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Crystal and Molecular Structure of Dichlorobis(azobenzene)palladium(II), a Possible Intermediate in the Ortho Palladation of Azobenzene

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The structure of dichlorobis(azobenzene)palladium(II) has been established by a crystallographic study. Crystals of this material are trigonal, space group $P3_1$ (or $P3_2$), with $a = 9.136$ (7) Å and $c = 23.340$ (18) Å. Calculated ($Z = 3$) and observed densities are 1.56 (2) and 1.60 g/cm^3, respectively. The structure analysis was based upon 2821 nonzero intensity data, collected by counter methods and refined by full-matrix least-squares techniques to a conventional discrepancy factor of 0.038. The palladium atom is bound, in a slightly distorted trans square-planar configuration, to two monodentate azobenzene ligands and two chloride ions. Important average bond distances include Pd–N = 2.024 (9) Å, Pd–Cl = 2.292 (2) Å, and N–N = 1.238 (9) Å. Steric crowding within the molecule leads to a twisting of the phenyl rings and a noncentrosymmetric molecular structure. Several features of the structure are consistent with the hypothesis that this complex may be an intermediate in the ortho palladation of azobenzene.

Introduction

The complex dichlorobis(azobenzene)palladium(II) has independently been reported by two research groups as a product of the reaction of dichlorobis(benzonitrile)palladium(II) with azobenzene.[1,2] Both groups assigned to this complex a trans square-planar structure with the azo ligand bound solely by a N:→Pd σ bond. This mode of metal coordination, though simple and reasonable, is not a common one for azobenzene.[3] Most frequently, azobenzene undergoes ortho metalation in its reactions with palladium and platinum complexes and also with a variety of other transition metal systems.[4,5] When dimeric $[PdCl(azb)]_2$ (azb = ortho-metalated azobenzene; azbH = azobenzene) is cleaved with triethylphosphine, it is the Pd–C bond rather than the Pd–N bond which is retained in the monomeric product.[6] Crystal structure information is available for a polymeric Cu(I) complex of azomethane, in which the azo group serves a bridging function[7] and for a cationic Pt(II) complex containing a σ-bonded phenyldiazene, $p\text{-FC}_6H_4N{=}NH$.[8] However, no structural data for a complex containing σ-bonded unmetalated azobenzene were available prior to this work.

This complex is also of interest from other viewpoints. It has been suggested as an intermediate in the ortho palladation of azobenzene,[1] a reaction which is the prototype for an important class of chemical transformations. Inspection of molecular models suggested a sterically crowded structure and it was felt that aspects of this structure could well be pertinent to the understanding of some details of the metalation reaction. Also of interest was the opportunity for comparison of the closely related pair of compounds $PdCl_2(azbH)_2$ and $PdCl_2(C_6H_5NO)_2$.[9] The metal-coordinated azo and nitroso groups in these molecules are isoelectronic, but steric constraints are considerably more severe in the azobenzene adduct. Finally, complexes of transition metals with simple azo ligands have attracted considerable attention because of the possible relationship of such complexes to intermediates in the biological fixation of nitrogen.

Experimental Section

Collection and Reduction of the Intensity Data. A sample of dichlorobis(azobenzene)palladium(II) was prepared by published methods.[1,2] Suitable single crystals could be obtained by allowing the reactants, dichlorobis(benzonitrile)palladium(II) and azobenzene, to mix by slow diffusion. Precession photographs revealed $\bar{3}$ diffraction symmetry and the lone systematic absence $00l$, $l \neq 3n$, consistent with the enantiomorphic space group pair $P3_1$ and $P3_2$. Lattice parameters (23°, λ(Mo Kα_1) 0.70930 Å), determined by refinement of the setting angles of 15 accurately centered reflections,[10] are $a = 9.136$ (7) Å and $c = 23.340$ (18) Å. Numbers in parentheses are standard deviations obtained from the least-squares fitting process. Calculated ($Z = 3$) and observed (flotation in C_6H_{14}–CCl_4 mixtures) densities are 1.56 (2) and 1.60 g/cm^3, respectively.

Intensity data were collected from an orange near-octahedral crystal of dimensions 0.37 × 0.28 × 0.27 mm mounted on a glass fiber in a general orientation. Bounding planes belonged to the {001}, {011}, and {10$\bar{1}$} forms. The mosaic spread of the crystal was very small, as evidenced by a typical value of 0.05° for the width at half-maximum of peaks obtained by narrow-source open-counter ω scans. The general procedures employed in data collection and processing have previously been described.[11] The takeoff angle was 2.4° and the diffracted beam was filtered through 3.0-mil Nb foil. A 4 × 4 mm counter aperture was positioned 28 cm from the crystal. The pulse-height analyzer was set to admit ~95% of the Mo Kα peak. The scan range extended from 0.75° in 2θ below the calculated position of the Kα_1 peak to 0.75° above the Kα_2 peak. The scan rate was 0.5°/min in 2θ and 20-sec background counts were taken at each end of the scan. Three standard reflections were measured at intervals of 100 reflections throughout data collection; variations in the intensities of these standards were within the bounds expected on the basis of counting statistics. Reflections with counting rates greater than ~10,000 counts/sec were automatically attenuated with copper foil. The intensities of all independent reflections with $2\theta \leq 55°$ were measured.

The data were processed according to previously published methods.[11] The p factor in the expression for the estimated standard deviations of the observed intensities was assigned a value of 0.04. Of the 3188 data processed, 2821 were above background by three or more standard deviations; only these data were employed in subsequent work. Test calculations, based upon a linear absorption coefficient of 10.66 cm,$^{-1}$ showed transmission factors ranging only from 0.76 to 0.78. Hence absorption corrections were not applied.

Solution and Refinement of the Structure. Solution of the structure was achieved by Patterson and difference Fourier techniques on the assumption of space group $P3_1$. Isotropic least-squares refinement of all atoms, with phenyl rings treated as rigid groups (C–C = 1.390 Å, C–H = 0.95 Å, C–C–C = C–C–H = 120°) converged to discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.050$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.065$. Final refinement employed anisotropic thermal parameters for the Pd, Cl, and N atoms and individual isotropic B values for the group carbon atoms. This refinement yielded $R_1 = 0.038$ and $R_2 = 0.048$ at convergence. A final difference Fourier map showed no peaks greater than 1.1 e/Å^3. In the final refinement cycle, no parameter shifted by more than half its estimated standard deviation. At this point, refinement to convergence was carried out in the alternative space group $P3_2$ in an effort to distinguish between the two possible enantiomorphic groups on the basis of differences in anomalous scattering by the Pd and Cl atoms. The results of the two refinements differed only slightly ($R_2 = 0.0481$ in $P3_1$ and 0.0491 in $P3_2$). Though we do not regard the distinction as unequivocal, all results are reported in terms of space group $P3_1$, since it yielded the lower weighted residual factor.

In all structure factor calculations, the atomic scattering factors tabulated in ref 12 were used for C and N, those of Cromer and Waber[13] were employed for Pd and Cl, and those of Stewart et al.[14] were used for H. The $\Delta f'$ and $\Delta f''$ values of Cromer[15] were used in correcting for the real and imaginary parts of anomalous scattering by the Pd and Cl atoms. In least-squares refinements, the function $\sum w(|F_o| - |F_c|)^2$ was minimized and weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard

Table I

Positional and Thermal Parameters for $(C_6H_5N_2C_6H_5)_2PdCl_2$

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.20442 (5)[b]	0.20441 (5)	0.1	99.3 (8)	99.7 (8)	9.9 (1)	55.3 (6)	−1.8 (2)	1.3 (2)
Cl(1)	0.45462 (26)	0.45455 (26)	0.10005 (8)	143 (3)	141 (3)	13.4 (3)	23 (2)	−1.9 (8)	2.0 (7)
Cl(2)	−0.04723 (23)	−0.04723 (23)	0.10005 (9)	112 (3)	114 (3)	20.7 (3)	48 (2)	−1.3 (8)	0.0 (8)
N(1)	0.1997 (7)	0.2222 (8)	0.1863 (4)	101 (10)	98 (9)	12 (1)	47 (8)	2 (2)	2 (3)
N(2)	0.1540 (8)	0.3049 (8)	0.2159 (2)	179 (12)	147 (11)	14 (1)	107 (10)	7 (3)	7 (3)
N(3)	0.2222 (8)	0.1993 (7)	0.0137 (4)	107 (10)	105 (10)	12 (1)	51 (8)	−1 (3)	−3 (2)
N(4)	0.3044 (8)	0.1538 (8)	−0.0159 (2)	136 (10)	160 (11)	13 (1)	92 (9)	−6 (3)	−7 (3)

Group Parameters[c]

Group	x_0	y_0	z_0	ϕ	θ	ρ
Ring 1	0.3447 (4)	0.0662 (4)	0.2507 (1)	−2.138 (6)	2.178 (3)	−1.982 (6)
Ring 2	−0.0084 (5)	0.4645 (5)	0.1666 (2)	−0.820 (4)	−2.625 (4)	0.441 (4)
Ring 3	0.0659 (4)	0.3443 (4)	−0.0505 (1)	0.054 (6)	−2.174 (3)	1.163 (6)
Ring 4	0.4650 (5)	−0.0084 (5)	0.0329 (2)	1.872 (4)	−2.609 (4)	−0.427 (4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Tabulated thermal parameters have been multiplied by 10^4. [b] Numbers in parentheses in tables and in the text are estimated standard deviations in the least significant figure. [c] The coordinates x_0, y_0, and z_0 are the fractional coordinates of the center of gravity of the group; the angles ϕ, θ, and ρ are the three rotation angles defined by R. J. Doedens in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 198–200. The angular coordinates are given in radians.

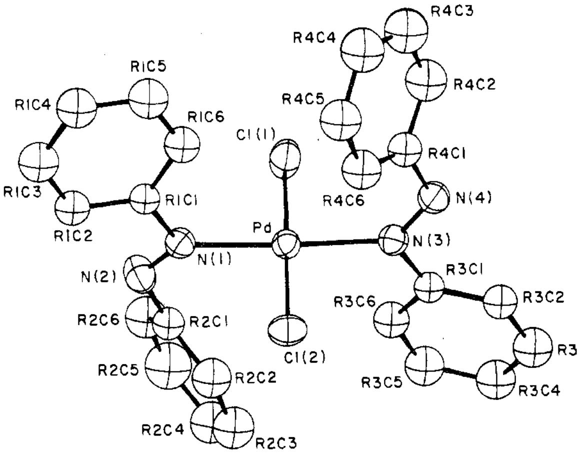

Figure 1. A view of the molecular structure of bis(azobenzene)dichloropalladium(II). Phenyl ring hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

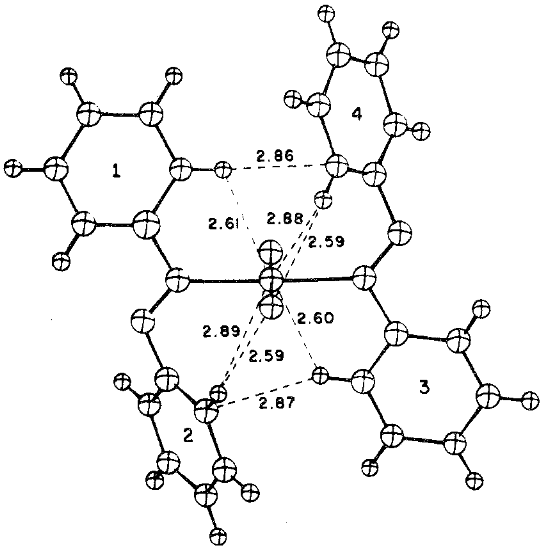

Figure 2. A second view of the molecular structure, with hydrogen atoms included and short intramolecular contacts indicated. For clarity, thermal parameters were arbitrarily set to 2.0 Å^2 for nonhydrogen atoms and 1.0 Å^2 for hydrogen atoms. Only the numbering of the phenyl rings is indicated; numbering of individual atoms may be determined by reference to Figure 1.

deviation of an observation of unit weight was 1.8. Calculation of structure factors for the 365 data with $F_o^2 < 3\sigma(F_o^2)$ showed 16 reflections with F_c exceeding F_o by as much as 3σ; of these, only four had $\Delta F/\sigma > 4$ and one had been misset.

Final atomic and group parameters are listed in Table I. Derived coordinates of group atoms together with isotropic thermal parameters for these atoms are tabulated in Table II. Intramolecular bond distances and angles are given in Table III. Principal amplitudes of thermal motion for atoms refined anisotropically are listed in Table IV and selected data on molecular planes are shown in Table V. A listing of observed and calculated structure factors is available.[16]

Description of the Structure and Discussion

Two overall views of the molecular structure of bis(azobenzene)dichloropalladium(II) are shown in Figures 1 and 2. The molecule has the expected trans square-planar stereochemistry, with each azobenzene ligand bound to the metal ion in a monodentate fashion via a Pd–N σ bond. This is the first structurally documented example of an azobenzene molecule coordinated in this manner to a single metal ion, though a similar type of bonding has recently been found for *p*-fluorophenyldiazene in the cationic Pt(II) complex $\{PtCl[P(C_2H_5)_3]_2(p\text{-}FC_6H_4N_2H)\}^+$ [8] and also for a substituted pyrazoline ligand in a tetracarbonyliron complex.[17] A number of other Pd and Pt complexes likely to contain simple azo ligands bound in this fashion have been reported.[1,18] Other observed modes of metal coordination for the azo function include the bridging configuration found in a copper(I) chloride–azomethane complex[7] and the olefin-like π bonding observed in two Ni(0) derivatives of azobenzene.[19,20] In addition to these types of coordination, azo ligands undergo a number of characteristic reactions[3] with metal complexes, including metalation (vide supra), addition of a pair of metal atoms across the N═N double bond,[21] and complete rupture of the azo linkage.[22]

As is evident from data tabulated in Table V, the metal atom and the four coordinated atoms are closely coplanar. Although the two chlorine atoms occupy equivalent coordination sites, their environments within the molecule differ significantly, as can be seen from the figures and from the nonbonded contacts listed in Table III. One of these chlorine atoms, designated Cl(2), is involved in two very short intramolecular contacts of 2.59 (1) Å with phenyl hydrogen atoms from different azobenzene ligands. These nonbonded interactions are substantially shorter than the sum of the hydrogen and chlorine van der Waals radii (3.0 Å).[23] The shortest corresponding contact for Cl(1) is a normal 3.09 (1) Å. One apparent

Table II. Positional and Thermal Parameters of Group Atoms

	x	*y*	*z*	*B*, Å^2
R1C1[a]	0.2708 (12)[b]	0.1420 (12)	0.2196 (2)	2.73 (11)
R1C2	0.2346 (9)	0.1079 (11)	0.2775 (2)	3.41 (12)
R1C3	0.3084 (7)	0.0320 (7)	0.3086 (2)	4.45 (16)
R1C4	0.4186 (12)	−0.0097 (13)	0.2819 (2)	4.40 (18)
R1C5	0.4549 (9)	0.0245 (11)	0.2239 (2)	4.70 (17)
R1C6	0.3810 (7)	0.1003 (6)	0.1928 (2)	3.73 (13)
R2C1	0.0730 (8)	0.3827 (8)	0.1887 (2)	3.19 (12)
R2C2	−0.0645 (7)	0.2970 (5)	0.1522 (3)	4.46 (16)
R2C3	−0.1458 (7)	0.3788 (8)	0.1301 (3)	5.00 (18)
R2C4	−0.0897 (10)	0.5463 (8)	0.1445 (3)	5.45 (21)
R2C5	0.0477 (9)	0.6320 (6)	0.1810 (3)	6.39 (24)
R2C6	0.1290 (6)	0.5502 (7)	0.2031 (3)	4.91 (18)
R3C1	0.1426 (12)	0.2710 (12)	−0.0195 (2)	2.85 (11)
R3C2	0.1089 (11)	0.2353 (9)	−0.0775 (2)	3.39 (12)
R3C3	0.0322 (7)	0.3086 (7)	−0.1085 (2)	4.38 (16)
R3C4	−0.0107 (13)	0.4176 (12)	−0.0815 (2)	4.48 (18)
R3C5	0.0229 (11)	0.4532 (9)	−0.0235 (2)	4.61 (17)
R3C6	0.0996 (6)	0.3799 (7)	0.0075 (2)	3.56 (13)
R4C1	0.3823 (8)	0.0730 (8)	0.0117 (2)	3.23 (12)
R4C2	0.5488 (7)	0.1286 (6)	−0.0039 (2)	4.80 (17)
R4C3	0.6316 (6)	0.0472 (9)	0.0174 (3)	6.05 (22)
R4C4	0.5478 (8)	−0.0897 (10)	0.0542 (3)	5.64 (22)
R4C5	0.3813 (8)	−0.1454 (7)	0.0698 (3)	5.09 (18)
R4C6	0.2985 (6)	−0.0640 (7)	0.0485 (3)	4.33 (16)
R1H2	0.1591 (14)	0.1364 (17)	0.2958 (3)	*c*
R1H3	0.2836 (11)	0.0086 (10)	0.3483 (2)	
R1H4	0.4692 (20)	−0.0616 (21)	0.3032 (3)	
R1H5	0.5304 (14)	−0.0041 (18)	0.2056 (3)	
R1H6	0.4059 (10)	0.1237 (9)	0.1531 (2)	
R2H2	−0.1028 (11)	0.1824 (6)	0.1423 (4)	
R2H3	−0.2399 (9)	0.3202 (12)	0.1051 (4)	
R2H4	−0.1454 (14)	0.6023 (12)	0.1293 (4)	
R2H5	0.0861 (13)	0.7466 (6)	0.1908 (5)	
R2H6	0.2231 (8)	0.6088 (11)	0.2281 (4)	
R3H2	0.1384 (17)	0.1607 (14)	−0.0959 (3)	
R3H3	0.0092 (10)	0.2843 (10)	−0.1482 (2)	
R3H4	−0.0633 (21)	0.4678 (20)	−0.1027 (3)	
R3H5	−0.0065 (17)	0.5278 (14)	−0.0050 (3)	
R3H6	0.1227 (9)	0.4042 (10)	0.0472 (2)	
R4H2	0.6062 (11)	0.2224 (8)	−0.0291 (3)	
R4H3	0.7456 (7)	0.0853 (13)	0.0067 (4)	
R4H4	0.6045 (12)	−0.1455 (14)	0.0687 (4)	
R4H5	0.3239 (12)	−0.2391 (9)	0.0950 (4)	
R4H6	0.1845 (7)	−0.1020 (11)	0.0592 (4)	

[a] A label of the form R*m*C*n* denotes carbon atom *n* of phenyl ring *m*; numbering of hydrogen atoms corresponds to that of the carbon atoms. [b] Standard deviations of group atomic coordinates are estimated from errors of group parameters by conventional error propagation techniques and may not be meaningfully used to estimate errors in distances or angles within a group. [c] Hydrogen atoms were assigned isotropic thermal parameters of 5.0 Å^2.

Table III. Intramolecular Distances (Å) and Angles (deg)

	(a) Bond Distances		
Pd–Cl(1)	2.285 (2)	N(3)–N(4)	1.237 (10)
Pd–Cl(2)	2.299 (2)	N(1)–R1C1	1.427 (14)
Pd–N(1)	2.024 (9)	N(2)–R2C1	1.407 (12)
Pd–N(3)	2.023 (9)	N(3)–R3C1	1.425 (14)
N(1)–N(2)	1.240 (10)	N(4)–R4C1	1.411 (12)
	(b) Nonbonded Contacts		
Pd···R1H6	2.61	Pd···R3H6	2.60
Pd···R2H2	2.89	Pd···R4H6	2.88
Pd···R1C6	3.12	Pd···R3C6	3.11
Pd···R2C2	3.21	Pd···R4C6	3.21
Cl(1)···R1H6	3.09	Cl(2)···R2H2	2.59
Cl(1)···R3H6	3.09	Cl(2)···R4H6	2.59
N(1)···R1H6	2.58	N(3)···R3H6	2.58
N(1)···R1H2	2.64	N(3)···R3H2	2.64
N(1)···R2H2	2.80	N(3)···R4H6	2.81
N(2)···R1H2	2.43	N(4)···R3H2	2.43
N(2)···R2H6	2.54	N(4)···R4H2	2.52
N(2)···R2H2	2.66	N(4)···R4H6	2.68
R1H6···R4C6	2.86	R3H6···R2C2	2.87
R1H6···R4C5	3.05	R3H6···R2C3	3.04
	(c) Bond Angles		
Cl(1)–Pd–Cl(2)	179.9 (1)	Pd–N(3)–R3C1	117.7 (6)
Cl(1)–Pd–N(1)	88.3 (2)	N(4)–N(3)–R3C1	112.7 (8)
Cl(1)–Pd–N(3)	88.4 (2)	N(3)–N(4)–R4C1	118.1 (6)
Cl(2)–Pd–N(1)	91.7 (2)	N(1)–R1C1–R1C2	121.7 (10)
Cl(2)–Pd–N(3)	91.7 (2)	N(1)–R1C1–R1C6	118.3 (5)
N(1)–Pd–N(3)	176.7 (2)	N(2)–R2C1–R2C2	123.2 (6)
Pd–N(1)–N(2)	129.0 (6)	N(2)–R2C1–R2C6	116.7 (5)
Pd–N(1)–R1C1	117.8 (6)	N(3)–R3C1–R3C2	121.7 (10)
N(2)–N(1)–R1C1	113.0 (8)	N(3)–R3C1–R3C6	118.3 (5)
N(1)–N(2)–R2C1	118.7 (6)	N(4)–R4C1–R4C2	115.8 (5)
Pd–N(3)–N(4)	129.3 (6)	N(4)–R4C1–R4C6	124.0 (6)

Table IV. Principal Root-Mean-Square Amplitudes of Thermal Vibration (Å)

Atom	Min	Intermed	Max
Pd	0.1573 (12)	0.1748 (12)	0.1810 (5)
Cl(1)	0.186 (2)	0.192 (2)	0.276 (3)
Cl(2)	0.184 (2)	0.203 (4)	0.239 (2)
N(1)	0.170 (8)	0.184 (15)	0.184 (10)
N(2)	0.183 (17)	0.193 (12)	0.247 (6)
N(3)	0.172 (10)	0.186 (11)	0.190 (13)
N(4)	0.182 (9)	0.186 (18)	0.234 (6)

consequence of the short Cl–H interactions involving Cl(2) is a small distortion from ideal square coordination about the Pd atom. This distortion involves a bending of N(1) and N(3) away from Cl(2); the resulting Cl–Pd–N angles deviate by ~1.7° from their ideal values.

Bond distances within the metal coordination sphere are normal. The Pd–N distances of 2.024 (9) and 2.023 (9) Å are equal within experimental error and longer by ~0.03 Å than the corresponding distances in the closely related nitrosobenzene adduct $PdCl_2(C_6H_5NO)_2$.[9] They are, however, within the range of previously observed Pd–trigonal N distances.[24] The Pd–Cl distances differ by an apparently significant amount (7σ); the longer distance of 2.299 (2) Å is observed for the chlorine atom involved in the two very short Cl–H contacts. Both metal–chlorine distances are within the range of comparable distances observed in closely related compounds (e.g., 2.295 (1) Å in $PdCl_2(C_6H_5NO)_2$[9] and 2.287 (2) Å in $PdCl_2[(CH_3)_2SO]_2$.[25] In addition to these bonding interactions, the Pd atom is involved in short intramolecular contacts to an ortho hydrogen atom of each phenyl ring. The shorter contacts (2.61, 2.60 Å) involve hydrogens on phenyl rings 1 and 3 while the longer ones (2.89, 2.88 Å) are to rings 2 and 4. The Pd···C distances associated with these two types of Pd···H contact are 2.97 and 3.21 Å.

In contrast to one earlier suggestion,[2] the coordinated azobenzene ligands possess the trans conformation. Other structural features of these ligands reflect their steric crowding. Each of the four phenyl rings is twisted substantially out of the plane defined by the azo group and the N–C bond to the ring in question. The torsion angles average 22.9° for the rings bound to coordinated N atoms and 48.3° for rings bound to free nitrogen atoms. There is even a small torsion (averaging 3.3°) about the N=N bond. As a consequence of the twisting of the phenyl rings, the molecule is dissymmetric. The absence of a molecular mirror plane is obvious; the lack of a molecular center of symmetry at the Pd atom may best be seen by inspection of the atomic coordinates in Tables I and II. Since the space group is $P3_1$, an *individual* crystal must be chiral. However, the two enantiomorphic crystal forms which must be present in the bulk sample cannot readily be distinguished because of the centrosymmetric crystal habit.

The N=N distances of 1.240 (9) and 1.237 (9) Å are comparable to the value found in free azobenzene (1.24 (3) Å).[26] A tabulation of representative N–N distances for metal-coordinated simple azo ligands is given in Table VI. It can be seen that the observed N–N distances cover a range of values, with the bulk of them equal to or slightly greater

Table V. Molecular Planes and Dihedral Angles[a]

1. Plane Containing Pd, Cl(1), Cl(2), N(1), and N(3)

$$-0.8626X + 0.4981Y - 0.0886Z = -0.2074$$

Distances to Plane, Å

Pd	0.0006	N(1)	−0.0006
Cl(1)	0.0003	N(2)	−0.0006
Cl(2)	0.0003		

2. Plane Containing N(1), N(2), and R1C1[b]

$$0.5802X + 0.8086Y - 0.0981Z = 1.4647$$

3. Plane Containing N(1), N(2), and R2C1

$$0.5483X + 0.8230Y - 0.1486Z = 1.2447$$

4. Plane Containing N(3), N(4), and R3C1

$$-0.4127X - 0.9053Y - 0.1008Z = 1.9219$$

5. Plane Containing N(3), N(4), and R4C1

$$-0.4380X - 0.8871Y - 0.1453Z = -1.9358$$

6. Phenyl Ring 1

$$-0.3676X - 0.9016Y - 0.2279Z = -2.8523$$

7. Phenyl Ring 2

$$0.5385X + 0.3022Y - 0.7866Z = -3.1318$$

8. Phenyl Ring 3

$$0.5910X + 0.7747Y - 0.2247Z = 1.8015$$

9. Phenyl Ring 4

$$-0.0092X - 0.6207Y - 0.7840Z = -0.6014$$

Angles between Perpendiculars to These Planes

Planes	Angle, deg	Planes	Angle, deg
1-2	84.9	4-5	3.1
1-3	87.1	2-6	23.1
1-4	85.1	3-7	48.6
1-5	87.1	4-8	22.7
2-3	3.5	5-9	48.0

[a] In calculations of all planes, all atoms were given unit weights. Equations of planes are expressed with respect to coordinates (*X, Y, Z*) referred to the orthogonal axis system (*a*, *b**, *c*). [b] The atoms defining each of the planes 2-9 are strictly coplanar.

than that in free azobenzene. Apparently significant lengthening is observed in some ortho-metalated complexes; still longer values, approaching those expected of a N–N single bond, are found in complexes of π-bonded azobenzene and in a series of bridged binuclear iron carbonyl species. The four N–C(phenyl) distances are of normal magnitudes. Although the differences in these distances are of dubious statistical significance, it is interesting to note that they fall into two pairs with the shorter distances occurring for the two rings involved in the very close H···Cl contacts. The N–N–C angles also fall into two distinct pairs, with those at N(1) and N(3) being about 5° smaller than those at N(2) and N(4).

Most of the differences between the structures of $PdCl_2(azbH)_2$ and $PdCl_2(C_6H_5NO)_2$ may be rationalized on the basis of the steric effects of the additional phenyl rings in the former molecule. In addition to the very short H···Cl contacts already discussed, each of these phenyl rings participates in a short C···H contact with an ortho hydrogen atom from another phenyl ring (R1H6···R4C6 = 2.86 Å; R3H6···R2C2 = 2.87 Å). The result of the molecular crowding is a noncentrosymmetric structure with inequivalent Cl atoms and phenyl rings twisted well out of the plane of the azo linkage. Thus, phenyl rings 1 and 3 in the azobenzene complex are twisted by nearly twice as great an angle (22.9° vs. 11.8°) as are the analogous rings in the nitrosobenzene adduct. The small difference in Pd–N distances between these two compounds may stem from the crowded nature of the azobenzene complex, though some difference in trans influence between the azo and aryl nitroso ligands is also conceivable.

The structure and chemical properties of this complex are consistent with the hypothesis that it, or a comparable species containing a single azobenzene ligand, is an intermediate in the ortho palladation of azobenzene. Coordination of azobenzene to Pd by a Pd–N σ bond presumably occurs early in the course of the metalation reaction.[5a] It has already been noted that conversion of $PdCl_2(azbH)_2$ to the chloro-bridged dimer $[PdCl(azb)]_2$ occurs readily under certain conditions and also that small amounts of the monomer are formed during the early stages of preparation of the dimer from $PdCl_4^{2-}$ and azobenzene in methanol.[1] Several aspects of the structure are of possible pertinence to this chemical behavior. The nonequivalence of the two chlorine atoms and the very short contacts of Cl(2) with phenyl ring ortho hydrogen atoms are possible factors involved in elimination of a single Cl^- ion from the metal complex. The short contacts of the Pd atom with the ortho C–H bonds are also likely to be important to the overall metalation pathway; however, it should be noted that the two shortest of these involve the phenyl ring which is not ultimately metalated. Many of the steric constraints found in $PdCl_2(azbH)_2$ would also be present in a complex containing a single azobenzene per metal atom (e.g., $PdCl_3(azbH)^-$). Hence such a species must also be considered as a potential intermediate in the formation of $[PdCl(azb)]_2$ by metalation reactions.

Table VI. N-N Bond Distances in Metal-Coordinated Azo Groups

Compd	N-N, Å	Ref
Free azbH[a]	1.24 (3)[b]	26
$[PdCl(azb)]_2$	1.23	27
$PtCl(PEt_3)_2(FC_6H_4N_2H)^+$	1.235 (10)	8
$PdCl_2(azbH)_2$	1.240 (9), 1.237 (9)	This work
$Cu_2Cl_2(H_3CN_2CH_3)$	1.26 (3)	7
$Ni(\pi\text{-}C_5H_5)azt$	1.27	28
$Rh(O_2CMe)(azb)_2$	1.27 (1), 1.29 (1)	29
$IrCl_2(MeOC_6H_3N_2H)(PPh_3)_2$	1.272 (9)	30
$IrClCO(PPh_3)_2(FC_6H_3N_2H)^+$	1.28 (3)	31
$Ru[\pi\text{-}(C_5H_4)C_6H_4PPh_2]F_9azb$	1.310 (7)	32
$(RhClCOazb)_2$	1.31 (2), 1.34 (2)	33
$Fe_2(CO)_6(MeN_2Me)$	1.366 (8)	34
$Ni[P(p\text{-}tol)_3]_2azbH$	1.371 (6)	20
$Ni(t\text{-}C_4H_9NC)_2azbH$	1.385 (5)	19

[a] Abbreviations used in this table: azt, ortho-metalated azotoluene; F_9azb, ortho-metalated perfluoroazobenzene; *p*-tol, *p*-tolyl; Me, methyl; Et, ethyl; Ph, phenyl. [b] Value for the nondisordered azobenzene molecule.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50190G-10-75.

References and Notes

(1) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2247 (1969).

(2) R. Murray, *Inorg. Nucl. Chem. Lett.*, **5**, 811 (1969).

(3) For a review of structural and chemical aspects of metal complexes of azo ligands, see A. J. Carty, *Organomet. Chem. Rev., Sect. A*, **7**, 191 (1972).

(4) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).

(5) (a) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970), and references therein; (b) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc. A*, 3204 (1970), and references therein.

(6) R. W. Siekman and D. L. Weaver, *Chem. Commun.*, 1021 (1968); D. L. Weaver, *Inorg. Chem.*, **9**, 2250 (1970).

(7) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960).

(8) S. D. Ittel and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4804 (1974).

(9) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 537 (1973).

(10) Computer programs employed in this structure analysis have previously

been listed: R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 840 (1973). All computations were carried out on the local PDP-10 computer.
(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).
(12) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.
(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(15) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(16) Supplementary material.
(17) C. Krüger, *Chem. Ber.*, **106**, 3230 (1973).
(18) J. F. Van Baar, K. Vrieze, and D. J. Stufkens, *J. Organomet. Chem.*, **81**, 247 (1974).
(19) R. S. Dickson and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 2988 (1972).
(20) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **57**, 389 (1973).
(21) R. P. Bennett, *Inorg. Chem.*, **9**, 2184 (1970).
(22) M. M. Bagga, W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 1534 (1969).
(23) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p 260.
(24) Some representative values are listed in ref 9.
(25) M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Crystallogr.*, **23**, 788 (1967).
(26) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966).
(27) R. C. Elder, personal communication.
(28) V. A. Semion, I. V. Barinov, Yu. A. Ustynyuk, and Yu. T. Struchkov, *J. Struct. Chem. (Engl. Transl.)*, **13**, 512 (1972).
(29) R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2138 (1972).
(30) P. L. Bellon, G. Caglio, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 897 (1974).
(31) F. W. B. Einstein and D. Sutton, *J. Chem. Soc., Dalton Trans.*, 434 (1973).
(32) M. I. Bruce, R. C. F. Gardner, B. L. Goodall, F. G. A. Stone, R. J. Doedens, and J. A. Moreland, *J. Chem. Soc., Chem. Commun.*, 185 (1974).
(33) R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2141 (1972).
(34) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **8**, 2709 (1969).

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Binding Sites in Transition Metal–Pyrimidine Complexes and Evidence for a Measurable Trans Influence in Copper(II) Complexes.

Crystal and Molecular Structure of an N(1)-Bonded Copper(II)–Thymine Complex, (Aquo)(diethylenetriamine)(thyminato)copper(II) Bromide Dihydrate

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The synthesis and structural characterization of the complex (aquo)(diethylenetriamine)(thyminato)copper(II) bromide, $CuBrO_3N_5C_9H_{20}$, are reported. The complex crystallizes, as the dihydrate, in the monoclinic system, space group $P2_1/n$, with $a = 6.341$ (1) Å, $b = 12.840$ (8) Å, $c = 20.805$ (12) Å, $\beta = 95.50$ (3)°, $V = 1686.1$ Å^3, $Z = 4$, $d_{\text{measd}} = 1.68(1)$ g cm^{-3}, and $d_{\text{calcd}} = 1.68$ g cm^{-3}. Intensities for 4938 independent reflections (560 zeros) were collected by counter methods. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix, least-squares refinement has led to final R(excluding zeros), weighted R, and goodness-of-fit values of 0.077, 0.062, and 1.4, respectively. The primary coordination sphere about the copper is approximately square pyramidal. The tridentate diethylenetriamine ligand, with its terminal nitrogen atoms in trans positions, and N(1) of the coordinated thymine monoanion define the equatorial plane. This complex represents the first report of metal binding to the N(1) position of pyrimidines. The coordination sphere about the copper is completed by an axially bonded water molecule, Cu–O = 2.465 (3) Å. Comparison of the Cu–N(middle nitrogen atom of the diethylenetriamine ligand) distance in the thyminato complex, 2.009 (3) Å, and the closely related cyano complex, 2.036 (4) Å, indicates a significant trans influence in carbon-bonded cyano complexes of copper(II). The square-pyramidal complex cations form columns along the short a axis such that the coordinated water molecule lies approximately below the copper atom of a translationally related complex. The complexes form hydrogen-bond dimers about centers of symmetry via the coordinated thymine monoanion. The bromide anion and the waters of crystallization play an important role in both the stability of the cationic columns and the complete three-dimensional structural network.

Introduction

Thymine and uracil and their natural nucleoside and nucleotide derivatives have no unprotonated heterocyclic nitrogens at neutral pH's. Coordination of metals to these heterocyclic sites is less favorable than in the other common nucleic acid constituents which have at least one nitrogen atom with an available lone pair.[1] Consequently, metal complexes of these two bases and their derivatives have been less extensively investigated. In some respects, however, these heterocycles are the most interesting of the bases. For example, platinum complexes react with uracils and thymines to produce "platinum blues" which have proven to be powerful anticancer agents.[2] Additionally, mercury(II) and monoalkyl derivatives of mercury(II) appear to interact preferentially with the thymine moieties in DNA.[3,4] The binding site implicated by the available evidence is N(3).[3,4]

Early line-broadening studies of thymidine suggested that little interaction between this nucleoside and Cu(II) took place.[5] Later it was shown using the same technique that the similar nucleoside, uridine, did form complexes with Cu(II), but at relatively high metal concentration.[6] Relaxation studies using ^{13}C NMR have revealed similar spectral changes for C(5), C(2), and C(4) for the nucleosides of cytosine, uracil, and thymine.[7] The changes in the cytosine derivative are seen at much lower concentrations, however. The relaxation results are consistent with binding at N(3). ^{1}H NMR line broadening was less evident in studies using thymine because the broadening results largely from the scalar coupling contribution to T_2,[8,9] which is particularly large at C(5). Thymine has no proton on C(5) but has a methyl substituent at this position.

Irrespective of the importance of the metal interactions in drugs and in influencing nucleic acid conformations, thymine and uracil and their derivatives are interesting ligands, worthy of study because of their multifaceted coordination possibilities. In addition to possible coordination of a metal to N(3), it is likely that coordination could take place at N(1), O(2), and O(4) and, in uracil derivatives, at C(5).[7] The favored reaction site will depend on the metal, the pH, the reaction time, etc.