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The Crystal and Molecular Structure of Tetra-*n*-butylammoniumcopper(III) Bis(maleonitrile dithiolate) and the Geometry of the Monovalent Copper(III) Bis(maleonitrile dithiolate) Ion[1]

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The crystal and molecular structure of tetra-n-butylammoniumcopper(III) bis(maleonitrile dithiolate) has been determined from an X-ray diffraction study of a single crystal specimen. The monoclinic unit cell, space group I2/c, with $a = 15.59 \pm 0.02$, $b = 13.83 \pm 0.01$, $c = 27.94 \pm 0.03$ Å., and $\beta = 93.86 \pm 0.03°$, contains eight formula units. Atomic parameters were refined by least-squares methods using three-dimensional data out to $\sin \theta/\lambda = 0.482$. The anion is closely planar with the sulfur atoms in a square arrangement around the copper atom. The symmetry of the anion is mmm to a very close degree. In contrast with the cobalt complex examined previously, the copper atoms are not well separated in the structure and the shortest copper–copper distances are 4.026 and 4.431 Å. All four of the n-butyl chains in the cation have the *trans* conformation. Positions of all 36 independent hydrogen atoms were determined from an electron density difference function.

Introduction

In a previous paper[2] we reported our work on the structure of $((n\text{-}C_4H_9)_4N)_2 \cdot Co(S_2C_4N_2)_2$, a member of a series of compounds of general formula $R'_z(M'S_4C_4R_4)^{-z}$ where $z = 0, 1, 2$; M′ = Co, Ni, Cu, Pd, Pt, Zn, Rh; R = CN, CF_3, C_6H_5, etc., and $R' = (n\text{-}C_4H_9)_4N^+$, $(CH_3)_4N^+$, etc. We report in this paper a structure determination of another member of the series, *viz.*, $(n\text{-}C_4H_9)_4N^+Cu(S_2C_4N_2)_2^-$. We were encouraged to examine this material because it was being used as a host crystal for paramagnetic resonance experiments. Maki, *et al.*,[3] have already used the results of this crystallographic study to identify the principal axes of the g-value tensor and the hyperfine tensor with the symmetry directions of the anion and to explain some other features of the resonance results.

Experimental

X-Ray Diffraction.—Dr. N. Edelstein of Harvard University kindly supplied us with some well-formed, needle-like, dark red crystals of the complex $(n\text{-}C_4H_9)_4N^+Cu(S_2C_4N_2)_2^-$. The melting point, analysis, and preparation of these crystals are described in a paper by Davison, *et al.*[4]

X-Ray photographs obtained by the Weissenberg technique and copper radiation established the diffraction symmetry of the crystal. A single crystal, in the form of a long thin plate of approximate dimensions 0.27 × 0.11 × 0.07 mm. and mounted about a b^* axis, was used for collecting the intensity data. Intensities were measured with a General Electric XRD-5 goniostat equipped with a scintillation counter and a pulse height discriminator. Mo Kα radiation was used and the unit cell dimensions are based on $\lambda = 0.70926$ Å. for Mo Kα_1.

The space group permits 2803 independent reflections in the sphere with $\sin \theta/\lambda$ less than 0.482 ($2\theta < 40°$), and, of these, 1834 were measured with counting times of 10 sec. each. All reflections in the sphere were recorded up to $2\theta = 30°$. Above 30°, it was found that most of the intensities were quite weak and only the reflections that gave some ease and economy in setup were measured. Of the 1834 measured reflections, 396 were assigned zero intensity and the maximum count was 4100 counts/sec. for the 002 reflection.

No corrections were made for either absorption or extinction. With $\mu = 10.5$ cm.$^{-1}$ for Mo radiation, μR is 0.14 or less, making absorption effects rather small.

Calculations were made with an IBM 7094 computer using a full matrix least-squares refinement program written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, with minor modifications, and Fourier and distance programs written by Zalkin (all unpublished). We minimized the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2$, where F_o and F_c are the observed and calculated structure factors, respectively, and w is the weighting factor.

Atomic scattering factors were taken as the values given by Ibers[5] for neutral Cu, S, N, C, and H. Dispersion corrections[6] of 0.3 and 0.1 electron were added to the Cu and S scattering factors, respectively. The imaginary part of the dispersion correction was ignored.

Results

Unit Cell and Space Group.—A body centered unit cell contains eight formula units $(n\text{-}C_4H_9)_4NCu(S_2C_4N_2)_2$ and is monoclinic with dimensions: $a = 15.59 \pm 0.02$, $b = 13.83 \pm 0.01$, $c = 27.94 \pm 0.03$ Å., $\beta = 93.86 \pm 0.03°$, $V = 6010.5$ Å.^{3}.

Reflections are absent unless $h + k + l = 2n$ and $h0l$ reflections are absent unless $l = 2n$. This is consistent with either the centric space group I2/c (C_{2h}^6) or the noncentric space group Ic (C_s^4). The success of our structure determination confirms our choice of the former.

With eight formula units of $(n\text{-}C_4H_9)_4NCu(S_2C_4N_2)_2$ in the unit cell, the density calculated from the X-ray data is 1.30 g./cc. This compares with the value of 1.30 g./cc. found by a flotation method using a mixture of benzene and carbon tetrachloride.

Determination of the Structure.—When all the data had been collected, the observed intensities were corrected for Lorentz and polarization effects, and a three-dimensional Patterson function was calculated using

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

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

[3] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

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

[5] J. A. Ibers in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 202.

[6] D. H. Templeton, *ibid.*, p. 215.

TABLE I

FINAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS, TOGETHER WITH THEIR STANDARD DEVIATIONS, FOR ALL ATOMS EXCEPT HYDROGEN

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B[c]	$\sigma(B)$[c]
Cu	0.1366	0.0001	0.1851	0.0001	0.2326	0.0001	[a]	...
S(1)	0.1412	0.0003	0.3401	0.0003	0.2201	0.0001	[a]	...
S(2)	0.1366	0.0003	0.0302	0.0003	0.2451	0.0001	[a]	...
S(3)	0.0916	0.0003	0.2160	0.0003	0.3031	0.0001	[a]	...
S(4)	0.1780	0.0003	0.1534	0.0003	0.1621	0.0001	[a]	...
N(1)	0.2477	0.0009	0.2738	0.0010	0.0545	0.0006	8.8	0.4
N(2)	0.1830	0.0009	0.5132	0.0011	0.1239	0.0005	8.5	0.4
N(3)	0.0375	0.0009	0.0986	0.0010	0.4136	0.0005	8.2	0.4
N(4)	0.0979	0.0008	0.8519	0.0010	0.3385	0.0005	7.3	0.3
N(5)	0.3307	0.0006	0.3446	0.0007	0.9111	0.0003	3.8	0.2
C(1)	0.1719	0.0008	0.3466	0.0010	0.1618	0.0005	4.3	0.3
C(2)	0.1903	0.0008	0.2659	0.0010	0.1392	0.0005	4.7	0.3
C(3)	0.2217	0.0010	0.2701	0.0012	0.0928	0.0007	7.3	0.4
C(4)	0.1799	0.0010	0.4402	0.0013	0.1412	0.0006	6.4	0.4
C(5)	0.1043	0.0008	0.0247	0.0010	0.3035	0.0005	4.2	0.3
C(6)	0.0864	0.0008	0.1029	0.0010	0.3274	0.0005	4.2	0.3
C(7)	0.0584	0.0010	0.0973	0.0012	0.3752	0.0007	6.9	0.4
C(8)	0.1011	0.0010	0.9287	0.0012	0.3235	0.0005	6.1	0.4
C(9)	0.3670	0.0008	0.4373	0.0009	0.9327	0.0004	4.0	0.3
C(10)	0.3306	0.0009	0.4681	0.0010	0.9789	0.0005	5.5	0.4
C(11)	0.3730	0.0009	0.5634	0.0011	0.9966	0.0005	5.7	0.4
C(12)	0.3343	0.0010	0.6019	0.0012	0.0392	0.0006	7.6	0.4
C(13)	0.3531	0.0009	0.2592	0.0010	0.9436	0.0005	5.0	0.3
C(14)	0.4456	0.0010	0.2435	0.0012	0.9582	0.0006	7.1	0.4
C(15)	0.4466	0.0013	0.1561	0.0013	0.9935	0.0007	9.0	0.5
C(16)	0.5316	0.0020	0.1486	0.0021	0.0195	0.0010	17.4	1.0
C(17)	0.3748	0.0008	0.3331	0.0009	0.8637	0.0005	4.5	0.3
C(18)	0.3412	0.0011	0.2454	0.0013	0.8349	0.0006	7.9	0.4
C(19)	0.3944	0.0010	0.2409	0.0012	0.7873	0.0006	7.6	0.4
C(20)	0.3717	0.0012	0.1512	0.0013	0.7598	0.0006	8.9	0.5
C(21)	0.2335	0.0008	0.3475	0.0009	0.9031	0.0004	4.4	0.3
C(22)	0.1982	0.0009	0.4306	0.0010	0.8725	0.0005	5.3	0.3
C(23)	0.1004	0.0011	0.4318	0.0012	0.8731	0.0006	7.2	0.4
C(24)	0.0611	0.0011[b]	0.5162	0.0012[b]	0.8431	0.0006[b]	10.7	0.4[b]

[a] Treated anisotropically—see Table III. [b] Not actually calculated, but estimated from similar atoms. [c] In Å.^{2}.

the 1143 terms whose intensities were measured as 2 counts/sec. or more. With eight molecules in the unit cell, it was probable that all atoms would be in general positions, so that little assistance was obtained from the symmetry of the space group and the use of special positions in locating the positions of the copper atoms. However, plausible positions for the copper atom and the four independent sulfur atoms, all in general positions, 8(f) $(0, 0, 0;\ {}^1/_2, {}^1/_2, {}^1/_2) \pm (x, y, z;\ x, \bar{y}, {}^1/_2 + z)$, were found from the Patterson function by inspection of the highest peaks around the origin and using our knowledge of the geometry of the anion as found in the cobalt compound.

A three-dimensional electron density Fourier was calculated with phases based on the copper and the four sulfur atoms. This function readily revealed the locations of the other 29 heavier atoms, all in general 8(f) positions.

A least-squares refinement with all 34 of these atoms, each having an isotropic temperature factor of the form $\exp(-B\lambda^{-2}\sin^2\theta)$, and using the 1143 terms, each with unit weight, resulted in a conventional unreliability factor $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$ of 0.11 after three cycles of refinement. The end two carbon atoms of one of the butyl chains (C(15) and C(16)) were found to be merging, so an electron density map of the immediate vicinity of these two atoms was calculated using the results of this least-squares refinement. It was then evident that C(16) had been wrongly located. Three further cycles of least-squares refinement using the correct location for C(16) resulted in a drop of R to 0.092 for all the heavy atoms.

The copper and the sulfur atoms were given anisotropic temperature factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$, with $4\beta_{ij} = a_i^*a_j^*B_{ij}$, a_i^* being the length of the ith reciprocal axis. Three cycles of refinement including these anisotropic temperature factors resulted in a value of R of 0.079.

An electron density difference function with all the atoms except hydrogen subtracted out was calculated using the results of this last refinement and using all 1143 terms. Possible locations for 28 hydrogen atoms were found in this difference function and all these positions were used in three cycles of least-squares refinement. At this stage we had 62 atoms in the calculation and this resulted in a total of parameters greater than the capacity of our program and computer. Therefore, in this calculation, we refined only the positions of the 28 hydrogen atoms (each with an isotropic temperature factor) and held the parameters of the other 34 atoms fixed. Of the hydrogen atom positions, 22 appeared

TABLE II

FINAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS

Atom	x	y	z	B, Å.^{2}	Atom	x	y	z	B, Å.^{2}
H(1) C(9)	0.37	0.49	0.91	2.3	H(1) C(17)	0.44	0.32	0.88	0.5
H(2)	0.43	0.43	0.95	9.2	H(2)	0.35	0.38	0.85	2.3
H(1) C(10)	0.32	0.42	0.00	4.7	H(1) C(18)	0.38^a	0.25	0.82	5.8
H(2)	0.29	0.48	0.97	7.8	H(2)	0.34^a	0.20	0.85	1.6
H(1) C(11)	0.43	0.54	0.01	4.2	H(1) C(19)	0.38^a	0.29^a	0.77^a	5.5
H(2)	0.38	0.61	0.97	10.2	H(2)	0.47	0.24	0.80	4.9
H(1) C(12)	0.36	0.65	0.04	4.6	H(1) C(20)	0.32^a	0.18	0.74	9.6
H(2)	0.27	0.58	0.03	6.9	H(2)	0.40^a	0.10^a	0.77	12.1
H(3)	0.34	0.56	0.07	8.9	H(3)	0.31^a	0.11	0.76	19.1
H(1) C(13)	0.33	0.20	0.92	5.5	H(1) C(21)	0.22	0.29	0.88	2.7
H(2)	0.32	0.27	0.97	1.5	H(2)	0.21	0.35	0.93	−2.0
H(1) C(14)	0.48^a	0.24^a	0.93^a	8.0^a	H(1) C(22)	0.21	0.49	0.89	1.3
H(2)	0.45	0.28	0.97	6.3	H(2)	0.22	0.43	0.84	4.8
H(1) C(15)	0.43	0.15	0.03	−4.3	H(1) C(23)	0.08	0.38	0.86	3.1
H(2)	0.45	0.12	0.97	5.9	H(2)	0.10	0.46	0.90	5.9
H(1) C(16)	0.49^a	0.10^a	0.04^a	5.0^a	H(1) C(24)	0.08	0.57	0.86	4.6
H(2)	0.54^a	0.11^a	0.99^a	5.0^a	H(2)	0.00^a	0.53	0.87	10.7
H(3)	0.57^a	0.19^a	0.03^a	5.0^a	H(3)	0.05^a	0.49	0.81	8.6

[a] Parameters chosen from a difference function and used in the least-squares refinement, but not refined.

TABLE III

FINAL ANISOTROPIC THERMAL PARAMETERS, TOGETHER WITH THEIR STANDARD DEVIATIONS, FOR THE COPPER AND THE FOUR SULFUR ATOMS

Atom	B_{11}	$\sigma(B_{11})$	B_{22}	$\sigma(B_{22})$	B_{33}	$\sigma(B_{33})$	B_{12}	$\sigma(B_{12})$	B_{13}	$\sigma(B_{13})$	B_{23}	$\sigma(B_{23})^a$
Cu	4.7	0.1	4.0	0.1	4.4	0.1	−0.1	0.1	0.2	0.1	−0.2	0.1
S(1)	7.9	0.3	4.0	0.2	4.5	0.2	0.3	0.2	1.9	0.2	−0.2	0.2
S(2)	8.6	0.3	3.8	0.2	5.6	0.2	0.0	0.2	1.5	0.2	0.1	0.2
S(3)	6.3	0.2	4.3	0.2	4.9	0.2	0.5	0.2	0.9	0.2	0.3	0.2
S(4)	10.7	0.3	3.9	0.2	4.9	0.2	−0.2	0.2	2.3	0.2	−0.7	0.2

[a] All in Å.^{2}.

satisfactory, with the remaining 6 either unsuitably located or with very high temperature factors.

Several errors in the data, due to mis-setting of the goniostat or mispunching of a data card, were corrected and all the measured data included in the calculation. As there were so many weak intensities, a considerable number of them were recounted but little variation from previous measurements was found. Terms with intensity less than 2 counts/sec. were given $^1/_4$ weight and all the rest given unit weight, making 1834 terms in all.

Three cycles of least squares were calculated using these new data and only the 34 heavy atoms, with the copper and the four sulfur atoms having anisotropic temperature factors, and these gave a value of R of 0.12. Another electron density difference function was calculated using the results of this latest refinement and including only the terms for which $\sin \theta/\lambda < 0.36$. In addition to the previous 22 hydrogen atom locations, 11 new sites were found with only the three around C(16) missing.

The 33 hydrogen atoms were included in two cycles of least-squares refinement where only the heavy atoms were refined, followed by two cycles where the heavy atoms were held fixed and the hydrogen atom positions were refined. R fell to 0.106 after these four cycles of refinement and all but 9 of the 33 hydrogen atoms were satisfactorily located. A card punching error resulted in the incorrect location of one of the nine and this was corrected in the next refinement. The remaining eight were rather imprecisely located in extended areas of electron density in the difference function and the least-squares refinement had moved them, through admittedly small distances, to unsuitable locations.

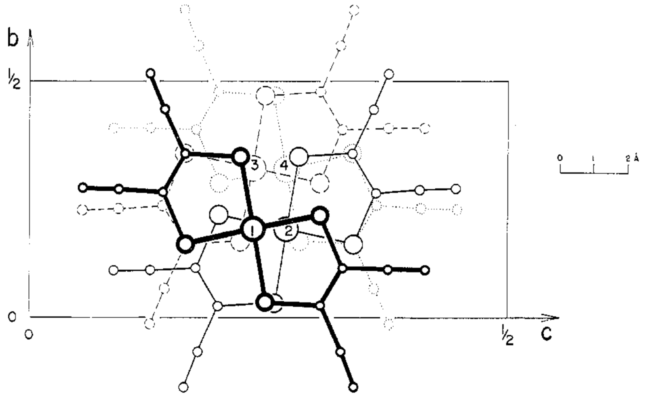

Fig. 1.—A projection down the a axis showing the stacking of the $Cu(MNT)_2^-$ anions as viewed down a stack. The copper atoms labeled 1, 2, 3, and 4 have x coordinates of 1.14, 0.86, 0.64, and 0.36, respectively.

Yet another difference function, calculated after two further cycles of refinement of the heavy atoms only, showed no better locations for the eight doubtful hydrogen atoms, but did show possible locations for the three hydrogen atoms around C(16). These last eleven hydrogen atoms were included in subsequent least-squares calculations with an average temperature factor, but were never allowed to refine. Two cycles with all 70 atoms included, but only the 34 heavy atoms allowed to refine, resulted in $R = 0.104$.

As in the cobalt crystal[2] the dispersion corrections to

Table IV

Observed Structure Factor Magnitudes (FOBS) and Calculated Structure Factors (FCAL)

```
 H,K= 0, 0
  L FOB FCA
  2 418-379
  4 119 113
  6   0  13
  8 172 174
 10 203-198
 12 111 105
 14  25  14
 16  43 -42
 18  29  31
 20  22 -21
 22  30  32
 24   0   6
 26  18  21

 H,K= 0, 1
  L FOB FCA
  1 363-326
  3 380 368
  5  66 -48
  7  63  60
  9   0  -5
 11  22  27
 13   0   0
 15  45 -53
 17  40  46
 19  36 -40
 21  22  20
 23  24 -28
 25  56  54

 H,K= 0, 2
  L FOB FCA
  0 281-261
  2 167 159
  4 151-133
  6  76  77
  8 190 179
 10  15   5
 12  59  55
 14  59 -60
 16 121 121
 18  68 -70
 20   0   5
 22  53 -56
 24  44  45
 26  33 -40

 H,K= 0, 3
  L FOB FCA
  1  44  36
  3  47  52
  5  47  39
  7  25 -33
  9  31 -33
 11  85  76
 13  54 -46
 15   0  -8
 17  41  45
 19   0  -8
 21  23 -21
 23  42  37
 25  36 -40

 H,K= 0, 4
  L FOB FCA
  0   0  -8
  2  23 -29
  4  71  69
  6  80 -70
  8  55 -46
 10   0   4
 12 117-109
 14  30 -25
 16 120 121
 18  86 -88
 20  75  72
 22  20 -25
 24  18 -19

 H,K= 0, 5
  L FOB FCA
  1  96  95
  3  48 -51
  5  16  24
  7 141 133
  9  35  41
 11   0  -7
 13  43 -44
 15  46  51
 17 138-135
 19 166 158
 21  38 -47
 23   0 -16

 H,K= 0, 6
  L FOB FCA
  0 177 168
  2 263-260
  4 150 146
  6  93 -90
  8 158 148
 10  53 -51
 12 107 105
 14  11   3
 16 103-105
 18  48  51
 20  24 -29
 22   0   3

 H,K= 0, 7
  L FOB FCA
  1 223-223
  3 289 279
  5 194-184
  7  38  47
  9 112-113
 11  86  87
 13   0 -10
 15   0   4
 17  56  62
 19  24 -21
 21   0  -1

 H,K= 0, 8
  L FOB FCA
  0  85 -85
  2  98 110
  4  99-103
  6  81  83
  8 108-103
 10   0  18
 12  27 -10
 14  34 -34
 16  23 -17
 18   0 -12
 20  36  40

 H,K= 0, 9
  L FOB FCA
  1  20  25
  3   0  -8
  5  78  75
  7  15 -33
  9  22 -14
 11  39  36
 13   0 -10
 15   0  21
 17   0 -16
 19   0  16

 H,K= 0,10
  L FOB FCA
  0  97 -90
  2  12 -21
  4  27  40
  6  50 -43
  8   0   9
 10  23  31
 12  48 -42
 14  30 -24
 16  40  41

 H,K= 0,11
  L FOB FCA
  1  52 -54
  3   0   9
  5  52 -51
  7  24  37
  9   0  22
 11   0   7
 13   0 -15
 15  58  59

 H,K= 0,12
  L FOB FCA
  0  54  55
  2   0  -2
  4  17 -29
  6   0   5
  8   0  10
 10   0 -20

 H,K= 0,13
  L FOB FCA
  1  31 -41
  3  51  41
  5  37 -39

 H,K= 1, 1
  L FOB FCA
-20   0  -4
-18   0  21
-16  19   9
-14  31  34
-10   0   1
 -8  83 -91
 -6 120-119
 -4 202 187
 -2  59 -50
  0 256 235
  2 122-107
  4   0   0
  6  24 -24
  8  30 -34
 10  43 -38
 12 160 156
 14 159-156
 16  69  70
 18  65 -70
 20  15  31

 H,K= 1, 2
  L FOB FCA
-19   0  13
-17  53 -53
-15  75  74
-13  17 -29
-11   0  16
 -9  82  78
 -7 199-190
 -5 149-148
 -3 206-203
 -1 280 272
  1  48 -39
  3  57  54
  5 239-230
  7  98  97
  9  39  37
 11  76  72
 13 149-142
 15 183 182
 17 137-130
 19  21  17

 H,K= 1, 3
  L FOB FCA
-18  42 -40
-16  90  87
-14  64 -69
-12  46  48
-10  56  64
 -8  71  71
 -6  90  93
 -4 236 235
 -2  65  65
  0  91 -87
  2 195 193
  4 210 203
  6 139-134
  8  26 -24
 10  63  65
 12  52 -56
 14  81  80
 16  34 -42
 18  21  25

 H,K= 1, 4
  L FOB FCA
-17  81  83
-15  71 -69
-13  89  88
-11  52 -56
 -9  16  25
 -7   0  -8
 -5  48 -51
 -3  58  53
 -1  76 -69
  1  50  43
  3 199-192
  5  99 102
  7 104 104
  9   0 -10
 11 139-134
 13 111 105
 15  74 -73
 17  63  62

 H,K= 1, 5
  L FOB FCA
-16  69 -66
-14 124 119
-12  94 -91
-10  64  55
 -8  41  36
 -6  23 -27
 -4 155 150
 -2 195-184
  0  67  74
  2 151-148
  4 176 166
  6 140-132
  8  74  74
 10  86 -84
 12  54  56
 14 138-138
 16 121 124

 H,K= 1, 6
  L FOB FCA
-15  52  51
-13  90 -97
-11  64  67
 -9  84 -98
 -7   0   7
 -5  89  87
 -3 159-162
 -1 217 212
  1  75 -75
  3 164 156
  5  89 -97
  7 108  99
  9 103-104
 11   0  13
 13  86 -83
 15  95  98

 H,K= 1, 7
  L FOB FCA
-14   0 -12
-12  72  80
-10 158-159
 -8  77  76
 -6   0 -10
 -4 106-105
 -2 100 106
  0 105 -99
  2  40 -37
  4 112-109
  6  26  31
  8  19 -20
 10  20  33
 12  36 -35
 14  22 -25

 H,K= 1, 8
  L FOB FCA
-11  64 -72
 -9 122 123
 -7  92 -90
 -5  28  27
 -3  19  27
 -1  64 -63
  1  27  27
  3  82  89
  5  48 -54
  7   0  -3
  9   0  -6
 11  64  71

 H,K= 1, 9
  L FOB FCA
 -8  26 -40
 -6   0  21
 -4   0   3
 -2  96-105
  0   0   8
  2  80  81
  4   0   3
  6   0  12
  8  43 -41

 H,K= 1,10
  L FOB FCA
 -3  22 -18
 -1  58  50
  1  15 -14
  3   0  10
  5  59  56
  7  68 -56

 H,K= 1,11
  L FOB FCA
  0  33  26
  2  33 -35
  6  62 -60

 H,K= 1,12
  L FOB FCA
  1  90 -83
  5  43 -45
  7 106 107

 H,K= 1,13
  L FOB FCA
  0  44 -44
  2  36  36

 H,K= 2, 0
  L FOB FCA
-26  18  19
-24  17  14
-22  23  20
-20  18  -9
-18  42  47
-16  79 -89
-14 325 319
-12 427-417
-10 424 411
 -8 224-218
 -6 313 324
 -4 149 153
 -2 241 230
  0 198-176
  2 160-158
  4 135 126
  6  62 -62
  8  84  79
 10 163-159
 12 314 308
 14 300-298
 16 177 183
 18 125-123
 20  22  27
 22  40 -36
 24   0  -3
 26   0  12

 H,K= 2, 1
  L FOB FCA
-19   0  -6
-17  56 -52
-15 195 193
-13 197-209
-11 284 285
 -9 230-217
 -7  68 -74
 -5  76 -74
 -3 152 138
 -1   0 -18
  1 106 104
  3  76  64
  5  89 -88
  7  23  18
  9  38 -44
 11 106 104
 13 249-245
 15 223 217
 17 151-154
 19  64  59

 H,K= 2, 2
  L FOB FCA
-20   0  10
-18  33  24
-16  62  65
-14 105-103
-12 247 236
-10 129-131
 -8   0 -17
 -6 120-123
 -4   0   3
 -2 270-266
  0  80  77
  2 199 204
  4 233-225
  6  23  25
  8  83 -76
 10  39  40
 12  83 -78
 14 120 125
 16 133-142
 18  47  52
 20  22 -17
 24  25  24

 H,K= 2, 3
  L FOB FCA
-19  53 -54
-17   0  12
-15  33 -39
-13  72  63
-11   0   9
 -9  91  85
 -7  77 -74
 -5  65 -64
 -3 261 257
 -1  55 -49
  1 182-192
  3 103 -99
  5 225-221
  7   0   3
  9  28  36
 11  24 -31
 13  82  81
 15  39 -45
 17  29  25
 19  44 -42

 H,K= 2, 4
  L FOB FCA
-22  24 -16
-18  30  45
-16  76 -80
-14  27 -26
-12   0   5
-10  17  28
 -8   0   9
 -6  15 -21
 -4 181 165
 -2  54 -71
  0  34 -35
  2 139-135
  4 136-134
  6  78  69
  8 153-153
 10  17 -12
 12   0   9
 14   0  13
 16   0  -6
 18  22 -18
 22   0  -3

 H,K= 2, 5
  L FOB FCA
-17  22  -9
-15  65 -70
-13  73  65
-11  89 -94
 -9  18 -26
 -7  87 -87
 -5 112 106
 -3 230-224
 -1 143 125
  1  31  33
  3  49 -54
  5 306 293
  7 221-215
  9  81 -76
 11  46 -45
 13  48  53
 15  86 -89
 17  22  32

 H,K= 2, 6
  L FOB FCA
-20  24 -25
-16  41 -47
-14 136 150
-12 122-124
-10 114 123
 -8 100 -95
 -6  70  85
 -4 113-121
 -2 194 199
  0  78 -85
  2  79 -73
  4 165 153
  6   0  -7
  8 116 117
 10 138-144
 12  57  55
 14  92 -98
 16 116 113
 20  54  47

 H,K= 2, 7
  L FOB FCA
-13 145-147
-11 149 153
 -9  90 -97
 -7 114 125
 -5 117-114
 -3 151 154
 -1  72 -71
  1   0   8
  3  58  62
  5 136-130
  7 114 109
  9  66 -67
 11  71  76
 13 117-115
 15 122 117

 H,K= 2, 8
  L FOB FCA
-18  46 -53
-14  68 -78
-12  84  86
-10  82 -85
 -8  96  95
 -6  63 -70
 -4  52  56
 -2   0 -14
  0   0  13
  2   0 -15
  4   0  -8
  6  57  58
  8  58 -63
 10  56  62
 12  93 -91
 14  99  89
 18  49  50

 H,K= 2, 9
  L FOB FCA
 -9  58  58
 -7  61 -67
 -5  42  50
 -3  29  25
 -1   0  -3
  1  44  49
  3  26  27
  5   0   5
  7  30 -22
  9  66  70
 11  75 -66
 13   0  14
 15  34 -28

 H,K= 2,10
  L FOB FCA
-16  44 -42
-12   0  22
 -8  56 -47
 -4   0 -12
  0  66  66
  2  52  59
  4  80 -75
  8   0  13
 10  23 -35
 12  34  33
 14   0  -2
 16   0   7

 H,K= 2,11
  L FOB FCA
  1   0 -10
  9   0  -9
 11  18  22
 13   0  -5

 H,K= 2,12
  L FOB FCA
-10   0   5
 -6  25  31
 -2  65  64
  0  35 -25
  2  25 -27
  4  55  55
  6  39 -42
 10  26 -16

 H,K= 2,13
  L FOB FCA
  1   0  17

 H,K= 3, 1
  L FOB FCA
-20  66 -60
-18  46  51
-16  19 -25
-14  83  85
-12 266-258
-10 169 161
 -8   0  11
 -6  80 -85
 -4 186-177
 -2 101-102
  0 224-224
  2  55  41
  4 353-354
  6  41  37
  8   0  -3
 10   0   5
 12  35 -33
 14  49  46
 16   0   2
 18   0 -12
 20   0  -2
 22   0  -5

 H,K= 3, 2
  L FOB FCA
-19   0  -3
-17  57 -54
-15 166 165
-13 167-173
 -9 148-151
 -7  61  62
 -5  50 -53
 -3 144 134
 -1  92 -87
  1  70  75
  3 298-290
  5   0  -1
  7  87 -85
  9  83  77
 11  66 -62
 13  18 -13
 15  14  19
 17  41 -44
 19  31  32
 21  28 -24

 H,K= 3, 3
  L FOB FCA
-24   0 -10
-18   0 -20
-16   0   8
-14   0  -8
-12  75  85
-10 117-111
 -8  58  63
 -6  46  59
 -4 157-144
 -2 136 137
  0 100 103
  2 107 -97
  4  24 -27
  6  37  35
  8  23  21
 10  21   8
 12  36 -37
 14   0  -5
 16  54 -56
 18  69  69
 20  76 -70
 22  54  54
 24  25 -21

 H,K= 3, 4
  L FOB FCA
-17  15  24
-15  60 -63
-13 104 108
-11 126-120
 -9  59  71
 -7  36 -36
 -5  22 -21
 -3  21 -21
 -1 131 123
  1  25 -28
  3  88  82
  5 173-165
  7  77 -79
  9   0  -5
 11   0  13
 13  27  28
 15  77 -84
 17  68  74
 19  58 -63
 21  24  26

 H,K= 3, 5
  L FOB FCA
-16  97-104
-14 116 119
-12 150-147
-10  93  89
 -8  82 -90
 -6  63  65
 -4  74 -77
 -2 215 216
  0 146-146
  2 104  93
  4 133-129
  6 154 157
 10  13  20
 12  34  36
 14  77 -74
 16  86  79
 18  32 -42
 20  41  36
 22   0  -7

 H,K= 3, 6
  L FOB FCA
-21   0  16
-15  96 102
-13  94-107
-11  74  80
 -9  65 -71
 -7  98  97
 -5  81 -80
 -3 121 114
 -1 161-155
  1 115 118
  3 149-142
  5 114 113
  7 136-134
  9  19  17
 11  49  50
 13  63 -68
 15  44  52
 17  46 -50
 19   0  13
 21  18 -18

 H,K= 3, 7
  L FOB FCA
-14  44 -46
-12   0  13
-10   0   8
 -8   0  -1
 -6  63 -65
 -4  50  54
 -2  52 -49
  0   0 -11
  2  19 -20
  4 185 180
  6  77 -74
  8  28 -24
 10  50  47
 12  95 -94
 14  80  77
 16  28 -22
 18  45  39
 20   0  -2

 H,K= 3, 8
  L FOB FCA
-11  43  44
 -9  59 -64
 -7  21  24
 -5  25 -29
 -3  40  31
 -1  71 -71
  1  24  21
  3  20  18
  5  20 -15
  7   0 -15
  9  43  51
 11 118-113
 13  53  60
 15  66 -52
 17  17  11
 19  18 -10

 H,K= 3, 9
  L FOB FCA
-18  25 -29
-12  56  55
 -8  49  48
 -6  37 -36
 -4  15  23
 -2  15 -21
  0  55  57
  2   0  17
  4  48 -53
  6  22  18
 12  74  73
 14  38 -35
 16  25  19
 18   0  15

 H,K= 3,10
  L FOB FCA
  3  27 -31
 13   0 -13
 15   0  -9

 H,K= 3,11
  L FOB FCA
  0  29 -25
  2  37  31
  4  17  11
  6   0  -3

 H,K= 3,12
  L FOB FCA
 -9  36 -49
 -3  66  68
  3  43 -48
  9   0   3

 H,K= 3,13
  L FOB FCA
  0  52  47

 H,K= 4, 0
  L FOB FCA
-26  79 -69
-24  43  49
-22  23 -23
-20  35  31
-18  42 -40
-16   0  -3
-14 155-148
-12  17  14
-10 202 205
 -8 148-138
 -6 106 112
 -4   0  -7
 -2  66  69
  0 675-713
  2 888 978
  4 573-598
  6  38  30
  8  81 -81
 10  66  63
 12 122-118
 14  75  82
 16  20 -22
 18  18 -17
 20  19  32
 22  17  -8
 24   0   4

 H,K= 4, 1
  L FOB FCA
-19  37 -30
-17  14  36
-15  51 -58
-13   0   6
-11 123-111
 -9   0  23
 -7  84  83
 -5  19  16
 -3 152 141
 -1   0  10
  1 357 332
  3 490-512
  5 234 226
  7 126-137
  9  65  58
 11  17 -23
 13  32  36
 15   0   1
 17  36 -29
 19  27  30
 21   0 -17
 23  25  22
 25  18 -24

 H,K= 4, 2
  L FOB FCA
-26  58  52
-22  41  57
-18  26  32
-16  90 -89
-14  87  84
-12 102-103
-10  37 -47
 -8  62 -67
 -6  51  40
 -4  31 -26
 -2 197-191
  0  67  64
  2 246-236
  4 126 125
  6  57 -40
  8  43  42
 10  34  43
 12  18 -15
 14  28  29
 16  55 -56
 18  53  58
 20  23 -33
 22   0  19
 24  25 -25

 H,K= 4, 3
  L FOB FCA
-17  51  44
-15   0 -24
-13  19  20
-11  31  23
 -9  96 -90
 -7  50  57
 -5  64 -66
 -3  44 -37
 -1  49  46
  1   0   3
  3  10 -19
  5  65 -64
  7  61  66
  9  34 -38
 11  36 -39
 13  27  36
 15  29 -34
 17   0   2
 19   0   5
 21   0   1
 23   0  10

 H,K= 4, 4
  L FOB FCA
-24   0   6
-20   0 -15
-16 117-122
-14 111 115
-12  46 -50
-10 116-109
 -8  12   7
 -6   0  10
 -4  97 -92
 -2  31  28
  0   0  -5
  2   0  -2
  4   0 -15
  6  50  41
  8   0   4
 10   0   4
 12  19  26
 14  29 -42
 16   0  -7
 18  71  64
 20  63 -66
 22  74  66
 24   0  -6

 H,K= 4, 5
  L FOB FCA
-15 140 138
-13 114-117
-11   0  -6
 -9   0 -11
 -7  22 -30
 -5   0 -11
 -3  33  29
 -1  62  65
  1  97 -93
  3   0 -16
  5 135-132
  7  18 -28
  9  59  59
 11   0   0
 13  15 -17
 15   0  15
 17  32  36
 19 113-107
 21  74  79
 23  26 -26

 H,K= 4, 6
  L FOB FCA
-22   0 -11
-18   0   5
-14  88 -87
-12  20  33
-10  34  44
 -8 114-116
 -6  82  81
 -4  54 -59
 -2 146 135
  0 158-161
  2 233 219
  4 142-156
  6 181 172
  8  95 -91
 10  90  97
 12  59 -59
 14  62  52
 18  34 -25
 20  35  40
 22  36 -42

 H,K= 4, 7
  L FOB FCA
-13  38  43
-11  21  21
 -9  57 -57
 -7  88  97
 -5 104-114
 -3 123 117
 -1 235-239
  1 168 168
  3 211-206
  5 213 210
  7 117-113
  9  65  69
 11  74 -77
 17   0  -3
 19  35  26
 21   0  -6

 H,K= 4, 8
  L FOB FCA
-20  57 -47
-16   0  -8
-12   0   2
-10   0   7
 -8  30  31
 -6  21 -30
 -4  81  83
 -2  85 -92
  0 126 127
  2  45 -48
  4  68  83
  6 122-122
  8  93  97
 10  58 -51
 12  39  37
 16   0   9
 18   0  13

 H,K= 4, 9
  L FOB FCA
 -5  37  39
 -3  37 -45
 -1  15  24
  1  40 -35
  3   0  16
  5  22 -16
 17   0  13

 H,K= 4,10
  L FOB FCA
-14  56  67
-10  34 -35
 -6   0   4
 -2  45  43
  0  16  21
  2  23 -15
  4   0  -5
  6  23  30
  8  58 -50
 10  24  11
 14   0 -16
 H,K= 4,11
  L FOB FCA
 -3  24  33
 -1  63 -59
  1  29  28
  3   0 -14
  5   0  18

 H,K= 4,12
  L FOB FCA
 -8   0 -10
 -4   0   8
  0   0 -17
  2  18  21
  4   0   0
  8   0   6

 H,K= 5, 1
  L FOB FCA
-18  43 -51
-16  50 -53
-14  61 -60
-12  18  14
-10   0   1
 -8   0   4
 -6  57 -59
 -4  29 -27
 -2  65  62
  0 191-197
  2 138 136
  4  63  70
  6   0  14
  8  47 -58
 10  22  17
 12  19 -24
 14  74  70
 16  76 -80
 22   0  20
 24   0 -17

 H,K= 5, 2
  L FOB FCA
-17  21  29
```

the copper and sulfur form factors had been given the wrong sign. Two additional cycles of least-squares refinement of the heavy atoms after correction of this error improved the agreement of some of the low-angle reflections, but left R at 0.104. No atom moved more than 0.003 Å. Thermal parameters (other than cross terms) of copper and sulfur increased 0.1 or 0.2 Å.^{2}, while those of carbon and nitrogen decreased about 0.2 Å.^{2}. In the last cycle no coordinate changed more than 0.00005 and no thermal parameter more than 0.01 Å.^{2}.

The parameters resulting from these last cycles are listed in Tables I, II, and III. The observed and calculated structure factors before correction of the dispersion error are compared in Table IV.

Standard deviations were estimated in the same way

Table IV (*Continued*)

L	FOB	FCA
-15	72	-71
-13	27	29
-11	69	-76
-9	0	4
-7	0	13
-5	107	-103
-3	51	49
-1	0	17
1	92	91
3	112	-109
5	121	117
7	68	-74
9	58	51
11	0	4
13	46	43
15	111	-106
17	102	100
21	34	38
23	0	-16
H,K= 5, 3		
-18	22	29
-16	42	-41
-14	52	59
-12	84	-75
-10	13	13
-8	0	9
-6	0	-2
-4	16	-20
-2	83	77
0	27	28
2	111	-118
4	70	64
6	0	13
8	0	3
10	29	-25
12	43	49
14	58	-48
16	43	42
22	0	-17
H,K= 5, 4		
-17	31	-26
-15	47	52
-13	77	-73
-11	78	86
-9	65	-73
-7	17	25
-5	17	27
-3	0	-8
-1	43	34
1	59	-53
3	88	95
5	109	-104
7	82	92
9	32	39
11	44	53
13	52	-54
15	74	77
21	17	-18
23	36	37
H,K= 5, 5		
-20	41	29
-16	38	38
-14	59	-62
-12	108	106
-10	104	-104
-8	29	30
-6	31	-45
-4	18	-20
-2	92	97
0	121	-118
2	76	88
4	64	-56
6	173	175
8	81	-74
10	56	61
12	41	-38
14	53	59
20	74	-73
22	41	41
H,K= 5, 6		
-13	52	50
-11	65	-72
-9	93	99
-7	88	-85
-5	33	39
-3	37	45
-1	147	-136
1	104	107
3	102	-102
5	89	81
7	68	-69
9	73	73
11	21	-34
13	62	52
21	51	51
H,K= 5, 7		
-12	22	-22
-10	67	63
-8	118	-115
-6	90	104
-4	0	8
-2	14	-20
0	110	108
2	83	-86
4	20	17
6	41	-43
8	39	38
10	22	-21
H,K= 5, 8		
-9	53	-58
-7	90	89
-5	81	-88
-3	0	19
-1	21	15
1	107	-108
3	0	-3
5	47	39
7	31	-28
9	0	-4
H,K= 5, 9		
-4	0	17
-2	22	25
0	31	-33
2	31	27
4	22	16
6	0	-10
10	44	-39
H,K= 5,10		
-15	36	36
-5	0	-3
-1	51	-42
1	40	46
3	0	-10
5	33	-34
7	34	34
9	45	-41
H,K= 5,11		
0	0	-1
2	0	17
4	42	-42
6	0	19
10	68	58
H,K= 5,12		
-1	31	-20
1	44	49
3	40	-40
5	36	35
H,K= 6, 0		
-24	0	-0
-22	20	-19
-20	19	-6
-18	42	-46
-16	0	13
-14	99	-94
-12	302	296
-10	345	-341
-8	389	385
-6	186	-188
-4	91	89
-2	88	-90
0	111	126
2	22	23
4	33	28
6	0	7
8	87	-79
10	13	8
12	120	-109
14	131	136
16	158	-146
18	128	123
20	81	-76
22	31	37
H,K= 6, 1		
-17	0	-6
-15	35	-40
-13	113	119
-11	172	-175
-9	261	265
-7	187	-184
-5	62	65
-3	54	-64
-1	66	57
1	98	-91
3	139	147
5	144	139
7	24	-20
9	18	18
11	30	-35
13	72	69
15	141	-146
H,K= 6, 2		
-24	18	21
-20	40	33
-16	0	-1
-14	17	18
-12	140	-138
-10	156	150
-8	106	-103
-6	44	45
-4	63	-51
-2	36	49
0	0	10
2	72	80
4	117	121
6	77	-76
8	67	73
10	13	-29
12	0	13
14	46	-49
16	84	88
20	48	46
H,K= 6, 3		
-21	54	44
-17	0	-11
-15	0	14
-13	0	-13
-11	19	28
-9	32	-34
-7	63	66
-5	34	-32
-3	24	-23
-1	103	113
1	0	-13
3	24	-30
5	0	17
7	0	-17
9	56	55
11	65	69
13	0	-16
15	37	41
21	35	-27
H,K= 6, 4		
-22	0	-3
-18	0	-18
-16	85	81
-14	47	-55
-12	20	24
-10	0	18
-8	19	17
-6	0	1
-4	0	-13
-2	96	95
0	63	-60
2	0	-12
4	42	-54
6	0	1
8	139	135
10	84	-82
12	0	16
14	0	6
18	0	5
22	0	5
H,K= 6, 5		
-15	31	-42
-13	37	-36
-11	86	83
-9	39	-48
-7	19	22
-5	19	-21
-3	68	63
-1	132	-129
1	102	99
3	26	28
5	57	-58
7	173	161
9	70	-65
11	30	34
13	34	-27
H,K= 6, 6		
-20	25	29
-18	0	8
-16	23	18
-12	109	109
-10	116	-117
-8	110	109
-6	84	-87
-4	93	93
-2	112	-121
0	138	128
2	82	-84
4	24	-29
6	32	38
8	62	-73
10	74	86
12	44	-47
16	79	-70
18	49	47
20	77	-73
H,K= 6, 7		
-11	141	-144
-9	132	135
-7	100	-95
-5	114	110
-3	95	-87
-1	105	103
1	88	-90
3	0	20
5	46	54
7	47	-54
9	53	53
11	16	-24
H,K= 6, 8		
-18	36	38
-14	34	39
-10	96	80
-6	92	83
-4	61	-64
-2	60	67
0	30	-29
2	0	1
4	15	-14
6	0	-8
8	22	26
10	65	-54
12	56	53
14	55	-53
H,K= 6, 9		
-15	36	32
-9	33	-29
-3	32	27
-1	0	-0
1	22	-34
3	39	35
5	0	10
9	34	-26
11	30	31
15	36	30
H,K= 6,10		
-12	0	-8
-8	0	15
-4	24	36
0	57	-56
2	41	40
4	0	12
6	42	-43
8	49	36
12	26	-27
H,K= 6,11		
-1	43	-42
1	65	64
3	25	-22
5	66	-70
H,K= 6,12		
-2	26	-40
0	32	38
2	0	-12
H,K= 7, 1		
-16	30	37
-14	0	-8
-12	104	108
-10	155	-146
-8	139	139
-6	30	-22
-4	29	-33
-2	0	-16
0	149	143
2	0	7
4	136	138
6	139	-139
8	62	60
10	0	5
12	0	6
14	0	-20
H,K= 7, 2		
-15	47	-52
-13	113	113
-11	85	-86
-9	136	136
-7	81	-79
-5	70	67
-3	118	-112
-1	17	15
1	0	4
3	144	145
5	101	-96
7	63	64
9	27	-32
11	60	60
13	0	-7
H,K= 7, 3		
-14	0	10
-12	0	-16
-10	83	82
-8	59	-59
-6	84	80
-4	0	5
-2	66	-75
0	0	-9
2	18	19
4	51	-49
6	40	41
8	27	-38
10	28	-29
12	15	-14
14	0	-6
H,K= 7, 4		
-13	26	-27
-11	81	84
-9	81	-82
-7	101	103
-5	0	-20
-3	0	-1
-1	0	-9
1	90	95
3	32	-39
5	74	74
7	24	-19
9	40	49
11	0	-8
13	0	-11
H,K= 7, 5		
-12	107	105
-10	103	-102
-8	92	91
-6	48	-48
-4	77	85
-2	63	-64
0	124	113
2	109	-116
4	52	49
6	128	-128
8	82	90
10	48	-48
14	0	5
H,K= 7, 6		
-11	90	-89
-9	79	83
-7	46	-40
-5	79	81
-3	57	-54
-1	94	86
1	98	-97
3	83	96
5	65	-58
7	117	121
9	61	-56
H,K= 7, 7		
-14	17	18
-8	0	-2
-6	0	6
-4	30	-30
-2	30	36
0	36	-33
2	0	4
4	37	-36
6	65	59
8	44	-45
10	28	31
14	68	-66
H,K= 7, 8		
-1	22	32
1	22	-28
3	47	56
5	0	7
7	32	-34
H,K= 7, 9		
-2	23	18
0	40	-48
4	0	4
6	33	-20
8	0	3
10	0	-5
14	18	30
H,K= 7,10		
-1	17	-24
1	0	4
3	0	-5
5	0	-6
7	25	36
H,K= 7,11		
-2	75	-70
0	36	29
4	25	25
6	0	5
H,K= 8, 0		
-22	73	65
-20	20	-13
-18	67	62
-16	0	-12
-14	74	70
-12	25	-23
-10	20	13
-8	27	28
-6	112	-116
-4	85	74
-2	40	35
0	74	84
2	375	-363
4	369	370
6	306	-297
8	62	62
10	54	-54
12	62	61
14	49	-42
16	52	55
18	17	-9
20	0	2
H,K= 8, 1		
-15	0	19
-13	30	-22
-11	90	92
-9	39	-47
-7	0	-0
-5	18	17
-3	26	-29
-1	84	87
1	0	-0
3	184	171
5	328	-329
7	141	137
9	83	-93
11	44	49
13	22	-21
H,K= 8, 2		
-22	51	-56
-18	33	-31
-14	43	-45
-12	80	81
-10	0	6
-8	0	-7
-6	33	-32
-4	26	27
-2	18	20
0	66	-62
2	80	86
4	53	-53
6	116	118
8	65	-64
10	0	18
12	0	4
14	0	-1
16	0	-1
18	24	-34
H,K= 8, 3		
-13	0	-16
-11	41	48
-9	57	62
-7	44	-40
-5	0	11
-3	62	-65
-1	19	-26
1	38	36
3	19	-26
5	14	27
7	28	-24
9	41	48
11	15	-23
H,K= 8, 4		
-20	0	-7
-16	33	38
-12	86	88
-10	0	-13
-8	0	-19
-6	34	36
-4	24	29
-2	31	-22
0	24	24
2	0	16
4	0	-11
6	35	-37
8	25	-32
10	0	-14
12	0	16
16	0	-7
20	18	22
H,K= 8, 5		
-11	90	-87
-9	30	36
-7	29	44
-5	0	-19
-3	25	21
-1	14	30
1	28	38
3	35	-38
5	46	56
7	30	-28
9	22	-31
H,K= 8, 6		
-18	25	-24
-14	88	88
-10	31	22
-8	0	7
-6	48	-52
-4	49	51
-2	59	-65
0	79	68
2	129	-132
4	67	70
6	106	-106
8	133	133
10	79	-72
14	73	-69
16	25	14
18	0	-5
H,K= 8, 7		
-5	62	59
-3	62	-68
-1	92	88
1	113	-108
3	142	130
5	100	-105
7	118	119
H,K= 8, 8		
-16	0	18
-12	0	9
-8	17	6
-6	23	16
-4	23	-31
-2	36	32
0	72	-81
2	56	62
4	69	-70
6	52	50
8	73	-71
10	64	66
12	56	-45
H,K= 8, 9		
-1	0	-15
5	0	4
7	24	-29
H,K= 8,10		
-10	0	-17
-6	0	22
-2	49	-40
0	0	14
2	18	13
4	18	24
6	0	1
8	31	23
H,K= 8,11		
-1	0	17
H,K= 9, 1		
-12	21	-19
-10	0	-2
-8	20	-26
-6	56	68
-4	0	-11
-2	14	-20
0	14	16
2	67	-74
4	52	51
6	0	16
8	0	5
10	0	-11
18	25	-27
H,K= 9, 2		
-13	0	-8
-11	64	66
-9	58	-65
-7	0	-13
-5	0	10
-3	0	14
-1	19	30
1	0	-15
3	0	21
5	85	-87
7	33	35
9	43	-46
H,K= 9, 3		
-18	49	-38
-12	44	46
-10	21	-24
-8	0	11
-6	35	-46
-4	0	-8
-2	0	-10
0	20	21
2	14	21
4	81	-84
6	0	-13
8	48	-53
10	47	51
12	0	-15
18	25	25
H,K= 9, 4		
-9	77	80
-7	55	-62
-5	0	3
-3	0	-3
-1	20	-23
1	0	-1
3	25	-29
5	70	68
7	96	-106
9	0	2
H,K= 9, 5		
-8	69	-70
-6	30	38
-4	42	-47
-2	0	11
0	39	45
2	63	-67
4	37	44
6	49	-42
8	80	75
12	17	20
H,K= 9, 6		
-15	24	23
-9	56	-56
-5	85	-77
-3	31	35
-1	0	8
1	62	-56
3	82	78
5	45	-48
9	70	-73
15	0	20
H,K= 9, 7		
-2	23	-19
0	16	-19
4	49	-49
6	66	66
8	0	-8
12	25	-34
H,K= 9, 8		
3	75	-70
5	0	8
9	0	15
H,K= 9, 9		
-12	26	26
-6	0	16
-2	0	7
0	0	2
4	17	23
6	0	-9
8	0	-17
H,K= 9,10		
3	26	23
5	0	-3
H,K=10, 0		
-20	0	-19
-18	13	13
-16	0	-1
-14	0	4
-12	118	-112
-10	167	162
-8	166	-161
-6	241	239
-4	177	-176
-2	0	-10
0	77	-82
2	0	6
4	66	-72
6	26	25
8	15	20
10	12	-11
12	28	25
14	17	-11
16	70	66
18	90	-85
H,K=10, 1		
-11	27	36
-9	164	-149
-7	185	177
-5	94	-97
-3	76	79
-1	67	-73
1	20	24
3	69	-74
5	0	12
7	0	8
15	60	55
H,K=10, 2		
-20	0	-13
-16	0	-16
-12	0	0
-10	90	-88
-8	68	72
-6	76	-71
-4	51	49
-2	0	-12
0	41	48
2	0	13
4	0	-17
6	15	15
8	38	-36
10	28	27
12	16	-20
14	0	4
16	0	-16
18	45	50
H,K=10, 3		
-9	0	-12
-7	34	-46
-5	40	37
-3	42	-47
-1	21	-29
1	47	49
3	0	1
5	30	-37
7	22	-30
15	25	-25
H,K=10, 4		
-18	44	-36
-14	53	61
-10	0	17
-6	0	-11
-4	0	5
-2	0	-9
0	30	27
2	37	-42
4	15	-0
6	0	-7
8	0	28
10	93	97
12	38	-38
14	0	5
H,K=10, 5		
-15	35	31
-5	0	6
-3	22	-20
-1	38	39
3	44	41
5	39	-42
15	0	-16
H,K=10, 6		
-16	0	-0
-12	54	-54
-8	90	-87
-4	60	-71
-2	56	56
0	75	-70
2	102	99
4	23	-14
6	0	2
8	17	-13
10	69	-65
12	35	41
14	18	-20
H,K=10, 7		
-3	47	48
5	17	19
H,K=10, 8		
-10	44	-35
-6	65	-57
-2	69	-62
0	0	25
2	24	-24
4	17	21
6	0	-3
8	0	-11
10	0	22
H,K=10, 9		
-3	25	-28
5	26	24
H,K=11, 1		
-6	44	51
-4	0	-11
-2	15	21
0	37	-32
2	22	16
4	0	-22
H,K=11, 2		
-5	66	-68
-3	31	35
-1	31	-36
1	27	35
11	34	-42
H,K=11, 3		
0	0	-24
H,K=11, 4		
11	30	27
H,K=11, 5		
0	40	-34
H,K=11, 6		
11	36	-30
H,K=11, 7		
0	49	41
H,K=11, 9		
0	37	26
H,K=12, 0		
-16	18	13
-14	44	-37
-12	34	39
-10	17	-15
-8	13	-12
-6	0	-8
-4	26	-26
-2	0	10
0	23	-22
2	57	58
4	110	-98
6	148	156
8	125	-124
10	57	54
12	33	-38
14	0	-1
H,K=12, 1		
-9	62	67
-3	16	7
3	32	-40
9	94	85
H,K=12, 2		
-14	18	19
-10	0	13
-6	16	20
-2	0	1
0	0	-3
2	28	-22
4	33	28
6	41	-45
8	48	52
10	49	-42
12	0	16
14	0	-16
H,K=12, 3		
-15	0	6
-9	0	-3
-3	33	29
3	33	35
9	25	-29
H,K=12, 4		
-12	56	-52
-8	0	-7
-4	0	1
-2	0	-10
0	0	-5
2	0	12
4	24	25
6	0	13
8	0	2
10	0	-8
12	0	-3
H,K=12, 5		
-9	55	-55
-3	0	3
3	0	6
9	18	6
H,K=12, 6		
-12	52	54
-10	36	-40
-6	0	-10
-2	65	59
0	30	-19
2	25	31
4	71	-67
6	36	38
8	51	-49
H,K=12, 7		
-9	0	26
-3	25	29
3	54	-53
H,K=13, 1		
0	0	2
H,K=13, 3		
0	0	6
H,K=13, 5		
0	0	6
H,K=14, 0		
-10	48	-46
-8	59	57
-6	106	-105
-4	109	100
-2	75	-71
0	30	25
2	21	-12
4	31	32
6	21	-26
H,K=14, 1		
7	0	12
H,K=14, 2		
-8	31	-21
-4	36	-41
-2	31	29
0	25	-26
2	0	5
4	0	1
6	0	2
H,K=14, 4		
-6	0	-6
-4	0	-7
-2	0	8
0	0	-1
2	0	10

as for the cobalt crystal,[2] and we give the same estimate (0.1 to 0.2 Å.) for the standard deviations of hydrogen atom coordinates.

Description of the Structure.—The stacking of the $Cu(MNT)_2^-$ ions is shown in a projection down the *a* axis in Fig. 1, and the arrangement of the tetra-*n*-butylammonium ions is shown in a similar projection in Fig. 2. An over-all picture of the projection is directly obtainable by inserting the contents of Fig. 1 into the almost unoccupied central rectangle in Fig. 2. The two figures illustrate the nature of the molecular arrangement in the structure. The anions are stacked in columns whose axes are parallel to *a* and these columns are surrounded by a latticework of cations making the two parts of the structure quite independent, with very little overlap in the *bc* plane. This arrangement is very different from that found in both $((C_4H_9)_4N)_2Co(S_2C_4N_2)_2$ by Forrester, *et al.*,[2] and in $((CH_3)_4N)_2$Ni-

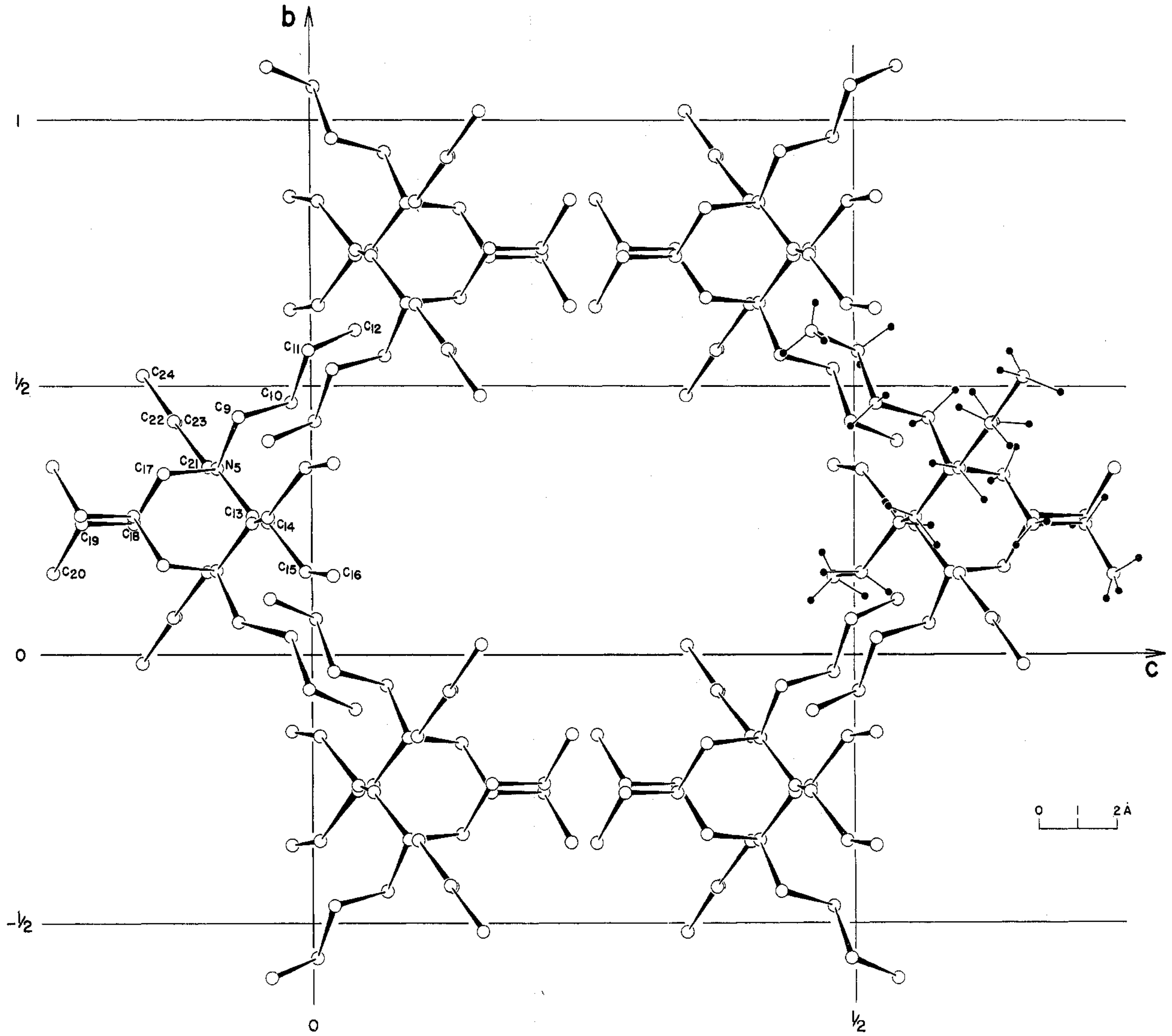

Fig. 2.—A projection down the *a* axis showing the latticework arrangement of the tetra-*n*-butylammonium ions. The small black circles are representative of each type of hydrogen atom. The stacked anions shown in Fig. 1 fit exactly into the almost unoccupied rectangle in the center of this figure.

$(S_2C_4N_2)_2$ by Eisenberg, *et al.*,[7] where the metal atoms are separated by about 10 Å.

A side view of the column of stacked anions is shown in Fig. 3. The four copper atoms per unit cell per stack are almost exactly above each other in the *a* direction while the anions are rotated in such a way as to give the stack mm symmetry in the *bc* projection.

The $Cu(MNT)_2^-$ Ion.—The dimensions of the anion are illustrated in Fig. 4 and compared in Table V with those found for the doubly charged anion in $((C_4H_9)_4N)_2Co(S_2C_4N_2)_2$. Despite the difference in the oxidation state, there is no significant difference in the molecular dimensions of the two anions, with standard deviations of about 0.02 Å.

The anion is approximately planar, but deviations from planarity are considerably greater than in the $Co(MNT)_2^{2-}$ ion. To assess the planarity, the distances of the atoms in the ion from a plane constructed to pass through the three points defined as: point 1, the mean position of atoms N(1), N(2), C(3), and C(4); point 2, the mean position of atoms C(7) and N(3); point 3, the mean position of atoms C(8) and N(4), were calculated, and these are listed in Table VI. The ion appears to be bent slightly into a crescent shape with only atom S(1) deviating substantially from this shape. Deviations range from 0.05 Å. on one side of the plane to 0.11 Å. on the other. The four sulfur atoms are twisted from square-planar in an irregular way. The S–Cu–S angles in the rings are 92°, in close agreement with 91 and 92° found in previous studies[2,7] of the divalent anion.

The chemically equivalent but crystallographically nonequivalent bonds in the anion, *viz.*, Cu–S(1), Cu–S(2), Cu–S(3), and CuS(4); C(1)–S(1), C(2)–S(4), C(5)–S(2), and C(6)–S(3); C(1)–C(2) and C(5)–C(6); C(2)–C(3), C(1)–C(4), C(5)–C(8), and C(6)–C(7); C(3)–N(1), C(4)–N(2), C(7)–N(3), and C(8)–N(4), differ by less than two standard deviations. Crystallographically the ion is not required to have any symmetry, but its geometry is such that it does not differ very much from mmm (D_{2h}) symmetry. The only deviations from

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

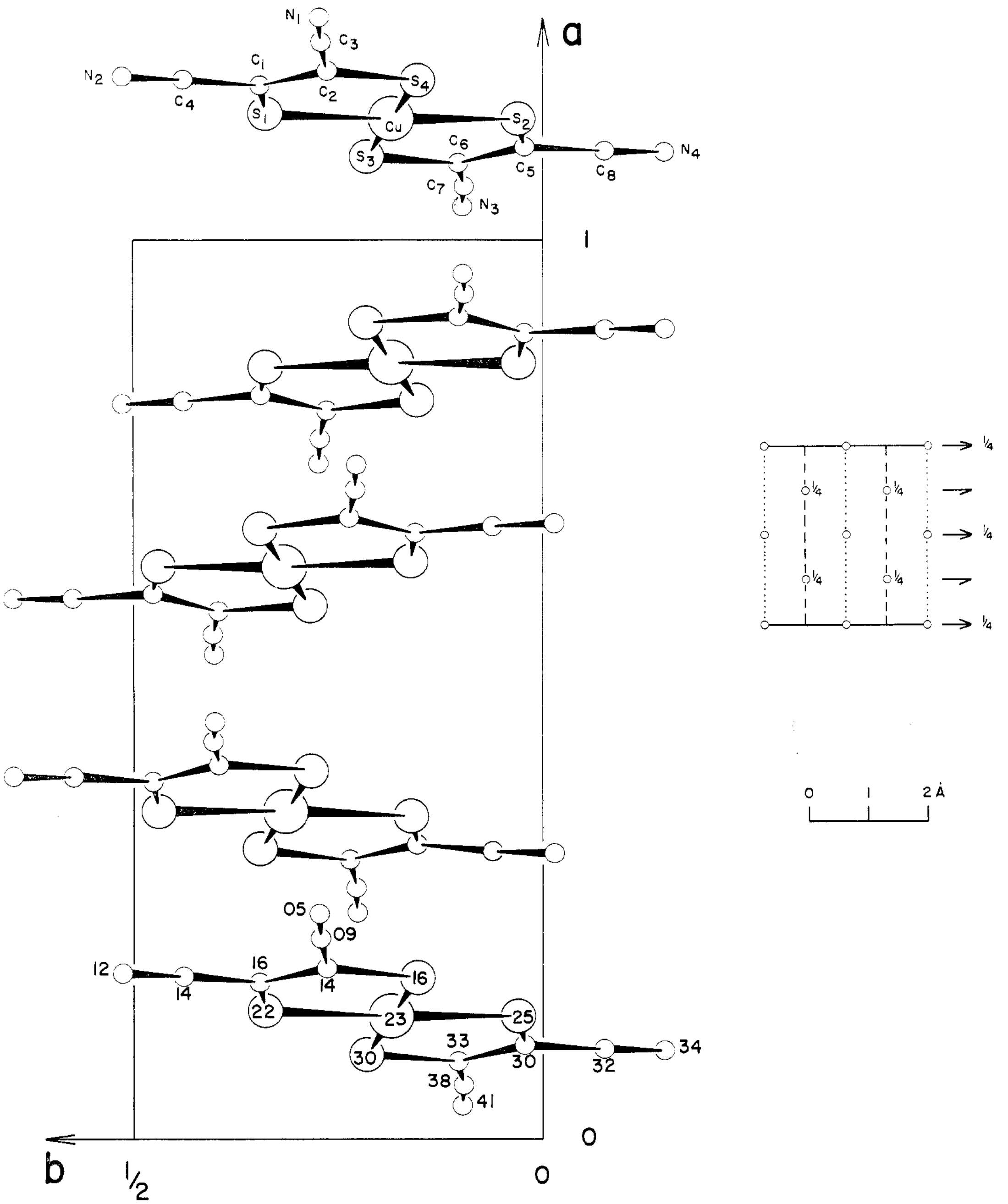

Fig. 3.—A projection down the *c* axis showing the stacking of the $Cu(MNT)_2^-$ anions from the side. The figures beside some of the atoms are the *z* coordinates (×100).

this symmetry which are statistically significant are the deviations from planarity, and these are considerably less than the amplitudes of thermal motion. Thus we prefer not to assign them any chemical significance. Neither our data nor our computing facilities justify anisotropic analysis of the motion of the carbon and nitrogen atoms. In the absence of such analysis, we will not belabor the thermal motion of the sulfur atoms except to point out that the large values of B_{11} correspond to large out-of-plane amplitudes.

In sharp contrast with the cobalt chelate,[2] where the closest distance of approach of the metal atoms is 9.81 Å., the copper atoms in this structure have nearest copper neighbors at 4.026 ± 0.005 and 4.431 ± 0.006 Å. These near neighbors give an explanation of decreased anisotropy in the e.s.r. properties found by Maki, *et al.*,[3] for the isomorphous nickel crystal. No atom from the cation except hydrogen (nearest at 4.74 Å.) approaches closer than 5.0 Å. to the copper atom, although some 14 different atoms from adjacent anions are at distances between 3.6 and 5.0 Å. from the copper.

The Tetra-*n*-butylammonium Ion.—The configuration of this ion can be seen in Fig. 2 and the important dimensions are listed in Table VII. All the butyl chains adopt the *trans* conformation, and the dihedral angles of these chains are listed in Table VIII. With the exception of the chain involving C(16) these angles are very small showing that the chains are very nearly planar.

The four C–N bonds are equal within the experi-

TABLE V

A COMPARISON OF THE INTERATOMIC DISTANCES AND ANGLES, TOGETHER WITH THEIR ESTIMATED STANDARD DEVIATIONS, IN THE $Cu(MNT)_2^-$ AND THE $Co(MNT)_2^{-2}$ IONS

(A) Distances

	$Cu(MNT)_2^-$		$Co(MNT)_2^{-2}$	
Atoms	Distance, Å.	E.s.d., Å.	Distance, Å.	E.s.d., Å.
Cu/Co–S(1)	2.174	0.004	2.163	0.003
Cu/Co–S(2)	2.170	0.004		
Cu/Co–S(3)	2.177	0.004		
Cu/Co–S(4)	2.158	0.005	2.159	0.003
S(1)–C(1)	1.73	0.010	1.731	0.007
S(2)–C(5)	1.74	0.010		
S(3)–C(6)	1.71	0.010		
S(4)–C(2)	1.70	0.010	1.715	0.007
C(1)–C(2)	1.32	0.020	1.34	0.010
C(5)–C(6)	1.31	0.020		
C(2)–C(3)	1.42	0.020	1.40	0.010
C(1)–C(4)	1.43	0.020	1.40	0.010
C(5)–C(8)	1.44	0.020		
C(6)–C(7)	1.44	0.020		
C(3)–N(1)	1.17	0.020	1.15	0.010
C(4)–N(2)	1.12	0.020	1.16	0.010
C(7)–N(3)	1.14	0.020		
C(8)–N(4)	1.15	0.020		

(B) Angles

	$Cu(MNT)_2^-$		$Co(MNT)_2^{-2}$	
Atoms	Angles, deg.	E.s.d., deg.	Angles,[a] deg.	E.s.d., deg.
S(1)–Cu/Co–S(3)	88.2	0.2	88.6[b]	0.1
S(1)–Cu/Co–S(4)	92.2	0.2	91.4[b]	0.1
S(2)–Cu/Co–S(3)	92.5	0.2		
S(2)–Cu/Co–S(4)	87.1	0.2		
Cu/Co–S(1)–C(1)	102.5	0.5	103.7	0.3
Cu/Co–S(2)–C(5)	101.4	0.5		
Cu/Co–S(3)–C(6)	101.9	0.5		
Cu/Co–S(4)–C(2)	101.9	0.5	103.8	0.3
S(1)–C(1)–C(2)	119.2	1.1	120.0	0.6
S(2)–C(5)–C(6)	121.6	1.1		
S(3)–C(6)–C(5)	122.5	1.1		
S(4)–C(2)–C(1)	123.9	1.1	121.1	0.5
S(1)–C(1)–C(4)	117.7	1.1	117.2	0.6
S(2)–C(5)–C(8)	115.1	1.0		
S(3)–C(6)–C(7)	116.3	1.1		
S(4)–C(2)–C(3)	115.9	1.1	118.1	0.5
C(1)–C(2)–C(3)	120.1	1.3	120.8	0.7
C(2)–C(1)–C(4)	123.0	1.3	122.8	0.7
C(5)–C(6)–C(7)	121.1	1.3		
C(6)–C(5)–C(8)	123.2	1.3		
C(1)–C(4)–N(2)	177.1	1.7	178.7	1.0
C(2)–C(3)–N(1)	179.8	1.7	178.2	0.8
C(5)–C(8)–N(4)	178.5	1.6		
C(6)–C(7)–N(3)	175.9	1.7		

[a] Because of the higher symmetry of the $Co(MNT)_2^{-2}$ ion there are two symmetrically equivalent values of each of these distances and angles. [b] Not independent angles.

mental accuracy and have an average value of 1.52 ± 0.01 Å. The six tetrahedral angles at the nitrogen atom (C–N–C) average 109.5° with a spread of ±5°. Both these results are in excellent agreement with the values found in the cobalt compound.

In the butyl chains, the mean C–C distance is 1.523 Å. Applying a thermal correction assuming that each carbon atom "rides" on its neighbor nearer to the central

TABLE VI

DISTANCES OF THE VARIOUS ATOMS IN THE $Cu(MNT)_2^-$ ION FROM THE PLANE THROUGH THE MEAN ATOMS {N(1), N(2), C(3), AND C(4)}, {C(7) AND N(3)}, AND {C(8) AND N(4)}

Atom	Distance (Å.) from plane	E.s.d. (Å.) of the atomic position
Cu	−0.064	0.002
S(1)	+0.032	0.004
S(2)	−0.094	0.004
S(3)	−0.065	0.004
S(4)	−0.114	0.005
C(1)	−0.030	0.014
C(2)	−0.036	0.014
C(3)	+0.011	0.016
C(4)	−0.011	0.016
C(5)	−0.051	0.014
C(6)	−0.030	0.014
C(7)	−0.019	0.016
C(8)	−0.008	0.016
N(1)	+0.053	0.015
N(2)	−0.053	0.015
N(3)	+0.019	0.015
N(4)	+0.008	0.014

TABLE VII

DISTANCES AND ANGLES INVOLVING THE CARBON AND NITROGEN ATOMS IN THE TETRA-*n*-BUTYLAMMONIUM ION

Atoms	Distance,[a] Å.	Atoms	Angles,[b] deg.
N(5)–C(9)	1.510	C(9)–N(5)–C(13)	111.0
N(5)–C(13)	1.517	C(9)–N(5)–C(17)	104.6
N(5)–C(17)	1.544	C(9)–N(5)–C(21)	112.4
N(5)–C(21)	1.520	C(13)–N(5)–C(17)	109.6
		C(13)–N(5)–C(21)	107.2
		C(17)–N(5)–C(21)	112.1
Mean C–N dist.	1.523	Mean C–N–C angle	109.5

Atoms	Distance,[c] Å.	Distance,[e] Å.	Atoms	Angle, deg.	E.s.d. deg.
C(9)–C(10)	1.51	1.52	N(5)–C(9)–C(10)	115.3	1.0
C(10)–C(11)	1.54	1.54	C(9)–C(10)–C(11)	109.6	1.1
C(11)–C(12)	1.47	1.49	C(10)–C(11)–C(12)	112.2	1.2
C(13)–C(14)	1.49	1.51	N(5)–C(13)–C(14)	117.2	1.1
C(14)–C(15)	1.56	1.58	C(13)–C(14)–C(15)	104.6	1.3
C(15)–C(16)	1.48[d]	1.55	C(14)–C(15)–C(16)	109.6	1.7
C(17)–C(18)	1.53	1.56	N(5)–C(17)–C(18)	112.0	1.1
C(18)–C(19)	1.62	...	C(17)–C(18)–C(19)	106.6	1.3
C(19)–C(20)	1.49	1.50	C(18)–C(19)–C(20)	109.8	1.4
C(21)–C(22)	1.51	1.52	N(5)–C(21)–C(22)	115.1	1.0
C(22)–C(23)	1.53	1.54	C(21)–C(22)–C(23)	109.0	1.2
C(23)–C(24)	1.54	1.57	C(22)–C(23)–C(24)	111.3	1.3
Mean C–C dist.	1.523	1.535	Mean angle	111.0	

[a] E.s.d. all ±0.016 Å. [b] E.s.d. all ±0.9°. [c] E.s.d. all ±0.02 Å. [d] E.s.d. ±0.035 Å. [e] Distance corrected for thermal motion assuming that atom C(*n* + 1) "rides" on atom C(*n*).

TABLE VIII

THE DIHEDRAL ANGLES FOR THE FOUR BUTYL CHAINS IN THE TETRA-*n*-BUTYLAMMONIUM ION

Plane (1) defined by atoms			Plane (2) defined by atoms			Dihedral angle, deg.
C(9)	C(10)	C(11)	C(10)	C(11)	C(12)	5.3
C(13)	C(14)	C(15)	C(14)	C(15)	C(16)	13.9
C(17)	C(18)	C(19)	C(18)	C(19)	C(20)	6.0
C(21)	C(22)	C(23)	C(22)	C(23)	C(24)	0.9

nitrogen atom increases the distance by 0.012 Å. and somewhat reduces the spread of the values. This assumption is reasonable as the temperature factors increase progressively along each carbon chain (see Table I) with the exception of C(18) and C(19). The mean value of the 12 N-C-C and C-C-C angles in the four chains is 111.0°, somewhat smaller than that found in the cobalt compound, although the four N-C-C angles all have higher than average values as found previously.

All the atoms in the tetra-*n*-butylammonium ion were located easily from an electron density Fourier with the exception of C(16) at the end of one of the butyl chains. This atom appears poorly resolved and has a high temperature factor in the least-squares refinement. However, a careful examination shows no better position available for this atom, and the bond angles and distances are very reasonable. We can only assume that this atom either has a high thermal vibration at the end of the chain or else there is a certain amount of disorder in this region. Needless to say, this effect makes it rather difficult to locate hydrogen atoms associated with this carbon atom, although density does appear in the appropriate region in the electron density difference function. Little reliability should therefore be placed on the exact location of these particular hydrogen atoms.

As described earlier, 24 of the hydrogen atoms were located from the difference Fourier in very suitable locations and their parameters refined by least-squares methods. The remaining 12 hydrogen atoms were also located from the difference Fourier. However, their parameters were not refined but merely used in the least-squares analysis to calculate structure factors. The carbon-hydrogen distances range from 0.6 to 1.2 Å. The mean C–H bond length (36 values) is 0.94 Å., somewhat smaller than the value of 1.09 Å. usually taken as the standard interatomic separation. With the exception of the hydrogen atoms associated with the end carbon atoms, together with those associated with C(15) and C(23), all of the hydrogen bond angles are within 20° of the tetrahedral angle. This is consistent with the estimated standard deviations of the hydrogen atom positional parameters.

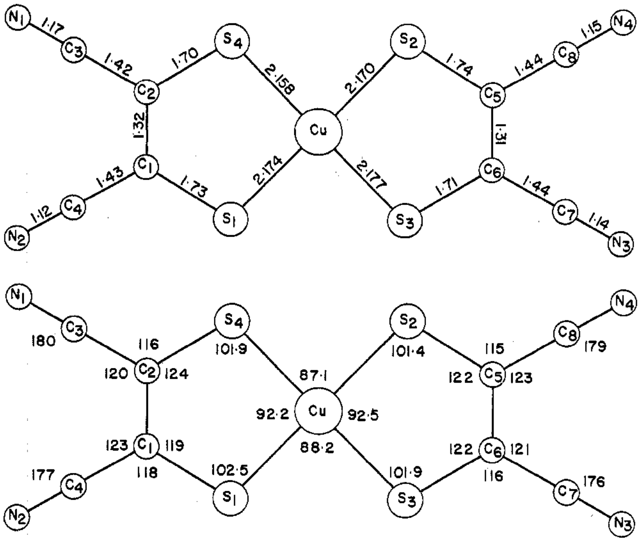

Fig. 4.—The molecular dimensions of the $Cu(MNT)_2^-$ anion.

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