

Crystal and Molecular Structures at -35°C of Two Crystal Forms of Bis(2,6-dimethylpyridine)chromium, a Bis Heterocyclic Sandwich Complex

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The molecular structure of the heterocyclic sandwich complex bis(2,6-dimethylpyridine)chromium, $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$, has been determined by single-crystal x-ray diffraction techniques using three-dimensional data gathered at -35°C by counter methods. Deep red crystals obtained by vacuum thermal gradient sublimation exhibit two distinct morphologies: form A, bulky prisms of triclinic symmetry, space group $P\bar{1}$, $a = 7.307(1) \text{ \AA}$, $b = 8.242(2) \text{ \AA}$, $c = 6.316(2) \text{ \AA}$, $\alpha = 112.50(3)^{\circ}$, $\beta = 104.01(2)^{\circ}$, $\gamma = 102.46(2)^{\circ}$, $Z = 1$; form B, thin plates of orthorhombic symmetry, space group $Pbcn$, $a = 9.421(1) \text{ \AA}$, $b = 10.496(2) \text{ \AA}$, $c = 12.725(2) \text{ \AA}$, $Z = 4$. In both forms the molecule is a true sandwich complex consisting of a Cr atom symmetrically π bonded to two 2,6-dimethylpyridine ligands. In form A, Cr is located at a crystallographic inversion center, and accordingly the molecule has C_i symmetry, while in form B, Cr resides on a crystallographic twofold axis, so that here the molecule has C_2 symmetry. Except for a difference in conformation, the molecular geometry of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ is the same in both crystal forms. Since the pyridine ligands of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ are known to rotate freely in solution, these two crystal modifications (i.e., A and B) represent two different rotameric conformations of this fluxional molecule. Full-matrix least-squares refinement of the structure has converged with a conventional R index (on $|F|$) of 0.086 for form A using the 1064 reflections with $I_0 > 2.0\sigma(I_0)$ and 0.045 for form B using 909 similarly selected observations.

Introduction

Numerous π -carbocyclic transition metal sandwich type complexes have been prepared since the discovery of the first such species, bis(π -cyclopentadienyl)iron or ferrocene, in 1952.¹ Among these are the bis(π -cyclopentadienyl)metal complexes of all 3d metals,² a host of bis(benzenoid)-transition metal compounds² (e.g., $(\text{C}_6\text{H}_6)_2\text{Cr}^3$), and several mixed π -carbocyclic ligand-metal systems (e.g., $(\text{C}_5\text{H}_5)(\text{C}_4\text{H}_4)\text{Co}^4$ and $(\text{C}_5\text{H}_5)(\text{C}_3(\text{C}_6\text{H}_5)_3)\text{Ni}^5$), as well as some lanthanide ($[\text{Ce}(\text{C}_8\text{H}_8)_2]^{-6}$) and actinide ($(\text{C}_8\text{H}_8)_2\text{U}$ and $(\text{C}_8\text{H}_8)_2\text{Th}^7$) π complexes.

In contrast to these successes have been the efforts to synthesize analogous sandwich compounds with π -heterocyclic ligands. Although various "half-sandwich" complexes of the form $\text{M}(\text{CO})_3\text{L}$, where $\text{M} = \text{Cr}$ or Mn and $\text{L} =$ neutral pyrrole or a pyrrolyl ligand,⁸ thiophene,⁹ substituted thiopyran,¹⁰ or tri- or pentamethylpyridine,¹¹ have been prepared, the only reported examples of "full" heterocyclic sandwich compounds are those of the mixed-ligand species (π -cyclopentadienyl)(π -pyrrolyl)iron or azaferrocene, $(\text{C}_5\text{H}_5)(\text{C}_4\text{H}_4\text{N})\text{Fe}$,¹² and its derivative $(\text{C}_5\text{H}_5)[\text{C}_4\text{H}(\text{C}-\text{H}_3)_2(\text{C}(\text{O})\text{CH}_3)\text{N}]\text{Fe}$.¹³ We now wish to present the crystal and molecular structures of two conformational isomers of bis(2,6-dimethylpyridine)chromium, $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$, a bis heterocyclic sandwich complex possessing identical (i.e., unimixed) ligands. A preliminary account of the synthesis and structure of this compound has appeared.¹⁴

Experimental Section

Because $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ decomposes in air (to a nonvolatile green substance $(\text{Cr}_2\text{O}_3?)$),¹⁵ all sample manipulations were performed under N_2 . Deep red crystals of the complex grown slowly by vacuum thermal gradient sublimation yielded crystals of two distinct morphologies: bulky prisms, henceforth form A, and thin plates, henceforth form B. In turn, a crystal of each form was attached to a glass fiber and then quickly transferred to a Syntex $P2_1$ diffractometer, where it was maintained in a stream of N_2 at ca. -35°C . Preliminary diffraction experiments (with the diffractometer) suggested triclinic symmetry for form A, a suggestion ultimately confirmed by successful solution and refinement of the structure in space group $P\bar{1}$, but indicated the orthorhombic symmetry of space group $Pbcn$ for form B. Crystal data for both forms of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ are available in Table I.

As described below, in form A the molecules of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ exhibit C_i symmetry. Comparison of the unit cell volumes of forms A and B (Table I) reveals that the unit cell of form B contains 4 molecules of the complex. Space group $Pbcn$ could accommodate 4 molecules per unit cell at one of two different symmetry sites; at one the molecules

would have C_i symmetry as in form A, but at the other they would have C_2 symmetry. If the C_2 sites were occupied in form B, then the molecular conformation of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ in B could be different from that in A. (Clearly, however, the $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ molecules in B could reside at sites of C_2 symmetry and still retain the conformation found in A.) The NMR spectrum of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ in toluene- d_8 shows free rotation of the pyridine rings to -65°C .^{14,15} Hence, isolation of different rotameric conformations of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ would be consistent with this behavior.

A summary of data collection details is provided in Table I. Data reduction and assignment of standard deviations (with $p = 0.02$) to the measured intensities were carried out as described before.¹⁶ Analysis of the check reflections of each data set (Table I) showed $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$ to be stable during data collection (N_2 stream, -35°C), so that corrections for decomposition were not needed. Following data collection, attempts to determine the diffractometer setting angles for the faces of the data crystal of form A failed, owing to rapid crystal decomposition in air; hence we were unable to apply an absorption correction to these data. However, a procedure (to cope with the air sensitivity of $(\text{C}_7\text{H}_9\text{N})_2\text{Cr}$) was devised to achieve this for the data crystal of form B, so that these data were corrected for absorption.

Solution and Refinement of the Structures

Triclinic Form A. A difference Fourier map phased with Cr at the unit cell origin clearly revealed the positions of all nonhydrogen atoms. Full-matrix least-squares refinement, in centric space group $P\bar{1}$, first treating these atoms isotropically and then anisotropically, converged at $R = \sum \|F_o\| - |F_c| / \sum \|F_o\| = 0.097$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.118$ for the 1064 reflections with $I_0/\sigma(I_0) > 2.0$, where $\sigma(I_0)$ is the estimated standard deviation of a reflection of intensity I_0 .¹⁶ The function minimized in refinement¹⁷ is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors were used for Cr,¹⁸ N,¹⁹ C,¹⁹ and H,²⁰ and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections²¹ for anomalous scattering were applied to the Cr scattering function.

A difference Fourier map then indicated the hydrogen positions at heights of 0.6–1.1 and 0.3–0.7 $e \text{ \AA}^{-3}$ for ring and methyl hydrogen atoms, respectively. For comparison, the carbon atoms of the initial difference map ranged in density from 6.5 to 6.9 $e \text{ \AA}^{-3}$. In the final cycles of least-squares refinement, the ring hydrogens were treated isotropically, but the methyl hydrogens which did not refine properly were constrained to idealized tetrahedral positions ($\text{C}-\text{H} = 0.95 \text{ \AA}$ and $\text{N}-\text{C}-\text{C}(\text{methyl})-\text{H}$ torsion angles learned from form B). At convergence, the final error indices are $R = 0.086$ and $R_w = 0.106$, and a standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - s)]^{1/2}$, is 5.30, where m (1064) is the number of observations $|F_o|$ and s (91) is the number of variables in least-squares refinement. When all 1131 reflections examined during data collection

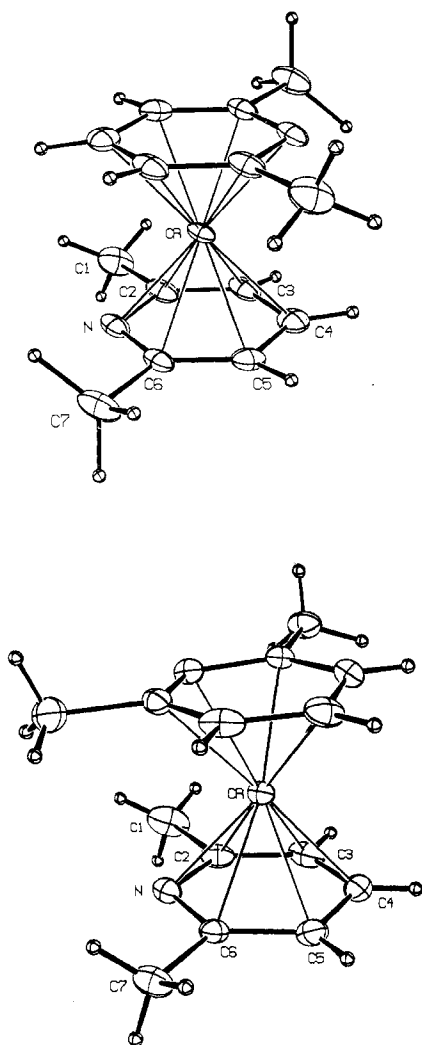


Figure 1. Molecular conformations of $(C_7H_9N)_2Cr$ in forms A (top) and B (bottom), with the atom numbering scheme. Non-hydrogen atoms are shown as ellipsoids of 30% probability, and hydrogen atoms, as spheres of radius 0.1 Å.

are used in structure factor calculations, $R = 0.090$ and $R_w = 0.106$.²²

In the final cycle of refinement no nonhydrogen atomic parameter shifted by more than 1.5% of an estimated standard deviation (esd), and no ring hydrogen parameter, by more than 4.0% of its esd. The largest peaks of a final difference Fourier map (ca. $1.0 \text{ e } \text{Å}^{-3}$) were located between the Cr atom and the pyridine rings.

Orthorhombic Form B. Interpretation of the Patterson map led to the locations of the Cr atoms—at sites of C_2 symmetry—and to the positions of the nitrogen and carbon atoms of the pyridine rings. From the ensuing difference Fourier map, the positions of the methyl carbon atoms (heights of 4.2 and $4.5 \text{ e } \text{Å}^{-3}$) were determined. Least-squares refinement of the positions of the chromium and dimethylpyridine atoms, first isotropically and then anisotropically, was carried out to virtual convergence. The positions of all hydrogen atoms were readily determined from a difference Fourier map, and then included as isotropic atoms in refinement. Least-squares convergence was attained with final R , R_w , and standard deviation of an observation of unit weight indices (with $m = 909$ and $s = 114$) of 0.045, 0.035, and 1.55, respectively. As before, only those data with $I_o/\sigma(I_o) > 2.0$ were carried into structure refinement. Use of all 1451 reflections measured in data collection in structure factor calculations gives R and R_w values of 0.089 and 0.039, respectively.²² There were no indications that corrections for secondary extinction should be applied to either data set.

In the last cycle of refinement no nonhydrogen or ring hydrogen parameter shifted by more than 4.1% of its esd, and no methyl hydrogen parameter by more than 15% of its esd. The largest peak on a final difference Fourier map ($0.3 \text{ e } \text{Å}^{-3}$) was not associated with an established part of the structure.

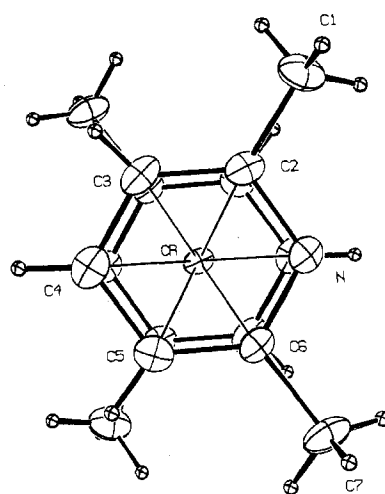


Figure 2. Views of the $(C_7H_9N)_2Cr$ molecule in forms A (top) and B (bottom), normal to the pyridine rings. As shown, rotation of ca. 132° about the molecular axis of conformer A yields conformer B. The same restrictions used for Figure 1 (see caption) were applied to these drawings.

Discussion

Figure 1 shows the relative conformations of the $(C_7H_9N)_2Cr$ molecules in forms A and B and indicates the atom numbering scheme employed herein. Final atomic positional and thermal parameters with corresponding standard deviations as estimated from the least-squares inverse matrix are presented in Table II. Bond lengths and bond angles are given in Tables III and IV.

The crystal structures of both A and B are composed of discrete molecules of $(C_7H_9N)_2Cr$, in which each Cr atom is symmetrically sandwiched between two 2,6-dimethylpyridine molecules thereby forming a "full heterocyclic sandwich" complex, as distinguished from a "half heterocyclic sandwich" such as azaferrocene.¹² In triclinic form A, the Cr atom occupies a crystallographic inversion center, and thus the molecule has C_i symmetry and its pyridine rings are rigorously parallel (i.e., the dihedral angle between the pyridine mean planes is zero by symmetry). In orthorhombic form B, Cr resides on a crystallographic twofold axis which is approximately parallel to the N–C(4) direction. Hence, the pyridine rings are again strictly parallel by symmetry, but now the molecule has C_2 symmetry and, as shown in Figure 2, methyl

Table I. Experimental Summary for $(C_7H_9N)_2Cr$

| | Form A | Form B |
|--|---|---|
| | Crystal Data at $-35\text{ }^\circ\text{C}^a$ | |
| a , Å | 7.307 (1) | 9.421 (1) |
| b , Å | 8.242 (2) | 10.496 (2) |
| c , Å | 6.316 (2) | 12.725 (2) |
| α , deg | 112.50 (3) | 90 |
| β , deg | 104.01 (2) | 90 |
| γ , deg | 102.46 (2) | 90 |
| V , Å ³ | 320.2 (3) | 1258.4 (6) |
| d_{calcd} , ^b g cm ⁻³ | 1.392 | 1.416 |
| Systematic absences | None | $0kl, k = 2n + 1; h0l, l = 2n + 1; hk0, h + k = 2n + 1$ |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $P1$ or $\bar{P}1$ (No. 1 or 2) ^c | $Pbcn$ (No. 60) |
| Z | 1 | 4 |
| No. of molecules per crystallographic asymmetric unit | $1/2$ | $1/2$ |
| Crystallographic site symmetry occupied by molecule | $\bar{1} (C_1)$ | $2 (C_2)$ |
| $F(000)$, electrons | 140 | 560 |
| Fw | 267.31 | 267.31 |
| | Data Collection at $-35\text{ }^\circ\text{C}$ (Syntex $P2_1$ Autodiffractometer Equipped with Graphite Monochromator and Syntex LT-1 Inert-Gas Low-Temperature Delivery System) | |
| Radiation (Mo $K\alpha$), Å | 0.710 69 | 0.710 69 |
| Mode | ω scan | ω scan |
| Scan range | Symmetrically over 1.0° about $K\alpha_{1,2}$ maximum for both A and B | |
| Background | Offset 1.0 and -1.0° in ω from $K\alpha_{1,2}$ maximum | |
| Scan rate, deg min ⁻¹ | Variable, 1.0–4.0 | Constant, 1.0 |
| Check reflections | 4 remeasured after every 96 reflections for both data sets; analysis ^d of these data indicated only random fluctuation in intensity for both specimens with all correction factors less than 0.5σ | |
| 2θ range, deg | 4.0–50.0 | 4.0–55.0 |
| Octants of reciprocal space examined | $\pm h, \pm k, l$ | hkl |
| Reflections measured | 1131 | 1451 |
| Data crystal dimensions, mm | $0.12 \times 0.14 \times 0.25$ | $0.064 \times 0.44 \times 0.29$ |
| Data crystal faces ^e | | {110}, { $\bar{1}\bar{1}0$ }, {001} |
| Absorption coeff, $\mu(\text{Mo } K\alpha)$, cm ⁻¹ | 9.09 | 9.25 |
| Transmission factor range ^f | | 0.79–0.94 |

^a Unit cell parameters were obtained by least-squares refinement of the setting angles of 53 reflections with $18^\circ < 2\theta < 25^\circ$ for form A and 30 reflections with $15^\circ < 2\theta < 22^\circ$ for form B. ^b Due to rapid decomposition of this material in the atmosphere the densities were not measured. ^c Shown by successful refinement to be $P1$ (see text). ^d W. H. Henslee and R. E. Davis, *Acta Crystallogr., Sect. B*, **31**, 1511 (1975). ^e The triclinic data crystal decomposed before the forms of its faces were determined (see text). To determine the setting angles for the faces of the data crystal of form B, each face, as viewed with a telescope, was placed (approximately) in diffracting condition on the Syntex diffractometer. The approximate setting angles for each face were then matched with setting angles calculated from the orientation matrix. ^f An absorption correction was not applied to data set A (see text).

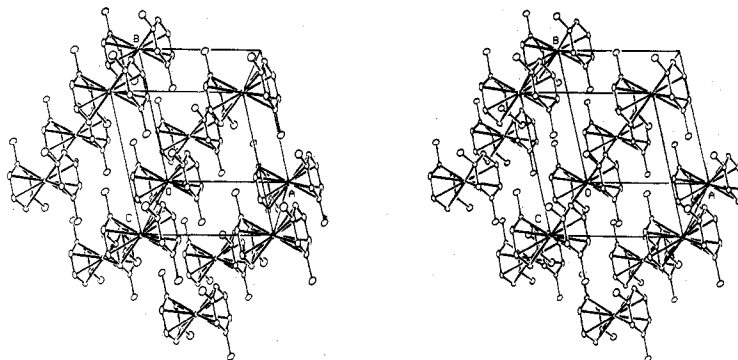


Figure 3. Stereoview of the packing of $(C_7H_9N)_2Cr$ in triclinic form A. Ellipsoids of 10% probability are shown. Hydrogen atoms are omitted for the sake of clarity. Each molecule is surrounded by 12 others in an approximately cubic close-packed arrangement.

groups of C(1) and C(7) are staggered. As may be seen in Figure 2, the conformation of form A may be converted to that of form B by rotation (132°) of one pyridine ligand relative to the other about the molecular axis passing through the rings and the Cr atom.

The principal barriers to the observed free rotation of the rings in solution would arise from the repulsive interactions of the methyl groups on opposite rings. The van der Waals methyl–methyl contact distance is about 4.00 \AA .²³ The closest intramolecular methyl–methyl approaches in $(C_7H_9N)_2Cr$ are 4.49 \AA in A and 3.97 \AA in B, clearly nonrepulsive separations. Furthermore, as shown in Figures 1 and 2, the dispositions of

the methyl groups in both A and B are such that these intramolecular repulsions are minimized, making the conformers in A and B the most stable rotational isomers of $(C_7H_9N)_2Cr$, since for other conformations the methyl group interactions must be stronger.

A variety of rotational conformations have been found from structural studies of substituted π -cyclopentadienyl–transition metal complexes.²⁴ For example in ferrocenedicarboxylic acid,²⁵ the carboxyl groups (one per C_5H_5 ring) as well as the cyclopentadienyl rings are virtually eclipsed, but in diacetylferrocene²⁶ the acetyl substituents (one per C_5H_5 ring) occupy positions on opposite sides of the iron atom while the

Table II.

a. Fractional Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Nonhydrogen Atoms of $(C_7H_9N)_2Cr^a$

| Atom | x | y | z | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-----------------|--------------|--------------|-------------|----------|----------|----------|----------|----------|----------|
| Form A | | | | | | | | | |
| Cr ^b | 0 | 0 | 0 | 138 (9) | 231 (10) | 223 (9) | 64 (7) | -5 (6) | 35 (8) |
| N | 0.245 (1) | 0.085 (1) | 0.334 (1) | 20 (2) | 38 (3) | 26 (3) | 7 (2) | -2 (2) | 8 (2) |
| C(1) | 0.265 (1) | -0.227 (1) | 0.196 (2) | 40 (4) | 45 (5) | 60 (6) | 19 (5) | 3 (4) | 24 (4) |
| C(2) | 0.251 (1) | -0.069 (1) | 0.141 (1) | 19 (4) | 36 (5) | 34 (5) | 11 (5) | 1 (4) | 7 (4) |
| C(3) | 0.250 (1) | -0.067 (1) | -0.078 (1) | 16 (4) | 46 (5) | 31 (5) | 11 (2) | 4 (4) | 3 (4) |
| C(4) | 0.240 (1) | 0.086 (1) | -0.120 (2) | 18 (4) | 48 (5) | 39 (5) | 5 (2) | 10 (4) | 13 (4) |
| C(5) | 0.236 (1) | 0.242 (1) | 0.079 (1) | 20 (4) | 35 (5) | 43 (5) | 2 (2) | 4 (4) | 14 (4) |
| C(6) | 0.237 (1) | 0.237 (1) | 0.294 (1) | 19 (4) | 33 (5) | 26 (5) | 5 (2) | 0 (4) | 5 (4) |
| C(7) | 0.235 (1) | 0.402 (1) | 0.509 (2) | 42 (4) | 39 (5) | 38 (5) | 9 (5) | 3 (4) | -7 (4) |
| Form B | | | | | | | | | |
| Cr ^b | 0 | 0.214 90 (7) | 1/4 | 207 (3) | 290 (4) | 211 (3) | 0 | -11 (5) | 0 |
| N | 0.101 3 (3) | 0.343 1 (3) | 0.355 9 (2) | 27 (1) | 34 (2) | 26 (2) | -2 (2) | -2 (1) | -2 (1) |
| C(1) | -0.122 4 (6) | 0.445 8 (6) | 0.399 9 (5) | 39 (3) | 71 (4) | 49 (3) | 19 (3) | -5 (2) | -23 (3) |
| C(2) | -0.037 8 (3) | 0.325 4 (4) | 0.387 2 (3) | 28 (2) | 42 (2) | 22 (2) | 9 (2) | -1 (1) | -5 (1) |
| C(3) | -0.095 9 (4) | 0.205 1 (4) | 0.401 9 (3) | 24 (2) | 68 (3) | 23 (2) | -9 (3) | 2 (2) | 3 (2) |
| C(4) | -0.014 2 (5) | 0.096 2 (4) | 0.385 7 (3) | 43 (2) | 41 (2) | 35 (2) | -13 (3) | -10 (2) | 13 (2) |
| C(5) | 0.130 9 (4) | 0.112 7 (4) | 0.361 4 (3) | 35 (2) | 34 (2) | 34 (2) | 5 (2) | -8 (2) | 3 (2) |
| C(6) | 0.183 7 (3) | 0.235 4 (3) | 0.345 4 (3) | 28 (2) | 31 (2) | 23 (2) | 0 (2) | -6 (1) | 0 (1) |
| C(7) | 0.337 2 (4) | 0.255 6 (4) | 0.317 4 (3) | 25 (2) | 55 (3) | 35 (2) | 1 (2) | -2 (2) | -6 (2) |

b. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for Hydrogen Atoms of $(C_7H_9N)_2Cr^c$

| Atom ^d | x | y | z | U | Atom ^d | x | y | z | U |
|-------------------|------------|-------------|-------------|----------|-------------------|------------|-----------|-----------|----------|
| Form A | | | | | | | | | |
| H(3) | 0.269 (14) | -0.145 (14) | -0.200 (18) | 0.06 (3) | H(1,3)* | 0.192 | -0.234 | 0.303 | 0.08 |
| H(4) | 0.225 (10) | 0.076 (9) | -0.276 (14) | 0.02 (1) | H(7,1)* | 0.168 | 0.473 | 0.451 | 0.08 |
| H(5) | 0.222 (11) | 0.340 (11) | 0.029 (13) | 0.03 (3) | H(7,2)* | 0.164 | 0.359 | 0.598 | 0.08 |
| H(1,1)* | 0.207 | -0.343 | 0.049 | 0.08 | H(7,3)* | 0.368 | 0.481 | 0.618 | 0.08 |
| H(1,2)* | 0.400 | -0.210 | 0.276 | 0.08 | | | | | |
| Form B | | | | | | | | | |
| H(3) | -0.183 (3) | 0.199 (3) | 0.419 (3) | 0.03 (1) | H(1,3) | -0.100 (6) | 0.508 (5) | 0.354 (5) | 0.11 (3) |
| H(4) | -0.043 (3) | 0.020 (3) | 0.392 (3) | 0.03 (1) | H(7,1) | 0.352 (3) | 0.319 (3) | 0.267 (3) | 0.03 (1) |
| H(5) | 0.182 (3) | 0.046 (3) | 0.353 (3) | 0.04 (1) | H(7,2) | 0.378 (3) | 0.184 (3) | 0.280 (3) | 0.04 (1) |
| H(1,1) | -0.113 (5) | 0.478 (4) | 0.467 (4) | 0.09 (1) | H(7,3) | 0.388 (4) | 0.273 (3) | 0.373 (3) | 0.04 (1) |
| H(1,2) | -0.204 (4) | 0.429 (5) | 0.390 (4) | 0.07 (1) | | | | | |

^a See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are the estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature factor expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^b For Cr the anisotropic thermal parameters are given $\times 10^4$. ^c The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound. ^d Parameters of atoms marked with asterisks are not refined values but, as stated in the text, represent idealized coordinates. These atoms were assigned isotropic thermal parameters of 6.0 Å^2 .

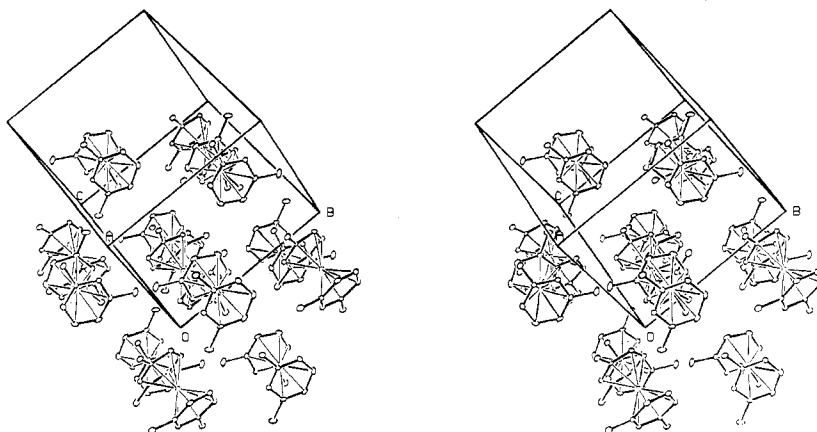


Figure 4. Stereoview of the packing of $(C_7H_9N)_2Cr$ in orthorhombic form B. As in form A, each molecule is surrounded by 12 others in an approximately cubic close-packed manner. The same considerations used to produce Figure 3 (see caption) were used in this drawing.

ring carbons remain eclipsed. Hodgson and Raymond²⁷ found that molecules of the fluxional species $(C_8H_4(CH_3)_4)_2U$ crystallize as two distinct rotational conformers in the same crystal; in one form the methyl groups are approximately eclipsed, but in the other they are approximately staggered.

It was determined by these workers that the eclipsed form experiences more and stronger *intermolecular* methyl-methyl contacts than does the staggered form and that rotation of the rings of the eclipsed conformer to alleviate *intramolecular* methyl repulsions is hindered by the existent *intermolecular*

Table III. Bond Lengths (Å) for $(C_7H_9N)_2Cr^a$

| | Form A | Form B |
|-------------|------------|-----------|
| Cr-N | 2.151 (6) | 2.131 (3) |
| Cr-C(2) | 2.129 (8) | 2.126 (4) |
| Cr-C(3) | 2.129 (7) | 2.137 (3) |
| Cr-C(4) | 2.161 (8) | 2.134 (4) |
| Cr-C(5) | 2.129 (9) | 2.164 (4) |
| Cr-C(6) | 2.115 (8) | 2.125 (3) |
| N-C(2) | 1.405 (11) | 1.382 (4) |
| N-C(6) | 1.373 (11) | 1.378 (4) |
| C(1)-C(2) | 1.491 (13) | 1.504 (7) |
| C(2)-C(3) | 1.386 (13) | 1.390 (6) |
| C(3)-C(4) | 1.394 (14) | 1.394 (6) |
| C(4)-C(5) | 1.423 (13) | 1.413 (6) |
| C(5)-C(6) | 1.372 (12) | 1.395 (5) |
| C(6)-C(7) | 1.517 (12) | 1.505 (5) |
| C(1)-H(1,1) | 0.95* | 0.92 (5) |
| C(1)-H(1,2) | 0.95* | 0.80 (4) |
| C(1)-H(1,3) | 0.95* | 0.90 (6) |
| C(3)-H(3) | 0.86 (11) | 0.86 (3) |
| C(4)-H(4) | 0.94 (9) | 0.85 (3) |
| C(5)-H(5) | 0.99 (9) | 0.86 (3) |
| C(7)-H(7,1) | 0.95* | 0.94 (3) |
| C(7)-H(7,2) | 0.95* | 0.97 (3) |
| C(7)-H(7,3) | 0.95* | 0.87 (4) |

^a Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figures 1 and 2 for identity of the atoms. Values marked with asterisks are idealized distances and hence are unrefined.

Table IV. Bond Angles (deg) for $(C_7H_9N)_2Cr^a$

| | Form A | Form B |
|----------------|-----------|-----------|
| C(2)-N-C(6) | 116.8 (7) | 116.9 (2) |
| N-C(2)-C(1) | 114.7 (8) | 114.9 (4) |
| N-C(2)-C(3) | 121.0 (8) | 122.3 (3) |
| C(1)-C(2)-C(3) | 124.3 (8) | 122.7 (3) |
| C(2)-C(3)-C(4) | 122.3 (8) | 120.5 (3) |
| C(2)-C(3)-H(3) | 129 (8) | 119 (2) |
| C(4)-C(3)-H(3) | 108 (8) | 120 (2) |
| C(3)-C(4)-C(5) | 115.8 (9) | 117.8 (4) |
| C(3)-C(4)-H(4) | 119 (5) | 126 (2) |
| C(5)-C(4)-H(4) | 125 (5) | 116 (2) |
| C(4)-C(5)-C(6) | 121.1 (8) | 119.4 (4) |
| C(4)-C(5)-H(5) | 110 (5) | 118 (2) |
| C(6)-C(5)-H(5) | 129 (5) | 123 (2) |
| C(5)-C(6)-N | 122.9 (7) | 122.8 (3) |
| C(5)-C(6)-C(7) | 121.9 (8) | 120.5 (3) |
| N-C(6)-C(7) | 115.1 (7) | 116.7 (3) |

^a Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figures 1 and 2 for identity of the atoms. As stated in the text, the positions of the methyl hydrogens of form A were idealized. For form B, refinement of the methyl hydrogen positions yielded the following values: C-C(methyl)-H, 108 (3)-115 (3)[°]; H-C(methyl)-H, 99 (3)-110 (3)[°].

methyl-methyl contacts.

The situation with $(C_7H_9N)_2Cr$ is similar, although perhaps

less apparent than in $(C_8H_4(CH_3)_4)_2U$. The molecules of $(C_7H_9N)_2Cr$ in both forms experience several intermolecular methyl-methyl interactions. In A, these contacts range from 3.91 to 4.22 Å (average 4.12 Å) and probably are not significant. In B, however, these interactions are slightly more acute, ranging from 3.52 to 4.35 Å (average 3.99 Å). Consistent with the shorter intermolecular methyl contacts in B is its smaller average molecular volume, 314.6 (2) Å³ compared to 320.2 (3) Å³ in A (see Table I). Thus, conformer A is somewhat less crowded than conformer B, and as such should be more stable. However, the similarity in molecular packing in the two crystal forms is noteworthy. In both forms, each molecule is surrounded by 12 other molecules in an approximately cubic close-packed manner. These packing arrangements may be seen in Figures 3 and 4.

Despite the difference in molecular conformation, corresponding geometrical features of the complex in forms A and B are in excellent agreement (see Tables III and IV). Moreover, as illustrated in Table V, selected distances of the structures of $(C_7H_9N)_2Cr$ compare favorably with analogous distances of other chromium-arene and chromium-heterocyclic π complexes. In addition, the dimensions of the pyridine ligands of $(C_7H_9N)_2Cr$ agree with those of the uncomplexed pyridine rings of D-glucitol-pyridine (C-C = 1.37 (1) Å, C-N = 1.330 (6) Å)³³ and pyridinium dicyanomethylide (C-C = 1.39 (1) Å, C-N = 1.37 (1) Å),³⁴ and the internal ring angles of $(C_7H_9N)_2Cr$ exhibit variations similar to those noted for these uncoordinated pyridine rings.

The least-squares planes calculated through the atoms of the pyridine ligands of $(C_7H_9N)_2Cr$ (see Table VI) demonstrate that these rings are planar in A, but slightly boat shaped in B, with atoms N and C(4) displaced by 0.025 (3) and 0.033 (4) Å toward the Cr atom. These deviations from planarity in B are even more pronounced when the best plane is computed through the positions of the four coplanar ring atoms (viz., C(2), C(3), C(5), and C(6)); in A, atoms N and C(4) lie in this plane, but in B, N and C(4) lie 0.030 (3) and 0.056 (4) Å on the Cr side of this plane. Nonetheless, the Cr-N and Cr-C(4) distances in B are, as in A, equal to the other four Cr-C bond lengths.

The positions of the ring hydrogen atoms are too poorly determined for meaningful evaluation of their displacements from the pyridine best planes. However, it does appear that methyl carbons C(1) and C(7) lie out of these planes and away from the Cr atoms. Although these deviations are small (0.03 (1) Å in A, 0.016 (6) and 0.037 (4) Å in B), the apparent direction of these deviations is at variance with that reported in several other structures (e.g., the hydrogen atoms of $(C_6H_6)_2Cr^3$ and $(C_6H_6)Cr(CO)_3^{28}$ and the methyl carbons of $(C_8H_4(CH_3)_4)_2U^{27}$). It should be noted, however, that small and perhaps insignificant displacements of ring-substituent atoms away from the π -bonded metal atoms were

Table V. Selected Mean Distances (Å) in Some Chromium-Ring π Complexes^a

| Compd | Cr-ring atom | Cr-mean plane ^b | (C-C) _{π} | (C-N) _{π} | Ref |
|--|-----------------------|----------------------------|-----------------------------------|-----------------------------------|-----------|
| $(C_7H_9N)_2Cr$, form A | 2.136 (15) | 1.620 (1) | 1.39 (4) | 1.38 (1) | This work |
| $(C_7H_9N)_2Cr$, form B | 2.136 (10) | 1.620 (1) | 1.40 (2) | 1.380 (4) | This work |
| $(C_6H_6)_2Cr$ { x-ray diffraction ^c | 2.146 (2) | 1.609 (1) | 1.420 (3) | | 3a |
| { electron diffraction | 2.150 (2) | 1.613 (2) | 1.423 (2) | | 3b |
| $(C_6H_6)Cr(CO)_3$, neutron diffraction | 2.243 (14) | | 1.41 (1) | | 28 |
| $(C_6(CH_3)_6)Cr(CO)_3$ | 2.233 (14) | 1.70 | 1.42 (4) | | 29 |
| $[(C_6H_5)_2C(O)OCH_3]Cr(CO)_2P(C_6H_5)_3$ | 2.198 (4) | | 1.40 (1) | | 30 |
| $[C_5H_5(C_2H_5)_2N(CH_3)]Cr(CO)_3$ { 3-ethyl isomer | 2.21 (6) ^d | 1.684 | 1.40 (4) | 1.401 (8) | 31 |
| { 5-ethyl isomer | 2.20 (5) ^d | 1.680 | 1.43 (5) | 1.405 (11) | 31 |
| $[C_5H_5(CH_3)N(CH_3)]Cr(CO)_3$ | 2.19 (6) ^d | 1.703 | 1.39 (2) | 1.386 (7) | 32 |

^a Numbers in parentheses are the estimated standard deviations, if available, in the last significant digits. A mean distance is given by $\bar{X} = \sum_i^n X_i/n$, and its standard deviation, by $[\sum(X_i - \bar{X})^2/(n-1)]^{1/2}$, where n is the number of observations X_i . ^b A mean plane is defined only by those ring atoms which are π bonded to Cr. ^c Distances corrected for the effect of thermal motion. ^d The Cr to ring methylene carbon distance (see reference given in last column) is not included in this calculation.

Table VI. Selected Mean Planes^a

| Atom | Deviations from planes, ^c Å | |
|-------|---|------------|
| | Form A | Form B |
| | $-0.8995X_A^b - 0.2394Y_A - 0.3655Z_A + 1.6203 = 0$ | |
| | $-0.2560X_B^b - 0.0368Y_B - 0.9660Z_B + 4.7766 = 0$ | |
| N* | 0.002 (6) | 0.025 (3) |
| C(2)* | -0.002 (8) | -0.017 (4) |
| C(3)* | -0.002 (8) | -0.012 (3) |
| C(4)* | 0.006 (8) | 0.033 (4) |
| C(5)* | -0.005 (8) | -0.025 (4) |
| C(6)* | 0.001 (8) | -0.003 (3) |
| C(1) | -0.03 (1) | -0.016 (6) |
| C(7) | -0.03 (1) | -0.037 (4) |
| H(3) | -0.11 (10) | -0.00 (3) |
| H(4) | 0.11 (8) | 0.05 (3) |
| H(5) | 0.05 (9) | -0.02 (4) |
| Cr | 1.620 (1) | 1.620 (1) |
| | $-0.8989X_A^b - 0.2383Y_A - 0.3677Z_A + 1.6221 = 0$ | |
| | $-0.2584X_B^b - 0.0424Y_B - 0.9651Z_B + 4.8007 = 0$ | |
| C(2)* | -0.001 (8) | -0.007 (4) |
| C(3)* | 0.001 (8) | 0.007 (3) |
| C(5)* | -0.001 (8) | -0.007 (4) |
| C(6)* | 0.002 (8) | 0.007 (3) |
| N | 0.000 (6) | 0.030 (3) |
| C(1) | -0.028 (10) | -0.011 (6) |
| C(4) | 0.011 (8) | 0.056 (4) |
| C(7) | -0.04 (1) | -0.032 (4) |
| H(3) | -0.10 (10) | 0.02 (3) |
| H(4) | 0.02 (8) | 0.08 (3) |
| H(5) | 0.06 (9) | 0.00 (4) |
| Cr | 1.622 (1) | 1.635 (1) |

^a Orthonormal (A) coordinate system with axes X , Y , and Z parallel to unit cell vectors a , $c^* \times a$, and c^* for triclinic form A, and to a , b , and c for orthorhombic form B. Coordinates of atoms marked with asterisks were used to define the planes.

^b The subscripts "A" and "B" refer to form A and form B, respectively. ^c Numbers in parentheses are the estimated standard deviations in the last significant digits. A negative deviation from the plane indicates that the atom with coordinates given in Table II lies between the plane and the origin.

found in the structures of $(C_6(CH_3)_6)Cr(CO)_3$ ²⁹ and 1,1'-bis(pentamethyldisilanyl)ferrocene.³⁵

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Supplementary Material Available: Listings of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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