## Title

THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRA-n-BUTYL AMMONIUM COPPER (III) BIS-(MALEONITRILE DITHIOLATE) AND THE GEOMETRY OF THE MONOVALENT COPPER (III) BIS-(MALEONITRILE DITHIOLATE) ION

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## Publication Date

1964-06-01

UCRL-11506

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Berkeley, California

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To be published in J. Inorganic Chem.

UCRL-11506

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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June 1964

UCRL-11506

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
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# The Crystal and Molecular Structure of Tetra-n-Butyl Ammonium Copper (III) bis-(Maleonitrile Dithiolate) and the Geometry of the Monovalent Copper (III) bis-(Maleonitrile Dithiolate) Ion[1]

BY J. D. FORRESTER, ALLAN ZALKIN AND DAVID H. TEMPLETON.

The crystal and molecular structure of tetra-n-butyl ammonium copper(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 $\beta = 93.86 \pm 0.03^\circ$, 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, $(\underline{n}\text{-}C_4H_9)_4N^+ \; Cu(S_2C_4N_2)_2^-$ . We were encouraged to examine this material as it had considerably different e.s.r. properties from the first structure and interpretation of these phenomena would be aided considerably by some knowledge of the structure.

Maki et al[3] have already used the results of this crystallographic study in a detailed review of the electronic structures of several members of this family of compounds.

## 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 $(\underline{n}\text{-}Bu_4N)^+ \; Cu(S_2C_4N_2)_2^-$ . 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 x 0.11 x 0.07 mm and mounted about a $\underline{b}^*$ 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. MoKα radiation was used and the unit cell dimensions are based on $\lambda = 0.70926$ Å for $MoK\alpha_1$.

The space group permits 2803 independent reflections in the sphere with $\sin\theta/\lambda$ less than 0.482 ($2\theta < 40^\circ$), and of these, 1834 were measured with counting times of 10 sec. each. All reflections in the sphere were recorded up to $2\theta = 30^\circ$. Above $30^\circ$, it was found that most of the intensities were quite weak and only the reflections that gave some ease and economy in set up were measured. Of the 1834 measured reflections, 396 were assigned zero intensity and the maximum count was 4,100 counts per sec. for the 002 reflection.

No corrections were made for either absorption or extinction. With $\mu = 10.5 \text{ cm}^{-1}$

for Mo radiation, $\mu R$ 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 minimised the function $\sum \underline{w}(|\underline{F}_o| - |\underline{F}_c|)^2 / \sum \underline{w}\underline{F}_o^{\,2}$, where $\underline{F}_o$ and $\underline{F}_c$ are the observed and calculated structure factors, respectively, and $\underline{w}$ 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 electrons 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 $(\underline{n}\text{-}C_4H_9)_4N\ Cu(S_2C_4N_2)_2$ and is monoclinic with dimensions:-

$$\underline{a} = 15.59 \pm 0.02,\ \underline{b} = 13.83 \pm 0.01,\ \underline{c} = 27.94 \pm 0.03\ \text{Å}$$

$$\beta = 93.86 \pm 0.03^\circ,\ \underline{V} = 6010.5\ \text{Å}^3.$$

Reflections are absent unless $\underline{h}+\underline{k}+\underline{\ell} = 2\underline{n}$ and $\underline{h}0\underline{\ell}$ reflections are absent unless $\underline{\ell} = 2\underline{n}$. This is consistent with either the centric space group $\underline{I}2/\underline{c}$ ($\underline{C}_{2h}^{6}$) or the non-centric space group $\underline{Ic}$ ($\underline{C}_{s}^{4}$). The success of our structure determination confirms our choice of the former.

With eight formula units of $(\underline{n}\text{-}C_4H_9)_4N\ Cu(S_2C_4N_2)_2$ 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 polarisation effects, and a three dimensional Patterson function was calculated using the 1143 terms whose intensities were measured as two counts or greater. 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 :-

$$8(f) \quad (0,\ 0,\ 0;\ 1/2,\ 1/2,\ 1/2) \pm (\underline{x},\ \underline{y},\ \underline{z};\ \underline{x},\ \bar{\underline{y}},\ 1/2 + \underline{z})$$

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 $\exp(-\underline{B}\lambda^{-2}\sin^2\theta)$, and using the 1143 terms, each with unit weight, resulted in a conventional unreliability factor $\underline{R} = \sum ||\underline{F_o}| - |\underline{F_c}|| / \sum |\underline{F_o}|$ 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 $\underline{R}$ to 0.092 for all the heavy atoms.

The copper and the sulfur atoms were given anisotropic temperature factors of the form $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{hk} - 2\beta_{13}\underline{h\ell} - 2\beta_{23}\underline{k\ell})$, with $4\beta_{ij} = \underline{a}_{\underline{i}}^* \underline{a}_{\underline{j}}^* \underline{B}_{\underline{ij}}$, $\underline{a}_{\underline{i}}^*$ being the length of the $\underline{i}$th reciprocal axis. Three cycles of refinement including these anisotropic temperature factors resulted in a value of $\underline{R}$ o~~n~~f 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 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 mis-punching 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 two counts per 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 4 sulfur atoms having anisotropic temperature factors, and these gave a value of $\underline{R}$ 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. $\underline{R}$ 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 9 and this was corrected in the next refinement. The remaining 8 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.

Yet another difference function, calculated after two further cycles of refinement of the heavy atoms only, showed no better locations for the 8 doubtful hydrogen atoms, but did show possible locations for the three hydrogen atoms around C(16). These last 11 hydrogen atoms were included in subsequent least squares calculations with an average temperature factor but were never allowed to refine. Two cycles of refinement with all 70 atoms included, but only the 34 heavy atoms allowed to refine resulted in a final value of R of 0.104.

In the final cycles, with the exceptions of C(15), C(16) and C(18), no heavy atom parameter changed by more than 4% of a standard deviation and most moved by considerably less than this.

The positional and thermal parameters resulting from these last cycles of refinement are listed in Tables I, II and III and the observed and calculated structure factors are compared in Table IV.

Standard deviations of the parameters of the heavy atoms were calculated assuming that the discrepancies in the structure factors represent random errors and with neglect of the effect of the hydrogen parameters. Limitations of our computer program and computer, did not permit us to estimate the standard deviations of the hydrogen parameters by the method of least squares. From the results of the hydrogen bond distance calculations however, we estimate the standard deviation of the hydrogen parameters to be 0.1 to 0.2 Å.

Description of the Structure.—The stacking of the Cu(MNT)$_2^{-1}$ ions is shown in a projection down the a axis in Fig. 1 and the arrangement of the tetra-n-butyl ammonium ions is shown in a similar projection in Fig. 2. An overall 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 $((C_4H_9)_4N)_2\ Co(S_2C_4N_2)_2$ by Forrester et al[2] and in $((CH_3)_4N)_2\ Ni(S_2C_4N_2)_2$ 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 whilst the anions are rotated in such a way as to give the stack mm symmetry in the bc projection.

The Cu(MNT)$_2^{-1}$ 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 $((C_4H_9)_4N)_2\ Co(S_2C_4N_2)_2$. 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 approximately boat shaped with only atom S(1) deviating to any extent from this shape. Deviations range from 0.05 Å on one side of the plane to 0.11 Å on the other and because of the shape of the ion, no attempt was made to calculate a least squares plane through it.

The four sulfur atoms around the copper are considerably distorted out of the plane, but in an irregular fashion. However, this arrangement is very close to square planar and the Cu-S-Cu angles within the rings are again found to be somewhat greater than 90°, as found in previous studies (Forrester et al[2], Eisenberg et al[7]).

The chemically equivalent but crystallographically non-equivalent bonds in the anion, viz, Cu-S(1), Cu-S(2), Cu-S(3) and Cu-S(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) are equal to better 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.

In sharp contrast with the Co chelate, where the closest distance of approach of the metal atoms is 9.81 Å, the copper atoms in this structure have nearest copper neighbours at 4.026 ± 0.005 and 4.431 ± 0.006 Å. This is consistent with the e.s.r. results found by Maki et al[3] as it allows the necessary coupling needed to explain the observed phenomena in the copper compound. 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-Butyl Ammonium Ion.*—The configuration of this ion can be seen in Fig. 2 and the important dimensions are listed in Tables VII and VIII. All the butyl chains adopt the trans conformation and the dihedral angles for these chains are listed in Table IX. 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 to within the experimental 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 neighbour nearer to the central 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*-butyl ammonium 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 for the hydrogen atoms are listed in Table VIII. 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.

We thank Prof. A. H. Maki and Dr. N. Edelstein for providing us with excellent crystals of the material and for their co-operation in and helpful discussion of the problem.

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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## TABLE I

### FINAL CO-ORDINATES AND ISOTROPIC THERMAL PARAMETERS, TOGETHER WITH THEIR STANDARD DEVIATIONS, FOR ALL ATOMS EXCEPT HYDROGEN

| Atom | x | σ(x) | y | σ(y) | z | σ(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 | 0.1622 | 0.0001 | a | - |
| N(1) | 0.2477 | 0.0009 | 0.2738 | 0.0010 | 0.0545 | 0.0006 | 9.0 | 0.4 |
| N(2) | 0.1830 | 0.0009 | 0.5133 | 0.0011 | 0.1239 | 0.0005 | 8.7 | 0.4 |
| N(3) | 0.0374 | 0.0009 | 0.0986 | 0.0010 | 0.4136 | 0.0005 | 8.4 | 0.4 |
| N(4) | 0.0979 | 0.0008 | 0.8517 | 0.0010 | 0.3385 | 0.0005 | 7.5 | 0.3 |
| N(5) | 0.3307 | 0.0006 | 0.3446 | 0.0007 | 0.9111 | 0.0003 | 3.9 | 0.2 |
| C(1) | 0.1719 | 0.0008 | 0.3466 | 0.0010 | 0.1619 | 0.0005 | 4.5 | 0.3 |
| C(2) | 0.1903 | 0.0008 | 0.2659 | 0.0010 | 0.1392 | 0.0005 | 4.8 | 0.3 |
| C(3) | 0.2217 | 0.0010 | 0.2701 | 0.0012 | 0.0928 | 0.0007 | 7.4 | 0.4 |
| C(4) | 0.1799 | 0.0010 | 0.4402 | 0.0013 | 0.1413 | 0.0006 | 6.6 | 0.4 |
| C(5) | 0.1044 | 0.0008 | 0.0247 | 0.0010 | 0.3035 | 0.0005 | 4.3 | 0.3 |
| C(6) | 0.0864 | 0.0008 | 0.1030 | 0.0010 | 0.3273 | 0.0005 | 4.4 | 0.3 |
| C(7) | 0.0583 | 0.0010 | 0.0974 | 0.0012 | 0.3752 | 0.0007 | 7.1 | 0.4 |
| C(8) | 0.1012 | 0.0010 | 0.9287 | 0.0012 | 0.3235 | 0.0005 | 6.3 | 0.4 |
| C(9) | 0.3670 | 0.0008 | 0.4373 | 0.0009 | 0.9326 | 0.0004 | 4.2 | 0.3 |
| C(10) | 0.3305 | 0.0009 | 0.4681 | 0.0010 | 0.9790 | 0.0005 | 5.6 | 0.4 |
| C(11) | 0.3730 | 0.0009 | 0.5635 | 0.0011 | 0.9966 | 0.0005 | 5.9 | 0.4 |
| C(12) | 0.3343 | 0.0010 | 0.6020 | 0.0012 | 0.0393 | 0.0006 | 7.8 | 0.4 |
| C(13) | 0.3531 | 0.0009 | 0.2591 | 0.0010 | 0.9436 | 0.0005 | 5.2 | 0.3 |
| C(14) | 0.4458 | 0.0010 | 0.2435 | 0.0012 | 0.9582 | 0.0006 | 7.2 | 0.4 |
| C(15) | 0.4465 | 0.0013 | 0.1561 | 0.0013 | 0.9935 | 0.0007 | 9.2 | 0.5 |
| C(16) | 0.5317 | 0.0020 | 0.1487 | 0.0021 | 0.0196 | 0.0010 | 17.7 | 1.0 |
| C(17) | 0.3750 | 0.0008 | 0.3332 | 0.0009 | 0.8637 | 0.0005 | 4.6 | 0.3 |
| C(18) | 0.3411 | 0.0011 | 0.2453 | 0.0013 | 0.8349 | 0.0006 | 8.1 | 0.4 |
| C(19) | 0.3944 | 0.0010 | 0.2410 | 0.0012 | 0.7873 | 0.0006 | 7.8 | 0.4 |
| C(20) | 0.3717 | 0.0012 | 0.1511 | 0.0013 | 0.7598 | 0.0006 | 9.1 | 0.5 |

TABLE I (Contd.)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C(21) | 0.2334 | 0.0008 | 0.3475 | 0.0009 | 0.9031 | 0.0004 | 4.5 | 0.3 |
| C(22) | 0.1982 | 0.0009 | 0.4306 | 0.0010 | 0.8725 | 0.0005 | 5.4 | 0.3 |
| C(23) | 0.1005 | 0.0011 | 0.4317 | 0.0012 | 0.8732 | 0.0006 | 7.4 | 0.4 |
| C(24) | 0.0610 | 0.0011[b] | 0.5163 | 0.0012[b] | 0.8430 | 0.0006[b] | 11.0 | 0.4[b] |

[a] Treated anisotropically - see Table III.

[b] Not actually calculated, but estimated from similar atoms.

[c] In Å$^2$.

## TABLE II

### FINAL CO-ORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS

| Atom | x | y | z | B(Å$^2$) | Atom | x | y | z | B(Å$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| H1 C9 | 0.37 | 0.49 | 0.91 | 2.3 | H1 C17 | 0.44 | 0.32 | 0.88 | 0.5 |
| H2 | 0.43 | 0.43 | 0.95 | 9.2 | H2 | 0.35 | 0.38 | 0.85 | 2.3 |
| H1 C10 | 0.32 | 0.42 | 0.00 | 4.7 | H1 C18 | 0.38[a] | 0.25 | 0.82 | 5.8 |
| H2 | 0.29 | 0.48 | 0.97 | 7.8 | H2 | 0.34[a] | 0.20 | 0.85 | 1.6 |
| H1 C11 | 0.43 | 0.54 | 0.01 | 4.2 | H1 C19 | 0.38[a] | 0.29[a] | 0.77[a] | 5.5 |
| H2 | 0.38 | 0.61 | 0.97 | 10.2 | H2 | 0.47 | 0.24 | 0.80 | 4.9 |
| H1 C12 | 0.36 | 0.65 | 0.04 | 4.6 | H1 C20 | 0.32[a] | 0.18 | 0.74 | 9.6 |
| H2 | 0.27 | 0.58 | 0.03 | 6.9 | H2 | 0.40[a] | 0.10[a] | 0.77 | 12.1 |
| H3 | 0.34 | 0.56 | 0.07 | 8.9 | H3 | 0.31[a] | 0.11 | 0.76 | 19.1 |
| H1 C13 | 0.33 | 0.20 | 0.92 | 5.5 | H1 C21 | 0.22 | 0.29 | 0.88 | 2.7 |
| H2 | 0.32 | 0.27 | 0.97 | 1.5 | H2 | 0.21 | 0.35 | 0.93 | -2.0 |
| H1 C14 | 0.48[a] | 0.24[a] | 0.93[a] | 8.0[a] | H1 C22 | 0.21 | 0.49 | 0.89 | 1.3 |
| H2 | 0.45 | 0.28 | 0.97 | 6.3 | H2 | 0.22 | 0.43 | 0.84 | 4.8 |
| H1 C15 | 0.43 | 0.15 | 0.03 | -4.3 | H1 C23 | 0.08 | 0.38 | 0.86 | 3.1 |
| H2 | 0.45 | 0.12 | 0.97 | 5.9 | H2 | 0.10 | 0.46 | 0.90 | 5.9 |
| H1 C16 | 0.49[a] | 0.10[a] | 0.04[a] | 5.0[a] | H1 C24 | 0.08 | 0.57 | 0.86 | 4.6 |
| H2 | 0.54[a] | 0.11[a] | 0.99[a] | 5.0[a] | H2 | 0.00[a] | 0.53 | 0.87 | 10.7 |
| H3 | 0.57[a] | 0.19[a] | 0.03[a] | 5.0[a] | H3 | 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 | $\underline{B}_{11}$ | $\sigma(\underline{B}_{11})$ | $\underline{B}_{22}$ | $\sigma(\underline{B}_{22})$ | $\underline{B}_{33}$ | $\sigma(\underline{B}_{33})$ | $\underline{B}_{12}$ | $\sigma(\underline{B}_{12})$ | $\underline{B}_{13}$ | $\sigma(\underline{B}_{13})$ | $\underline{B}_{23}$ | $\sigma(\underline{B}_{23})$ [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 4.6 | 0.1 | 3.8 | 0.1 | 4.2 | 0.1 | -0.1 | 0.1 | 0.2 | 0.1 | -0.2 | 0.1 |
| S(1) | 7.8 | 0.3 | 3.9 | 0.2 | 4.4 | 0.2 | 0.3 | 0.2 | 1.9 | 0.2 | -0.2 | 0.2 |
| S(2) | 8.5 | 0.3 | 3.7 | 0.2 | 5.4 | 0.2 | -0.1 | 0.2 | 1.5 | 0.2 | 0.1 | 0.2 |
| S(3) | 6.2 | 0.2 | 4.2 | 0.2 | 4.8 | 0.2 | 0.5 | 0.2 | 0.9 | 0.2 | 0.3 | 0.2 |
| S(4) | 10.6 | 0.3 | 3.8 | 0.2 | 4.9 | 0.2 | -0.2 | 0.2 | 2.3 | 0.2 | -0.7 | 0.2 |

[a] All in Å$^2$.

## TABLE IV

## OBSERVED STRUCTURE FACTOR MAGNITUDES (FOBS) AND CALCULATED STRUCTURE FACTORS (FCAL)

(Table in two parts, to be reproduced photographically).

```
 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  96  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  56
 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  16 -19
 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 -20
  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
  6 191 172
  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
```

```
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
```

```
  L FOB FCA
-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
  L FOB FCA
 -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
  L FOB FCA
 -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
  L FOB FCA
-15  36  36
 -5   0  -3
 -1  51 -47
  1  40  46
  3   0 -10
  5  33 -34
  7  34  34
  9  45 -41

  H,K= 5,11
  L FOB FCA
  0   0  -1
  2   0  17
  4  42 -42
  6   0  19
 10  68  58

  H,K= 5,12
  L FOB FCA
 -1  31 -20
  1  44  49
  3  40 -40
  5  36  35

  H,K= 6, 0
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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  36
 13  34 -27

  H,K= 6, 6
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
 -1  43 -42
  1  65  64
  3  25 -22
  5  66 -70

  H,K= 6,12
  L FOB FCA
 -2  26 -40
  0  32  38
  2   0 -12

  H,K= 7, 1
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
 -1  22  32
  1  22 -28
  3  47  56
  5   0   7
  7  32 -34

  H,K= 7, 9
  L FOB FCA
 -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
  L FOB FCA
 -1  17 -24
  1   0   4
  3   0  -5
  5   0  -6
  7  25  36

  H,K= 7,11
  L FOB FCA
 -2  75 -70
  0  36  29
  4  25  25
  6   0   5

  H,K= 8, 0
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
 -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
  L FOB FCA
-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
  L FOB FCA
 -1   0 -15
  5   0   4
  7  24 -29

  H,K= 8,10
  L FOB FCA
-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
  L FOB FCA
 -1   0  17

  H,K= 9, 1
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-18  49 -38
-12  44  46
-10  71 -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
  L FOB FCA
 -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
  L FOB FCA
 -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
  L FOB FCA
-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
  L FOB FCA
 -2  23 -19
  0  16 -19
  4  49 -49
  6  66  66
  8   0  -8
 12  25 -34

  H,K= 9, 8
  L FOB FCA
  3  75 -70
  5   0   8
  9   0  15

  H,K= 9, 9
  L FOB FCA
-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
  L FOB FCA
  3  26  23
```

```
  5   0  -3

  H,K=10, 0
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
 -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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
-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
  L FOB FCA
 -3  47  48
  5  17  19

  H,K=10, 8
  L FOB FCA
-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
  L FOB FCA
 -3  25 -28
  5  26  24

  H,K=11, 1
  L FOB FCA
 -6  44  51
 -4   0 -11
 -2  15  21
  0  37 -32
  2  22  16
  4   0 -22

  H,K=11, 2
  L FOB FCA
 -5  66 -68
 -3  31  35
 -1  31 -36
  1  27  35
 11  34 -42

  H,K=11, 3
  L FOB FCA
  0   0 -24

  H,K=11, 4
  L FOB FCA
 11  30  27

  H,K=11, 5
  L FOB FCA
  0  40 -34

  H,K=11, 6
  L FOB FCA
 11  36 -30

  H,K=11, 7
  L FOB FCA
  0  49  41

  H,K=11, 9
  L FOB FCA
  0  37  26

  H,K=12, 0
  L FOB FCA
-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
  L FOB FCA
 -9  62  67
 -3  16   7
  3  32 -40
  9  94  85

  H,K=12, 2
  L FOB FCA
-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
  L FOB FCA
-15   0   6
 -9   0  -3
 -3  33  29
  3  33  35
  9  25 -29

  H,K=12, 4
  L FOB FCA
-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
  L FOB FCA
 -9  55 -55
 -3   0   3
  3   0   6
  9  18   6

  H,K=12, 6
  L FOB FCA
-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
  L FOB FCA
 -9   0  26
 -3  25  29
  3  54 -53

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

  H,K=13, 3
  L FOB FCA
  0   0   6

  H,K=13, 5
  L FOB FCA
  0   0   6

  H,K=14, 0
  L FOB FCA
-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
  L FOB FCA
  7   0  12

  H,K=14, 2
  L FOB FCA
 -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
  L FOB FCA
 -6   0  -6
 -4   0  -7
 -2   0   8
  0   0  -1
  2   0  10
```

## TABLE V

### A COMPARISON OF THE INTERATOMIC DISTANCES AND ANGLES, TOGETHER WITH THEIR ESTIMATED STANDARD DEVIATIONS, IN THE $Cu(MNT)_2^{-1}$ AND THE $Co(MNT)_2^{-2}$ IONS

A) DISTANCES

| | $Cu(MNT)_2^{-1}$ | | $Co(MNT)_2^{-2}$ | |
|---|---|---|---|---|
| Atoms | Distance[b] | e.s.d.[b] | Distance[b] | e.s.d.[b] |
| Cu or Co -S(1) | 2.174 | 0.004 | 2.163 | 0.003 |
| -S(2) | 2.170 | 0.004 | | |
| -S(3) | 2.177 | 0.004 | | |
| -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 | | |

[a] Because of the higher symmetry of the $Co(MNT)_2^{-2}$ ion there are two symmetrically equivalent values of each of these distances.

[b] In Å.

TABLE V. (Contd.)

B) ANGLES

| | $Cu(MNT)_2^{-1}$ | | $Co(MNT)_2^{-2}$ | |
|---|---|---|---|---|
| Atoms | Angles | e.s.d. | Angles[a] | e.s.d. |
| S(1)-Cu/Co-S(3) | 88.2° | 0.2° | 88.6[b] | 0.1° |
| S(4) | 92.2 | 0.2 | 91.4[b] | 0.1 |
| S(2)-Cu/Co-S(3) | 92.5 | 0.2 | | |
| 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 angles.

[b] Not independent angles.

# TABLE VI

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

| 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-BUTYL AMMONIUM ION

A) C-N distances and angles

| Atoms | Distance[a] | Atoms | Angles[b] |
|---|---|---|---|
| N(5)-C(9) | 1.510 Å | C(9) -N(5)-C(13) | 111.0° |
| -C(13) | 1.517 | -C(17) | 104.6 |
| -C(17) | 1.544 | -C(21) | 112.4 |
| -C(21) | 1.520 | C(13)-N(5)-C(17) | 109.6 |
| | | -C(21) | 107.2 |
| | | C(17)-N(5)-C(21) | 112.1 |
| Mean C-N distance - | 1.523 Å | Mean C-N-C angle - | 109.5° |

[a] estimated standard deviations all ± 0.016 Å

[b] estimated standard deviations all ± 0.9°

TABLE VII (Contd.)

| Atoms | Distance[a] | Distance[c] | Atoms | Angle | e.s.d. |
|---|---|---|---|---|---|
| C(9) -C(10) | 1.51 Å | 1.52 Å | 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[b] | 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 distance = | 1.523 Å | 1.535 Å | Mean angle = | 111.0° | |

[a] estimated standard deviations all ± 0.02 Å

[b] estimated standard deviation ± 0.035 Å

[c] distance corrected for thermal motion assuming that atom C(*n*+1) "rides" on atom C(*n*).

## TABLE VIII

## CARBON-HYDROGEN DISTANCES IN THE TETRA n-BUTYL AMMONIUM ION.

| Atoms | Distances[b] | Atoms | Distances[b] |
|---|---|---|---|
| C(9) -H(1)C(9) | 1.04 Å | C(17)-H(1)C(17) | 1.00 Å |
| -H(2) | 1.00 | -H(2) | 0.86 |
| C(10)-H(1)C(10) | 0.94 | C(18)-H(1)C(18) | 0.72[a] |
| -H(2) | 0.75 | -H(2) | 0.75[a] |
| C(11)-H(1)C(11) | 0.92 | C(19)-H(1)C(19) | 0.85[a] |
| -H(2) | 1.09 | -H(2) | 1.03 |
| C(12)-H(1)C(12) | 0.87 | C(20)-H(1)C(20) | 1.01[a] |
| -H(2) | 1.01 | -H(2) | 0.87[a] |
| -H(3) | 0.91 | -H(3) | 1.08[a] |
| C(13)-H(1)C(13) | 0.99 | C(21)-H(1)C(21) | 1.06 |
| -H(2) | 0.89 | -H(2) | 0.88 |
| C(14)-H(1)C(14) | 0.98[a] | C(22)-H(1)C(22) | 0.97 |
| -H(2) | 0.64 | -H(2) | 1.01 |
| C(15)-H(1)C(15) | 1.07 | C(23)-H(1)C(23) | 0.86 |
| -H(2) | 0.87 | -H(2) | 0.94 |
| C(16)-H(1)C(16) | 1.12[a] | C(24)-H(1)C(24) | 0.82 |
| -H(2) | 1.00[a] | -H(2) | 1.17[a] |
| -H(3) | 0.86[a] | -H(3) | 1.00[a] |

Mean carbon-hydrogen distance - 0.94 Å

[a] positions located from difference fourier and not refined by least squares

[b] estimated standard deviations all ± 0.1 to 0.2 Å

## TABLE IX

## THE DIHEDRAL ANGLES FOR THE FOUR BUTYL CHAINS IN THE TETRA n-BUTYL AMMONIUM ION

| Plane (1) Defined by atoms | Plane (2) Defined by atoms | Dihedral angle |
|---|---|---|
| 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 |

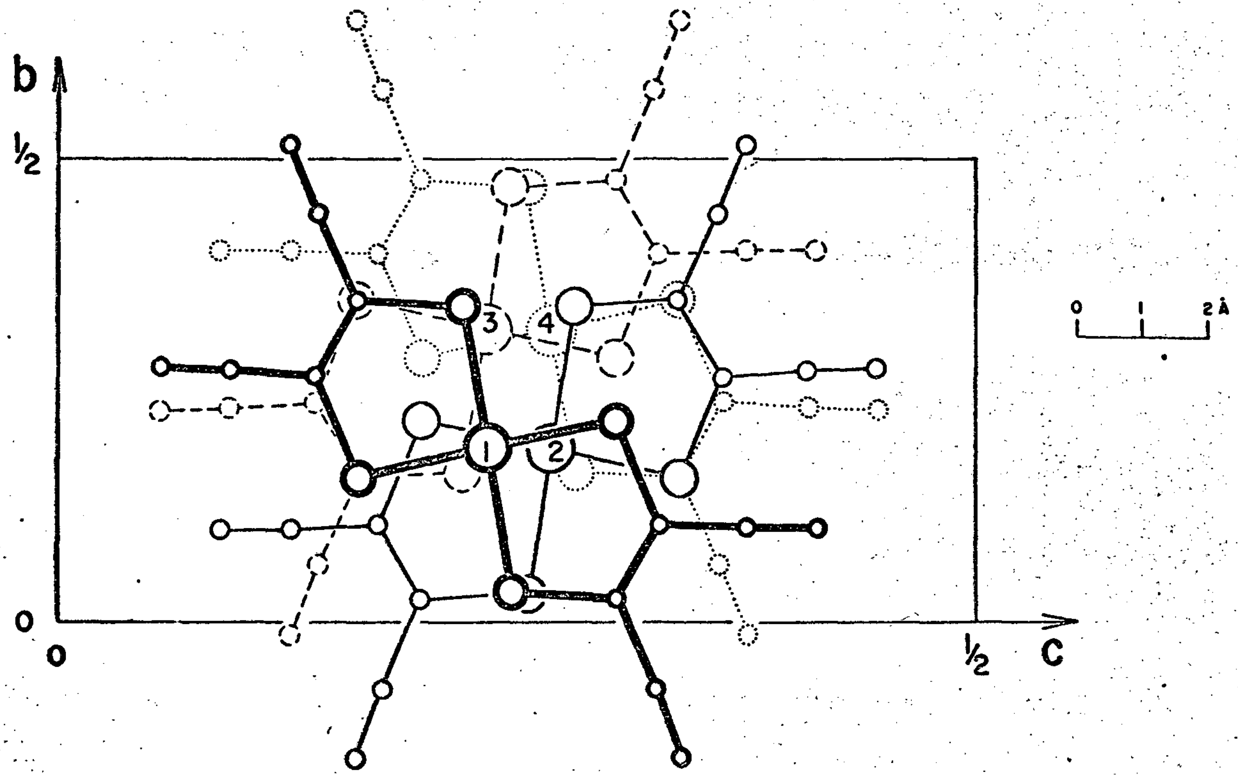
## Figure Captions

MUB 2344 Fig. 1.—A projection down the a axis showing the stacking of the $Cu(MNT)_2^{-1}$ anions as viewed down a stack. The copper atoms labelled 1, 2, 3 and 4 have x co-ordinates of 1.14, 0.86, 0.64 and 0.36 respectively.

MUB 2434 Fig. 2.—A projection down the a axis showing the latticework arrangement of the tetra-n-butyl ammonium 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.

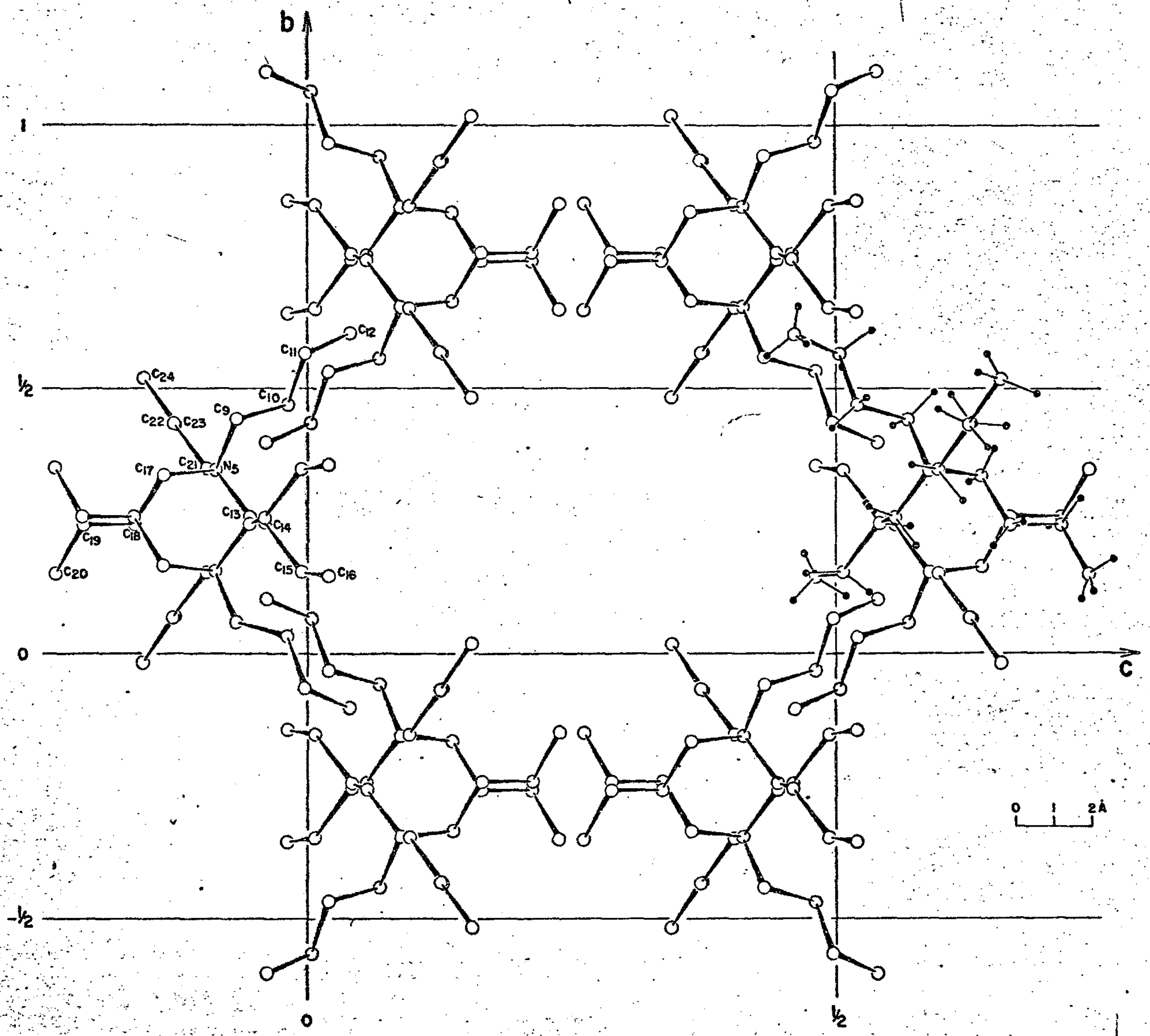
MUB 2343 Fig. 3.—A projection down the c axis showing the stacking of the $Cu(MNT)_2^{-1}$ anions from the side. The figures beside some of the atoms are the z co-ordinates (X100).

MUB 2433 Fig. 4.—The molecular dimensions of the $Cu(MNT)_2^{-1}$ anion.



MUB-2344

FIG. 1



MUB-2434

FIG. 2

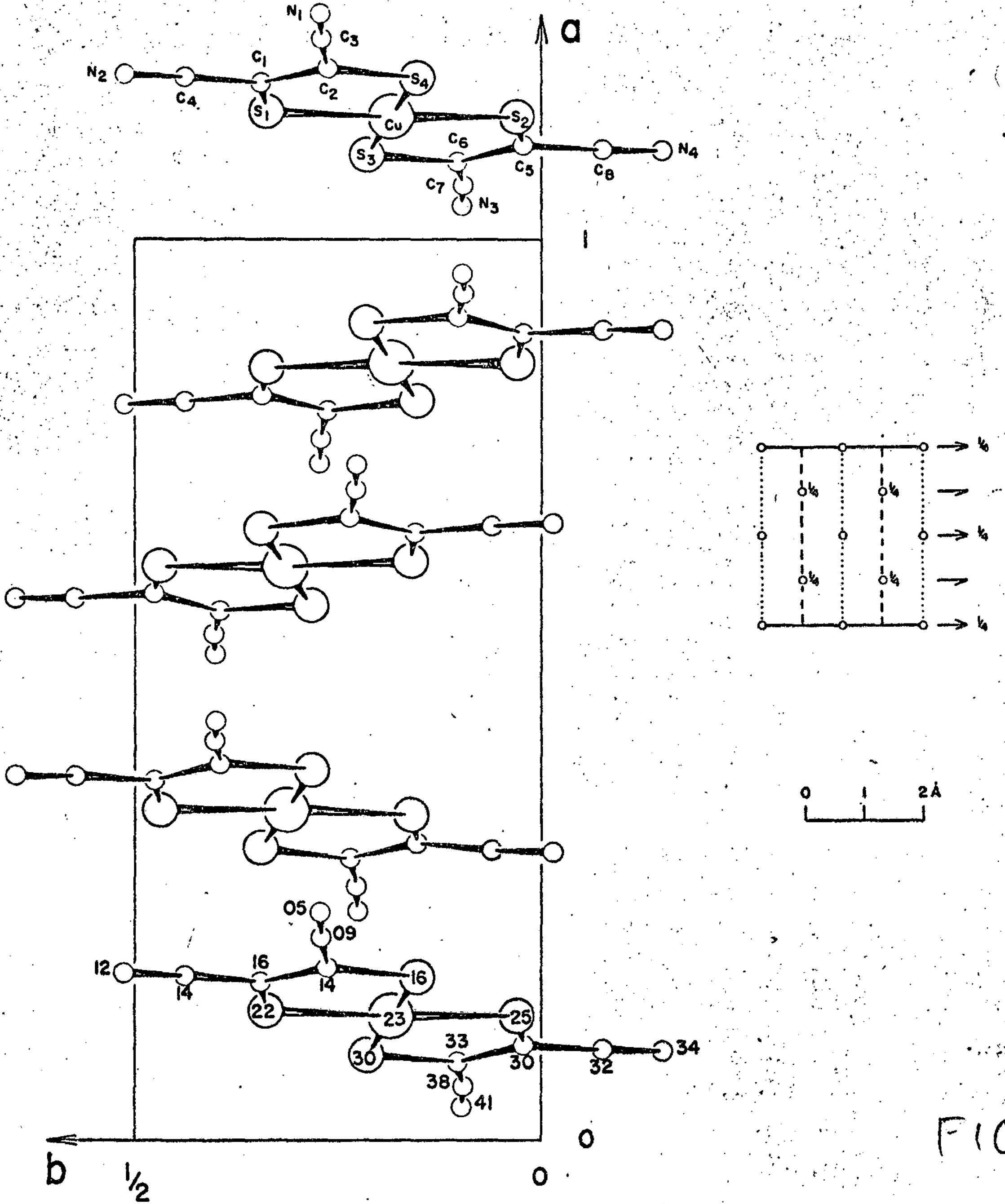
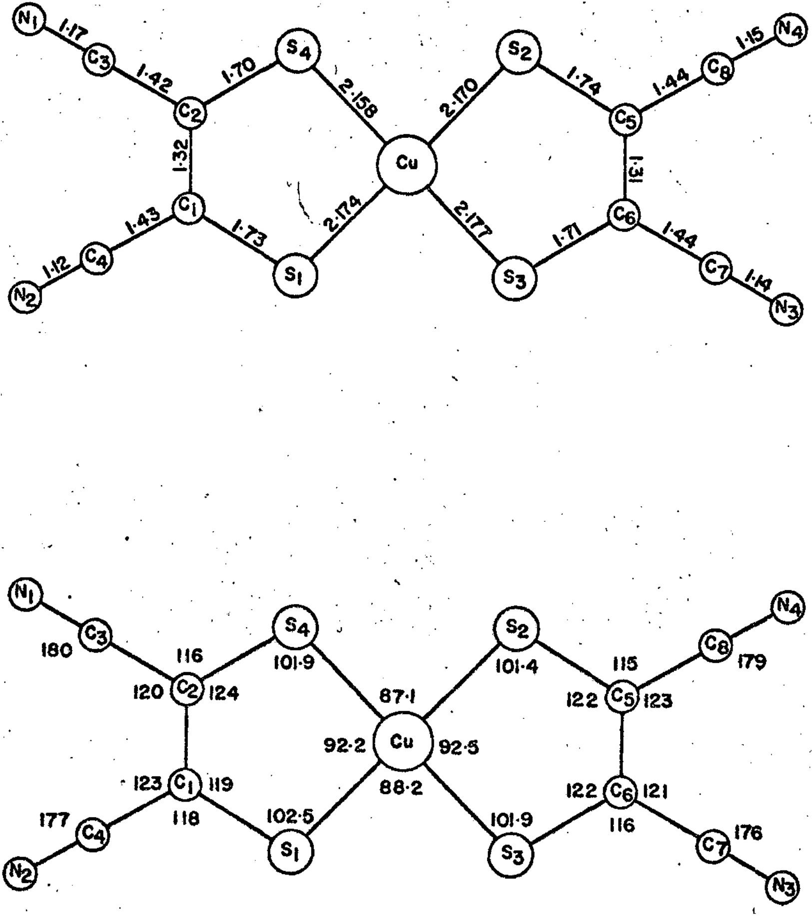


FIG 3

MUB-2343



MUB-2433

FIG. 4