cdot HCl$.

Three of the *n*-butyl chains are well resolved and show the usual zigzag pattern typical of unsaturated hydrocarbon chains. The fourth chain, which points toward a similar chain of another tetra-*n*-butylammonium ion, shows some apparent disorder of the last two carbon atoms. A section through this portion of the *n*-butyl chain is shown in Figure 1, which illustrates why our attempts to locate these two carbon atoms precisely were fruitless. Although they were included in the least-squares refinement at the most likely positions, they did not converge to reasonable positions. Similar

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(17) J. D. McCullough, *Acta Cryst.*, **17**, 1067 (1964).
(18) A. Caron and J. Donohue, *ibid.*, **15**, 1052 (1962).

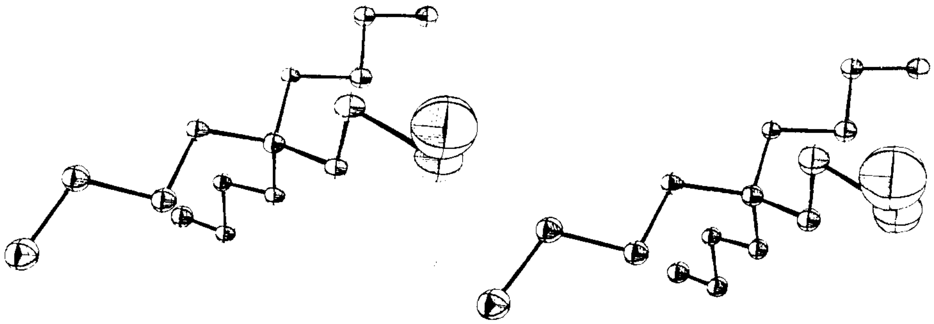

Figure 7.—The tetra-*n*-butylammonium cation. The large amplitudes of motion indicated for two of the carbon atoms are perhaps indicative of disorder in the end of this chain (stereo view).

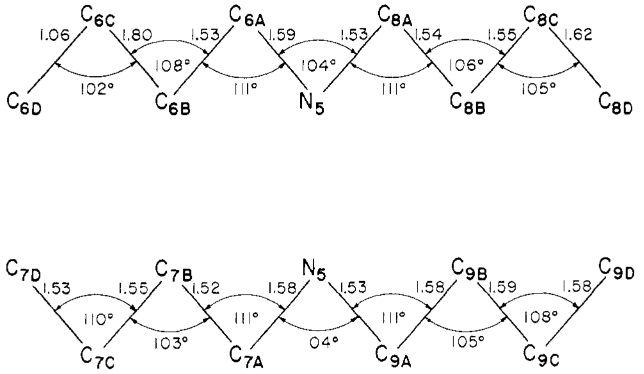

Figure 8.—Bond distances and angles in the two planar chains of the tetra-*n*-butylammonium ion. Standard deviations are 0.03 A for the distances and 1.5° for the angles. The values involving C_{6C} and C_{6D} are not to be taken seriously because of the disorder in this end of the chain (see text).

difficulties with the terminal CH_3 of a tetra-*n*-butylammonium cation were found by Forrester, *et al.*,[7] in the $Cu(MNT)_2^-$ complex. The mean C–C bond length, excluding the terminal carbon atoms C_{6C} and C_{6D}, is 1.56 A (σ_μ = 0.02 A). The individual values of the bond lengths (σ = 0.03) and angles (σ = 1.5°) are given in Figure 8.

Conclusions

We have studied the crystal and molecular structures of $(n\text{-}C_4H_9)_4NFe(MNT)_2$ which we find to be composed of discrete, tightly bound dimers in which the Fe is surrounded by five sulfur atoms in a square-pyramidal arrangement. The unpaired electrons of the Fe(III) ions interact, probably *via* the sulfur bridges. to produce an antiferromagnetically coupled system, The tetra-*n*-butylammonium cations contain three normal *n*-butyl chains while the fourth one has a $-CH_2-CH_3$ group which is probably disordered owing to interactions with a similar group from an adjacent tetra-*n*-butylammonium cation.

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