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Structure of *trans*-Chlorobis(triethylphosphine)(*p*-fluorophenylhydrazine)platinum(II) Tetrafluoroborate

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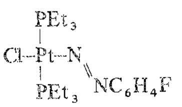
The title compound $[Pt(P(C_2H_5)_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$ is part of a system proposed as a model for the reduction of dinitrogen to ammonia. The structure of the complex has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by full-matrix least-squares techniques to a final R index (on F) of 0.045 based on 3015 reflections above background. The material crystallizes in the orthorhombic space group D_{2h}^{16}-$Pnma$ with four molecules in a cell of dimensions $a = 16.062$ (7), $b = 13.625$ (6), and $c = 12.085$ (5) Å. The ions have crystallographically imposed mirror symmetry and the platinum atom has square-planar coordination with Pt–P = 2.328 (2) Å, Pt–Cl = 2.303 (2) Å, and Pt–N(1) = 2.081 (7) Å. The hydrazine ligand, including the phenyl group, lies in a plane approximately perpendicular to the coordination plane. The N(1)–N(2) bond is 1.436 (11) Å and the Pt–N(1)–N(2) angle is 113.2 (5)°. There is an extensive hydrogen-bonding system connecting the anions and cations. The structure of this reduced species is compared with structures of other complexes in the same model system.

Introduction

Not only may unstable or unisolable molecules be stabilized on transition metals, but these coordinated molecules may undergo reactions to produce products not attainable in the absence of the metals. In truly catalytic systems the stabilized intermediates are not isolable because of their short lifetimes, but in other systems they often can be isolated.

One area of research in which there is currently considerable interest is the biological fixation of nitrogen. A wide variety of model systems has been proposed, but one difficulty is that in the systems which are better models for the actual biological process[1] the intermediate species cannot be isolated or characterized. The model system proposed by Parshall[2] in 1965 is still one of the more complete cycles in that each of the intermediate species I–III can be isolated and characterized. These species are being studied structurally because of the paucity of information on such metal–nitrogen systems and on their structural relationships. Compound II, the subject of an earlier structural investigation,[3] is an example of a very unstable molecule, an aryldiazene, stabilized by coordination to a transition metal. The cationic complex II can be deprotonated to yield a neutral aryldiazenido complex I which is currently being investigated structurally.[4] The σ-bonded aryldiazene can also be hydrogenated under mild conditions to give the cationic arylhydrazine complex III the structure of which is reported here. Continued hydrogenation of the arylhydrazine complex results in the formation of ammonia and aniline. Although it has been shown[5] that the diaryl-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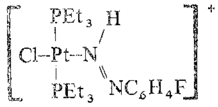
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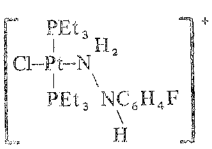
III

diazene, azobenzene, when π bonded in a nickel(0) complex,[6] can be reduced to an uncoordinated diarylhydrazine, attempts to prepare a coordinated hydrazine from that complex have been unsuccessful.[7]

Experimental Section

Preparation. The compound [$Pt(P(C_2H_5)_3)_2(H_2NNHC_6H_4F)Cl$][$BF_4$] was prepared by literature methods.[2c] Suitable crystals were obtained by slow evaporation of an ethanol–dichloromethane solution of the complex.

Crystallographic Data. The crystals of [$Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl$][$BF_4$] display from six to around twenty faces and a morphology consistent with the orthorhombic system. Precession and Weissenberg photographs using Cu Kα radiation show *mmm* symmetry and systematic absences $0kl$ ($k + l = 2n + 1$) and $hk0$ ($h = 2n + 1$), consistent with space groups $D_{2h}{}^{16}$-*Pnma* or $C_{2v}{}^{9}$-$Pn2_1a$.

Intensity measurements were made with Mo radiation using a Picker FACS-I computer-controlled four-circle X-ray diffractometer equipped with a scintillation counter and pulse height analyzer. The crystal, of approximate dimensions 0.50 mm × 0.55 mm × 0.66 mm, was mounted in air with the *a* axis misset from the spindle axis. Cell constants and their standard deviations were derived from a least-squares refinement of the setting angles of twelve reflections.[8] The reflections were centered on the Mo Kα_1 peak, λ 0.70930 Å, using a narrow source. The unit cell parameters are $a = 16.062$ (7) Å, $b = 13.625$ (6) Å, $c = 12.085$ (5) Å, $V = 2627.9$ Å^3. The density calculated for four molecules per unit cell is 1.71 g/cm^3, which agrees with the experimental value of 1.71 (2) g/cm^3 measured by a flotation technique in dichloromethane–bromoform.

The mosaicity of the data crystal was measured by means of narrow-source, open-counter ω scans and was found to be acceptable although there was some slight character to the peaks. Intensities were measured by means of the θ–2θ scan technique using Mo radiation and a graphite monochromator. The takeoff angle of 2.4° resulted in the intensity of a reflection being about 80% of its maximum value as a function of takeoff angle. Peaks were measured in 2θ from 0.9° below the Mo Kα_1 peak to 0.9° above the Mo Kα_2 peak. Backgrounds, measured at each end of the scan, were for 10 sec out to $2\theta = 30°$, for 20 sec to $2\theta = 44°$, for 40 sec to $2\theta = 55°$, and for 100 sec out to $2\theta = 62°$ where data collection was terminated because there were relatively few reflections above background. All reflections were scanned at 2°/min. The counter was positioned 30 cm from the crystal and was preceded by an aperture of 4.5 × 4.5 mm.

The intensities of six standard reflections were measured after every 100 reflections. During data collection the intensity of the strongest of the standards, $0\bar{4}0$, increased evenly to about 20% above its initial intensity, another standard increased slightly, and the other standards remained constant. We assume that the increase in the intensity of the $0\bar{4}0$ reflection resulted from decreasing effects of extinction as radiation damage of the crystal occurred. There was also marked yellowing of the crystal as the radiation exposure increased. In view of the constant nature of the weaker standards, we made no corrections of intensity with exposure.

Solution and Refinement of the Structure. All data were processed as described previously;[8] a value of 0.04 was used for *p* in the estimation of $\sigma(F_o{}^2)$. A total of 5234 reflections were processed, but of these 3015 unique reflections obey the condition $F_o{}^2 > 3\sigma(F_o{}^2)$. Only these reflections were used in subsequent calculations. The structure was solved using a Patterson synthesis,[9] in which it was possible to locate the Pt, P, and Cl positions consistent with space group *Pnma*. Three cycles of refinement using 1000 inner data, each followed by a difference Fourier synthesis, led to positions for all nonhydrogen atoms. The resultant structure in *Pnma* was one in which the mirror plane of the cation included all atoms save for those of PEt_3 and the mirror plane of the anion included the B atom and two F atoms. Refinement of the structure was carried out by full-matrix least-squares techniques. Throughout the refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight, w, is $4F_o{}^2/\sigma^2(F_o{}^2)$. The agreement indices R and R_w are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2}$. The scattering factors for nonhydrogen atoms were from the new tabulation;[10] the values for hydrogen were those of Stewart, *et al.*[11] The anomalous dispersion terms of Cromer[10] for Pt, P, Cl, and F were applied to the calculated structure factors.[12] A cycle of refinement in which the phenyl ring was constrained to a rigid group[13] of D_{6h} symmetry with C–C bond distances of 1.397 Å and in which all nonhydrogen atoms were assigned isotropic thermal parameters led to values of R and R_w of 0.092 and 0.109, respectively. It was noticed that the thermal parameter of N(2) was unusually high, where the numbering scheme is Pt–N(1)–N(2)–C_6H_4F.

At this point, all intensities were corrected for absorption. Calculated transmission factors ranged from 0.068 to 0.184, based on a linear absorption coefficient of 56.8 cm^{-1}.

A further cycle of isotropic refinement was followed by two cycles in which the nongroup atoms of the complex were allowed to vibrate anisotropically. The calculation resulted in agreement factors of 0.067 and 0.084, respectively. The thermal ellipsoid of N(2) was elongated perpendicular to the mirror plane and the N–N distance was 1.36 Å, much shorter than expected.

Since Fourier syntheses resulted in reasonable positions for the methyl hydrogen atoms and since a sensitive test for acentricity using second harmonic generation failed to detect the absence of a center of symmetry, we believe that the correct space group is *Pnma*. These positions and those of the methylene and hydrazine hydrogen atoms were idealized assuming tetrahedral geometry, C–H distances of 1.00 Å, and N–H distances of 0.95 Å. In ensuing calculations the phenyl hydrogen atom positions were idealized assuming planar-trigonal geometry. The hydrogen atoms were assigned isotropic thermal parameters equivalent to the values of the atoms to which they were attached. A fixed contribution from these hydrogen atoms was added to all subsequent structure factor calculations.

The short N–N distance and the large thermal motion of N(2) perpendicular to the mirror plane strongly suggested that part or all of the $N_2C_6H_4F$ group is disordered above and below this mirror plane. This was confirmed on the basis of a difference synthesis computed with this group omitted. The resultant orientation of the $N_2C_6H_4F$ group suggested that N(1) is on the mirror, that N(2) is about 0.5 Å off the mirror, and that the C_6H_4F portion approaches the mirror as one moves toward F. Accordingly, the N(2)–C_6H_4 portion was placed off the mirror, but N(1) and F were left on the mirror.

Another cycle of refinement in which N(2) and the rigid phenyl ring were assigned isotropic thermal parameters and not constrained to the plane resulted in agreement factors of 0.051 and 0.061, respectively. Another cycle in which the F(1) was allowed to leave the mirror plane as an isotropic atom and N(2) was allowed to vibrate anisotropically was followed by a redetermination of the hydrogen atom positions. Two final cycles of refinement, which included the new fixed hydrogen atom contribution and an isotropic extinction correction, resulted in R and R_w of 0.045 and 0.054, respectively, for 3015 observations and 135 variables.

An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of scattering angle, $|F_o|$, and Miller indices revealed no unexpected trends. The error in an observation of unit weight is 1.88 e. The final value of the isotropic extinction term is 6.3 (4) × 10^{-6} e^{-2}. The maximum density on a final difference Fourier synthesis is a residual of 1.6 e/Å^3 near Pt. This may be compared with peak heights of about 3.2 e/Å^3 for the C atoms in an earlier difference synthesis.

The final atomic positional and thermal parameters along with their standard deviations as estimated from the inverse matrix are given in Table I. Table II lists the idealized positional coordinates for the hydrogen atoms together with their assigned thermal parameters.[14] The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III;[14] only the reflections which were used in the refinement are listed in this table. Table IV presents the root-mean-square amplitudes of vibration.[14]

Description of the Structure and Discussion

The structure consists of the packing of discrete ions connected in chains by hydrogen-bond interactions between the hydrazine hydrogen atoms and the fluorine atoms of the tetrafluoroborate anion. Figure 1 presents the labeling scheme for the complex. The hydrogen atoms are labeled according to the carbon atoms to which they are affixed. The atom F(4) of the $BF_4{}^-$ is hydrogen bonded to HN(2), F(3) is not hydrogen bonded, and F(2), which does not lie on the mirror plane, is hydrogen bonded to HN(1) of another molecule. Figure 2 presents a stereoscopic view of the complex with one of the hydrogen-bond interactions. Figure 3 presents a stereoscopic view of the packing in one unit cell and the disorder of the

Table I. Positional and Thermal Parameters for Atoms of $[Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$

Atom	x^a	y	z	β_{11} or B^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.20415 (2)	1/4	0.08990 (2)	29.5 (1)	51.2 (2)	53.6 (2)	0	0.00 (1)	0
P	0.2074 (1)	0.4208 (1)	0.0878 (1)	41.0 (6)	51.8 (8)	88.3 (13)	0.0 (6)	2.5 (8)	3.7 (8)
Cl	0.2770 (2)	1/4	−0.0743 (2)	48.9 (9)	76.3 (15)	67.0 (17)	0	13.9 (10)	0
F(1)	0.0352 (4)	0.2679 (8)	0.7392 (6)	5.9 (2)					
F(2)	0.4696 (3)	0.1705 (4)	0.3251 (8)	69 (3)	88 (4)	336 (11)	0 (3)	61 (5)	−15 (5)
F(3)	0.4114 (11)	1/4	0.4571 (11)	237 (14)	332 (22)	144 (12)	0	71 (12)	0
F(4)	0.3518 (5)	1/4	0.3129 (14)	38 (3)	356 (20)	391 (22)	0	−36 (8)	0
B	0.4260 (7)	1/4	0.3568 (13)	34 (4)	101 (10)	113 (12)	0	21 (6)	0
N(1)	0.1352 (4)	1/4	0.2357 (5)	31 (2)	69 (4)	52 (5)	0	−4 (3)	0
N(2)	0.1818 (5)	0.2837 (7)	0.3298 (8)	33 (3)	67 (6)	59 (6)	−3 (4)	−5 (4)	3 (5)
C(1)	0.1427 (3)^c	0.2668 (6)	0.4324 (4)	3.3 (2)					
C(2)	0.0561 (3)	0.2688 (7)	0.4423 (4)	3.8 (2)					
C(3)	0.0192 (2)	0.2640 (9)	0.5469 (5)	4.5 (2)					
C(4)	0.0689 (3)	0.2574 (13)	0.6414 (4)	4.7 (3)					
C(5)	0.1556 (3)	0.2555 (14)	0.6315 (4)	4.3 (2)					
C(6)	0.1924 (2)	0.2602 (10)	0.5269 (5)	3.7 (2)					
C(7)	0.1829 (6)	0.4710 (7)	−0.0447 (8)	75 (4)	80 (6)	111 (7)	20 (4)	11 (5)	26 (5)
C(8)	0.0991 (7)	0.4365 (9)	−0.0849 (7)	84 (6)	125 (8)	104 (8)	29 (6)	−19 (5)	13 (6)
C(9)	0.3092 (6)	0.4713 (8)	0.1298 (12)	58 (4)	78 (6)	243 (15)	−17 (4)	0 (6)	−20 (8)
C(10)	0.3796 (6)	0.4545 (11)	0.0639 (13)	50 (4)	163 (13)	309 (21)	−19 (6)	16 (8)	−65 (13)
C(11)	0.1375 (5)	0.4788 (6)	0.1868 (7)	65 (4)	67 (4)	98 (6)	1 (3)	−1 (4)	−15 (4)
C(12)	0.1343 (7)	0.5905 (6)	0.1849 (9)	92 (6)	67 (5)	155 (10)	8 (4)	4 (6)	−27 (6)

[a] Numbers in parentheses here and throughout the paper are estimated standard deviations in the least significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The values of β have been multiplied by 10^4. [c] The positions of the six phenyl carbon atoms have been derived from the refined group parameters: $x_c = 0.1058$ (2), $y_c = 0.2621$ (7), $z_c = 0.5369$ (3), $\delta = -1.624$ (8), $\epsilon = -2.705$ (3), and $\eta = 1.502$ (9).

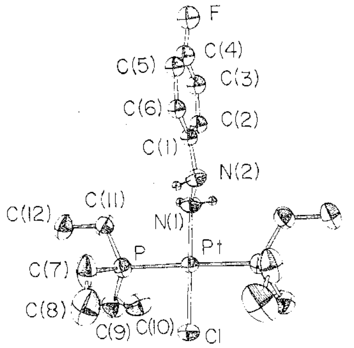

Figure 1. View of the complex $[Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl]^+$ showing the labeling of the atoms. The 50% thermal ellipsoids of all atoms except hydrogen are shown. Hydrogen atoms attached to carbon atoms have been omitted for the sake of clarity.

hydrazine molecules. Selected distances and angles are presented in Table V. Table VI presents selected dihedral angles.

The complex is square-planar as indicated by the bond angles about Pt in Table V. The Pt–P bond distance of 2.328 (2) Å is comparable with that found in the structure of II[3] (Pt–P = 2.320 (6) Å) and normal for *trans*-trialkylphosphines.[15] The variations in the bond distances and angles within the PEt_3 group appear to arise from the rather large effects of thermal motion. This thermal motion is manifested in the probability

Table V. Selected Distances (Å) and Bond Angles (deg) in $[Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$

	Bond Distances		
Pt–P	2.328 (2)	P–C(9)	1.845 (9)
Pt–Cl	2.303 (2)	P–C(11)	1.820 (8)
Pt–N(1)	2.081 (7)	C(7)–C(8)	1.507 (13)
N(1)–N(2)	1.436 (11)	C(9)–C(10)	1.404 (15)
N(2)–C(1)	1.408 (11)	C(11)–C(12)	1.523 (11)
C(4)–F(1)	1.308 (9)	B–F(2)	1.345 (8)
F(4)· · ·HN(2)	1.90	B–F(2)′	1.345 (8)
F(2)· · ·HN(1)	2.07	B–F(3)	1.234 (18)
P–C(7)	1.786 (9)	B–F(4)	1.306 (16)
	Nonbonded Distances		
HN(1)–HC(2)	2.13	P–Cl	3.241 (3)
N(2)–C(2)	2.443 (10)	N(1)–P	3.155 (5)
N(2)–F(4)	2.776 (12)	C(6)–F(3)	3.621 (18)
N(1)–F(2)	2.966 (8)	N(2)–N(2)′	0.918 (19)
	Bond Angles		
P–Pt–Cl	88.82 (4)	C(5)–C(4)–F(1)	119.5 (5)
P–Pt–N(1)	91.20 (4)	Pt–P–C(7)	112.8 (3)
Cl–Pt–N(1)	178.4 (2)	Pt–P–C(9)	112.9 (4)
P–Pt–P′[a]	177.18 (8)	Pt–P–C(11)	114.4 (3)
Pt–N(1)–N(2)	113.2 (5)	P–C(7)–C(8)	111.5 (6)
N(1)–N(2)–C(1)	114.4 (7)	P–C(9)–C(10)	119.9 (10)
N(2)–C(1)–C(2)	121.1 (5)	P–C(11)–C(12)	116.4 (6)
N(2)–C(1)–C(6)	118.4 (6)	N(2)–HN(2)–F(4)	150
C(3)–C(4)–F(1)	119.7 (6)	N(1)–HN(1)–F(2)	156

[a] A prime indicates atoms which have been reflected through the crystallographic mirror at $y = 1/4$.

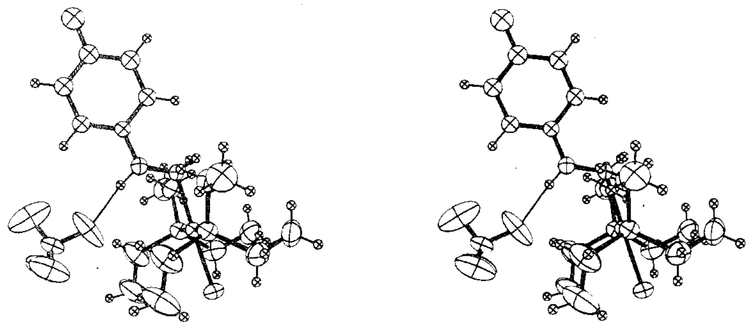

Figure 2. Stereoview of $[Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$ showing the hydrogen bond N(2)-HN(2)· · ·F(4).

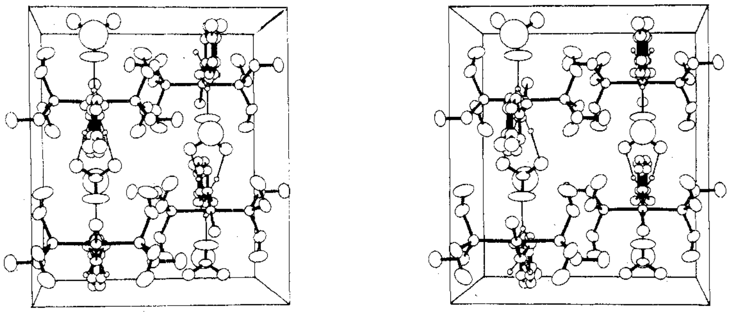

Figure 3. Stereoview of the packing in one unit cell of $[Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$. The *y* direction is to the right, the *x* direction is vertical, and the *z* direction is into the paper. The disorder of the hydrazine molecules is shown.

Table VI. Selected Interplanar Angles (deg) in $[Pt(PEt_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$

	Dihedral		
Pt-N(1)-N(2) N(1)-N(2)-C(1)	−168.3 (6)	C(1)-N(2)-N(1) C(1)-C(3)-C(5)	−29.1 (9)
Pt-N(1)-N(2) C(1)-C(3)-C(5)	−23.5 (7)	N(1)-N(2)-C(1) P-P′-N(1)	114.4 (6)
Pt-N(1)-N(2) P-N(1)-P′	−110.3 (4)		
	Vector Plane-Normal		
N(2)-C(1) C(1)-C(3)-C(5)	96.8 (7)	N(2)-N(1) N(1)-Pt-P	149.1 (5)
F(1)-C(4) C(1)-C(3)-C(5)	−99.0 (10)	N(2)-N(1) N(1)-P-P′	29.8 (5)
F(1)′-C(4) C(1)-C(3)-C(5)	−77.8 (10)	Pt-P C(7)-C(9)-C(11)	178.8 (2)

ellipsoids in the figures and in the root-mean-square amplitudes of vibration in Table IV. Application of a riding model for the C–C portion of the group increases the C(7)–C(8), C(9)–C(10), and C(11)–C(12) distances to 1.52, 1.45, and 1.55 Å, respectively.

The Pt–Cl distance of 2.303 (2) Å, though perhaps longer than the corresponding distance in II (2.291 (2) Å), is still short, indicating that the hydrazine has little trans influence.[16] This result is expected for a trans-coordinated sp^3 nitrogen atom.[17]

The Pt–N(1) bond length is 2.081 (7) Å. The corresponding distance from the structure of II is 1.973 (7) Å. In going from an sp^2-hybridized to an sp^3-hybridized nitrogen atom, the atomic radius increases by about 0.05 (1) Å.[18] This lengthening of the Pt–N(1) bond indicates that the hydrazine is not bound as tightly to the platinum atom but a review of Pt–N distances[19] indicates that the distance observed is very similar to other distances involving sp^3-hybridized nitrogen atoms.

The N(1)–N(2) bond distance is the feature most indicative of the reduction in bond order taking place in going from I to II to III. The corresponding values are about 1.16, 1.235 (10), and finally 1.436 (11) Å for this complex. These marked changes indicate a change in bond order from ~3 to 2 to 1, and continued hydrogenation of III ultimately reduces that bond order to 0 with the liberation of ammonia and aniline.

The N(1)–N(2) bond length is comparable with other known hydrazine bond lengths. Some typical lengths are 1.46 (4) Å found in a crystal structure of a zinc–hydrazine complex,[20] 1.449 (4) Å for hydrazine by electron diffraction,[21] and 1.453 (5) Å for hydrazine by infrared measurements.[22]

The plane defined by Pt–N(1)–N(2) was perpendicular to the coordination plane defined by P–N(1)–P′ when the hydrazine molecule was on the mirror plane. Instead, N(2) has moved off of the crystallographic mirror and the angle is now 69.7 (4)°. This deviation from 90° is comparable with that found in the structure of II (73.8 (7)°), but in that case there was no imposed symmetry. There is no chemical reason, steric or otherwise, that the hydrazine could not remain on a plane perpendicular to the coordination plane of the complex. In the solid state, deviation from 90° can be attributed entirely to hydrogen-bonding effects. Atom N(2) of the hydrazine has only one hydrogen atom in addition to the phenyl group. If this hydrogen atom, HN(2), is to point toward the nearby fluorine atom, F(4), of BF_4^-, then it must move toward the crystallographic plane. This is accomplished by moving N(2) (and thus the phenyl group also) off of the plane. The hydrogen-bond contact then becomes much more favorable (F(4)–HN(2) = 1.90 Å). This effect could have been accomplished by moving F(4) off of the plane and keeping the hydrazine on the plane, but this would have interfered with the two symmetrical, somewhat weaker hydrogen bonds to another molecule of complex, F(2)–HN(1) and F(2)′–HN(1)′. These two hydrogen-bond distances are longer (2.07 Å), but their combined effect together with the N(2)–H···F(4) hydrogen bond links the cationic complexes together in chains running along the *x* direction.

The Pt–N(1)–N(2) and N(1)–N(2)–C(1) angles have gone from sp^2 values (125.3 (6) and 120.0 (8)° respectively) for complex II to sp^3 values 113.2 (5) and 114.4 (7)° expected for a coordinated hydrazine.

The N(2)–C(1) distance of 1.408 (11) Å is the same as found in the structure of II (1.410 (12) Å). The phenyl ring, as described by C(1)–C(3)–C(5), makes an angle of −23.5° with the C(1)–N(2)–N(1) plane. In the structure of II this angle was 26.7 (9)° to relieve a close contact between HC(2) and HN(1). In the present structure there is no such close contact because the N(1) hydrogen atom is off the plane. The twist is presumably caused by intermolecular packing.

The results presented here demonstrate that the diazene of complex I has been reduced by hydrogenation to yield a hydrazine complex III. This reduction in N=N bond order under rather mild conditions may be of significance as a model for biological nitrogen fixation.

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Supplementary Material Available. Table II, the positional coordinates of the hydrogen atoms, Table III, the structure amplitudes, and Table IV, the root-mean-square amplitudes of vibration, 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 Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036.

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Synthesis of Diiminosuccinonitrile Complexes. Preparation and Structure of Bis(diiminosuccinonitrilo)platinum(II) *trans*-Dichlorobis(benzonitrile)platinum(II)

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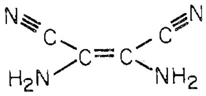
The complex bis(diiminosuccinonitrilo)platinum(II), [Pt(DISN)$_2$], and the analogs [Pd(DISN)$_2$] and [Ni(DISN)$_2$] have been prepared by the reaction in aqueous solution of the appropriate divalent metal halide with diaminomaleonitrile, oxygen, and a base. The reaction of diiminosuccinonitrile with bis(cyclooctadiene)nickel(0) also yields [Ni(DISN)$_2$]. [Pt(DISN)$_2$] can be prepared from PtCl$_4$, diaminomaleonitrile, and a base. An unusual material [Pt(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$] has been prepared by mixing stoichiometric quantities of the two components. The structure of this material has been determined from three-dimensional X-ray data collected by counter methods. The space group is C_{2h}^3-$C2/m$ with $a = 23.274$ (6) Å, $b = 12.439$ (3) Å, $c = 4.480$ (2) Å, $\beta = 98.68$ (1)°, $Z = 2$, $\rho_{\text{measd}} = 2.28$ (1) g/cm^3, and $\rho_{\text{calcd}} = 2.278$ g/cm^3. The structure has been refined by full-matrix least-squares techniques to a conventional R index (on F) of 0.029 for the 734 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$. The material consists of independent [Pt(DISN)$_2$] and [PtCl$_2$(C$_6$H$_5$CN)$_2$] molecules. The planar molecules form separate columns with interplanar distances of about 3.40 Å. The columns are held together by hydrogen bonds between the molecules. The bond distances found within the [Pt(DISN)$_2$] molecule suggest that the ligand has a delocalized electronic structure and that the compound is best described as a platinum(II) complex.

Introduction

Square-planar transition metal complexes with unsaturated electron-rich ligands are of considerable interest. Since such ligands alter the normal electronic environments of transition metals, these transition metal complexes have unusual properties, including spectroscopic, magnetic, and redox. Included among these interesting compounds are numerous complexes containing ligands with sulfur donors (dithiolates),[1-3] nitrogen or oxygen donors,[3-7] and, more recently, carbon donors.[8]

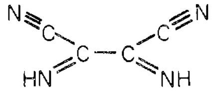
One ligand which can serve potentially in such a manner is diaminomaleonitrile (DAMN). This ligand, which is a substituted olefin, is electron rich and can coordinate to a metal in a number of different ways.



DAMN

Miles, *et al.*,[9] have shown that DAMN will react with Na$_2$PdCl$_4$ in acidic solution to give *trans*-dichlorobis(diaminomaleonitrile)palladium(II). The DAMN ligand serves as a monodentate amine and the complex has a trans square-planar geometry as deduced from an X-ray study. In addition, brief mention was made of the preparation in basic solution of neutral complexes of Ni(II), Pd(II), and Pt(II), which contain two DAMN molecules as the only ligands. These neutral complexes were thought to be analogs of the well-characterized metal complexes formed by the reaction of *o*-phenylenediamine with a variety of divalent metal halides in basic solution.[4,5] The *o*-phenylenediamine-derived complexes are formally complexes of the anion of benzoquinonediimine (BQDI). The complexes [M(BQDI)$_2$] (M = Co, Ni, Pd, or Pt) are intensely colored, have an extensive electrochemistry, and are themselves analogs of certain dithiolate complexes where the N–H group of the ligand is replaced by a sulfur atom.[4]

We find, on the basis of the details reported here, that these neutral complexes prepared from DAMN can be described as complexes of the anion of diiminosuccinonitrile (DISN).



DISN

The complexes [M(DISN)$_2$] (M = Ni, Pd, or Pt) have an intense blue or green color and are analogs of the well-known metal complexes of maleonitriledithiol (MNT).[1,2]

We wish to report greatly improved synthetic methods for the preparations of the DISN complexes and to report the molecular structure of [Pt(DISN)$_2$]. In an attempt to synthesize [Pt(DISN)$_2$] in a greater yield we used *cis*-dichlorobis(benzonitrile)platinum(II), [PtCl$_2$(C$_6$H$_5$CN)$_2$], as