UCRL-16975

University of California
Ernest O. Lawrence Radiation Laboratory

THE X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF VARIOUS COMPOUNDS

Berkeley, California

DISCLAIMER

Research and Development

UCRL-16975

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF VARIOUS COMPOUNDS

Roger C. Pettersen
(Ph.D. Thesis)

August 1966.

THE X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF VARIOUS COMPOUNDS

Contents

THE X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF VARIOUS COMPOUNDS

Roger C. Pettersen

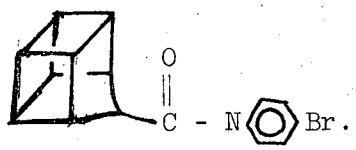
Lawrence Radiation Laboratory and
Chemistry Department
University of California
Berkeley, California

August 1966

ABSTRACT

Using techniques of x-ray crystallography, the structures of three new chemical compounds have been determined. The first, tetra-amminediaquonickel (II) hexacyanoferrate (II), $[Ni(NH_3)_4(H_2O)_2]_2Fe(CN)_6$, crystallizes in space group R32 with hexagonal cell dimensions, $a_1 = a_2 = 12.213$ A, $c = 17.005$ A, $\alpha = \beta = 90.00°$ and $\gamma = 120.00°$. The iron and nickel atoms lie along the c axis or three-fold axis. The ammonia, water and cyanide ligands are bonded to the heavy atoms in octahedral arrangements.

The second structure is the para-bromo-aniline derivative of homo-cubane carboxylic acid,



This substance crystallizes in space group $P\bar{1}$ with cell dimensions, $a = 10.092$ A, $b = 12.321$ A, $c = 11.649$ A, $\alpha = 100.62°$, $\beta = 88.32°$ and $\gamma = 114.10°$. The symmetry of the homo-cubane cage was of particular interest. Two asymmetric units were present in the unit cell, giving two independent measurements of the same molecule. The C - C bond lengths for the cages were all equal within the estimated standard deviations, the average for all of them being 1.56 ± 0.03 A. If the

bond angles are considered, one of the cages has mm2 point symmetry and the other 2 point symmetry. Hydrogen bonding was also discovered between the carbonyl oxygen atom and the nitrogen atom of adjacent molecules.

The third structure determined is ferricinium picrate, $C_{16}H_{12}N_3O_7Fe$. It is related to the "sandwich compound" ferrocene, $Fe(C_5H_5)_2$, where the iron atom is located midway between parallel planes of five-membered carbon rings. The oxidation state of the iron in ferrocene is +2, whereas it is +3 in the ferricinium ion, $Fe(C_5H_5)_2^+$. Ferricinium picrate crystallizes in space group Cmcm with cell dimensions a = 12.478 A, b = 20.274 A, c = 6.912 A, and $\alpha = \beta = \gamma = 90.00°$. The results of the structure determination show the ferricinium ion to be a sandwich also, but with a slightly larger distance between the planes of the two five-membered carbon rings.

INTRODUCTION

Modern methods of x-ray crystallography have become a powerful tool in the determination of precise sizes and shapes of chemical molecules, and of the repetitive atomic structure within a crystal. The scope of crystallographic research has been greatly altered by the recent availability of large electronic computers. The computer has significantly increased the size of the structures possible to be determined by x-ray methods. At the time of this writing it is possible to refine structures of over 400 parameters by full-matrix least squares calculations. This number will certainly increase in the near future. The accuracy of measuring reflection intensities has improved over the old method of visual estimation from photographic films. Present methods use a sodium iodide scintillation counter equipped with a pulse-height analyzer and decade scaler. A fully refined structure can be expected to give bond distances accurate to 1-1.5% and bond angles to 1-2%.

This work is concerned with the application of x-ray methods to the determination of three different crystal structures. They are not related to one another by any simple chemical or structural analysis, and will be treated in three separate sections in this thesis. Each section contains its own introduction and the points of interest for the particular structure. This is followed by the work of the structure determination, and the discussion and conclusions.

I. THE CRYSTAL STRUCTURE OF TETRAAMINEDIAQUONICKEL (II) HEXACYANOFERRATE (II). $[Ni(NH_3)_4(H_2O)_2]_2Fe(CN)_6$

A. Introduction

This portion of the work is concerned with the structure determination of tetraaminediaquonickel (II) hexacyanoferrate (II), $[Ni(NH_3)_4(H_2O)_2]_2Fe(CN)_6$. This complex has not been reported in the literature, although similar compounds such as $[Ni(NH_3)_4(H_2O)_2]SO_4$ and $[Co(NH_3)_4(H_2O)_2]TlCl_6$ are known.[1]

An unusual two step process leads to the formation of crystals of $[Ni(NH_3)_4(H_2O)_2]_2Fe(CN)_6$.[2] Conditions for formation are not overly critical. The initial step calls for mixing a 1M $K_2Fe(CN)_6$ solution with an approximately equimolar quantity of 1M $Ni(NO_3)_2$ in 6M ammonia. Very small, lavender, needle-shaped crystals are formed almost immediately. These are allowed to settle, and the excess liquid is drawn off with a pipet and syringe. The second step involves the slow transformation of the lavender crystals to the deep-blue rhombohedral-shaped crystals of $[Ni(NH_3)_4(H_2O)_2]_2Fe(CN)_6$ by allowing the former to remain slightly exposed to air in a loosely capped container for 24 hours or more. Presumably the transformation occurs as ammonia slowly escapes. The deep-blue crystals are washed in water, carefully dried in air, and then must be sealed in a small vial to prevent further loss of ammonia and subsequent decomposition.

It was originally postulated by Rock[3] that the nickel formed a tetrahedral complex with four ammonia ligands, with three additional waters of crystallization somewhere in the structure. The chemistry of the preparation could then be described as follows:

$$Ni(NH_3)_6^{+2} + Fe(CN)_6^{-4} \xrightarrow{NH_4OH} \underset{\text{lavender crystals}}{[Ni(NH_3)_6]_2Fe(CN)_6} \xrightarrow{\text{exposure to air}} NH_3\uparrow$$

$$[Ni(NH_3)_4]_2Fe(CH)_6 \cdot 3H_2O$$

The deep blue crystals were very well-formed and appeared suitable for an x-ray structure analysis. This work was brought to a successful completion and will be described in detail following the introduction. The results indicate an octahedral complex for the nickel (II), in disagreement with Rock's postulate.

Because of the disagreement, two independent chemical analyses were done on samples from the same batch of crystals. The first was a combustion analysis for carbon, hydrogen and nitrogen.[4] The other was a Kjeldahl distillation and a nickel determination with dimethylgloxime to find the ratio of ammonia to nickel.[5] These two methods gave results which agreed to about 2.5%, probably within experimental error. The ammonia-nickel ratio as determined from both analyses is 4.3:1.

Thus the more accurate chemical description of the substance is $[Ni(NH_3)_{4.3}(H_2O)_{1.7}]_2Fe(CN)_6$. Crystallographically, the water and ammonia ligands must be treated as equivalent and as randomly distributed, because the nickel lies along a three-fold axis. A similar case was reported by M. Linhard, et al. when they worked the structure for $[Co(NH_3)_4(H_2O)_2]TlCl_6$ and found it to have the sodium chloride structure.[6] A three-fold axis through the cobalt requires that the ammonia and water ligands be equivalent by symmetry, and further requires a random arrangement of these ligands about the cobalt.

An attempt was made to identify the lavender crystals by mounting a single crystal in a capillary and taking x-ray photographs. The substance was too unstable at room temperature and decomposed before any pattern appeared on the film. No attempt was made at a chemical analysis because of the instability.

The detailed chemical mechanism leading to the formation of $[Ni(NH_3)_4(H_2O)_2]_2Fe(CN)_6$ is still not understood. A possible explanation is that the lavender crystals have the composition $[Ni(NH_3)_6]_2Fe(CN)_6$ and that the partial loss of ammonia ligands on exposure to air is replaced with H_2O from the moist crystals.

B. Crystal Data

A well-formed, rhombohedral-shaped single crystal was mounted in a glass capillary wetted with ammonia. The long body-diagonal corresponds with the optical extinction axis or c crystallographic axis in the hexagonal system. A polarizing microscope was used for visual alignment along this axis. Weissenberg photographs of the first three layers indicated that the alignment axis had three-fold symmetry. The theory and use of the Weissenberg camera as well as other methods of photographing single crystals with x-rays can be found in books by Henry, Lipson and Wooster,[7] and by Buerger.[8] The reflections were indexed on the basis of an hexagonal coordinate system. Proper indexing gave the extinction rule $-h + k + \ell = 3n$, which confirmed a rhombohedral space group symmetry.

The hexagonal unit cell data are: $a_1 = a_2 = 10.213 \pm 0.012$ A, $c = 17.005 \pm 0.005$ A, $\alpha = \beta = 90.00°$, $\gamma = 120.00°$. The space group is R32 and Z = 3. The calculated density is 1.744 gm/cc., the measured density is 1.743 gm/cc. as determined by the flotation method in a mixture of ethylene dichloride and chloroform. The crystal dimensions were 0.17mm on the rhombohedral axes, and 0.25mm on the long, body-diagonal axis. The linear absorption coefficient is $\mu = 25.7$ cm^{-1} for molybdenum radiation. In this case the product of the largest crystal dimension and the linear absorption coefficient is less than one and a correction for absorption was not made.

The unit cell dimensions and the intensity data were measured with the aid of a General Electric XRD-5 spectrogoniometer. The goniometer is equipped with a sodium iodide scintillation detector, pulse-height analyzer and decade scaler. Molybdenum x-rays filtered with zirconium ($\lambda = 0.70169$ Å) were used throughout the course of this work.

Three angles are used in making the settings on the goniometer for the various reflections. 2θ is the Bragg angle of diffraction,

ϕ is the angle of rotation about the axis on which the crystal is mounted, and X is the angle the mount axis makes with a perpendicular to the plane of the goniometer.

The crystal was carefully aligned on an 00ℓ reflection with the X angle set at 90.00°. The alignment was considered satisfactory when a 360° rotation about the ϕ angle produced less than a 5% variation in the intensity. The cell dimensions were measured at as high a 2θ angle as possible. The $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks could be resolved above $2\theta = 40°$, and measurements on higher order reflections gave cell dimensions precise to 0.01%.

The goniometer angle settings for the desired set of reflections were calculated on the IBM 7044 computer. To measure the intensities, the prescribed settings were made for each reflection and a ten second count was taken. A background curve was determined as a function of the 2θ angle using random values for ϕ and X. The value of the background as determined by the 2θ angle for each reflection was subtracted from the total intensity measurement. Intensities were measured for 601 independent reflections whose general indices are $hki\ell$.

An additional 284 intensities were measured whose general indices are $\bar{h}\bar{i}k\ell$. The equivalence of these reflections with the $hki\ell$ reflections confirmed a $\bar{3}m$ Laue symmetry. Comparison of the two independent measurements of these equivalent reflections quickly revealed gross errors in setting the angles erroneously with the goniometer. Four such cases were found and the intensities corrected. The pairs of equivalent reflections were assigned an arithmetic average for the structure analysis.

C. Structure Determination

The intensity data were corrected for Lorentz and polarization effects. No attempt was made to correct for absorption. The $\bar{3}$m Laue symmetry limited the choice of space groups to R32, R3m and R$\bar{3}$m. A trial structure was first attempted for the highest space group symmetry R$\bar{3}$m. Since there are three formula units per cell, the iron atom was fixed at the special position (0,0,0) and the nickel atoms at (0,0,z; $z \cong 0.33$). Coordinates for the cyanide ligands were estimated from a previously determined ferrocyanide structure.[9] The ammonia ligands were put in a tetrahedral arrangement for the nickel complex. Atomic scattering factors were taken from volume III of the International Tables.[10] Scattering factors for neutral nitrogen were used throughout the calculations for the nickel ligands.

An IBM 7044 computer was used to compute structure factors for the trial structure, followed by a full-matrix least squares refinement. Three cycles of least squares refinement gave good isotropic Debye-Waller thermal parameters for all the atoms with the exception of the one ammonia ligand confined along the three-fold symmetry axis. The R factor was 23.2% where

$$R = \frac{\sum_i ||F_i|_o - |F_i|_c|}{\sum_i |F_i|_o} .$$

The F_o's are the observed structure factors, and the F_c's are the calculated structure factors.

Because of the difficulty with the one ammonia ligand along the three-fold axis, a second trial structure with six ammonia ligands in an octahedral arrangement around the nickel was submitted for refinement. The structure refined to an R = 6.9% after three cycles and gave reasonable isotropic thermal parameters for all the atoms.

To test for waters of crystallization or other structure, a three dimensional Fourier series was calculated by the IBM 7044 on the basis of the observed structure factors and from the phases calculated from the least squares refinement. No further structure appeared in the Fourier analysis.

All atoms of the structure were then allowed to refine with anisotropic Debye Waller temperature factors. The anisotropic temperature factors have the form $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)$. The final results are given in terms of B_{ij} where $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$ and a^*_i is the $i^{\underline{th}}$ reciprocal cell length. The final R factor is 5.7% for anisotropic refinement. The sum of the squares of the residuals is $172.447 = \Sigma_i(|F_i|_o - |F_i|_c)^2$.

As mentioned previously, two other space groups are possible for this structure. Space group R3m does not offer any particular advantage over $R\bar{3}m$ because the mirror planes constraining the ligands are present in both cases. For this reason it was not considered as a reasonable alternate structure.

On the other hand, space group R32 removes this constraint of the mirror plane, and the ligand atoms are free to move. For this space group the anisotropic temperature factors for the iron and nickel atoms have the same form as in space group $R\bar{3}m$, but the ligand atoms have anisotropic temperature factors of the form $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)$. A full-matrix least squares refinement carried out for this structure gave very similar agreement. The R factor is 5.7% and the sum of the squares of the residuals is $167.098 = \Sigma_i(|F_i|_o - |F_i|_c)^2$.

The confidence of the lower symmetry structure can be tested according to Hamilton's method.[11] Hamilton's test is based on the ratio of the statistical R' factors., where

$$R' = \left[\frac{\Sigma_i w_i(|F_i|_o - |F_i|_c)^2}{\Sigma_i w_i |F_i|_o^2} \right]^{1/2}$$

for each of the two cases. w_i is a weighting factor. The scale factors for the refinements in both space group $R\bar{3}m$ and space group R32 are identical to five figures, so it is possible to compare directly the sum of the squares of the residuals. Using Hamilton's method, the hypothesis is that space group R32 gives a significant improvement in the agreement. The following facts are needed:

Space group	Parameters	Sum of squares of residuals	Number of reflections
R32	42	167.098	601
$R\bar{3}m$	30	172.447	601

A script $\mathscr{R}$ will be used for the ratio of the statistical R' factors.

$$\mathscr{R} = \frac{172.447}{167.098} = 1.016.$$

Hamilton's tables are given in terms of $\mathscr{R}_{b,N,\alpha}$. The term b is the dimension of the linear hypothesis to be tested, in this case it is the number of parameters refined in the two space groups. N is the number of reflections minus the number of parameters for the refinement to be tested, i.e., the number of degrees of freedom. α is the confidence level for the test. Hamilton's table gives the following values for $\mathscr{R}$:

$$\mathscr{R}_{12,559,0.50} = 1.009$$
$$\mathscr{R}_{12,559,0.25} = 1.012$$
$$\mathscr{R}_{12,559,0.10} = 1.015$$
$$\mathscr{R}_{12,559,0.05} = 1.018$$

Thus the confidence level is somewhere between 90-95% that R32 gives a significant improvement in the agreement. This level of confidence is most likely somewhat reduced because a weighting scheme was not used in the refinement other than to assign all reflections an equal weight of unity. Although the method is not perfect, as Hamilton points out in his paper, it is at least, or more meaningful than arguments based on estimated standard deviations. At this level of confidence it appears reasonable to accept the R32 structure as being the better description.

The parameters of both structures are included here for completeness and comparison. The coordinates and anisotropic thermal parameters are given in Table I for space group $R\bar{3}m$ and in Table II for space group R32. The estimated standard deviations from the least squares refinement are also included for each. Table III contains the observed and calculated structure factors for the 601 independent reflections.

Table I. Fractional structure coordinates and their estimated standard deviations for tetraamminediaquonickel (II) hexacyanoferrate (II). Space group $R\bar{3}m$.

Atom	X	Y	Z	σ_x	σ_y	σ_z
Fe	0.0000	0.0000	0.0000	--	--	--
Ni	0.0000	0.0000	0.3162	--	--	0.0001
N 1	0.0997	2x	-0.2482	0.0003	$2\sigma_x$	0.0003
N 2	0.0980	2x	0.3904	0.0003	$2\sigma_x$	0.0003
N 3	0.1435	2x	0.1031	0.0004	$2\sigma_x$	0.0003
C	0.0892	2x	0.0654	0.0004	$2\sigma_x$	0.0003

Anisotropic thermal parameters and their estimated standard deviations for tetraamminediaquonickel (II) hexacyanoferrate (II). Space group $R\bar{3}m$. Units are A^2.

Atom	B11	B22	B33	B12	B13	B23	σ_{B11}	σ_{B22}	σ_{B33}	σ_{B12}	σ_{B13}	σ_{B23}
Fe	1.907	B11	1.942	$\frac{1}{2}$B11	0.000	0.000	0.046	σ_{B11}	0.069	$\frac{1}{2}\sigma_{B11}$	--	--
Ni	1.830	B11	1.893	$\frac{1}{2}$B11	0.000	0.000	0.032	σ_{B11}	0.046	$\frac{1}{2}\sigma_{B11}$	--	--
N 1	3.040	2.315	2.158	$\frac{1}{2}$B22	0.000	-0.367	0.172	0.208	0.177	$\frac{1}{2}\sigma_{B22}$	--	0.162
N 2	2.479	1.788	2.421	$\frac{1}{2}$B22	0.000	-0.446	0.151	0.184	0.180	$\frac{1}{2}\sigma_{B22}$	--	0.153
N 3	5.274	2.281	2.855	$\frac{1}{2}$B22	0.000	-0.292	0.283	0.231	0.222	$\frac{1}{2}\sigma_{B22}$	--	0.195
C	2.532	2.285	2.114	$\frac{1}{2}$B22	0.000	0.204	0.172	0.233	0.195	$\frac{1}{2}\sigma_{B22}$	--	0.180

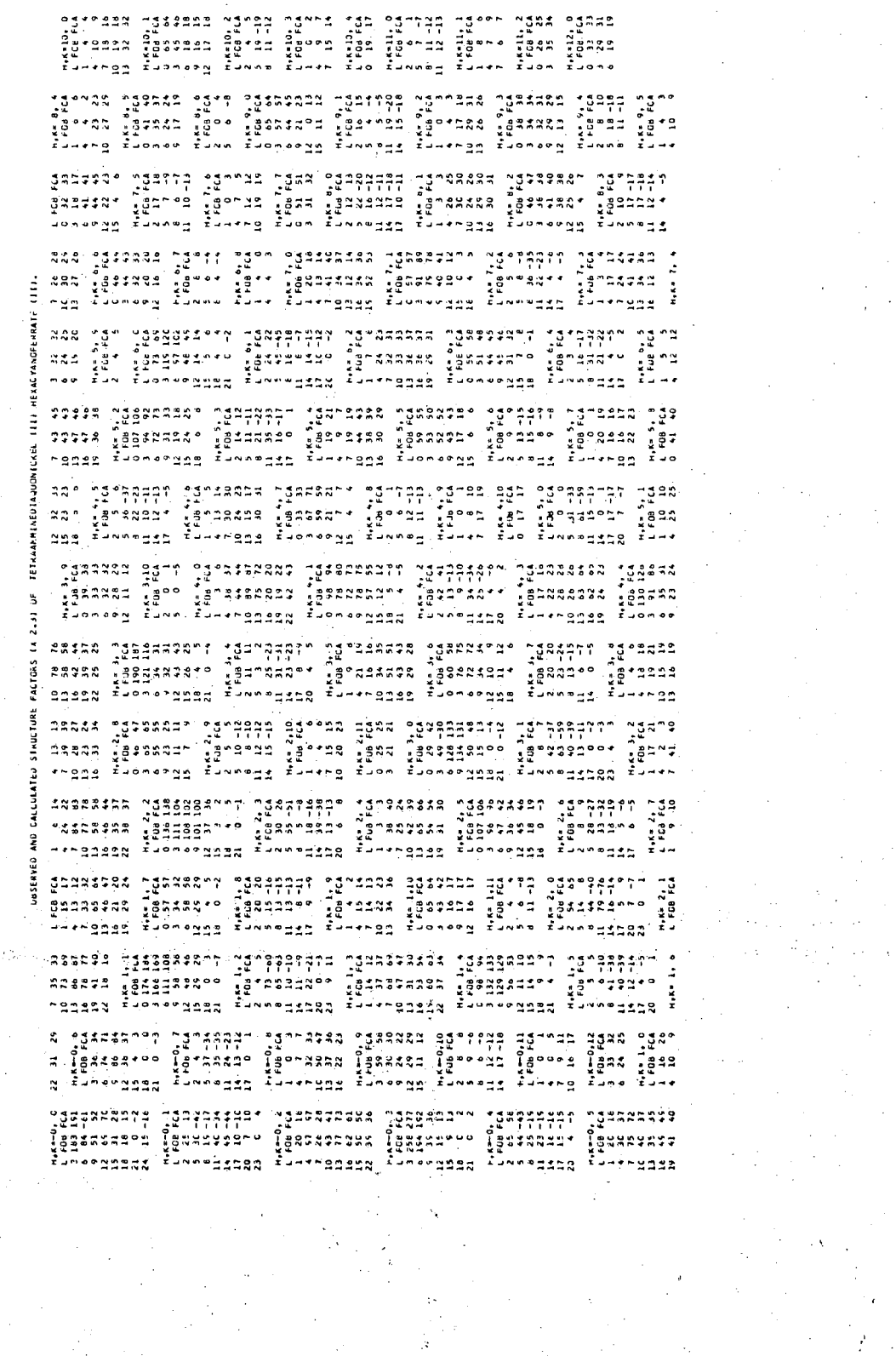
Table II. Fractional structure coordinates and their estimated standard deviations for tetraamminediaquonickel (II) hexacyanoferrate (II). Space group R32.

Atom	X	Y	Z	σ_x	σ_y	σ_z
Fe	0.0000	0.0000	0.0000	--	--	--
Ni	0.0000	0.0000	0.3162	--	--	0.0001
N 1	0.1999	0.0943	0.2480	0.0007	0.0022	0.0003
N 2	0.0926	0.1961	0.3908	0.0026	0.0007	0.0003
N 3	0.1512	0.2873	0.1031	0.0027	0.0008	0.0004
C	0.0853	0.1790	0.0656	0.0022	0.0008	0.0004

Anisotropic thermal parameters and their estimated standard deviations for tetraamminediaquonickel (II) hexacyanoferrate (II). Space group R32. Units are A^2.

Atom	B11	B22	B33	B12	B13	B23	σ_{B11}	σ_{B22}	σ_{B33}	σ_{B12}	σ_{B13}	σ_{B23}
Fe	1.927	B11	1.945	$\frac{1}{2}$B11	0.000	0.000	0.048	σ_{B11}	0.070	$\frac{1}{2}\sigma_{B11}$	--	--
Ni	1.847	B11	1.905	$\frac{1}{2}$B11	0.000	0.000	0.034	σ_{B11}	0.047	$\frac{1}{2}\sigma_{B11}$	--	--
N 1	2.310	2.513	2.244	0.774	0.339	1.020	0.217	0.500	0.190	0.480	0.171	0.453
N 2	2.323	1.727	2.485	0.697	-1.374	-0.414	0.416	0.189	0.186	0.342	0.398	0.157
N 3	5.698	2.390	2.839	1.924	-0.446	-0.299	0.881	0.243	0.225	0.687	0.716	0.201
C	1.349	2.319	2.152	-0.074	-0.683	0.346	0.378	0.261	0.204	0.437	0.513	0.203

Table III. Observed and calculated structure factors for tetraammine-diaquonickel (II) hexacyanoferrate (II). Space group R32.



D. Discussion of the Structure

The refined structure is illustrated in Fig. 1. The rhombohedral unit cell is outlined by eight iron atoms. The nickel atoms are located on the long body-diagonal or three-fold axis. The hexagonal unit cell is in solid outline and comprises one-third of the total hexagonal prism. For clarity the complete hexagonal structure is not shown in the figure.

Table IV lists the significant interatomic distances and the estimated standard deviations for the $R\bar{3}m$ and R32 structures.

Table IV. Interatomic distances for both structures of tetraamminediaquonickel (II) hexacyanoferrate (II), and the estimated standard deviations. (in angstrom units)

	$R\bar{3}m$	R32
Fe --- Ni	5.377 ± 0.002	5.377 ± 0.002
Ni --- Ni	6.251 ± 0.003	6.251 ± 0.003
Fe --- C	1.929 ± 0.006	1.936 ± 0.007
Fe --- N 3	3.084 ± 0.004	3.087 ± 0.008
Ni --- N 1	2.109 ± 0.006	2.115 ± 0.006
Ni --- N 2	2.143 ± 0.005	2.150 ± 0.006
C --- N 3	1.155 ± 0.007	1.157 ± 0.011

The bond distances of both structures agree within the limits of the estimated standard deviations. However, these deviations are at best a lower limit and most likely somewhat larger. It may be safely asserted that interatomic distances for both structures agree well within the experimental error.

The distances given in Table IV agree with those given in the literature. M. A. Porai-Koshits, et al.,[12] worked the structures of $Ni(NH_3)_4(NO_2)_2$ and $Ni(NH_3)_4(NCS)_2$. They reported a value of 2.07 ± 0.03 A for the Ni---NH_3 distance for the first structure and 2.15 ± 0.02

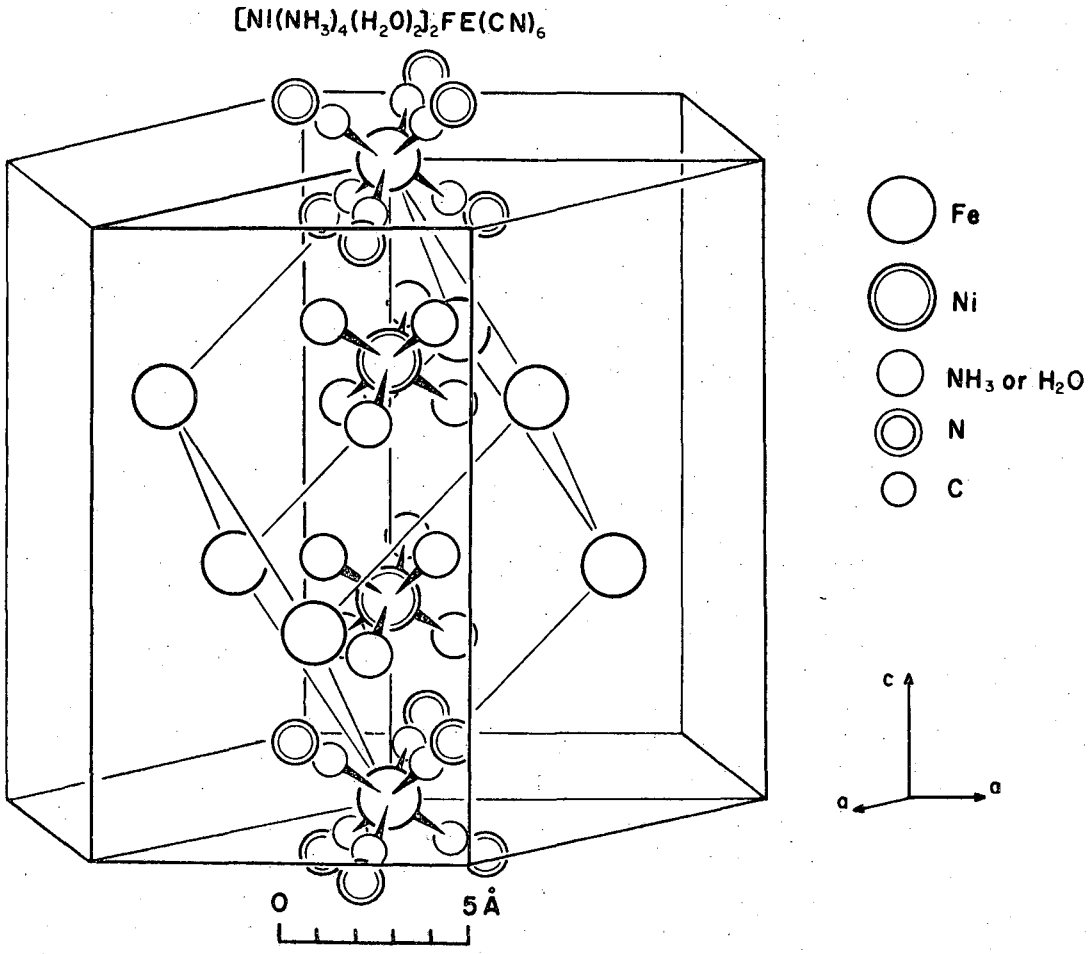


Fig. 1. The crystal structure of tetraamminediaquonickel (II) hexacyanoferrate (II).

A for the Ni ---NH_3 distance in the second. The comparison is not completely valid because some of the ligands are water in this work, and because of the influence of the NO_2 and NCS ligands in the Russian work. A value of 1.158 ± 0.002 A is reported[13] for the -C≡N distance based upon HCN, CH_3CN, BrCN, ClCN and ICN which is in good agreement with the -C≡N distance in this work.

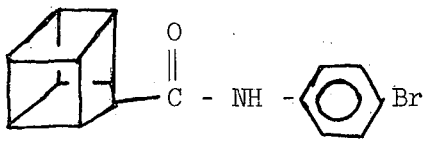
The bond angles differ somewhat between the two structures due to the freedom of motion of the ligands in the R32 space group. The iron-carbon-nitrogen bond angle is 179° in $R\bar{3}m$ and 173° in R32. The other angles the ligands make with the heavy atoms are all within 2° of 90° for both structures.

II. THE CRYSTAL STRUCTURE OF HOMO-CUBANE

A. Introduction

The hydrocarbon cubane (C_8H_8 = ) was first synthesized by Eaton and Cole in 1964.[14] The crystal structure determination followed soon after,[15] and the molecule was found to have cubic symmetry to within the limits of experimental error. The two independent carbon-carbon bond distances determined for the structure of the cubane molecule were 1.549 ± 0.003 A and 1.553 ± 0.003 A. The work for this thesis is concerned with the x-ray structure determination of homo-cubane, a molecule which is similar to cubane, and which appears in derivative form as an intermediate in the synthesis of cubane.[14,16] Homo-cubane is simply the cubane molecule with an added bridge carbon (C_9H_9 = ). The x-ray analysis was undertaken to determine the exact shape of this highly strained molecule.

To make the structure analysis possible, a heavy atom derivative was prepared by Dauben and Whalen. Their interest in this structure is a part of a study of the synthesis and rearrangements of various strained cage compounds.[17] They prepared the para-bromo aniline derivative of homo-cubane carboxylic acid,



especially for this structure analysis.

B. Crystal Data

A single crystal of the homo-cubane derivative was mounted on a small glass fiber using a small drop of General Electric baking varnish No. 1202. The crystal was aligned visually with a polarizing microscope along an extinction axis. The dimensions of the crystal are 0.20×0.29×0.45 mm. The chemical formula is $C_{16}H_{14}NOBr$, and the molecular weight is 308gm/mole. The linear absorption coefficient is $\mu = 33.55\ cm^{-1}$ (Mo K_α radiation). A correction for absorption was not made. The density of the crystals was measured by the flotation method in a mixture of ethylene dichloride and ethylene dibromide. The measured density is 1.568 gm/cc. Weissenberg photographs indicated no symmetry elements to be present. The space group as determined by the structure work is triclinic, $P\bar{1}$. The unit cell dimensions are: a = 10.092 ± 0.020 A, b = 12.321 ± 0.020 A, c = 11.649 ± 0.020 A, $\alpha = 100.62 \pm 0.05°$, $\beta = 88.32 \pm 0.10°$, $\gamma = 114.10 \pm 0.10°$. The cell volume is 1297.9 A^3 and the calculated density is 1.579 gm/cc. The number of molecules per unit cell is four.

The cell dimensions and the intensity data were measured on the General Electric XRD-5 spectrogoniometer in a manner as described in the first section of this thesis. 2465 intensity data were taken, of which 2252 were non-zero.

C. Structure Determination

The intensities were corrected for Lorentz and polarization effects and used to compute a three-dimensional Patterson function. The theory and use of the Patterson function can be found in Buerger's book.[18] The x,y,z coordinates of the two largest Patterson peaks were at (0.450, 0.075, 0.500) and (0.250, 0.175, 0.275). The next two peaks, which were about half the size were at (0.325, -0.250, 0.225) and (0.200, -0.100, 0.225). Space group $P\bar{1}$ gives Harker peaks at 2x, 2y, 2z. Assigning the two smaller peaks as Harker peaks, the coordinates of the two independent bromine atoms were determined. Five cycles of full-matrix least squares refinement with these two bromine atoms gave an agreement factor of 45%. A three-dimensional difference Fourier summation was computed using the phases and structure factors calculated in the last cycle of the least squares refinement. The differences between the observed and calculated structure factors were used as the coefficients in the Fourier series. The positions of the remaining carbon, nitrogen and oxygen atoms were determined from the difference Fourier summation. The two bromine atoms were refined using anisotropic Debye-Waller temperature factors and the remaining atoms using isotropic Debye-Waller temperature factors. Four cycles of full-matrix least squares refinement gave an agreement factor of 10.3%.

A second difference Fourier summation was computed using the phases and intensities calculated from the last refinement and the observed intensities. The largest peaks of the difference Fourier accounted for most of the hydrogen atoms which were at reasonable distances from the carbon and nitrogen atoms. Smaller peaks were also found which were due to the remaining hydrogen atoms.

The positions of the hydrogen atoms were refined isotropically by using a diagonal approximation of the least squares. The remaining 38 atoms were refined anisotropically in the same calculation. Refinement was completed on the Control Data 6600 computer with full-matrix least squares

calculations. The hydrogens were not refined in the final full-matrix calculations, but used only for the structure factor equations. The final agreement factor is 6.0% using 2252 non-zero reflections. The weighted sum of the squares of the residuals is 470.62 with all weights taken as unity.

Table V lists the fractional coordinates and their estimated standard deviations for the bromine, carbon, oxygen and nitrogen atoms as refined by the full-matrix least squares calculations. Table VI lists the anisotropic thermal parameters for the same atoms. Fractional coordinates and the isotropic thermal parameters for the hydrogen atoms are listed in Table VII. The hydrogen atom parameters are not considered as having the accuracy of the heavier atoms, but are included here only to give a rough idea of their positions and thermal motion. Table VIII lists the observed and calculated structure factors for the 2465 intensity data. The asterisks mark the data where a zero intensity was observed. These reflections were assigned zero weight in the least squares calculations.

Table V. Fractional coordinates and their estimated standard deviation for the para-bromo aniline derivative of homo-cubane carboxylic acid.

Atom	X	Y	Molecule A Z	σ_x	σ_y	σ_z
Br	0.0960	0.9449	0.1148	0.0001	0.0001	0.0001
C-B1	0.0481	0.7867	0.1405	0.0010	0.0009	0.0008
C-B2	0.1230	0.7554	0.2192	0.0010	0.0011	0.0009
C-B3	0.0891	0.6399	0.2370	0.0010	0.0010	0.0008
C-B4	-0.0211	0.5499	0.1745	0.0009	0.0009	0.0008
C-B5	-0.0953	0.5781	0.0942	0.0010	0.0010	0.0008
C-B6	-0.0602	0.6936	0.0771	0.0010	0.0011	0.0008
N	-0.0683	0.4303	0.1945	0.0008	0.0008	0.0006
C-C0	0.0114	0.3654	0.2149	0.0011	0.0010	0.0008
O	0.1418	0.4071	0.2137	0.0007	0.0007	0.0006
C-C1	-0.0668	0.2393	0.2357	0.0010	0.0009	0.0008
C-C2	0.0155	0.1986	0.3193	0.0011	0.0010	0.0009
C-C3	-0.0955	0.0806	0.3573	0.0013	0.0011	0.0010
C-C4	-0.2391	0.0992	0.3481	0.0011	0.0010	0.0009
C-C5	-0.2000	0.2221	0.3059	0.0009	0.0009	0.0008
C-C6	-0.1471	0.2851	0.4317	0.0010	0.0009	0.0008
C-C7	-0.0025	0.2657	0.4418	0.0011	0.0010	0.0009
C-C8	-0.0813	0.1448	0.4882	0.0012	0.0011	0.0009
C-C9	-0.2204	0.1625	0.4784	0.0011	0.0011	0.0008

Table V. Continued

	Molecule B					
Atom	X	Y	Z	σ_x	σ_y	σ_z
Br	0.6558	0.8716	0.6174	0.0001	0.0001	0.0001
C-B1	0.5928	0.7351	0.4986	0.0010	0.0009	0.0008
C-B2	0.4582	0.6570	0.5002	0.0011	0.0010	0.0008
C-B3	0.4072	0.5574	0.4136	0.0009	0.0009	0.0008
C-B4	0.4957	0.5364	0.3262	0.0009	0.0008	0.0007
C-B5	0.6321	0.6144	0.3279	0.0010	0.0009	0.0007
C-B6	0.6816	0.7130	0.4138	0.0010	0.0009	0.0009
N	0.4384	0.4362	0.2374	0.0007	0.0007	0.0006
C-C0	0.5068	0.3703	0.1737	0.0010	0.0009	0.0008
O	0.6333	0.3910	0.1910	0.0007	0.0006	0.0006
C-C1	0.4198	0.2707	0.0821	0.0009	0.0008	0.0007
C-C2	0.4792	0.1693	0.0480	0.0010	0.0008	0.0008
C-C3	0.3992	0.0948	-0.0672	0.0010	0.0009	0.0008
C-C4	0.3632	0.1900	-0.1268	0.0010	0.0009	0.0008
C-C5	0.4299	0.3108	-0.0381	0.0010	0.0008	0.0008
C-C6	0.5755	0.3132	-0.0864	0.0010	0.0008	0.0008
C-C7	0.6098	0.2196	-0.0272	0.0010	0.0009	0.0008
C-C8	0.5393	0.1191	-0.1350	0.0010	0.0009	0.0008
C-C9	0.5066	0.2125	-0.1904	0.0010	0.0009	0.0007

Table VI. Anisotropic thermal parameters for the para-bromo aniline derivative of homo-cubane carboxylic acid. Units are A^2.

	Molecule A					
Atom	B11	B22	B33	B12	B13	B23
Br	6.45	6.49	5.99	2.23	1.37	1.04
C-B1	3.19	6.38	2.68	1.52	0.65	0.30
C-B2	3.47	5.89	4.05	0.66	0.20	-0.15
C-B3	3.29	6.15	2.80	1.07	-1.06	0.21
C-B4	2.02	5.49	3.24	1.35	0.68	0.51
C-B5	3.04	5.65	3.62	1.71	-0.14	0.03
C-B6	3.65	7.25	3.50	2.77	0.14	1.11
N	2.54	5.70	4.27	1.01	0.11	1.03
C-CO	3.28	6.83	3.14	2.35	-0.34	-0.18
O	2.71	8.56	5.24	2.12	-0.51	0.94
C-C1	4.31	5.27	3.37	1.90	-0.06	-0.06
C-C2	4.58	6.54	5.46	2.83	1.01	1.19
C-C3	7.44	6.41	6.00	3.18	1.34	0.87
C-C4	4.35	6.50	4.98	1.24	-0.54	-0.05
C-C5	2.52	5.83	3.76	1.33	-0.54	0.33
C-C6	3.71	6.05	4.04	2.06	-0.38	0.16
C-C7	4.19	6.44	5.41	1.92	-0.68	0.69
C-C8	5.63	8.29	4.93	3.05	-0.35	1.35
C-C9	4.29	8.28	3.11	2.86	0.06	0.33

Note: The estimated standard deviations for the thermal parameters of the bromine atoms are about ±0.06 and about ±0.50 for the remaining atoms.

Table VI. Continued.

Molecule B

Atom	B11	B22	B33	B12	B13	B23
Br	6.50	6.61	5.27	2.30	-1.55	-1.71
C-B1	3.50	4.73	3.42	1.62	-1.12	0.47
C-B2	3.63	6.51	3.93	2.75	0.19	-0.37
C-B3	2.46	5.26	3.50	1.47	0.55	0.31
C-B4	2.10	4.03	3.48	1.18	-0.24	0.88
C-B5	3.24	5.37	2.97	1.76	0.60	0.59
C-B6	3.32	4.68	4.67	1.00	-0.04	0.65
N	2.00	4.94	3.38	1.21	-0.02	-0.15
C-C0	2.37	5.65	3.24	1.16	0.34	0.92
O	2.72	7.17	4.96	2.00	-0.34	-1.17
C-C1	2.67	4.62	3.42	0.41	-0.03	0.45
C-C2	3.91	4.33	4.12	1.79	0.94	0.98
C-C3	4.69	4.35	3.65	1.16	0.63	-0.37
C-C4	4.78	4.89	3.47	1.57	-0.61	-0.50
C-C5	3.73	4.12	4.04	1.36	-0.14	0.20
C-C6	3.76	3.69	3.88	0.91	0.00	0.27
C-C7	3.97	5.30	3.61	2.36	0.33	0.76
C-C8	4.46	5.00	3.69	2.04	0.89	0.66
C-C9	4.49	5.75	2.70	2.11	0.26	0.87

Note: The estimated standard deviations for the thermal parameters of the bromine atoms are about ±0.06 and about ±0.50 for the remaining atoms.

Table VII. Fractional coordinates and isotropic thermal parameters for the hydrogen atoms of the para-bromo aniline derivative of homocubane carboxylic acid as refined by least squares diagonal approximation.

	Molecule A				Molecule B			
Atom	X	Y	Z	B	X	Y	Z	B
H-B2	0.189	0.820	0.257	1.65	0.401	0.666	0.544	1.63
H-B3	0.148	0.618	0.291	0.27	0.313	0.490	0.418	2.69
H-B5	-0.169	0.508	0.046	2.79	0.690	0.603	0.272	0.55
H-B6	-0.104	0.720	0.035	0.27	0.771	0.776	0.412	1.08
H-N	-0.156	0.377	0.191	1.80	0.347	0.406	0.226	4.20
H-C1	-0.103	0.183	0.177	0.52	0.286	0.224	0.112	2.58
H-C2	0.145	0.195	0.275	8.13	0.495	0.110	0.108	2.86
H-C3	-0.095	-0.029	0.326	9.11	0.342	-0.008	-0.066	2.80
H-C4	-0.312	0.046	0.320	2.54	0.238	0.172	-0.178	2.73
H-C5	-0.267	0.246	0.272	0.82	0.405	0.391	-0.043	0.25
H-C6	-0.159	0.372	0.457	1.43	0.655	0.398	-0.083	1.25
H-C7	0.077	0.357	0.480	4.19	0.702	0.225	0.005	1.05
H-C8	0.010	0.099	0.539	10.13	0.584	0.052	-0.174	2.59
H-C9	-0.299	0.161	0.541	4.00	0.513	0.221	-0.267	1.61

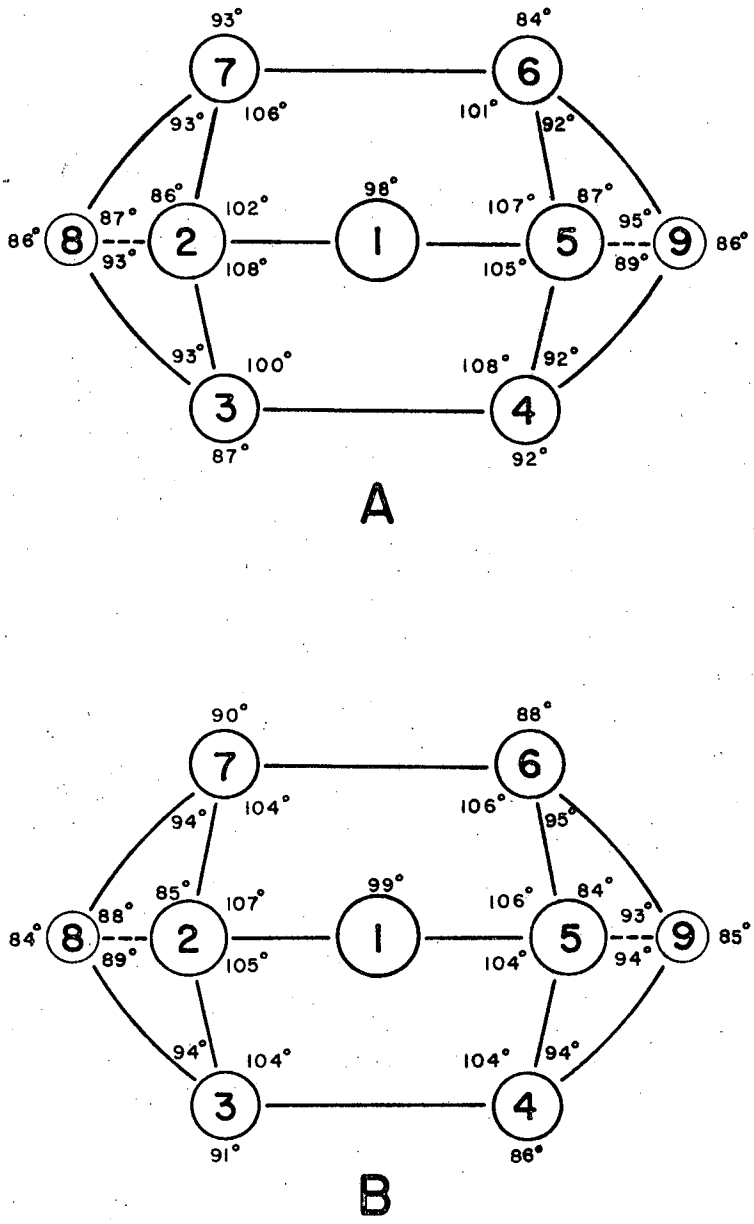
Table VIII. Observed and calculated structure factors for the para-bromo aniline derivative of homo-cubane carboxylic acid.

D. Discussion of the Structure

Two independent measurements of the molecular structure were available from the completed crystal structure since there were four molecules in the unit cell. This provided an extra measure for the accuracy of the structure, and a check on the symmetry of the homocubane. In particular, the twelve carbon-carbon bonds of the benzene rings averaged to 1.36 ± 0.03 A, where 0.03 A is the standard deviation for each measurement. This standard deviation is approximately double the estimated standard deviation as calculated from the final least squares refinement. For this reason, the estimated standard deviations from the least squares refinement have been doubled for the carbon-carbon bonds in the cage structure. The benzene bond angles average to 120.0 ± 3.0°. For the same reason, 3.0° is taken as the standard deviation for the bond angles in the cage structure.

Figure 2 shows a distorted view of the bond angles of the cage structure of both molecules. The bond distances are listed in Table IX.

HOMO-CUBANE



MUB-9366

Fig. 2. A distorted view of the homo-cubane cages showing the bond angles.

Table IX. Carbon-carbon bond distances for the homo-cubane cage (in angstrom units).

Bond	Molecule		Bond	Molecule	
	A	B		A	B
C1 - C2	1.56	1.58	C4 - C9	1.55	1.55
C1 - C5	1.51	1.56	C5 - C6	1.52	1.55
C2 - C3	1.56	1.52	C6 - C7	1.58	1.60
C2 - C7	1.56	1.54	C6 - C9	1.58	1.51
C3 - C4	1.57	1.63	C7 - C8	1.56	1.54
C3 - C8	1.56	1.55	C8 - C9	1.52	1.57
C4 - C5	1.57	1.55			

Note: Each bond distance has an estimated standard deviation of ±0.03A as discussed in the text.

The average for both molecules of bonds of:

C2 - C3 type:	1.55 ± 0.02 A (8 bonds)
C3 - C4 type:	1.60 ± 0.03 A (4 bonds)
C3 - C8 type:	1.55 ± 0.02 A (8 bonds)
C1 - C2 type:	1.56 ± 0.03 A (4 bonds)
C8 - C9 type:	1.55 ± 0.04 A (2 bonds)
All bonds :	1.56 ± 0.03 A (26 bonds)

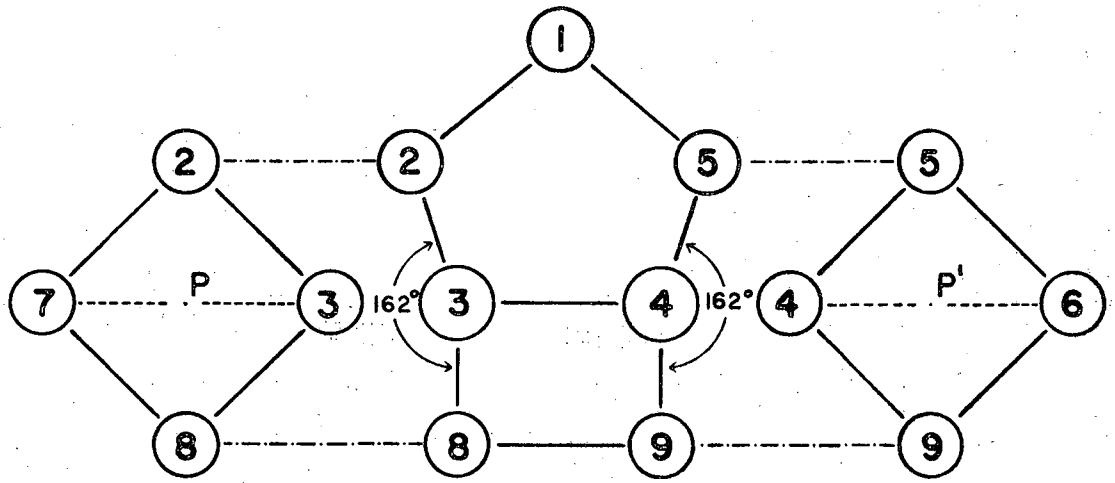
Within the limits of error, the carbon-carbon bond distances are equal, and the cages are symmetrical. If the bond angles are considered, and a standard deviation of ±3.0° is assigned, molecule B has mm2 point symmetry, whereas molecule A is twisted so that its only symmetry is a two-fold axis through the bridge carbon. There is no apparent explanation for this twisting. The bond lengths are in agreement with those found for cubane which are 1.549 ± 0.003 A and 1.553 ± 0.003 A.[15] The eight hydrogen bond lengths on the aromatic rings average to 0.9 ± 0.1 A. Those for the homo-cubane cage (18 bonds) average to 1.1 ± 0.2 A. The two H - N distances average to 0.85 ± 0.01 A.

Another interesting measurement is the amount of puckering in the two cyclobutane rings: C2 - C3 - C8 - C7 and C4 - C5 - C6 - C9. A hypothetical atomic position was calculated for the midpoint between carbons C3 and C7 and between carbons C4 and C6 for both molecules and shown as P and P' in Fig. 3. The left and right portions of the figure show the projections of the two cyclobutane rings of interest. The center portion is a projection of the complete molecule onto a plane along the C3 - C7 and C4 - C6 diagonal axes to show the amount of ring puckering. The individual angles calculated for the amount of puckering are:

Molecule A		Molecule B	
C2 - P - C8	162°	C2 - P - C8	160°
C5 - P'- C9	162°	C5 - P'- C9	163°

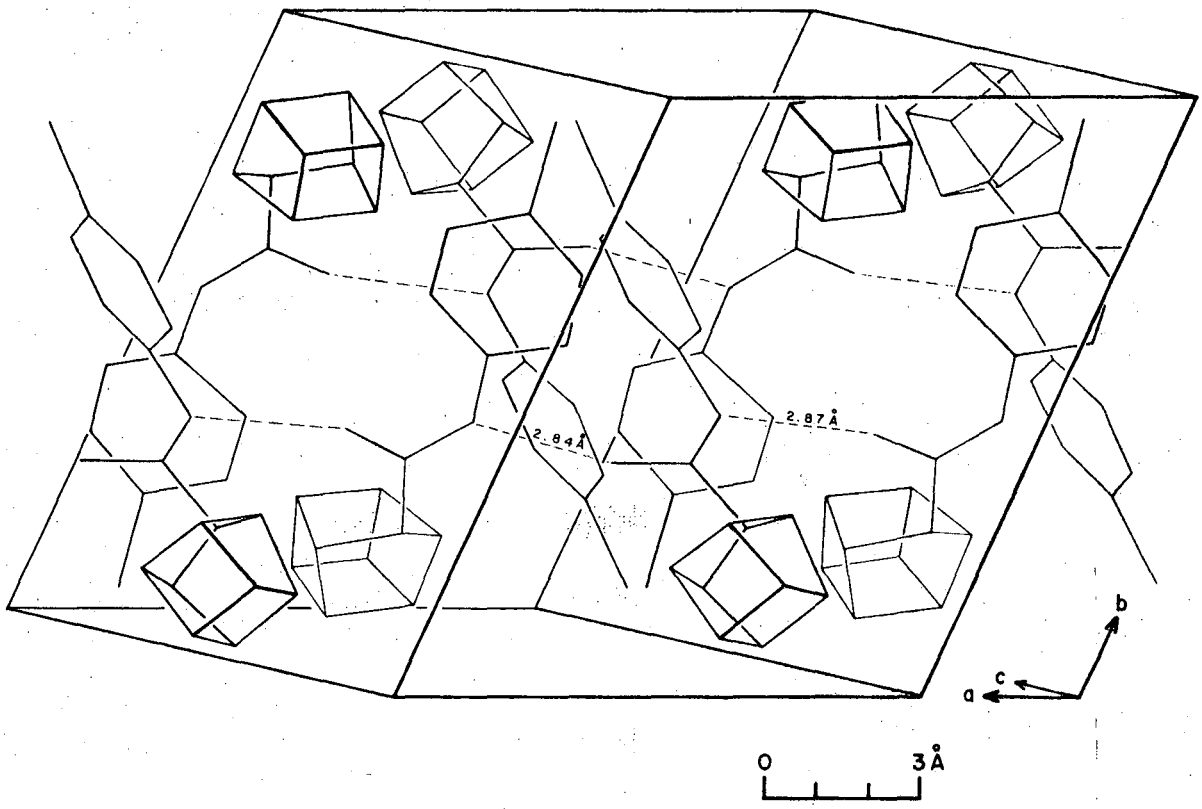
The average for all angles is 162 ± 1.3°.

Figure 4 shows the packing of the molecules in the triclinic cell. This packing arrangement is influenced by the presence of intermolecular hydrogen bonding between the carboxyl oxygens and the nitrogens. The respective interatomic distances are: $oxygen_A$ - $nitrogen_B$, 2.87 ± 0.03 A, and $oxygen_B$ - $nitrogen_A$, 2.84 ± 0.03 A.



MUB-11557

Fig. 3. A projection to show the amount of puckering in the four-membered rings of the homo-cubane cage.



THE PARA-BROMO ANILINE DERIVATIVE
OF HOMO-CUBANE CARBOXYLIC ACID

MUB-9213

Fig. 4. The cyrstal structure of the para-bromo aniline derivative of homo-cubane carboxylic acid.

III. THE CRYSTAL STRUCTURE OF FERRICINIUM PICRATE. $C_{16}H_{12}N_3O_7Fe$.

A. Introduction

The crystal structure for ferrocene, $Fe(C_5H_5)_2$, has been reported,[19] and examples of structures of various derivatives can also be found. (20, 21, 22, 23, 24). These compounds are "sandwich compounds," with the iron atom between parallel five-membered rings of carbon atoms. The constitution of these compounds corresponds to the +2 oxidation state of iron. The analogous compounds of +3 iron, $Fe(C_5H_5)_2^+$, are called ferricinium compounds. This portion of the work is concerned with the structure of the ferricinium ion in the salt ferricinium picrate.

The substance was found to form long, needle-shaped crystals, suitable for a single crystal x-ray structure determination.[25] The results of the work show the ferricinium ion also to be a sandwich, similar to ferrocene, but with a slightly larger distance between the planes of the two rings.

B. Crystal Data

The chemical formula of the substance is $C_{16}H_{12}N_3O_7Fe$, and the molecular weight is 414 gms/mole. A single crystal of dimensions $0.146 \times 0.246 \times 0.308$ mm was mounted on the tip of a small glass fiber with a small drop of General Electric baking varnish No. 1202. The crystal was aligned visually along the needle-axis, and later aligned more precisely on the goniometer. Weissenberg photographs show the crystal to be orthorhombic. The cell dimensions as measured on the goniometer are: $a = 12.478 \pm 0.006$ A, $b = 20.274 \pm 0.006$ A, $c = 6.912 \pm 0.012$ A. The cell volume is 1748.6 A^3. The density as measured by flotation in a mixture of bromoform and benzene is 1.575 gms/cc. The calculated density is 1.572 gms/cc. The number of molecules per unit cell is four, the space group is Cmcm. The linear absorption coefficient is $\mu = 9.35$ cm^{-1} (Mo K_α). No correction was made for absorption.

The intensities of 1249 reflections were measured on the General Electric XRD-5 spectrogoniometer. The spectrogoniometer and the method of measuring the intensity data were described in the first section of this thesis on pages 4-5.

C. Structure Determination

Preliminary Weissenberg photographs indicated the structure to be orthorhomic and C-face centered. The h0ℓ reflections were present only for $\ell = 2n$, indicating a c glide perpendicular to the b axis. These extinctions limit the choice of space group to three: $Cmc2_1$, C2cm, and Cmcm.

To test for the correct space group, the point group symmetry was sought by looking at various reflections to see if there was an anomalous dispersion effect. By looking at the proper reflections, the effect can distinguish between the three possible choices of mm2, 2mm or mmm point symmetry. The test was done with both copper and molybdenum radiation. Cooper was used because it gives a more pronounced dispersion effect when scattering from iron, although the absorption is also more pronounced. Table X lists the results of these measurements.

The trend seems to indicate $hk\ell = \overline{hk}\ell = hk\overline{\ell} = \overline{hk\ell}$, which does not correspond with any of the three choices of point group symmetry, but rather is indicative of 2/m symmetry. However, the discrepancy can be explained by absorption. The dimensions of the crystal were measured at various ϕ angles and the mass absorption coefficient was computed. Table XI lists these figures.

Table X. Anomalous dispersion test for point group symmetry of ferricinium picrate.

Reflection (hkℓ)		φ	Intensity			
			Copper		Molybdenum	
			Uncorrected	Corrected for absorption × 10^2	Uncorrected	Corrected for absorption × 10
1.	711	26°	7126 cps.	360 cps.	1872 cps.	229 cps.
	$\bar{7}11$	206°	7148	361	1895	231
	$71\bar{1}$	26°	7517	380	1880	230
	$\bar{7}11$	206°	7411	374	1884	230
	$7\bar{1}1$	196°	7405	319	1888	226
	$\bar{7}1\bar{1}$	16°	7495	319	1883	226
	$7\bar{1}\bar{1}$	196°	7237	308	1910	229
	$\bar{7}11$	16°	7362	313	1919	230
2.	441	52°	7910	447	2081	260
	$\bar{4}41$	232°	7952	449	2081	260
	$44\bar{1}$	52°	8264	467	2059	258
	$\bar{4}41$	232°	8241	466	2070	260
	$4\bar{4}1$	348°	9850	396	2139	255
	$\bar{4}4\bar{1}$	168°	9755	392	2139	255
	$4\bar{4}\bar{1}$	348°	9869	396	2188	261
	$\bar{4}41$	168°	9778	393	2153	256

Table X. Continued

Reflection (hkℓ)	φ	Intensity			
		Copper		Molybdenum	
		Uncorrected	Corrected for absorption × 10^2	Uncorrected	Corrected for absorption × 10
3. 591	69°	4631 cps.	246 cps.	1185 cps.	146 cps.
$\bar{5}\bar{9}1$	249°	4656	248	1179	145
$59\bar{1}$	69°	4813	256	1201	148
$\bar{5}9\bar{1}$	249°	4627	246	1185	146
$5\bar{9}1$	333°	5364	191	1237	145
$\bar{5}\bar{9}\bar{1}$	153°	5354	191	1229	144
$5\bar{9}\bar{1}$	333°	5354	191	1200	142
$\bar{5}91$	153°	5308	190	1217	143
4. 371	76°	7496	424	1806	225
$\bar{3}\bar{7}1$	256°	7628	431	1803	224
$37\bar{1}$	76°	7670	433	1811	225
$\bar{3}7\bar{1}$	256°	7476	423	1808	225
$3\bar{7}1$	326°	8972	319	1882	221
$\bar{3}\bar{7}\bar{1}$	146°	9113	324	1845	217
$3\bar{7}\bar{1}$	326°	9090	323	1871	220
$\bar{3}71$	146°	8938	318	1842	216

Table XI. Mass absorption coefficients for various ϕ angles as determined by the dimensions of the ferricinium picrate crystal.

ϕ	Dimension (t)	μt_{Cu}	μt_{Mo}
12°(192°)	0.193 mm	1.45	0.180
25°(205°)	0.216	1.62	0.202
50°(230°)	0.231	1.73	0.216
68°(248°)	0.223	1.67	0.209
75°(255°)	0.231	1.73	0.216
130°(310°)	0.146	1.10	0.137
145°(325°)	0.169	1.27	0.158
152°(332°)	0.169	1.27	0.158
168°(348°)	0.185	1.39	0.173

$\mu_{Mo} = 9.35\ cm^{-1}$
$\mu_{Cu} = 75.0\ cm^{-1}$

A simple $e^{-\mu t}$ factor was used to make a correction for the absorption on both the molybdenum and copper data. The corrected molybdenum data within each set agree to 1-2% as shown in Table X. The absorption factor over-corrects for the copper data, most likely because of the limitations of the simple model for larger absorption effects. However, the centric pairs match up in all cases to within 3%, and in most cases to better than 1%, eliminating the possibility of mm2 or 2mm point symmetry.

Continuing with the structure determination, the 1249 independent reflection intensities were corrected for Lorentz and polarization effects and used to compute a three-dimensional Patterson function. The iron-iron vector peak was found at x = 0.00, y = 0.38, z = 0.50. For

special position c, the space group Cmcm gives Harker peaks at (0, 2y, 1/2), so that the iron atom position was immediately determined. Most of the remaining structure was evident from the vector peaks with the iron atom translated to the origin.

The space group Cmcm requires that two mutually perpendicular mirror planes pass through the molecule. One of the mirrors forces the picrate to be planar, lying in xy planes at z = 1/4 and z = 3/4. The picrates are also bisected by the second mirror plane. The two mirror planes further require the cyclopentadiene rings to be eclipsed. However, the evidence gathered from the least squares refinements indicates the structure to be highly disordered.

In particular, the nitro groups are twisted out of the plane of the picrate, and the cyclopentadiene rings are more of a smear of electron density than ten distinct carbon atoms. A three-dimensional Fourier calculated on the basis of the phases from a refinement with an agreement factor of 9.2%, clearly showed a "doughnut-shaped" electron density for the cyclopentadiene rings. Large anisotropic thermal parameters were observed in the z direction (B33) for all the oxygens and one of the nitrogens (N1) of the picrate, and for all the carbons of the ferricinium.

One oxygen (O3) on the nitro group ortho to the phenol oxygen was observed to be considerably disordered. During the early stages of the least squares refinement, all the atoms of the nitro groups had isotropic thermal parameters less than 10, with the exception of the O3 which refined to a B = 36. A difference Fourier calculated on the basis of all the structure except for the O3, clearly gave two large resolved peaks on either side of the plane of the benzene ring at the O3 position. In the final stages, all the atoms were refined anisotropically. The O3 was allowed to move off the z = 1/4 mirror plane and treated as two half-atoms in the least squares calculation. The final refinement puts O3 0.88A in the z direction off the mirror plane, although this cannot be considered an accurate distance.

The disorder is more apparent when the root mean square displacement along the c axis is calculated from the B_{33}'s. Using the formula $B_{33} = 8\pi^2 \bar{u}_{33}^2$, the following values of $\bar{u}_{33}$ are found:

Atom	$\bar{u}_{33}$	Atom	$\bar{u}_{33}$
C1	0.66 A	O2	0.42 A
C2	0.39 A	O3	0.41 A
C3	0.40 A	O4	0.36 A
O1	0.41 A	N1	0.48 A

With such large displacements, the mathematical model of the thermal motion breaks down and the alternative is a disordered structure where the nitro groups are tilted out of the plane of the benzene ring in a random manner, and the cyclopentadiene rings are a "doughnut-shaped" smear of electron density.

The fractional coordinates and their estimated standard deviations for the structure are listed in Table XII. Table XIII lists the anisotropic thermal parameters and their estimated standard deviations. The final agreement factor for this structure is 8.3% using 996 non-zero data. The weighted sum of the squares of the residuals is 236.45 with all weights taken as unity. Table XIV lists the observed and calculated structure factors for the 1249 independent reflections. The asterisks mark the intensities which were observed to be zero. These reflections were assigned zero weight in the least squares calculations.

As was mentioned earlier, two other space groups are possible given the observed $hk\ell$ extinctions. These are $Cmc2_1$ and C2cm. A complete refinement was done for $Cmc2_1$ and a partial refinement for C2cm.

Space group $Cmc2_1$ has only one mirror plane which is perpendicular to the plane of the picrate. This allows free rotation of the nitro groups out of the plane of the benzene ring. Results of a full-matrix least squares calculation with all atoms anisotropic show that all the atoms of

Table XII. Fractional coordinates and their estimated standard deviations for the structure of ferricinium picrate.

Atom	X	Y	Z	σ_x	σ_y	σ_z
Fe	(0.0000)*	0.1862	(0.2500)	--	--	--
C1	0.1344	0.2446	(0.2500)	0.0007	0.0005	--
C2	0.1338	0.2012	0.0843	0.0006	0.0005	0.0016
C3	0.1360	0.1394	0.1486	0.0005	0.0004	0.0014
C4	(0.0000)	0.4416	(0.2500)	--	0.0005	--
C5	0.0939	0.4823	(0.2500)	0.0006	0.0004	--
C6	0.0950	0.5503	(0.2500)	0.0007	0.0004	--
C7	(0.0000)	0.5840	(0.2500)	--	0.0005	--
O1	(0.0000)	0.3812	(0.2500)	--	0.0004	--
O2	0.2123	0.3963	(0.2500)	0.0005	0.0003	--
O3	0.2716	0.4818	0.3756	0.0006	0.0004	0.0017
O4	0.0855	0.6825	(0.2500)	0.0006	0.0003	--
N1	0.1990	0.4511	(0.2500)	0.0006	0.0004	--
N2	(0.0000)	0.6536	(0.2500)	--	0.0005	--

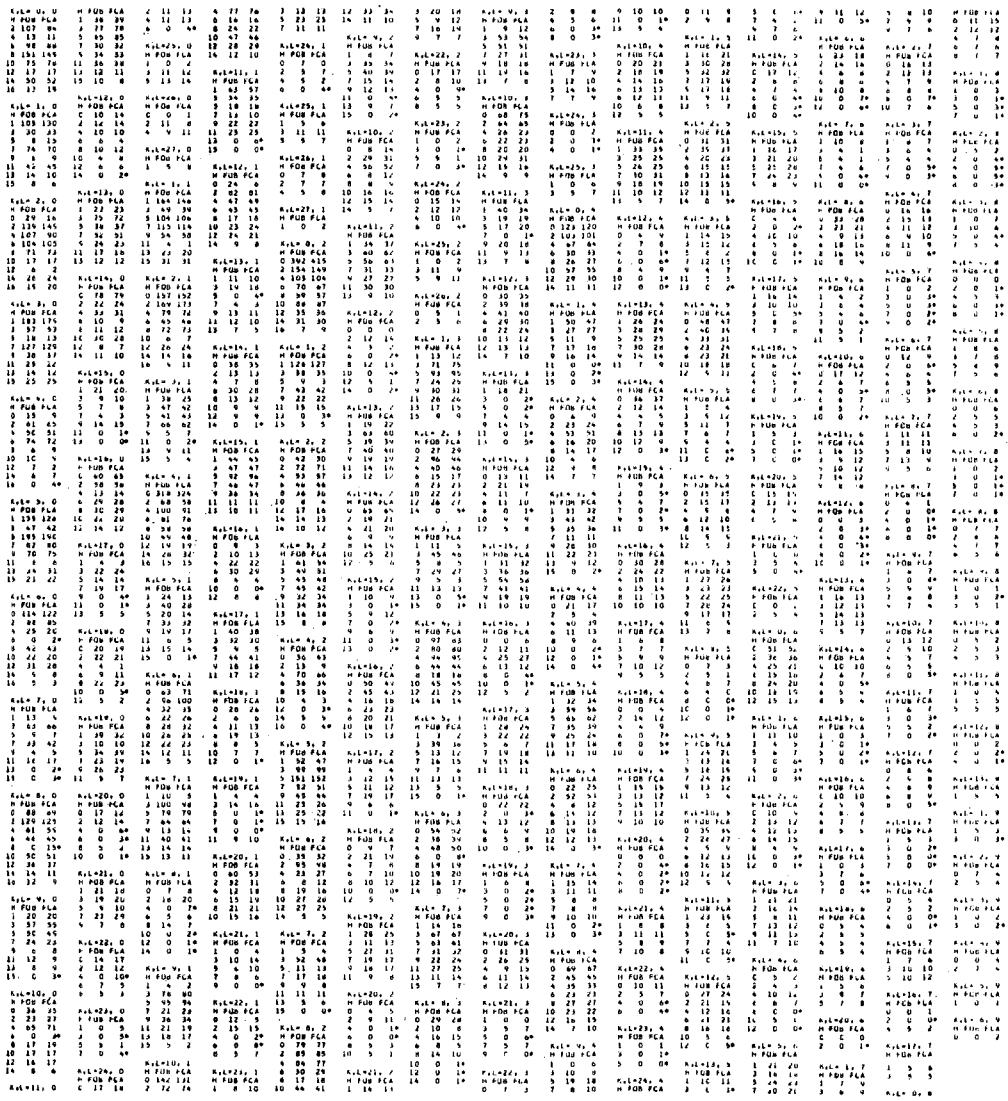
*Coordinates in parentheses were constrained in the least squares calculation.

Table XIII. Anisotropic thermal parameters and their estimated standard deviations for the structure of ferricinium picrate. Units are $Å^2$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\sigma_{B_{11}}$	$\sigma_{B_{22}}$	$\sigma_{B_{33}}$	$\sigma_{B_{12}}$	$\sigma_{B_{13}}$	$\sigma_{B_{23}}$
Fe	3.089	3.826	5.721	(0.000)*	(0.000)	(0.000)	0.059	0.067	0.088	--	--	--
C1	2.128	3.260	34.510	-0.625	(0.000)	(0.000)	0.310	0.375	2.629	0.303	--	--
C2	4.393	12.716	11.926	0.083	1.480	4.888	0.316	0.693	0.742	0.446	0.420	0.649
C3	3.991	9.245	12.960	1.304	0.307	-3.215	0.271	0.448	0.744	0.318	0.361	0.485
C4	3.666	2.990	6.564	(0.000)	(0.000)	(0.000)	0.446	0.408	0.671	--	--	--
C5	3.759	4.292	6.396	0.354	(0.000)	(0.000)	0.327	0.364	0.464	0.272	--	--
C6	4.242	4.215	7.861	-0.684	(0.000)	(0.000)	0.369	0.357	0.560	0.308	--	--
C7	4.393	3.052	5.146	(0.000)	(0.000)	(0.000)	0.499	0.409	0.562	--	--	--
O1	4.488	3.605	13.182	(0.000)	(0.000)	(0.000)	0.398	0.353	0.860	--	--	--
O2	5.289	5.384	14.651	1.416	(0.000)	(0.000)	0.336	0.328	0.687	0.291	--	--
O3	4.391	7.113	13.665	-0.402	-2.675	0.642	0.355	0.558	0.843	0.361	0.483	0.561
O4	7.812	3.762	10.066	-1.377	(0.000)	(0.000)	0.409	0.255	0.494	0.284	--	--
N1	4.137	3.861	18.789	0.325	(0.000)	(0.000)	0.354	0.328	1.065	0.301	--	--
N2	5.877	4.021	5.860	(0.000)	(0.000)	(0.000)	0.562	0.450	0.571	--	--	--

*Thermal parameters in parentheses were constrained in the least squares calculation.

Table XIV. Observed and calculated structure factors for ferricinium picrate.



the picrate remain within 0.02z of the z = 1/4 plane. The O3 was an exception and it moved to z = 0.12. All atoms had B_{33} thermal parameters as large or larger than those refined in the centric space group, further evidence that the structure is indeed disordered. The cyclopentadiene rings refined to an asymmetric structure in space group $Cmc2_1$. When the more symmetric ferricinium structure from the centric refinement was introduced, it refined back to the asymmetric structure. The agreement factor is R = 7.3% and the weighted sum of the squares of the residuals is 181.03. All weights were assigned to unity except for the zero intensities which were given zero weight.

Space group C2am offers no particular advantage over the centric space group since the mirror plane still requires the picrate to be planar. For this reason, refinement was not completed for this space group.

D. Discussion of the Structure

The space group Cmcm requires that two mutually perpendicular mirror planes pass through the molecule. The picrate anions lie in xy mirror planes at z = 1/4 and z = 3/4. They are also bisected by the yz mirror planes at x = 0 and x = 1/2. The iron and four atoms of the picrate lie at the intersection of the two mirror planes. The cyclopentadiene rings are in planes perpendicular to x, at x = 0.13 and x = -0.13. Figure 5 illustrates one molecule of ferricinium picrate in a projection along the c axis. The O3 atom (dotted in the figure) was allowed to move off the z = 1/4 mirror and treated as two half-atoms in the least squares calculation. The reason for this is discussed earlier in the text. Eight carbons of the cyclopentadiene rings also lie off the z = 1/4 mirror, and are illustrated by two concentric circles, the outer one solid and the inner one dotted. Because of the disorder in the structure, the bond distances and bond angles as given in the figure cannot be considered too reliable.

The disordered structure for the picrate in this work is in agreement with similar structures determined by other workers. In preliminary

results for potassium picrate,[26] the ortho nitro group is rotated 26° and the para group 6° out of the plane of the benzene ring. For picryl azide,[27] $C_6H_2N_6O_6$, the two ortho groups are rotated 14° and 58° respectively and the para group 7° out of the plane.

The disorder of the cyclopentadiene rings can be explained by a smearing of the electron density in the ring, also observed by Dunitz, Orgel and Rich for the ferrocene structure.[19] Because of this smearing, the iron-carbon and carbon-carbon bond lengths are not known to better than 0.02 A. An average iron-carbon distance in ferricinium of 2.06 A agrees within the accuracy of Dunitz, et al.[19]

A more reliable measurement is from the iron to the plane of the cyclopentadiene ring. The value calculated for this structure, taking an average value of x, is 1.684 ± 0.005 A. In the ferrocene structure, the distance from the iron to the center of gravity of the ring is 1.660 A. It was suggested by I. Pavlik and J. Klikarka[28] on the basis of infrared spectra measured for ferricinium picrate, that the iron-cyclopentadiene ring bond is weaker and more ionic than for ferrocene. This could account for the increased distance between the iron and the planes of the cyclopentadiene rings.

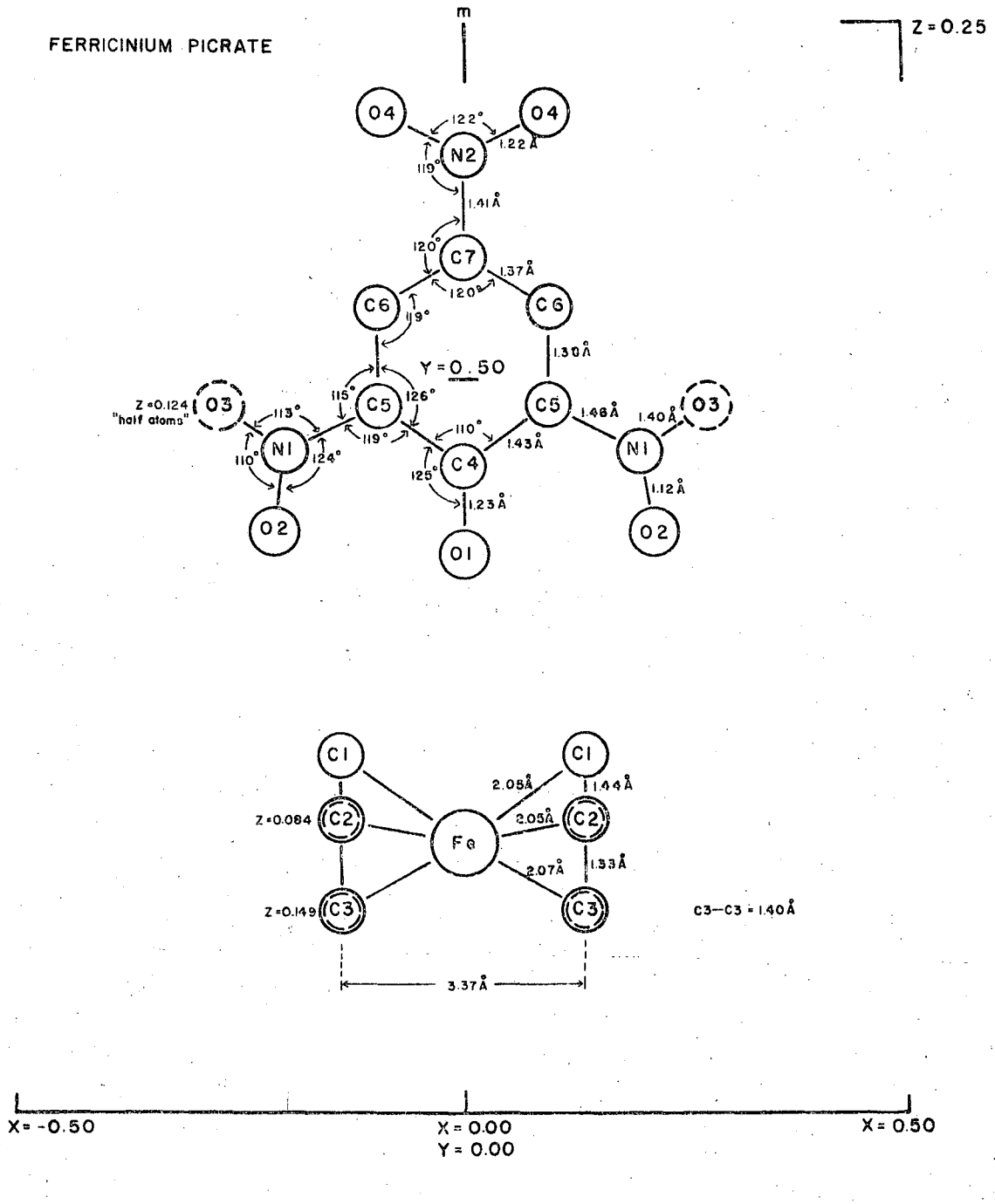


Fig. 5. The crystal structure of ferricinium picrate.

ACKNOWLEDGEMENTS

I am grateful to Professor David Templeton for his continued support and interest in this work. Our many discussions, particularly in regard to the interpretation of the results were most helpful. I am also indebted to Dr. Allan Zalkin for the use of his many computer programs and for his help in becoming acquainted with the methods of solving crystal structures. I wish to thank Dr. Ted Hopkins for his patience in answering many of my questions. I wish to thank Mrs. Helena Ruben for her help in the laboratory. I am also greateful to Mr. Tatzuo Ueki and Mr. Barry DeBoer for helpful discussions. I would like to thank Dr. Peter Rock, Dr. Dale Whalen and Dr. R. E. Bozak for preparing the crystal samples for this work.

I am indebted to the Lawrence Radiation Laboratory and the United States Atomic Energy Commission for their generous support of this work.

References

1. R. Abegg, Handbuch Der Anorganishen Chemie, IV Band 3 Abteiling 4 Teil, Lieferung 1-2, pp. 669-696.
2. The preparation was discovered by Dr. Peter Rock, Department of Chemistry, University of California, Davis, California.
3. Private communication with Dr. Peter Rock, July, 1964.
4. Analytical Laboratory, Department of Chemistry, Lewis Hall, University of California, Berkeley, California.
5. Analysis done by Mr. Ray Clem, Analytical Laboratory, Lawrence Radiation Laboratory, Berkeley, California.
6. M. Linhard, W. Manthey and K. Plieth, Z. Electrochem. 57, 862-866 (1953).
7. N. F. M. Henry, H. Lipson and W. A. Wooster, The Interpretation of X-ray Diffraction Photographs, MacMillan and Co., London, 1960.
8. M. J. Buerger, X-Ray Crystallography, John Wiley and Sons, New York, 1942.
9. Structure Reports, Volume 11, A. J. C. Wilson, editor, N. V. A. Oosthoek's Mij, Utrcht., p. 421, 1947-48.
10. International Tables for X-Ray Crystallography, Volume III, Physical and Chemical Tables, Kynoch Press, Birmingham, England, 1962, pp. 201-213.
11. Walter C. Hamilton, Acta Cryst. 18, 502-510 (1965).
12. M. A. Porai-Koshits, E. K. Iukhno, A. S. Antsishkina and L. M. Dikareva, Soviet Physics, Crystallography 2, 366-375 (1957), in English translation.
13. Interatomic Distances, Special Publication No. 11, The Chemical Society, London, 1958, p. S 17.
14. Eaton and Cole, J. Am. Chem. Soc. 86, 3157 (1964).
15. Everly B. Fleischer, J. Am. Chem. Soc. 86, 3889 (1964).
16. For a review and discussion of the many strained polycyclic compounds containing cyclobutane rings which have recently been synthesized, see Ph.D. Thesis by Dale L. Whalen, "Synthesis and Rearrangements of some Strained Cage Compounds," University of California, Berkeley, California.

17. Professor William Dauben, Department of Chemistry, University of California, Berkeley, California. Dale L. Whalen, see reference 16 for Ph.D. Thesis.

18. M. J. Buerger, Vector Space, John Wiley and Sons, New York, 1959.

19. J. D. Dunitz, L. E. Orgel, and A. Rich, Acta Crystallographica 9, 373 (1956).

20. N. D. Jones et al., Acta Crystallographica 19, 330 (1965).

21. Mary B. Laing and K. N. Trueblood, Acta Crystallographica 19, 373 (1965).

22. Z. L. Kaluski and Yu. T. Struchkov, Journal of Structural Chemistry 6, 296 (1965), translated into English from Russian.

23. Z. L. Kaluski, Yu. T. Struchkov, and R. L. Avoyan, Journal of Structural Chemistry 5, 683 (1964), translated into English from Russian.

24. O. V. Starovskii and Yu. T. Struchkov, Journal of Structural Chemistry 5, 231 (1964).

25. Prepared by Professor R. E. Bozak, California State College, Hayward, California.

26. Gus J. Palenik, U. S. Naval Ordnance Test Station, China Lake, California. The results are preliminary. The final work is to be published soon.

27. A. S. Bailey and C. K. Prout, Journal of the Chemical Society 4867 (1965).

28. I. Pavlik and J. Klikorka, Collection Czech. Chem. Commun. 30 (3), 664 (1965). Reference found in Chemical Abstracts 63, 1343f (1965).