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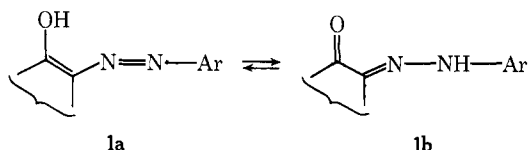
Resonance Interactions in Metal Chelates of *o*-Hydroxyazo Compounds. Crystal Growth, Structure, and Spectra of 1-(2-Pyridylazo)-2-naphtholatochlorocopper(II)

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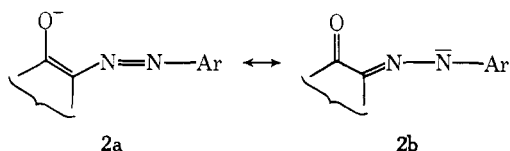
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Abstract: Single crystals of the title compound have been grown by a modified gel diffusion technique. The compound crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 15.817(3) \text{ \AA}$, $b = 8.255(1) \text{ \AA}$, $c = 10.404(3) \text{ \AA}$, $\beta = 103.46(2)^\circ$, $V = 1321.1(5) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd}} = 1.746 \text{ g cm}^{-3}$, $d_{\text{meas}} = 1.71 \text{ g cm}^{-3}$. Intensities were collected by counter methods on a card-controlled diffractometer operating in the θ - 2θ mode and employing Mo $K\alpha$ radiation. The structure, including hydrogen atoms, was solved by the heavy-atom method and refined by full-matrix least squares to $R_1 = 0.031$ and $R_2 = 0.040$. The pyridylazonephthol ligand (PAN) coordinates to copper as a planar tridentate chelate with strong covalent bonds through the pyridyl nitrogen (1.991 (2) \AA), the azo nitrogen adjacent to the naphthol group (1.964 (2) \AA), and the naphthol oxygen (1.984 (2) \AA). In the fourth position of an approximately square planar array about copper is found a strongly bound chloride ion (2.263 (1) \AA). Pairs of these Cu(PAN)Cl units combine to form a centrosymmetric dimer through weak bridging Cu-Cl bonds (2.647 (1) \AA) in the axial or fifth coordination site. The net coordination around copper is approximately square pyramidal, with the copper displaced 0.145 \AA from the equatorial plane toward the axial chlorine atom. The possibility for delocalization of electron density in anions of *o*-hydroxyazo compounds is discussed. The bond lengths observed in the ligand in Cu(PAN)Cl agree well with those predicted for a resonance hybrid involving roughly equal contributions from 12 canonical structures. Qualitative single-crystal polarized reflectance measurements indicate possible directions for the molecular transition moments.

The tautomeric equilibria of *o*-hydroxyazo compounds involve hydroxyazo, **1a**, and quinonehydrazone, **1b**, forms. The



factors affecting these equilibria have been studied using a variety of chemical,¹ spectroscopic,²⁻⁸ and crystallographic techniques.⁹⁻¹¹ These compounds are known to act as polydentate ligands to form chelates with a large number of metal ions.^{12,13} In these chelates, however, the ligands exist in their anionic form, and the tautomeric forms **1a** and **1b** of the ligand collapse to canonical forms **2a** and **2b** of a single anion structure. There is some question as to the extent of delocalization



of the negative charge in the ligands. In principle, X-ray structural analyses should provide a measure of the charge delocalization in these anions; a greater or lesser contribution from a canonical form to the anion structure should be reflected in the observed molecular dimensions. Yet, in the structure determinations reported of such transition metal chelates, the precision of the molecular parameters obtained has generally been too limited to be useful,¹⁴⁻¹⁶ except for one recently determined structure.¹⁷

The hydroxyazo compound, 1-(2-pyridylazo)-2-naphthol (HPAN), is an analytical reagent of some importance and has been used in the determinations for several metal ions.¹³ The anion, PAN, of this compound acts typically as a tridentate ligand in its reactions with cations to form chelates. Charge delocalization of the type described above is possible in the metal complexes of PAN. This possibility and the large variety of colored metal complexes formed by the ligand make the structural study of these complexes especially interesting. Additionally, it would be of interest to ascertain the role of the metal in the hues of the complexes.

In this paper we report on the growth of single crystals and on the structural characterization and spectra of 1-(2-pyridylazo)-2-naphtholchlorocopper(II), Cu(PAN)Cl. The copper(II) chelate was chosen as a representative metal complex for this particular ligand. The crystal structure of this chelate in the form of the perchlorate hydrate has been reported previously by other authors.¹⁶ The precision of their analysis, however, does not permit detailed conclusions about the anion structure to be drawn. It was felt that an anion other than ClO₄⁻ would enable more accurate structural data to be obtained, though the perchlorate could be crystallized much easier.

Since the metal complexes of azo dyes can usually be formed by reaction of solutions containing the metal ion and the ligand, respectively, a diffusion method seemed to be appropriate to grow single crystals of Cu(PAN)Cl. The technique of gel diffusion involving aqueous gels has been described in the preparation of single crystals of inorganic compounds.¹⁸⁻²⁰ More recently, the scope of the technique has been extended by its application to the growth of single crystals of organic charge-transfer complexes in gels involving organic solvents.²¹ In this study single crystals of Cu(PAN)Cl were grown using the gel diffusion technique with a gel containing organic solvents.

Experimental Section

Growth of Single Crystals of Cu(PAN)Cl. A gel was made from a solution of 450 mg of CuCl₂·2H₂O (MCB) in 5 mL of 1:1 benzene-methanol and 1 g of Sephadex-LH20 (Pharmacia Fine Chemicals). The powdered gel material was added rapidly to the copper chloride solution and a translucent gel formed almost immediately. The ratio of solid material to solution was adjusted by trial and error so that the gel set in a matter of seconds.

An analytically pure sample of HPAN was obtained by recrystallization from ethanol of a sample purchased from Aldrich. A dilute solution (ca. 20 mg in 5 mL) of HPAN in 1:1 benzene-methanol was added onto the surface of the gel, care being taken not to disturb the surface. A fresh solution of the ligand was added once a day after removing the spent solution. After 4 or 5 days, small crystals were observed in the body of the gel. These increased in size with the addition of more ligand solution. The crystals were separated from the gel by washing with a little CCl₄. Dark, intensely colored crystals in the form of both plates and prisms were obtained. Anal. Calcd for C₁₅H₁₀ClCuN₃O: C, 51.9; H, 2.9; N, 12.1. Found: C, 52.2; H, 3.0; N, 12.3.

Table I. Crystal Data for Cu(PAN)Cl

C ₁₅ H ₁₀ ClCuN ₃ O	mol wt 347.3
monoclinic (Mo Kα ₁ = 0.709 26 Å)	25 ± 1 °C
<i>a</i> = 15.817 (3), <i>b</i> = 8.255 (1), <i>c</i> = 10.404 (3) Å	
<i>β</i> = 103.46 (2)°, <i>V</i> = 1321.1 (5) Å ³	
density observed (floatation)	1.71 g cm ⁻³
density calculated (<i>Z</i> = 4)	1.746 g cm ⁻³
linear absorption coefficient, μ = 1.8 mm ⁻¹ (Mo Kα)	
total number of electrons per unit cell, <i>F</i> (000) = 700	
systematic absences: <i>h</i> 0 <i>l</i> for <i>h</i> odd, 0 <i>k</i> 0 for <i>k</i> odd	
space group, <i>P</i> 2 ₁ / <i>a</i> (<i>C</i> _{2h} ⁵)	
general positions, ±(<i>xyz</i> ; 1/2 + <i>x</i> , 1/2 - <i>y</i> , <i>z</i>)	

Spectroscopic Measurements. Visible spectra were recorded on a Pye Unicam SP 1800 ultraviolet and visible spectrophotometer. The polarized reflectance measurements were taken by Mr. C. D. Salzberg of our Laboratories on an E. Leitz Co. Ortholux petrographic microscope.²²

X-ray Diffraction Data. The unit cells of the two crystal forms were determined from precession photographs. The plate-like crystals are orthorhombic, space group *Pcab* (*D*_{2h}¹⁵) (systematic absences: 0*kl*, *l* odd; *h*0*l*, *h* odd; *hk*0, *k* odd), with lattice constants *a* = 17.83, *b* = 21.48, and *c* = 7.14 Å. Eight molecules of composition Cu(PAN)Cl per cell give a calculated density of 1.686 g cm⁻³ compared to 1.68 g cm⁻³ observed by floatation. No further work has been done with these crystals.

Crystal data for the prismatic crystals are collected in Table I. The morphology of the monoclinic crystals is 2/*m*, but they approximate hexagonal prisms with prism axis *c*, axial faces {100} and {110}, a prominent (001) end face, and two small unidentified end faces. Unit cell dimensions were refined by least squares from the diffractometer setting angles for 15 reflections accurately centered through narrow vertical and horizontal slits at a low take-off angle.

Diffracted intensities were measured with Zr-filtered Mo radiation on a card-controlled, Picker, four-circle diffractometer at 25 ± 1 °C. A scintillation detector was used and the pulse height analyzer was set for an approximately 90% window. The intensities were collected by the θ-2θ scan technique at a 2θ scan rate of 1°/min. The scan range was from 2θ_{α1} - 1.1° to 2θ_{α2} + 0.8° except for reflections at 2θ < 15°, for which the lower limits were chosen to avoid residual Kβ intensity. Background counts were taken for 20 s at each end of the scan. For high count rates, brass attenuators were automatically inserted in the diffracted beam. To monitor crystal and instrumental stability, the intensity of the 252 reflection was remeasured every 50th reflection. Its intensity dropped approximately 4% during data collection and was used to scale the data. All 2343 independent reflections in the *hkl* and *hkl* octants to 2θ = 50° were recorded. In addition, 281 of the 709 reflections with 50° < 2θ ≤ 55° were measured before X-ray tube failure terminated the data collection.

The measured intensities were reduced to structure amplitudes, *F*_o, by correcting for background, attenuation, scaling, Lorentz, and polarization effects. No absorption correction was applied, but the maximum error in intensity caused by absorption is estimated to be less than 9%. Observational variances were calculated according to the formula

$$\sigma^2(I) = \left(\frac{I\sigma(S)}{S}\right)^2 + \left(\frac{I\sigma(A)}{A}\right)^2 + S^2A^2 \left\{ 10P + 9 + \left(\frac{t_p}{2t_b}\right)^2 (10B_1 + 10B_2 + 18) \right\}$$

where the net intensity is

$$I = SA \left(10P + 4.5 - \frac{t_p}{2t_b} (10B_1 + 10B_2 + 9) \right)$$

S is a scaling factor based on the standard reflection, *A* is the attenuator factor, *P* is the integrated scan count recorded in time *t_p*, and *B*₁ and *B*₂ are the background counts, each obtained in time *t_b*. The appearance of the constants 4.5, 9, 10, and 18 is due to the recording of *P*, *B*₁, and *B*₂ as truncated decacounts.²³ Of the 2624 unique reflections measured, 442 had *I* < 2σ(*I*) and were considered unobserved. These intensities were set equal to 2σ(*I*), corrected to *F*_{lim}, and

Table II. Final Atomic Parameters (Standard Deviations) for the Nonhydrogen Atoms^a

atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cu	0.540 93 (2)	0.534 34 (4)	0.840 04 (3)	2.28 (2)	3.22 (2)	2.59 (2)	0.12 (1)	0.74 (1)	-0.22 (1)
Cl	0.486 08 (4)	0.713 36 (9)	0.995 77 (7)	3.41 (3)	2.68 (3)	3.20 (3)	0.60 (2)	1.33 (2)	0.10 (2)
O	0.3832 (1)	0.4962 (3)	0.7416 (2)	2.33 (8)	4.23 (10)	3.17 (9)	0.34 (7)	0.61 (7)	-0.32 (7)
N(1)	0.5288 (1)	0.4115 (3)	0.6907 (2)	2.17 (9)	2.68 (9)	2.20 (9)	0.05 (7)	0.57 (7)	0.34 (7)
N(2)	0.6084 (1)	0.3875 (3)	0.6820 (2)	2.31 (10)	3.08 (10)	2.48 (10)	-0.20 (8)	0.57 (8)	-0.24 (8)
N(3)	0.6340 (1)	0.5478 (3)	0.8763 (2)	2.29 (9)	2.65 (9)	2.60 (10)	-0.09 (8)	0.68 (7)	-0.03 (8)
C(1)	0.4578 (2)	0.3538 (3)	0.6040 (3)	2.35 (11)	2.94 (11)	2.26 (11)	0.04 (9)	0.43 (9)	0.30 (9)
C(2)	0.3799 (2)	0.4056 (4)	0.6409 (3)	2.75 (12)	2.95 (11)	2.60 (12)	-0.10 (10)	0.52 (10)	0.42 (10)
C(3)	0.2983 (2)	0.3531 (4)	0.5601 (3)	2.28 (12)	3.48 (13)	3.85 (14)	0.11 (10)	0.89 (10)	0.60 (11)
C(4)	0.2955 (2)	0.2594 (4)	0.4530 (3)	2.66 (12)	3.38 (13)	3.19 (14)	-0.59 (10)	-0.13 (10)	0.64 (11)
C(5)	0.3658 (2)	0.1101 (4)	0.3007 (3)	3.45 (14)	3.77 (14)	2.71 (13)	-0.87 (12)	0.06 (11)	0.17 (11)
C(6)	0.4397 (2)	0.0608 (4)	0.2627 (3)	5.10 (19)	4.02 (16)	2.49 (13)	-0.62 (13)	0.72 (12)	-0.42 (12)
C(7)	0.5202 (2)	0.1074 (4)	0.3355 (3)	4.11 (16)	4.22 (16)	3.05 (14)	-0.01 (12)	1.39 (12)	-0.25 (12)
C(8)	0.5289 (2)	0.2027 (4)	0.4459 (3)	3.11 (13)	3.42 (13)	2.73 (12)	-0.17 (11)	0.75 (10)	-0.07 (10)
C(9)	0.4552 (2)	0.2546 (3)	0.4883 (3)	2.95 (12)	2.37 (11)	2.25 (11)	-0.13 (9)	0.41 (9)	0.61 (8)
C(10)	0.3720 (2)	0.2070 (4)	0.4131 (3)	3.08 (12)	2.83 (11)	2.42 (11)	-0.39 (10)	0.22 (9)	0.80 (9)
C(11)	0.6665 (2)	0.4652 (3)	0.7860 (3)	2.43 (11)	2.37 (10)	2.33 (11)	-0.08 (9)	0.73 (9)	0.04 (9)
C(12)	0.7544 (2)	0.4553 (4)	0.7936 (3)	2.79 (12)	3.22 (12)	3.00 (13)	0.08 (10)	1.00 (10)	-0.21 (11)
C(13)	0.8111 (2)	0.5331 (4)	0.8963 (3)	2.04 (12)	3.82 (14)	4.12 (15)	-0.52 (11)	0.74 (10)	-0.31 (12)
C(14)	0.7779 (2)	0.6179 (4)	0.9875 (3)	2.95 (13)	3.84 (14)	3.46 (14)	-0.47 (11)	0.37 (11)	-0.87 (12)
C(15)	0.6902 (2)	0.6210 (4)	0.9764 (3)	3.14 (13)	3.43 (14)	2.92 (13)	-0.19 (10)	0.76 (10)	-0.73 (11)

^a The anisotropic thermal parameters (Å²) are of the form $\exp[-0.25(h^2a^*B_{11} + k^2b^*B_{22} + l^2c^*B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

included in the refinement and in the agreement indexes if the magnitude of the calculated structure factor exceeded F_{lim} . Subsequent study during the refinement of the structure of reflections with very poor agreement of the observed and calculated structure factors resulted in the elimination of four reflections (033; 613; 10,1, 3; 723) for demonstrable errors in data collection. A Wilson plot²⁴ yielded an overall temperature factor $B = 2.58 \text{ \AA}^2$ and a scale factor $K(F_o) = 0.692$.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method from three-dimensional Patterson and electron density maps. Refinement was by full-matrix least squares. The quantity minimized was $\sum w(|F_o| - |F_c^*|)^2$ where the calculated structure factor,

$$F_c^* = KF_c \left(1 + gF_c^2 \frac{1 + \cos^4 2\theta}{(1 + \cos^2 2\theta)\sin 2\theta} \right)^{-1/2}$$

included a correction for extinction.²⁵ The weights, w , were defined as

$$w^{-1} = \sigma^2(F_o^2)/4F_o^2 + (rF_o)^2$$

where r was chosen by inspection to be 0.018 to make the averages of $\sum w(|F_o| - |F_c^*|)^2$ approximately constant for groups of increasing F_o values.²⁶ The usual agreement indexes are defined as $R_1 = \sum |F_o| - |F_c^*| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c^*|)^2 / \sum wF_o^2]^{1/2}$. Atomic scattering factors for Cu(II), Cl, O, N, C, and H were taken from "International Tables for X-ray Crystallography",²⁷ as were the real and imaginary components of the anomalous scattering factors for Cu and Cl.

The position of the copper atom was obtained from a sharpened ($E^2 - 1$) Patterson map and the remaining 20 nonhydrogen atoms were located from a subsequent electron density map. Two cycles of refinement with isotropic temperature factors followed by one cycle with anisotropic temperature factors reduced R_1 to 0.047. A difference map showed the positions of the ten hydrogen atoms. One refinement cycle of the nonhydrogen atoms with anisotropic temperature factors and the hydrogen atoms with isotropic temperature factors gave $R_1 = 0.037$. The largest structure factors were obviously affected by extinction so the 187 largest F_o 's were refined with unit weights to determine the extinction coefficient g . Other reflections with large values of $w(|F_o| - |F_c^*|)^2$ were checked and, as noted above, four were eliminated from the data set. Two more cycles of refinement were followed by a redetermination of the extinction coefficient from the 142 largest F_o 's. Two final cycles completed the refinement with $R_1 = 0.031$ and $R_2 = 0.040$ for 2181 observed reflections and 41 unobserved reflections with $|F_c^*| > F_{lim}$. The goodness of fit $[\sum w(|F_o| - |F_c^*|)^2 / (\text{NO} - \text{NV})]^{1/2}$ where $\text{NO} = 2222$ independent observations and $\text{NV} = 230$ parameters) is 1.47. Of the 230 parameters

Table III. Final Atomic Parameters (Standard Deviation) for the Hydrogen Atoms

atom	x	y	z	B, Å ²	d, Å ^a
H(3)	0.252 (2)	0.380 (4)	0.588 (3)	2.9 (6)	0.88 (3)
H(4)	0.240 (2)	0.224 (4)	0.397 (3)	4.2 (7)	0.98 (3)
H(5)	0.311 (2)	0.084 (4)	0.255 (3)	3.5 (7)	0.91 (3)
H(6)	0.439(2)	-0.003 (4)	0.195 (4)	4.3 (8)	0.88 (4)
H(7)	0.573 (2)	0.081 (4)	0.309 (3)	3.8 (7)	0.96 (4)
H(8)	0.585 (2)	0.233 (4)	0.493 (3)	3.4 (7)	0.93 (3)
H(12)	0.776 (2)	0.400 (4)	0.731 (3)	3.1 (6)	0.93 (3)
H(13)	0.870 (2)	0.524 (3)	0.906 (3)	3.0 (6)	0.92 (3)
H(14)	0.814 (2)	0.677 (4)	1.052 (3)	4.2 (8)	0.91 (3)
H(15)	0.664 (2)	0.679 (3)	1.038 (3)	2.7 (6)	0.97 (3)

^a Carbon-hydrogen bond lengths.

varied in the last cycle, 228 changed less than 0.1σ , and the maximum shift was 0.29σ . A final difference map showed residual electron density between -0.28 and $+0.32 \text{ e/\AA}^3$ with some detail around copper.

The final positional and thermal parameters with standard deviations estimated from the least-squares process are given in Table II for the nonhydrogen atoms and in Table III for the hydrogen atoms. The other parameters were $g = 4.8 (5) \times 10^{-7}$ and $K(F_c) = 1.483 (3)$.

The crystallographic computations were performed with local modifications of the following programs: lattice refinement, PICK2;²⁸ electron density maps, FOURIE;²⁹ least-squares refinement, ORFLS;³⁰ illustrations, ORTEP-11.³¹ Data reduction and calculations of results were performed with local programs DACOR and RESULTS.

Results and Discussion

Coordination Geometry. The molecular configuration is shown stereoscopically in Figure 1. PAN coordinates to copper as a planar, tridentate chelate with strong, dative bonds through the pyridyl nitrogen, the azo nitrogen adjacent to the naphthol group, and the naphthol oxygen. This mode of attachment of PAN to Cu(II) is the same as that observed for Cu(PAN) (H₂O)ClO₄¹⁶ and strongly resembles that of 1-(2-thiazolylazo)-2-naphthol (TAN) to Cu(II) in Cu(TAN) (H₂O)₂ClO₄.^{14f} In the fourth position of an approximately square planar array about copper is found a strongly bound chloride ion. Pairs of these Cu(PAN)Cl units combine to form a centrosymmetric dimer through weak, bridging, Cu-Cl

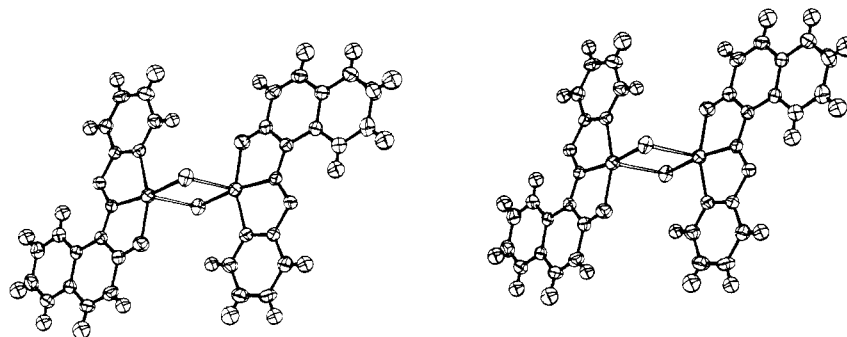


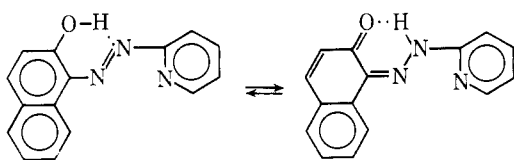
Figure 1. Stereoscopic view of a Cu(PAN)Cl dimer showing the 50% probability thermal ellipsoids.

bonds in the axial or fifth coordination position. The net coordination around copper is approximately square pyramidal, one of the more common configurations for Cu(II).^{32,33}

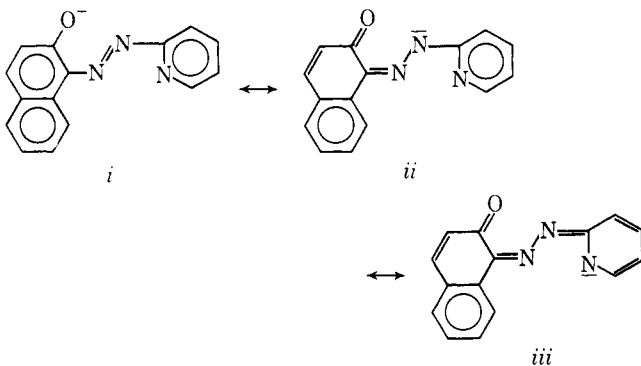
Bond lengths and angles around the copper and chlorine atoms are shown in Figure 2. The equatorial bond lengths, Cu-N(1) = 1.964 (2) Å, Cu-N(3) = 1.991 (2) Å, Cu-O = 1.984 (2) Å, and Cu-Cl = 2.263 (1) Å, compare well with values Cu-N = 2.00 Å, Cu-O = 1.94 Å, and Cu-Cl = 2.27 Å which are the sums of the covalent radii for Cu (1.28 Å),³⁴ N (0.72 Å),³⁵ O (0.66 Å),³⁶ and Cl (0.99 Å)³⁴ and with tabulated experimental values.^{32,33} As is usual for square pyramidal copper complexes,³³ the axial Cu-Cl bond at 2.647 (1) Å is appreciably longer (0.384 (1) Å) than the equatorial Cu-Cl bond. This distance represents a Pauling bond number, n , of 0.24 indicating that the bond is considerably weaker than the equatorial bonds.³⁴

The equatorial chelate atoms N(1), N(3), O, and Cl form only an approximate plane and individual atoms deviate as much as 0.03 Å from the plane. The copper atom is displaced 0.145 Å from the equatorial plane toward the axial chlorine atom, a condition typical of five-coordinate copper complexes.^{32,33} Additional distortion of the square pyramidal configuration arises because the five-membered chelate rings constrain the N(1)-Cu-N(3) and N(1)-Cu-O angles to be considerably less than 90°.

Ligand Geometry. For HPAN, there exists a tautomeric equilibrium between azophenol and quinonehydrazone forms.



Upon deprotonation of HPAN to PAN, these distinct tautomers yield a single anion which is a resonance hybrid of a number of canonical forms, the most important of which are i-iii. The absence of possible intramolecular hydrogen bonds



in PAN permits the rotation of the naphthol group by 180° around its adjacent C-N bond and leads to the formation of

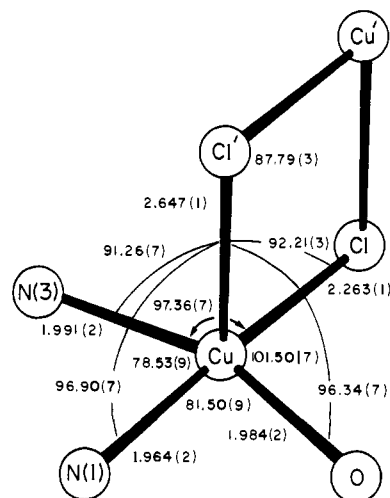


Figure 2. Coordination geometry about the Cu and Cl atoms. Atoms Cu' and Cl' belong to the second molecule of the centrosymmetric dimer. Additional angles are N(3)-Cu-O = 159.34 (10)° and Cl-Cu-N(1) = 170.06 (7)°.

metal complexes in which PAN acts as a tridentate ligand. By analogy to PAN, the metal complexes of PAN are also resonance hybrids of many canonical forms. A priori, it is difficult to predict the relative importance of these forms in the structure of Cu(PAN)Cl. The problem is more subtle than determining the proportion of tautomers in HPAN itself; the tautomers of HPAN are distinct chemical species characterized by different spectral and spectroscopic properties, but the canonical structures of PAN represent extreme possibilities of a single resonating structure. Although the structures of Cu(PAN) (H₂O)ClO₄,¹⁶ Cu(TAN) (H₂O)₂ClO₄,^{14f} and several TAN complexes of other cations^{14,17} have been determined, the limited precision of most of these structures has made it difficult to reasonably assess the relative contributions of the canonical forms. The good precision of the present structure permits such an analysis to be made.

Figure 3 shows the important canonical structures 3a, 3b, and 3c for Cu(PAN)Cl and also gives the Pauling³⁴ bond numbers, n , expected if each of the 12 forms contributes equally to the structure. From bond-length-bond-number correlation curves, bond lengths were predicted for these bond numbers. For carbon-carbon bonds, Table 7-9 of Pauling³⁴ was used. For carbon-nitrogen bonds, an equation analogous to Pauling's³⁴ eq 7.3 was deduced using 1.470 Å for a single bond,³⁵ 1.287 Å for a double bond from the sum of the double bond radii,³⁴ and 1.339 Å for aromatic bonds with $n = 1.5$.³⁷ The resultant equation relating bond length D_n with bond number n is

$$D_n^{C-N} = 1.470 - 0.183 \frac{5(n-1)}{3(n-1) + 2}$$

Table IV. Comparison of Observed Bond Lengths with Distances Predicted from Valence Bond Structures and with Distances Observed for Other Compounds

bond	Pauling bond number, <i>n</i>	distance predicted	observed distances			
			Cu(PAN)Cl	Parachlor Red ¹⁰	TAN (av) ¹¹	Co(TAN) ₂ ClO ₄ (av) ¹⁷
Carbon-Carbon Bonds						
C(1)-C(9)	1.17	1.46	1.448 (4)	1.450 (7)	1.431 (5)	1.440 (6)
C(4)-C(10)	1.17	1.46	1.436 (5)	1.444 (8)	1.419 (6)	1.415 (7)
C(2)-C(3)	1.17	1.46	1.433 (4)	1.459 (8)	1.418 (6)	1.427 (7)
C(1)-C(2)	1.33	1.42	1.438 (4)	1.477 (7)	1.411 (5)	1.424 (6)
C(9)-C(10)	1.42	1.41	1.422 (4)	1.387 (7)	1.417 (6)	1.421 (7)
C(8)-C(9)	1.42	1.41	1.406 (5)	1.395 (8)	1.401 (6)	1.397 (7)
C(5)-C(10)	1.42	1.41	1.401 (4)	1.408 (8)	1.407 (6)	1.402 (7)
C(13)-C(14)	1.42	1.41	1.378 (5)			
C(11)-C(12)	1.42	1.41	1.376 (4)			
C(6)-C(7)	1.42	1.41	1.376 (5)	1.396 (9)	1.400 (7)	1.376 (8)
C(12)-C(13)	1.58	1.38	1.383 (4)			
C(5)-C(6)	1.58	1.38	1.380 (5)	1.368 (9)	1.346 (7)	1.369 (8)
C(7)-C(8)	1.58	1.38	1.373 (5)	1.383 (8)	1.351 (6)	1.373 (7)
C(14)-C(15)	1.58	1.38	1.365 (5)			
C(3)-C(4)	1.83	1.35	1.348 (5)	1.328 (9)	1.330 (6)	1.339 (7)
Other Bonds						
N(2)-C(11)	1.17	1.41	1.401 (3)	1.394 (7)	1.380 (5)	1.373 (6)
N(3)-C(11)	1.42	1.35	1.355 (4)		1.290 (5)	1.324 (6)
N(3)-C(15)	1.42	1.35	1.344 (4)			
N(1)-C(1)	1.50	1.34	1.353 (3)	1.312 (6)	1.365 (5)	1.349 (6)
N(1)-N(2)	1.50	1.30	1.298 (3)	1.333 (6)	1.292 (4)	1.301 (5)
O-C(2)	1.50	1.28	1.279 (4)	1.248 (7)	1.321 (5)	1.291 (6)

This expression is similar to one derived by Donohue et al.³⁸ for older values of bond lengths. There is a lack of accurately known and unambiguous bond lengths for C-O and N-N bonds of intermediate order, so for these bonds we have assumed the functional form used for C-N bonds. For this purpose, N-N has been taken as 1.44 Å,³⁵ N=N as 1.24 Å,³⁹ C-O as 1.426 Å,³⁷ and C=O as 1.215 Å,³⁷ and the equations become

$$D_n^{N-N} = 1.44 - 0.20 \frac{5(n-1)}{3(n-1)+2}$$

and

$$D_n^{C-O} = 1.426 - 0.211 \frac{5(n-1)}{3(n-1)+2}$$

For $n = 1.5$, the C-O distance in carboxylate ions, 1.26 Å,³⁷ could be used and compares to 1.28 Å calculated from the above equation.

The bond lengths and angles observed for Cu(PAN)Cl are shown in Figure 4. For the PAN ligand, the observed and predicted bond lengths are compared in Table IV. The agreement is good, indicating that our assumption of 12 equivalent canonical forms is reasonable, and the PAN ligand structure is a superposition of roughly equal contributions from the canonical forms **3a**, **3b**, and **3c**. Also in Table IV are listed the comparable bond lengths for 2-nitro-4-chlorophenylazo-2'-naphthol (Parachlor Red)¹⁰ and for TAN,¹¹ structures determined with relatively good precision. The location of the hydrogen atoms indicated that Parachlor Red is in the hydrazone form, whereas TAN seems to exist as a tautomeric mixture with possibly more contribution from the azo form than from the hydrazone form. The tabulated bond lengths indicate that the bond character of PAN in Cu(PAN)Cl is somewhere between that of TAN and Parachlor Red. Also tabulated are the reasonably accurate distances in Co(TAN)₂ClO₄¹⁷ which, except for N(2)-C(11), which is shorter by 0.028 Å or 4σ, all agree within 3σ of the present structure. The possible resonance structures for Co(TAN)₂ClO₄ are slightly different from those of Cu(PAN)Cl; the largest difference predicted is a shortening of N(2)-C(11) in

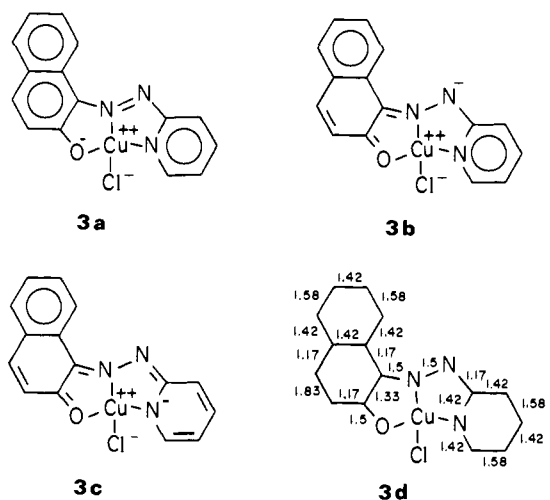


Figure 3. Canonical structures for Cu(PAN)Cl. The numbers of equivalent structures are six for **3a**, four for **3b**, and two for **3c**. The Pauling³⁴ bond numbers, n , based on equal contributions from the 12 structures are given in **3d**.

Co(TAN)₂ClO₄, which is what we observe. The finding of such extensive resonance in Cu(PAN)Cl is directly contradictory to the suggestion that the double bond character of the azo group was preserved and that there was essentially no delocalization of electrons in the chelate ring in the less accurately determined structure of Cu(PAN) (H₂O)ClO₄.¹⁶ We believe that the latter conclusion is unwarranted since the few bond lengths reported for Cu(PAN) (H₂O)ClO₄ are all within 3σ of our values.

A bond by bond comparison of the distances in Cu(PAN)Cl with those reported for other structures also shows the resonance nature of PAN in the complex. The length of the N(1)-N(2) bond (1.298 (3) Å) is intermediate between the average of 1.24 Å for the nitrogen-nitrogen double bond in several azobenzene derivatives³⁹ and the values for the single bond distances between sp² nitrogen atoms in benzalazine (1.412 (10) Å)⁴⁰ and in Parachlor Red (1.333 (6) Å).¹⁰

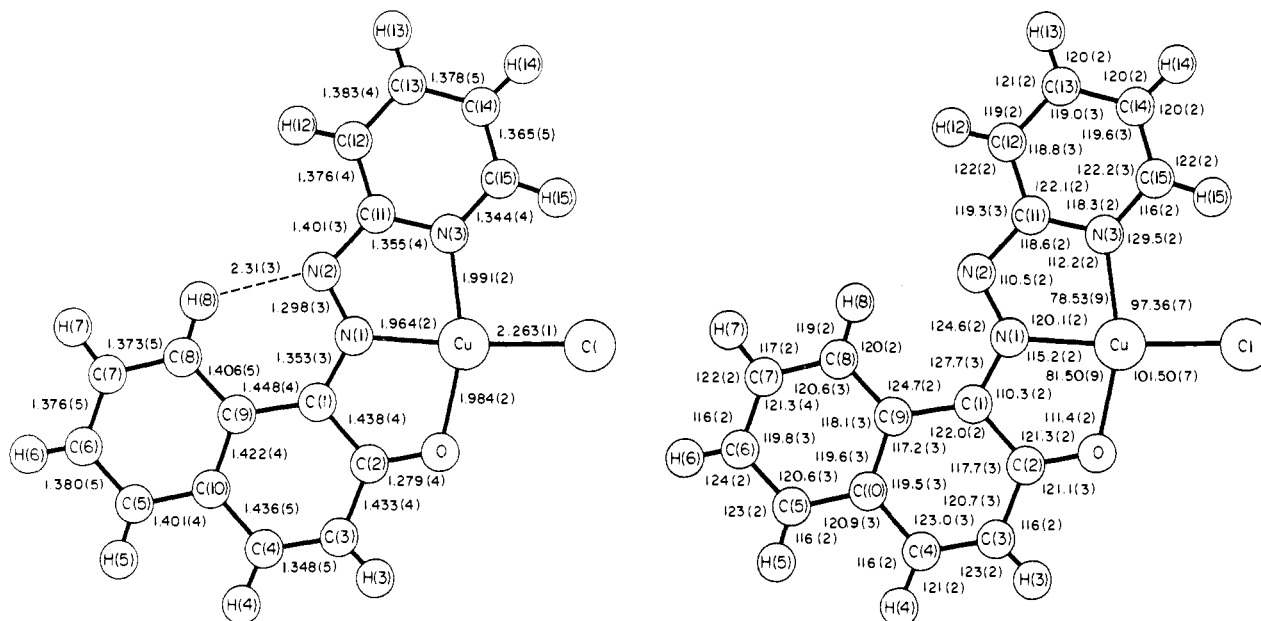


Figure 4. Bond lengths and angles for Cu(PAN)Cl. Standard deviations are given in parentheses.

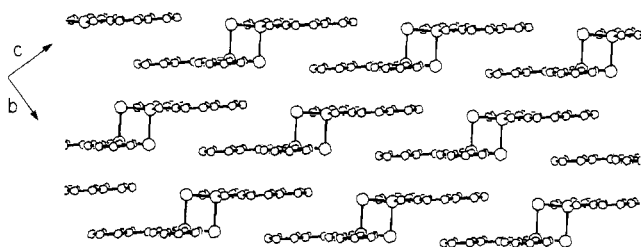


Figure 5. (100) projection of the structure. The horizontal axis is [011].

Complexes of acetone-methylphenylhydrazone with palladium(II)⁴¹ and platinum(II)⁴² have N-N bond lengths of 1.40 (2) and 1.41 (3) Å, respectively, and provide examples of metalized complexes with a formal single bond between sp^2 nitrogen atoms.

A comparison of N(1)-C(1) (1.353 (3) Å) with N(2)-C(1) (1.401 (3) Å) should be a sensitive measure of the relative contributions of the canonical structures of Figure 3. The comparable distances in Parachlor Red¹⁰ are 1.312 (6) and 1.394 (7) Å and indicate that N(1)-C(1) is intermediate between a double and a single bond whereas N(2)-C(1) is largely a single bond. The comparable distances in the acetone-methylphenylhydrazone complexes are 1.29 (2) and 1.46 (2) Å for the Pd(II) complex⁴¹ and 1.34 (3) and 1.43 (3) Å for the Pt(II) complex.⁴²

Two other relatively sensitive indicators of the resonance interactions are the C(2)-O bond and the naphthalenic carbon-carbon bonds, especially C(1)-C(2) and C(3)-C(4). The C(2)-O distance (1.279 (4) Å) is longer than the double bond value of 1.248 (7) Å found for the hydrogen-bonded carbonyl oxygen in Parachlor Red and shorter than the 1.32 Å found for the anionic, C-O single bonds in the α and β forms of copper 8-hydroxyquinolate.^{43,44} In form **3a** the bonds C(1)-C(2) and C(3)-C(4) should be equal with about $\frac{2}{3}$ double bond character, whereas in forms **3b** and **3c**, C(1)-C(2) would be a single bond and C(3)-C(4) would be double. In Cu(PAN)Cl, C(1)-C(2) (1.438 (4) Å) is significantly longer than C(3)-C(4) (1.348 (5) Å), but both bonds are between the values 1.477 (7) and 1.328 (9) Å for the hydrazone Parachlor Red¹⁰ which do correspond closely with ideal single and double bond values. The other naphthalenic C-C bonds show the ex-

pected trends for intermediate bond character, except possibly C(6)-C(7) which at 1.376 (5) Å is shorter than expected. This may be caused by the higher thermal vibration at the extremity of the molecule.

Consistent with the high degree of resonance interaction in PAN is the planarity of the ligand. The nonhydrogen atoms of PAN are reasonably coplanar with 0.035 Å maximum and 0.016 Å rms deviations. The copper and chlorine atoms lie considerably out of this plane (0.10 and -0.16 Å, respectively). A closer look at the atomic deviations reveals that they are systematic and that the ligand is better represented by two planes. The ten naphthol carbon atoms are coplanar to within 0.012 Å (rms deviation, 0.005 Å) and the six pyridyl atoms are coplanar to 0.010 Å (rms, 0.006 Å). The dihedral angle is only 1.2° so the distortion is slight. One contribution to the distortion probably comes from a short H(8)⋯N(2) intramolecular contact of 2.31 (3) Å.

Crystal Packing. The molecules pack plane to plane on edge in (100) sheets as shown in projection in Figure 5. The centrosymmetric dimers in these sheets are all related by translation, and successive layers are related by the glide planes. There are two different plane to plane overlaps. In the greater overlap, the planes of two PAN units are 3.33 Å apart, and the closest atomic approach is 3.369 (4) Å for N(1)⋯C(10) ($1-x, 1-y, 1-z$). The lesser overlap is between the ends of two naphthol groups and involves an interplanar separation of 3.43 Å. All intermolecular interatomic separations are consistent with van der Waals radii. Figure 6, a (010) stereoscopic view of the packing, gives an edge-on view of the layers and shows the relative orientation of the molecules from layer to layer.

Reflection Spectra. For a crystal in the space group $P2_1/a$, a molecular transition will give two allowed crystal transitions. The first, A_u , is polarized along the [010] direction and the second, B_u , is polarized in the (010) plane. If polarized reflectance measurements can be made along the b axis and in the (010) face, the direction of the molecular transition moments can usually be determined with reasonable accuracy. However, gel-grown crystals of Cu(PAN)Cl did not have the (010) face, and the quality of the other faces was not satisfactory for quantitative reflectance measurements. Hence only qualitative information could be extracted.

The absorption spectrum of Cu(PAN)Cl dissolved in p -dioxane shows high and low energy transitions which have λ_{max}

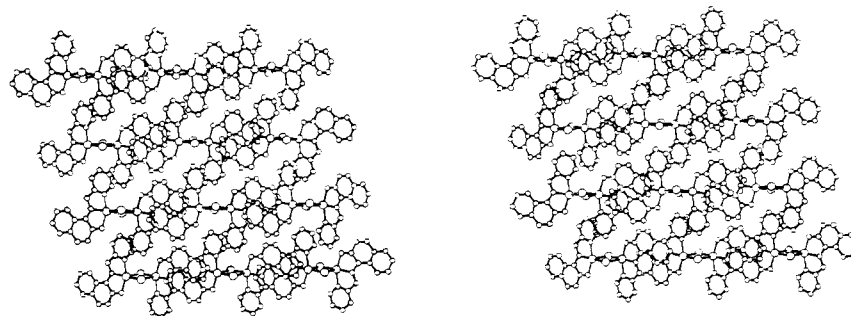


Figure 6. (010) stereoscopic view of the packing. The c axis is horizontal, left to right, and a is approximately vertical, bottom to top.

at about 425 and 570 nm, respectively. In the (110) face there is a moderate reflectance anisotropy for the latter transition and strong anisotropy for the former transition. The 570-nm maximum reflection direction makes an angle of 68° (counterclockwise) from c , and the 425-nm maximum reflection direction is at an angle of -7° (clockwise) from c .

In the (100) face, no strong anisotropy in the reflectance was observed at either wavelength. This indicates that the A_u state is much weaker than the B_u state for both transitions and suggests that the molecular transition moments have only small projections on b . For the (001) face, a strong reflectance maximum at 570 nm polarized along a and a weak reflectance maximum at 425 nm polarized along b were observed. These observations coupled with the crystal structure suggest that the moment for the 570-nm transition lies approximately along the C(4)–C(13) direction and the moment for the 425-nm transition lies approximately along the N(1)–Cu direction.

There is a possibility that the high energy absorption may have its origin not in an isolated molecular transition, but in a dimer transition, since the direction of the Cu–Cu' vector is also approximately parallel to the c axis. However, solution spectra in p -dioxane show that this absorption remains even after the complex is recrystallized from pyridine. This step would presumably cause the replacement of the chloro ligand by the pyridine ligand and thus result in the breakup of the dimeric structure. Hence, it is believed that the 425-nm transition has its origin within a single molecule of the metal complex.

Correlation between Ligand Tautomerism in HPAN and Ligand Resonance in Cu(PAN)Cl. There are several rapid and convenient methods (NMR, IR, visible spectroscopy, fluorescence) to determine the position of the hydroxyazo–quinonehydrazone tautomeric equilibrium for ligands such as HPAN both in solution and in the solid state. However, more involved methods, such as single-crystal X-ray structure analysis, as in the present case, seem to be required for an analysis of resonance interactions in the metal complexes. Therefore, it is of interest to determine if a correlation exists between the relative importance of the canonical forms (Figure 3) in Cu(PAN)Cl and the equilibrium amounts of the corresponding tautomers in HPAN itself.

There is some evidence to suggest that 1-arylaazo-2-naphthols exist predominantly in the hydrazone form in the solid state and in solution,⁶ but the tautomerism of HPAN specifically has not received much attention. The ^1H NMR spectrum of HPAN has been recorded by Betteridge and John. These workers have made an assignment of the signals based on an azonaphthol structure for the compound.⁴⁵ However, we believe that the spectrum is much better interpreted on the basis of a hydrazone structure for HPAN. This conclusion was reached by using the method of Kaul et al.⁷ and also by comparison of the ^1H NMR spectrum of HPAN with that of 1-phenylazo-2-naphthol, which is believed to exist largely as a hydrazone in CHCl_3 solution.⁴⁶

Therefore, whereas the canonical forms **3a** and **3b** seem to

contribute about equally to the hybrid anion structure in Cu(PAN)Cl, the hydrazone form dominates in the tautomeric equilibrium of the parent ligand. But it must be noted that the equilibrium between tautomers of hydroxyazo compounds is solvent sensitive and also that the resonance in Cu(PAN)Cl has been inferred from X-ray studies on only one of at least two crystalline modifications of the compound. Obviously more data will be required before correlations can be made between the electronic distribution in chelates such as Cu(PAN)Cl and the tautomeric distribution in the parent ligand.

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Supplementary Material Available: A listing of structure factor amplitudes, a table of least-squares planes, and a figure showing plane to plane overlap (18 pages). Ordering information is given on any current masthead page.

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Metalation of Ferrocene by *n*-Butyllithium-Pentamethyldiethylenetriamine

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Abstract: The reaction of ferrocene with *n*-butyllithium-pentamethyldiethylenetriamine (1:3 molar ratio) results in a dilithiated ferrocene derivative which upon carbonation and subsequent hydrolysis gives the dicarboxylic acid of ferrocene. The dilithium complex exhibits dynamic behavior in benzene or toluene with both cyclopentadienyl and base exchange being observed. The crystalline product obtained from a hexane-benzene solution in the presence of pentamethyldiethylenetriamine surprisingly contains only one triamine ligand per two lithium atoms and has the empirical formula $(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}(\text{N}_3\text{C}_9\text{H}_{23})\text{-Li}_2$. The molecular structure of this complex has been determined in the solid state and has been found to be dimeric, crystallographic symmetry $\bar{1}$, with the lithium atoms in two types of environments. All three pentamethyldiethylenetriamine nitrogen atoms are coordinated to one of the unique lithium atoms while the second unsolvated lithium atom bridges between one carbon atom of a cyclopentadienyl ring from each ferrocene monomer to form the dimer. A four-center electron-deficient bridge group is consequently observed consisting of the two unsolvated lithium atoms and two carbon atoms from two different ferrocene groups. The lithium atom-iron atom distance is short, 2.667 (8) Å, and is ascribed to bonding between the ferrocene e_g molecular orbital and the unsolvated lithium atom. The compound crystallizes in the monoclinic space group, $P2_1/n$, with lattice constants of $a = 13.557$ (5) Å, $b = 10.437$ (7) Å, $c = 15.50$ (6) Å, and $\beta = 106.24$ (2)°. The calculated density is 1.170 g cm⁻³ for two dimeric units per unit cell. The crystal structure was solved by diffractometer techniques using full-matrix least-squares analysis on a total of 4331 observations. The final agreement factor was $R_2 = 0.061$ for all data.

Introduction

Electrophilic substitution reactions have often been employed in the synthesis of ferrocene derivatives.^{2a} While many common electrophilic reactions, such as chlorination or nitration, have failed to yield the desired substitution product owing to the sensitivity of the iron atom to oxidation, alkali metal reagents have been used to resolve this problem. Ferrocene is first converted to a metalated derivative, which then is reacted with the electrophile to give the desired substituted molecule. Several authors have reported 1,1'-disubstituted ferrocenes prepared in this manner.^{2,3} Rausch and Ciappenelli⁴ found that the 1,1'-dilithio intermediate can be prepared in high yield, and with almost no accompanying monolithio by-product, using *n*-butyllithium *N,N,N',N'*-tetramethylethylenediamine (TMED).

Owing to our interest in the chemistry of interactions involving main group and transition metal organometallic compounds, we decided to further examine some of the products resulting from metalation of ferrocene using *n*-butyllithium. No infrared, nuclear magnetic resonance, or X-ray structural data had been reported for any metalated ferrocenes, nor had the degree of association been determined for these compounds. We selected the dilithiated compound for initial

study. Samples of dilithioferrocene-TMED were first prepared at the University of Massachusetts.⁴⁻⁶ Efforts to obtain suitable single crystals from these samples, as well as other samples, also prepared using *n*-butyllithium-TMED at the University of Illinois, were unsuccessful. Success was finally achieved by one of the authors (M.W.) using 1,1,4,7,7-pentamethyldiethylenetriamine (PMDT) rather than TMED in the metalation reaction. We have previously found that the use of PMDT generally results in significantly more soluble products than does the base TMED. An air-sensitive, red-orange, crystalline product was isolated from the reaction of *n*-butyllithium-PMDT and ferrocene, and it was demonstrated from a carbonation study that the compound contained two lithium atoms per iron atom. However, the NMR spectrum revealed that the compound contained only one PMDT per two lithium atoms. Since the structure could not be determined from these results, an X-ray structural investigation of dilithioferrocene-pentamethyldiethylenetriamine was undertaken. The results of that study are presented below.

Our characterization of the dilithioferrocene-PMDT complex in solution by NMR also revealed some interesting molecular dynamic behavior and the results of this study are also included.