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Chemical Crystallography at the High Flux Beam Reactor[*]

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Abstract

A brief description is given of the neutron diffraction facilities at the Brookhaven High Flux Beam Reactor. Present instrumentation includes two fully automated four-circle diffractometers. Cryogenic refrigerators and furnaces make possible the collection of three-dimensional intensity data from single crystals over the full temperature range 10-1200 K. Recent crystallographic research at the Reactor is illustrated by three representative studies-on ferrocene, $H_3Ni_4(C_5H_5)_4$, and pyridine-2,3-dicarboxylic acid. A survey of important areas for future work is attempted: these include metal hydrides, and charge-density studies by combined x-ray and neutron diffraction methods. New avenues are expected to open up with increasing use of the Reactor for collaborative research.

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Introduction

The unique neutron diffraction facilities at the Brookhaven High Flux Beam Reactor (HFBR) currently are being exploited in a wide variety of crystallographic studies. In this work, attention is focused on crystal structures where H atoms are important, and on disordered or partially ordered structures, since this is where neutron diffraction, alone or in conjunction with x-ray diffraction, offers unique advantages for determining molecular structure and investigating chemical bonding. Examples of recent work include studies of transition metal hydride coordination complexes,[1] binary[2] and ternary[3] metal hydrides, analyses of hydrogen bonding in carbohydrates,[4] investigations of the distributions of mobile ions in ionic conductors,[5,6] and combined x-ray and neutron diffraction (X-N) studies of charge-density distributions in hydrogen-bonded crystals.[7,8] In this lecture I will first briefly describe the instrumentation available for chemical crystallography at the HFBR, including the specialized low- and high-temperature facilities. Several refrigerators and furnaces make possible the collection of three-dimensional diffraction data from single crystals over the full temperature range 10-1200 K. After describing the instrumentation, I will go on to discuss the results obtained in three recent representative studies, and then conclude with some remarks on future plans.

Instrumentation

Two fully-automated four-circle diffractometers are currently in operation at the HFBR, and it is planned to install a third diffractometer during 1979. At the present reactor power of 40 million watts, the thermal neutron flux at the monochromator position for the crystallography beam ports (H6) is approximately 3×10^9 n·cm^{-2}·sec^{-1} with 20' in-pile collimation.[9] After monochromatization, this translates into an effective flux at the sample

position of about 6×10^6 n·cm^{-2}·sec^{-1} for neutron wavelengths near 1 Å. These fluxes will increase proportionately with the scheduled increase of reactor power to 60 million watts.

The diffractometers at the HFBR use Electronics and Alloys 55 cm i.d. χ-circles, which are offset from the ω-axis by approximately 9 cm. This arrangement allows large pieces of equipment, such as specially adapted closed-cycle helium refrigerators[a] and a heavy-duty furnace[10] to be mounted inside the χ-circles. All such equipment is compatible with both the diffractometers, thus allowing for maximum flexibility in operations.

The diffractometers are controlled by DEC PDP 11 computers, operating under the Reactor Experimental Control Facility.[11] A flexible crystallographic software package[12] has been written for this system, which includes all standard operations such as automated crystal centering and refinement of lattice constants, and collection of intensity data for any desired portion of reciprocal space. Raw step-scan profiles are recorded on magnetic tape, for subsequent off-line analysis.

<div align="center">Results</div>

Ferrocene

In the 1950's, the early x-ray diffraction studies of ferrocene[13-15] established the sandwich structure (I) and indicated that the Cp ligands[b]

I

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[a]Air Products and Chemicals, Inc., DISPLEX® Model CS-202.

[b]Abbreviations: Cp = η^5-cyclopentadienyl, Me = methyl, Ph = phenyl.

should be staggered, since the Fe atom lies at a center of inversion in space group $P2_1/a$. However, over the past twenty years a variety of evidence has been presented to indicate that the crystal structure is disordered at room temperature: from heat capacity measurements, a λ-point phase transition has been demonstrated to occur at 164 K, and this transition has been associated with an onset of rotational disorder of the Cp rings.[16] The original neutron diffraction measurements of Willis[17,18] were interpreted in terms of a disordered model, with one-third of the rings occupying positions rotated 36° with respect to the others, but these data were somewhat limited in resolution. Obviously, if rotational disorder of the rings is present, the supposition that individual ferrocene molecules in the crystal must be staggered is not valid. An electron diffraction study indicated that ferrocene in the gas phase has an eclipsed equilibrium configuration,[19] and the barrier to internal rotation was estimated to be 0.9(3) kcal/mole.[20]

We decided to carry out a new neutron diffraction study of ferrocene, in order to make as detailed an investigation of the disorder in the crystal structure as possible. We also wished to determine whether the protons were bent out of the planes of the Cp rings toward the Fe atom, as was indicated by the electron diffraction work to be the case in the gas phase. Complete three-dimensional neutron diffraction data out to $\sin\theta/\lambda \approx 0.65$ $\overset{\circ}{A}^{-1}$ were collected under ambient conditions and at a temperature just above the phase transition (173 K). Attempts to cool large single crystals through the phase transition were unsuccessful.

Our results confirm that the structure is indeed disordered above the phase transition.[21] The room-temperature nuclear scattering density map (Fig. 1(a)) shows markedly smeared peaks; the effect is especially pronounced for the H atoms at the 1 and 5 positions. This smearing is only slightly

reduced at 173 K (Fig. 1(b)), indicating that the disorder is not primarily dynamic in character. Rather it results from the presence of molecules in different orientations randomly distributed throughout the crystal. We have refined a two-fold disorder model, as indicated in Fig. 1(a), as well as carrying out refinements based on an ordered model, first with conventional anisotropic thermal parameters, and then including third- and fourth-order thermal tensors. In the disordered model, the rings are found to be twisted approximately 24^0 with respect to one another about an axis which does not coincide with the center of the rings. Such a model could be regarded as resulting from the superposition of two staggered or two (nearly) eclipsed configurations.[a] A possible configuration consistent with the present model, with the two Cp rings rotated about 12^0 from the eclipsed position, is indicated in Fig. 2. However, it is important to emphasize that there is no particular uniqueness to the two-fold model. The observed scattering density doubtless could be fit approximately equally well by a large number of disorder models. In fact, among the models we tried, the best fit[b] was obtained with ordered rings and incorporating higher-order thermal tensors.

At 173 K, all H atoms are found to be displaced out of the plane of the Cp rings toward the Fe atom. The mean displacement is $0.030(7)$ Å,[c] corresponding to an inclination of the C-H vector to the plane of $1.6(4)^0$. Based on gas-phase electron diffraction data, the inclination toward the metal was calculated to be $3.7(9)^0$.[22]

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[a] In order to allow an exactly eclipsed configuration, the two disordered rings would have to be rotated by 36^0.

[b] $R(F) = 0.06$ at room temperature for 687 independent reflections.

[c] Standard deviations of mean values have been calculated throughout as $\{\Sigma(X_i-\bar{X})^2/n(n-1)\}^{\frac{1}{2}}$, where n is the number of observations.

Tetrakis(η^5-cyclopentadienyl)tetranickeltrihydride, $H_3Ni_4Cp_4$

As part of our continuing collaboration with R. Bau's group at the University of Southern California, we have recently completed a neutron diffraction study of the tetrahedral cluster transition metal hydride complex, $H_3Ni_4Cp_4$.[23] This compound, one of the few known examples of polynuclear organometallic complexes with no carbonyl ligands, was isolated from the reaction of CpNi(NO) with $AlCl_3$ and $LiAlH_4$.[24] The presence of the three hydride ligands was inferred from the mass spectrum of the complex, which shows ions resulting from the loss of one, two, and three H atoms. A particularly interesting aspect of $H_3Ni_4Cp_4$ is its electronic configuration. Ni_4Cp_4, an unknown species, would have the expected "closed-shell" 60-electron configuration[25] and would be diamagnetic. Such a closed-shell complex is in fact known as $H_4Co_4Cp_4$.[26] $H_3Ni_4Cp_4$, however, has three additional electrons which are all unpaired,[24] making the complex a rare example of a paramagnetic metal cluster complex. Infrared spectroscopic data give no indication of the presence of the hydride ligands, but absorptions due to stretching vibrations of bridging hydrides frequently do not show up in IR spectra. Moreover, the paramagnetic nature of $H_3Ni_4Cp_4$ prevents the hydride ligands from being detected in the NMR spectrum.

An x-ray study of $H_3Ni_4Cp_4$ was conducted by Müller, Huttner and co-workers in 1973.[24] Although the hydride ligands were not located directly, these investigators were able to assign them to face-bridging positions, based on the observation that three of the Cp rings are tilted away from the fourth. From our neutron diffraction analysis, carried out at a temperature of 81 K,[a] we have confirmed the proposed structure (Fig. 3), and have determined accurate

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[a] R(F) = 0.11 for 2656 independent reflections with $\sin\theta/\lambda < 0.68$ $\overset{o}{A}^{-1}$.

values for bond distances and angles associated with the triply-bridging

hydride ligands, as summarized in Table I.

The complex has approximate C_{3v} symmetry, and the H_3Ni_4 core may be

envisaged as a tri-capped tetrahedron, or alternatively as a cube with one

corner missing (Fig. 4). No indication could be found for disorder of the

type in which H atoms partially occupy all four faces of the Ni_4 cluster.

The average metal-metal distance in $H_3Ni_4Cp_4$ (2.469(6) Å) is slightly

shorter than that measured at ambient temperature in nickel metal (2.492 Å).[27]

It is, however, considerably longer than the Ni-Ni single bond distances in

the molecules Ni_2Cp_2 (PhC≡CPh) (2.33 Å)[28] and $Ni_3Cp_3(CO)_2$ (2.39 Å),[29] which

contain bridging ligands, and the unbridged Ni-Ni bond distances in

$K_4[Ni_2(CN)_6]$ (2.32 Å)[30] and $Rb_4[Ni_2(CN)_6]$ (2.29 Å).[31] The length of the

Ni-Ni bonds in $H_3Ni_4Cp_4$ may reflect the delocalization of the three excess

electrons into antibonding Ni-Ni orbitals. Hoffmann and co-workers have

recently carried out extended Hückel calculations on $H_3Ni_4Cp_4$ and related

tetrahedral clusters.[32] They have shown that for the 60-electron Ni_4Cp_4

cluster, the lowest unoccupied level corresponds to a degenerate set of three

low-lying antibonding orbitals of t_1 symmetry, which in $H_3Ni_4Cp_4$ become

occupied by electrons from the H atoms. In addition to explaining the rather

long Ni-Ni distances in the cluster, this bonding picture rationalizes why a

fourth H atom cannot conveniently be added to $H_3Ni_4Cp_4$.

The present structure may be considered as a model for hydrogen

chemisorption on nickel metal. The H atoms are situated an average of

0.90(3) Å from the Ni_3 planes, and it seems reasonable that the absorption of

hydrogen gas on the {111} surfaces of a ccp metal, or the {001} surfaces of a

hcp metal, may lead to a configuration very similar to that found in $H_3Ni_4Cp_4$.[33]

A similar bonding situation is found in $HFeCo_3(CO)_9(P(OMe)_3)_3$.[34] In that

compound, the hydride ligand is found 0.978(3) $\overset{o}{A}$ above the Co_3 face of the $FeCo_3$ tetrahedral cluster.

The average Ni-C distance in $H_3Ni_4Cp_4$ (2.132(5) $\overset{o}{A}$) is very similar to that found in $Cp_2Ni_2(PhC\equiv CPh)$ (2.11(1) $\overset{o}{A}$)[28] and other cyclopentadienyl nickel complexes. The average absolute out-of-plane deviation of the C atoms in the Cp rings is only 0.003 $\overset{o}{A}$, while that for the H atoms is 0.025 $\overset{o}{A}$.[a] The H atoms on Cp(1) are systematically bent toward Ni(1) with an average displacement of 0.017(6) $\overset{o}{A}$, but no such trend is apparent for the other three rings. The observed displacements probably to a large degree reflect the influence of steric and packing factors.

Pyridine-2,3-dicarboxylic Acid (Quinolinic Acid)

We have recently studied the charge-density distribution in pyridine-2,3-dicarboxylic acid (quinolinic acid, QNA) by a combination of X-ray and neutron diffraction techniques. QNA possesses an interesting crystal structure, with a short intramolecular O(2)---H(5)---O(3) hydrogen bond.[35] The molecules occur in the zwitterion form in the crystal, as illustrated in Fig. 5, and are joined into layers by means of intermolecular hydrogen bonds N(1)-H(4)---O(4). There are no hydrogen bonds between layers. A neutron diffraction study at ambient temperature indicated that the short hydrogen bond (O---O : 2.398(3) $\overset{o}{A}$) is nearly linear and is asymmetric, with the proton displaced approximately 0.04 $\overset{o}{A}$ from the bond midpoint.[36] This observed asymmetry is almost certainly due to intramolecular electronic effects: the proton is located closer to the 3-carboxyl group (meta to the ring N atom) in agreement with the equilibrium position predicted by an INDO calculation.

Neutron diffraction measurements have been made for both normal quinolinic acid (H-QNA)[36,37] and material recrystallized from D_2O (D-QNA), in order to

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[a]The planes are fit to the five carbon positions.

evaluate the effects of deuterium substitution on the structure. A summary of the isotope effect in the short hydrogen bond is given in Table II. At both 100 and 298 K, the hydrogen moves approximately 0.025 $\overset{o}{A}$ further away from the bond midpoint, upon replacement with deuterium.[a] The fact that this effect is independent of temperature is consistent with the generally accepted interpretation of such isotope effects as zero-point energy phenomena.[38]

The deformation electron density in D-QNA has been computed by a modified X-N method, using data collected at 35 K.[39] The structure is centric (space group $P2_1/c$). X-ray data were measured with Nb filtered MoKα radiation, and extend to $\sin\theta/\lambda = 1.15 \ \overset{o}{A}{}^{-1}$ (5499 independent reflections).[b]

A section of the deformation map through the plane of the pyridine ring is shown in Fig. 6. This map was computed by the following procedure. Positional and anisotropic thermal parameters for C, N and O atoms were taken from a high-order x-ray refinement ($\sin\theta/\lambda > 0.65 \ \overset{o}{A}{}^{-1}$), while parameters for the H(D) atoms were taken from the neutron refinement. Systematic differences were found between the neutron and high-order x-ray thermal parameters for the C, N and O atoms, so the neutron thermal parameters for the H(D) atoms were adjusted, in an attempt to allow for these differences.

Well-defined maxima are found in all covalent bonds in the molecule, and peaks are observed near all four O atoms in regions normally associated with "lone-pair" density. The height of the peaks between D(5) and O(2), O(3) in the short intramolecular hydrogen bond is about 0.3 $e \cdot \overset{o}{A}{}^{-3}$, or roughly half that found in the covalent bonds. This may be compared to peak heights of approximately

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[a] The O(2)---O(3) distance exhibits no significant change upon deuteration. This observation is perhaps not too surprising, since the hydrogen bond is subject to intramolecular constraints.

[b] The neutron data extend to $\sin\theta/\lambda = 0.71 \ \overset{o}{A}{}^{-1}$; $R(F^2) = 0.03$ for 1694 independent reflections.

0.5 e·$Å^{-3}$ found in the hydrogen bond in sodium hydrogen diacetate (O···O = 2.48(1) $Å$).[40] In D-QNA, the asymmetric character of the intramolecular hydrogen bond is not readily apparent in the deformation map. It is interesting to compare the density in the intramolecular hydrogen bond with that in the intermolecular N(1)-D(4)---O(4) hydrogen bond (shown in the upper right portion of Fig. 6). The height of the "lone-pair" peak on O(4) pointing in the direction of D(4) is approximately 0.45 e·$Å^{-3}$. Both D(4) and D(5) fall within negative regions of the deformation map, as expected since they are acidic and should have net positive charge. D(4) occurs at a point of moderate density gradient, while D(5) lies near a local minimum.

Future Plans

Let me now conclude by attempting to summarize our future plans. Many of the types of crystallographic studies I have mentioned earlier should continue to play a central role in our neutron diffraction program. In particular, metal hydrides, and charge-density studies will receive great attention.

Interest in the metal hydrides stems from their potential importance as hydrogen-storage media, and from the fact that they provide an opportunity to study the details of bonding between hydrogen and metals, which can be done to high accuracy only by means of neutron diffraction. Metal hydride coordination complexes are often implicated as intermediates in homogeneous catalysis of hydrogenation reactions, and as I have indicated, cluster complexes may be regarded as providing models for the interaction of hydrogen with metal surfaces. We have just recently completed a study of a system with an octahedral cluster, $[HCo(CO)_{15}]^{-}[(Ph_3P)_2N]^{+}$,[41] which contains an interstitial hydride, located at the center of a Co_6 octahedron. In the future, increased emphasis can be

expected on large cluster systems, a number of which may prove to contain interstitial hydrides. The availability of reliable cryogenic refrigerators, and the high fluxes attainable at present neutron sources such as the HFBR, make work on large, complex systems very feasible.

In the area of charge-density analysis, considerable emphasis will likely be placed on relatively simple systems, which provide the possibility of making quantitative comparisons between theory and experiment. It would be very interesting to study simple salts, such as sulfates and phosphates, etc. Several first-row transition metal hydride complexes are likely candidates for investigation.

Other areas of interest, which I have not dealt with here, include ferroelectrics, and hydrogen-bonded organic materials of biochemical importance, such as the barbiturates and related compounds which are currently the subject of a collaborative effort at the HFBR with B. M. Craven. We hope that a number of new avenues of research will open up, as a wider spectrum of chemists becomes aware of the potential applications of neutron diffraction to solve structural problems, and with expanding use of the HFBR for collaborative research.

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Table I. Selected bond distances and angles in $H_3Ni_4Cp_4$

Distances (Å)

Ni(1)-H(1)	1.720(8)
Ni(1)-H(2)	1.718(9)
Ni(1)-H(3)	1.711(7)
Mean	1.716(3)
Ni(2)-H(1)	1.684(7)
Ni(2)-H(3)	1.674(8)
Ni(3)-H(1)	1.674(8)
Ni(3)-H(2)	1.661(9)
Ni(4)-H(2)	1.672(8)
Ni(4)-H(3)	1.704(8)
Mean	1.678(6)
Ni(1)-Ni(2)	2.490(3)
Ni(1)-Ni(3)	2.464(3)
Ni(1)-Ni(4)	2.478(3)
Mean	2.477(8)
Ni(2)-Ni(3)	2.458(3)
Ni(2)-Ni(4)	2.454(3)
Ni(3)-Ni(4)	2.471(3)
Mean	2.461(5)
H(1)···H(2)	2.317(11)
H(1)···H(3)	2.305(10)
H(2)···H(3)	2.326(9)
Mean	2.316(6)

Overall Mean Values

Ni-Ni	2.469(6)
Ni-H	1.691(8)
C-C (Cp rings)	1.408(5)
C-H	1.076(8)

Angles (°)

Ni(1)-H(1)-Ni(2)	94.0(4)
Ni(1)-H(1)-Ni(3)	93.1(4)
Ni(1)-H(2)-Ni(3)	93.6(4)
Ni(1)-H(2)-Ni(4)	93.9(4)
Ni(1)-H(3)-Ni(2)	94.7(4)
Ni(1)-H(3)-Ni(4)	93.0(3)
Mean	93.7(3)
Ni(2)-H(1)-Ni(3)	94.1(4)
Ni(3)-H(2)-Ni(4)	95.7(4)
Ni(2)-H(3)-Ni(4)	93.1(4)
Mean	94.3(8)

Overall Mean Values

Ni-H-Ni	93.9(3)
H-Ni-H	86.1(6)
Ni-Ni-Ni	60.0(2)

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Table II. Effect of deuterium substitution in the intramolecular

hydrogen bond in pyridine-2,3-dicarboxylic acid (distances in Å).

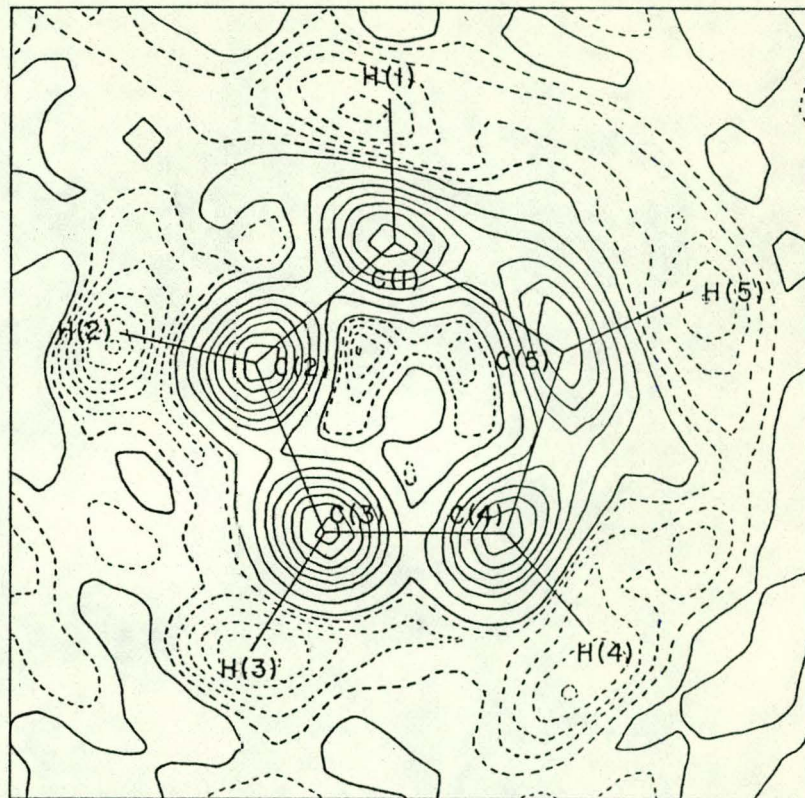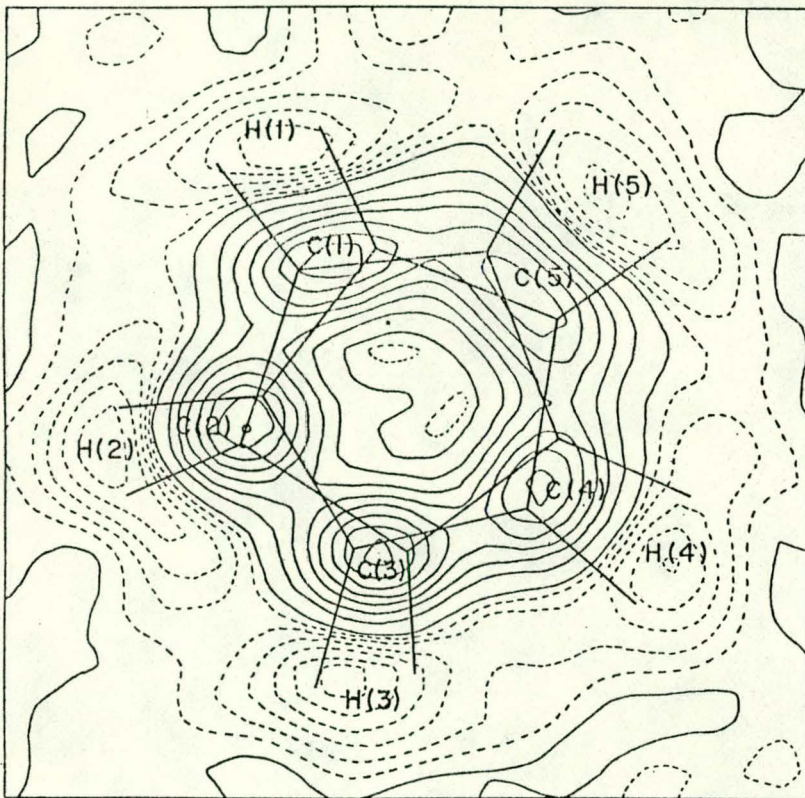|	O(2)···H(5)	O(3)···H(5)	O(2)···O(3)
100 K (H)	1.227(3)	1.176(3)	2.400(2)
100 K (D)	1.253(2)	1.150(2)	2.401(2)
298 K (H)	1.238(5)	1.163(5)	2.398(3)
298 K (D)	1.257(2)	1.138(2)	2.393(2)

Fig. 1. Observed nuclear scattering-density map sections through the
plane of the Cp ring in ferrocene. Negative contours are dashed and contour
intervals are 0.2 and 0.067 $\times 10^{-12}$ cm·Å^{-3}, for positive and negative contours,
respectively.

(a) Map at room temperature with atomic
positions from the two-fold dis-
ordered model superimposed

(b) Map at 173 K with atomic positions
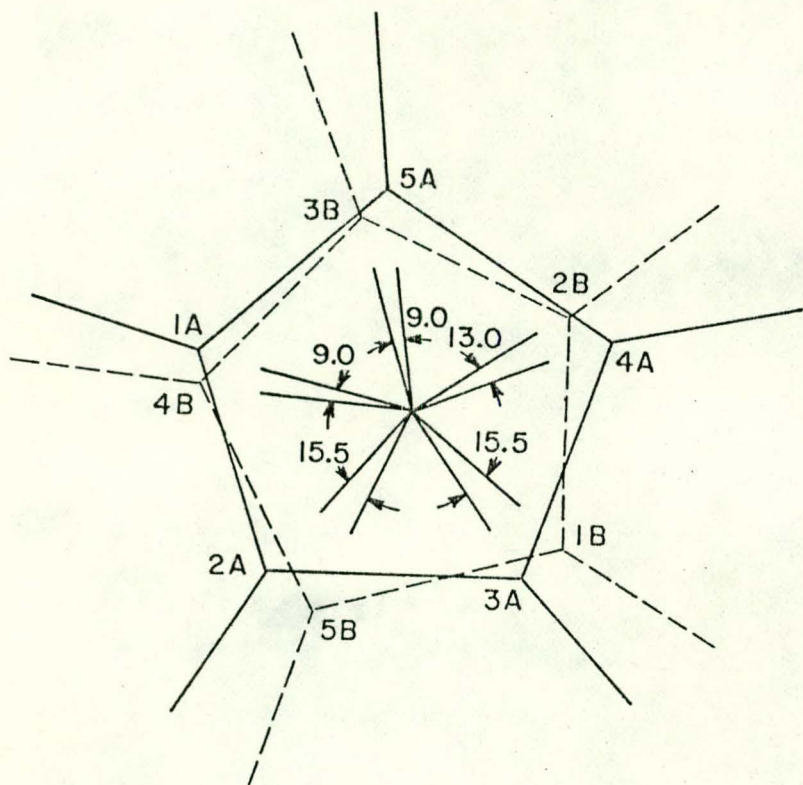from the ordered model incorpo-
rating higher-order thermal tensors
superimposed

Fig. 2. Possible (nearly) eclipsed configuration
for a ferrocene molecule, consistent with
the two-fold disordered model
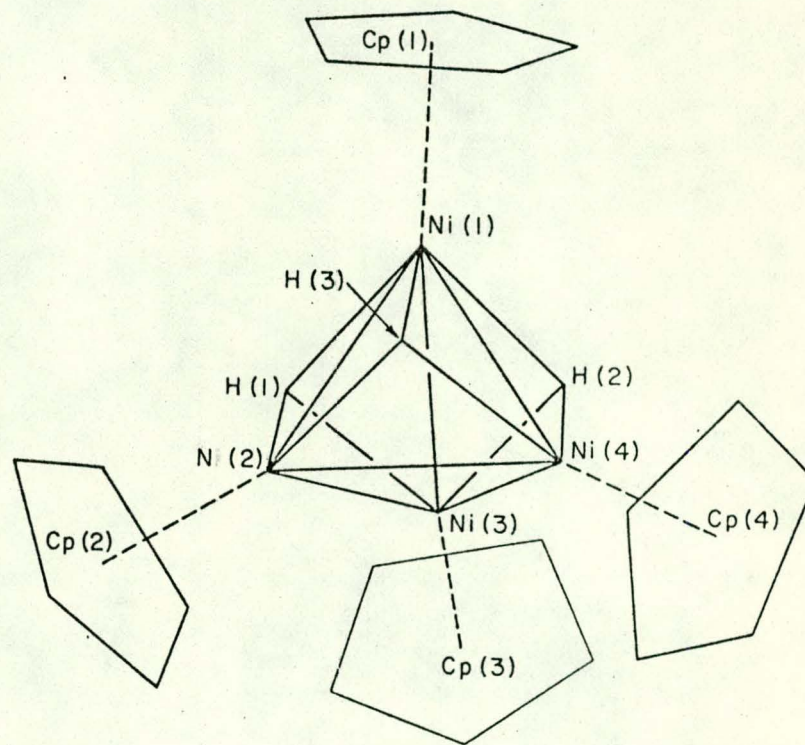
Fig. 3. Schematic view of $H_3Ni_4Cp_4$
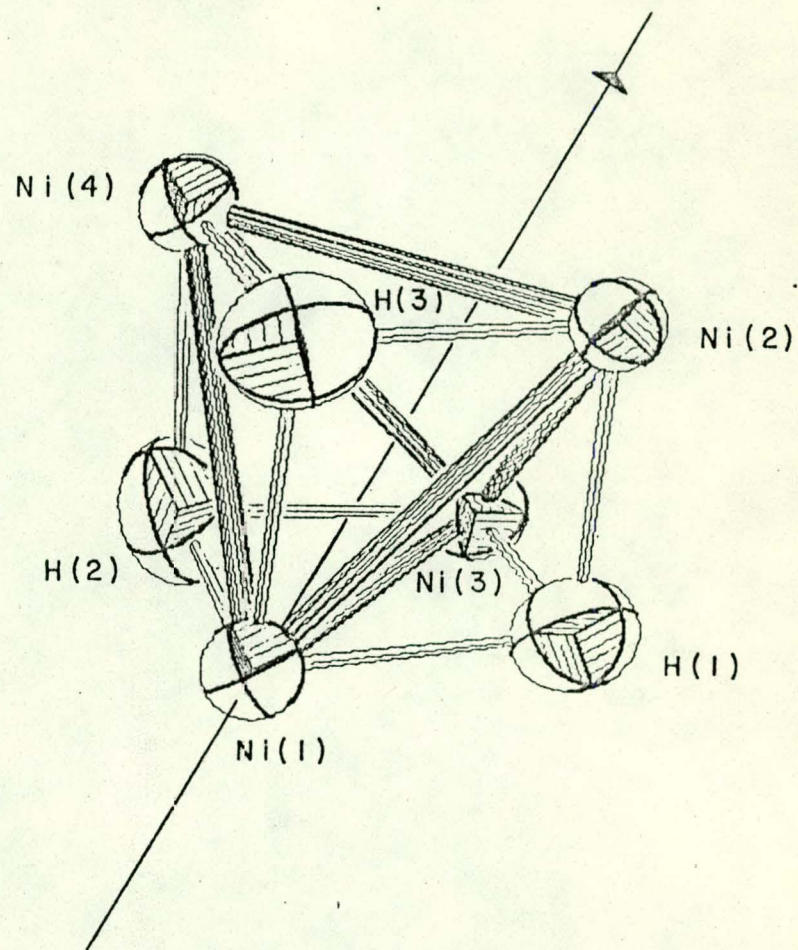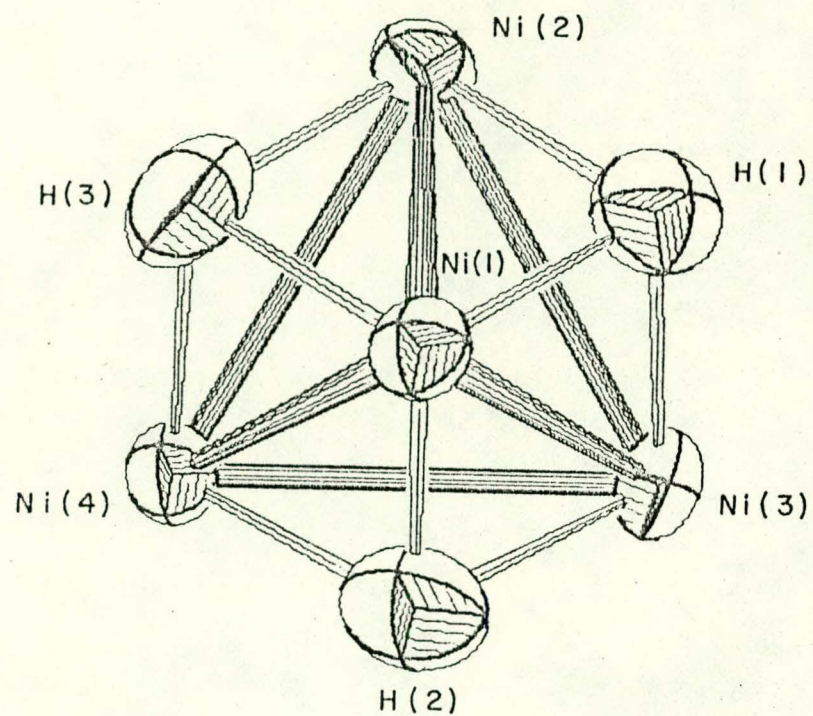with H atoms on the Cp
rings omitted for clarity

Fig. 4. The H3Ni4 core of H3Ni4Cp4, drawn with thermal ellipsoids enclosing 50 percent probability

(a) View approximately along the three-fold molecular axis

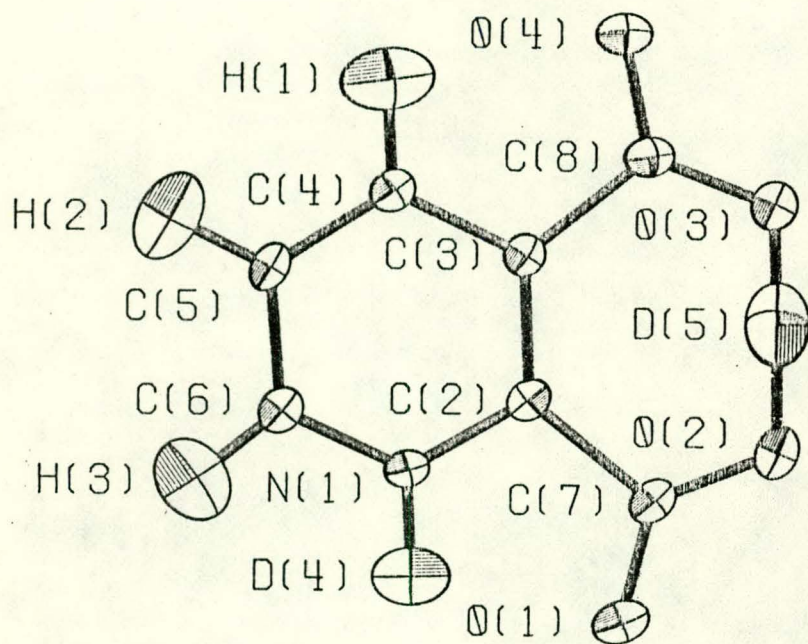(b) View approximately normal to the Ni(1)-Ni(2) bond

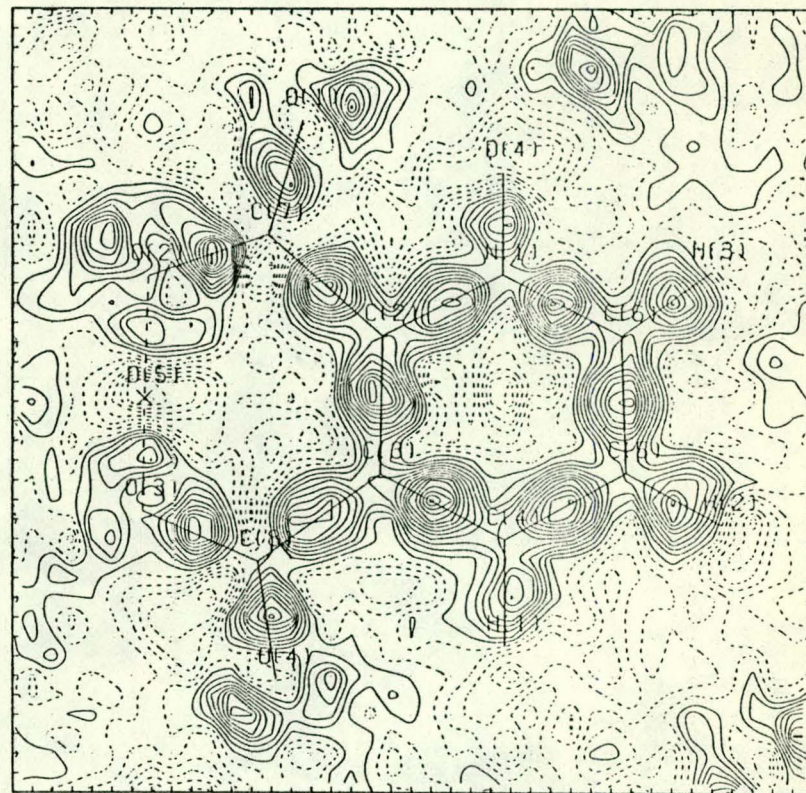Fig. 5. Molecular view of D-QNA at 35 K, with thermal ellipsoids drawn at the 97 percent probability level

Fig. 6. Modified X-N deformation electron density map for D-QNA at 35 K, computed from the complete set of x-ray data. The section is taken through the plane of the pyridine ring. Negative contours are dashed; the contour interval is 0.05 e·$\AA^{-3}$, which corresponds roughly to one esd