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Crystal and Molecular Structure of *trans*-μ-Dichloro-bis(phenylazophenyl-2*C*,*N*′)diplatinum(II)[1]

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The crystal structure of *trans*-μ-dichloro-bis(phenylazophenyl-2*C*,*N*′)diplatinum(II), $[(C_{12}H_9N_2)PtCl]_2$, has been determined by x-ray diffraction techniques. The compound crystallizes in the monoclinic system, space group $C2/c$, with a = 27.07 (3) Å, b = 4.087 (3) Å, c = 20.91 (2) Å, β = 106.46 (8)°, and Z = 4. Halves of the dimeric molecule are related by a center of symmetry. Each platinum atom is coordinated to the two bridging chloride ions, an ortho carbon atom of a phenyl ring, and the distant azo nitrogen atom such that the azobenzene ligand forms a five-membered chelate. The entire molecule is planar with the exception of the free phenyl rings which are twisted 39° about the C–N bond away from the bridging chloride ions. The σ bond between the aromatic carbon and platinum atoms causes a significant lengthening (0.134 (8)° Å) of the trans Pt–Cl distance.

Introduction

Since the original reports[2,3] of the ortho metalation of azobenzene, there has been considerable interest[4–6] in ortho-metalation reactions. From the original studies involving nitrogen donor atoms in the ortho-metalated ligand, interest has spread to ligands with sulfide,[7] thioester,[8] and phosphite[9] donor groups among others and to complexes in which the ortho-metalated complex contains a six-membered chelate ring.[10] Weaver[11] established by x-ray methods that a σ bond is formed between the ortho carbon atom of azobenzene and palladium. Hoare and Mills[12,13] showed further by x-ray studies that azobenzene forms a five-membered chelate ring in rhodium complexes. Doedens[14] and co-workers have recently added to their series of structures in this field that of a possible intermediate in the ortho palladation of azobenzene. However, due partly to the difficulty in obtaining suitable crystals, the structure of the original Cope and Siekman product, μ-dichloro-bis(phenylazophenyl-2*C*,N′)diplatinum(II), has not been reported until now.

Experimental Section

The title compound was prepared as previously described[2] and was recrystallized with some difficulty from tetrahydrofuran solution. Saturated solutions of the complex were prepared at room temperature and filtered into test tubes which then were tightly stoppered with corks. After 1 week the solutions had evaporated by diffusion through the cork to approximately one-fourth the original volume and a few small, needle-shaped single crystals were found in several of the test tubes. One of the largest single crystals (approximate dimensions 0.6 × 0.1 × 0.05 mm, mounted along the needle axis, coincident with b) was used for precession photographs and subsequent intensity measurements. Systematic absences determined from both photo-

Table I. Fractional Atomic Positional Parameters[a,b]

Atom	x	y	z
Pt	0.316 18 (3)	0.328 55 (24)	0.003 85 (3)
Cl	0.262 1 (2)	0.414 3 (19)	0.071 1 (2)
N(1)	0.414 8 (6)	0.341 1 (57)	−0.017 9 (7)
N(2)	0.369 4 (5)	0.263 4 (51)	−0.043 0 (7)
C(1)	0.360 4 (7)	0.133 0 (59)	−0.111 5 (9)
C(2)	0.397 5 (7)	−0.064 2 (60)	−0.127 8 (10)
C(3)	0.389 1 (9)	−0.175 5 (68)	−0.192 4 (11)
C(4)	0.345 7 (9)	−0.094 1 (71)	−0.241 5 (10)
C(5)	0.308 6 (8)	0.105 8 (68)	−0.226 7 (9)
C(6)	0.315 1 (7)	0.224 0 (65)	−0.161 5 (9)
C(7)	0.377 5 (7)	0.504 7 (63)	0.067 1 (9)
C(8)	0.422 0 (7)	0.473 8 (63)	0.044 8 (9)
C(9)	0.471 0 (7)	0.585 1 (75)	0.082 7 (10)
C(10)	0.475 5 (8)	0.724 4 (80)	0.144 3 (10)
C(11)	0.432 2 (8)	0.759 5 (79)	0.167 3 (10)
C(12)	0.384 6 (8)	0.650 4 (69)	0.130 3 (10)

[a] The estimated errors in the last digit are given in parentheses; this form is used throughout. [b] The numbering scheme is shown in the figures.

Table II. Anisotropic Thermal Parameters[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	28 (1)	67 (1)	30 (1)	−2 (1)	8 (1)	4 (1)
Cl	30 (2)	110 (6)	39 (2)	−9 (3)	13 (2)	−8 (3)
N(1)	29 (8)	92 (15)	31 (8)	−4 (10)	1 (6)	0 (10)
N(2)	16 (7)	83 (16)	40 (8)	6 (8)	5 (6)	2 (9)
C(1)	43 (11)	56 (14)	40 (10)	−7 (10)	17 (8)	−2 (10)
C(2)	42 (11)	59 (15)	47 (11)	6 (11)	15 (9)	13 (10)
C(3)	66 (14)	61 (16)	61 (13)	4 (14)	35 (11)	−5 (13)
C(4)	58 (14)	85 (21)	40 (11)	−9 (14)	20 (10)	2 (12)
C(5)	57 (13)	87 (19)	24 (9)	−14 (13)	6 (9)	5 (11)
C(6)	40 (11)	79 (19)	32 (9)	−6 (12)	8 (8)	6 (11)
C(7)	34 (10)	64 (15)	41 (10)	20 (11)	5 (8)	3 (11)
C(8)	35 (9)	69 (16)	33 (9)	3 (11)	5 (8)	1 (10)
C(9)	27 (9)	107 (24)	49 (12)	−7 (12)	7 (8)	9 (14)
C(10)	42 (12)	116 (25)	35 (11)	−7 (14)	−5 (9)	−4 (13)
C(11)	44 (11)	119 (26)	33 (11)	−9 (14)	6 (9)	5 (14)
C(12)	46 (12)	82 (17)	39 (11)	4 (13)	19 (9)	−9 (12)

[a] All values are multiplied by 1000. The thermal parameters are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

graphs and diffractometer measurements indicated possible choices for the space group[15] as *Cc*, No. 9, or *C*2/*c*, No. 15. Least-squares determination[16] of the cell constants gave the following values: a = 27.07 (3) Å, b = 4.087 (3) Å, c = 20.91 (2) Å, β = 106.46 (8)°, V = 2219 Å^3. Due to the few crystals available an accurate density determination was not possible; however, the crystals sink in carbon tetrachloride (with slow dissolution and decomposition). Thus, the density is greater than 1.6 g cm^{-3}. For four dimeric molecules in the unit cell the calculated density is 2.46 g cm^{-3}. The centric space group *C*2/*c* was assumed and this choice was later shown to be correct by the successful heavy-atom solution and structure refinement. This space group requires that the halves of the dimer be related either by a twofold axis or by a center of inversion.

Intensity measurements for 2311 unique reflections in the sphere $2\theta < 49.5°$ were made as previously described.[16] A symmetric θ–2θ scan of 2.0° was used. Scan rates varied from 1.5 to 12.0°/min depending on the intensity of the reflection. Four standard reflections were used to check stability and to account for long-term drift. The drift correction varied from 1.056 to 0.954 and appeared to result from instrument instability. Although absorption is a relatively severe problem for this compound (μ = 134.7 cm^{-1}), the small size of the crystal used reduced the problem somewhat. Unfortunately the crystal was destroyed before we could make exact geometric measurements on it. From the estimated size and shape of the crystal we anticipate that the maximum relative error in $|F_o|$ due to absorption will be ~10%. A value of 0.02 was used for the Ibers ignorance factor[17] in calculating the estimated errors in intensities. A total of 1670 reflections with $|F_o| > 3\sigma(F_o)$ were obtained.

A Patterson map was computed[18] and the positions of the platinum atoms were determined in accord with the dimeric formulation of two heavy atoms related by the center at $^1/_4$, $^1/_4$, 0. The remaining nonhydrogen atomic positions were determined from a Fourier map computed on the basis of the platinum positions. Least-squares refinement using unit weights progressed normally. The final model, 145 variables including anisotropic thermal parameters for all nonhydrogen atoms with the hydrogen atoms at their calculated positions (C–H = 1.07 Å), converged to a conventional R factor[19] of 5.2%. A final difference electron density map showed several peaks within 1 Å of the platinum atom and at approximately one-third to one-sixth the height anticipated for a carbon atom. There were no other peaks larger than one-tenth that expected for a carbon atom. Examination of groups of reflections ordered on $|F_o|$ and on $(\sin\theta)/\lambda$ revealed no significant trends in disagreement with the model. The scattering curves used were those for Pt, Cl, N, C,[20] and H.[21] The values of $|F_o|$ and F_c from the last cycle of refinement are given in Table A.[22]

Results

Atomic positional parameters and their estimated standard deviations for nonhydrogen atoms are listed in Table I. The calculated positions used for the hydrogen atoms are presented in Table B.[22] Anisotropic thermal parameters for nonhydrogen atoms have been collected in Table II and the rms dis-

Table III. Bond Lengths (Å)

Pt–Cl	2.326 (6)	Pt–Cl[a]	2.460 (5)
Pt–N(2)	1.98 (2)	Pt–C(7)	1.94 (2)
C(1)–C(2)	1.40 (3)	C(2)–C(3)	1.38 (3)
C(3)–C(4)	1.37 (3)	C(4)–C(5)	1.40 (4)
C(5)–C(6)	1.41 (3)	C(6)–C(1)	1.42 (3)
C(7)–C(8)	1.42 (3)	C(8)–C(9)	1.41 (3)
C(9)–C(10)	1.38 (3)	C(10)–C(11)	1.40 (3)
C(11)–C(12)	1.38 (3)	C(12)–C(7)	1.41 (3)
C(1)–N(2)	1.48 (3)	C(8)–N(1)	1.38 (3)
		N(1)–N(2)	1.23 (2)

[a] Chloride related by inversion center of the dimer.

Table IV. Bond Angles (deg)

Cl–Pt–Cl[a]	82.5 (2)	Cl–Pt–C(7)	95.5 (7)
Cl[a]–Pt–N(2)	104.3 (5)	C(7)–Pt–N(3)	77.6 (8)
Pt–C(7)–C(8)	113 (1)	Pt–C(7)–C(12)	131 (2)
Pt–N(2)–N(1)	122 (1)	Pt–N(2)–C(1)	126 (1)
C(1)–C(2)–C(3)	120 (2)	C(2)–C(3)–C(4)	122 (2)
C(3)–C(4)–C(5)	120 (2)	C(4)–C(5)–C(6)	121 (2)
C(5)–C(6)–C(1)	118 (2)	C(6)–C(1)–C(2)	120 (2)
C(7)–C(8)–C(9)	123 (2)	C(8)–C(9)–C(10)	118 (2)
C(9)–C(10)–C(11)	120 (2)	C(10)–C(11)–C(12)	121 (2)
C(11)–C(12)–C(7)	121 (2)	C(12)–C(7)–C(8)	116 (2)
N(1)–C(8)–C(7)	116 (2)	N(1)–C(8)–C(9)	121 (2)
N(2)–C(1)–C(2)	121 (2)	N(2)–C(1)–C(6)	119 (2)
N(1)–N(2)–C(1)	112 (2)	N(2)–N(1)–C(8)	111 (2)

[a] Chloride related by inversion center of the dimer.

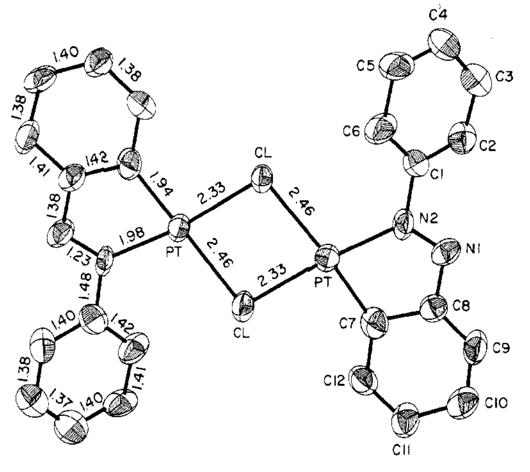

Figure 1. View of μ-dichloro-bis(azobenzene)diplatinum(II) in projection approximately onto the molecular plane. The normal to the molecular plane is at an angle of ~26° to the b axis.

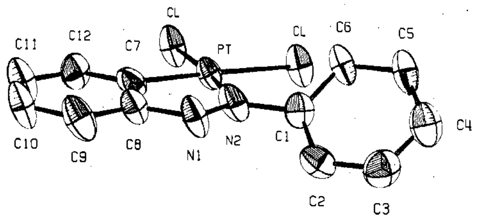

Figure 2. Side view of half of the dimeric molecule to illustrate the twist of the free phenyl ring (39°) and the directions of the thermal ellipsoids.

placements are shown in Figures 1 and 2. The molecule is dimeric with two chloride bridges and a trans configuration of the two 2-phenylazophenyl ligands, as shown in Figure 1. The bond lengths and angles appear in Tables III and IV, respectively. A series of weighted least-squares planes have been calculated for various fragments of the molecule and comprise Table C.[22] Both of the phenyl rings are found to be planar as is the platinum–azophenyl moiety.

Discussion

The structure of the title compound is that of two square coordinated platinum atoms bridged by a pair of chloride ligands. Coordination about each platinum atom is completed by two σ bonds to a 2-phenylazophenyl ligand, one to the ortho carbon atom of a phenyl ring and the other to the distant azo nitrogen atom to form a five-membered chelate ring as shown in Figure 1. The two 2-phenylazophenyl ligands are placed in a trans arrangement as required by the crystallographic inversion center. There are several structural details of considerable interest, viz., the presence of a structural trans effect, the twisting of the free phenyl ring out of the coordination plane, and the difference between C–N bond distances in the chelate ring and external to the chelate ring. However, it is important to note first the imprecision in the structure. The x-ray scattering is largely dominated by the platinum atoms (41% of total electron density), and although the structure has been refined to $R = 5.2\%$, there are relatively large uncertainties in the positions of the carbon and nitrogen atoms. The resultant estimated standard deviations in the C–C and C–N bond lengths are large, ~0.03 Å. However, these appear to be relatively conservative estimates, since all 12 C–C distances are within 1 esd of the accepted value of 1.395 Å, and both of the phenyl rings are found to be planar (vide supra). Our inability to correct for absorption leaves a bias in the data. We believe that this may affect the anisotropic thermal parameters significantly. In Figure 2, the major axes of thermal ellipsoids appear to be generally tipped relative to the molecular plane rather than perpendicular to it as might be expected. However, we doubt that uncorrected absorption has significantly altered the apparent bond lengths or molecular conformation.

van der Waals Contacts. Some aspects of the molecular conformation to be discussed below are undoubtedly affected by the packing forces in the crystal. Thus the free phenyl rings are placed such that their normals make an angle of 35.8° with the *b* axis, the short (4.087 Å) translation. This results in a perpendicular distance between phenyl rings in adjacent cells of 3.32 Å compared to the normal[23] inter-ring distance of 3.4 Å. The chlorine–chlorine distance of 4.09 Å in the *b* direction is larger than the sum of the chlorine van der Waals radii of 3.6 Å, and the interplanar spacing between bound phenyl rings is 3.69 Å. Only two H···H contacts are less than 2.4 Å, the sum of their van der Waals radii (2.36 and 2.38 Å). The influence of these forces on the twist angle of the free phenyl ring is discussed below.

Trans Effect. The σ bond between platinum and an aromatic carbon atom causes a significant structural trans effect. Thus, the Pt–Cl bond trans to C(7) is 2.460 (5) Å whereas that trans to N(2) is 2.326 (6) Å, yielding a difference of 0.134 (8) Å. This is within the range (0.1–0.2 Å) of trans effects for a σ-bonded carbon with platinum(II) given by Churchill.[24] In a palladium(II) complex containing a σ bond between the metal and the ortho carbon atom of a 2-phenylazophenyl moiety, Weaver[11] found trans Pd–Cl, 2.382 (5) Å, for a lengthening of ~0.08 Å. In rhodium(III) complexes[13,25] the carbon trans effect is ~0.19 Å and for iridium(III)[26] it is ~0.1 Å whereas it is less than 0.05 Å in manganese(0) complexes.[27]

Free Phenyl Twist. The structure of the molecule is such that H(6), the hydrogen atom on C(6) of the free phenyl ring, and the cis bridging chloride are brought into close proximity. Indeed, if the free phenyl ring were to lie in the molecular plane, then the H(6)···Cl contact would be 1.77 Å whereas the sum[23] of the van der Waals radii is 3.0 Å. This close contact is relieved in two ways. First, the free phenyl ring is moved away from the chloride such that the Pt–N(2)–C(1) angle[28] is 126 (1)° and the N(2)–Pt–Cl angle[29] opens to 104.3 (5)°. Second, the free phenyl ring is twisted 39° about the C(1)–N(2) bond with respect to the plane of the remainder of the complex, as illustrated in Figure 2. This increases the H(6)···Cl contact to the value of 2.7 Å found in this structure. A further twist of this ring would increase the H(6)···Cl contact distance but would reduce the distance between phenyl rings stacked along the *b* axis to less than the 3.32-Å value found here. Expanding the crystal along the *b* axis would allow a further twist of the free phenyl ring but the remainder of the contact distances (Cl···Cl and bound phenyl···bound phenyl; vide supra) would then be significantly greater than the optimal attractive distances. Thus, it appears a balance of these inter- and intramolecular forces results in the twist value of 39° found here. It may be assumed that the twist angle of the free phenyl ring will be somewhat greater in solution than in the solid state.

This interpretation of the twist angle is given some support by the findings of Hoare and Mills.[12 13] In the structure of di-μ-chloro-dicarbonylrhodium(I)bis(phenylazophenyl-2*C*,*N*′)rhodium(III),[13] they found the two free phenyl rings to be twisted 54 and 45° away from the bridging chloride ions. In the complex acetatobis(phenylazophenyl-2*C*,*N*′)rhodium(II),[12] where the bridging chloride ions have been replaced by the smaller acetate oxygen atoms, the twist angles are reduced to 14 and 22°. Bürgi and Dunitz[30] and also more recently Bernstein[31] have shown further that the free ligands in the isoelectronic series azobenzene, benzilidineaniline, and stilbene are quite flexible with respect to rotation about the C–N (or the analogous C–C) bond.

C–N Distance Differences. The twisting of the free phenyl ring is expected to reduce its conjugation to the bound, planar phenylazo moiety and should lengthen C(1)–N(2) relative to C(8)–N(1). The two distances are 1.48 (3) and 1.38 (3) Å, respectively, yielding a difference of 0.10 (5) Å. Although the difference is only possibly significant, it is in the expected direction. The N=N distance of 1.23 (3) Å is in agreement with that of the free ligand and is characteristic[14] of coordinated azobenzene ligands where one of the nitrogen atoms is involved in a σ bond to the metal atom. The remaining features of the structure are as expected.

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Registry No. *trans*-μ-Dichloro-bis(azobenzene)diplatinum(II), 15006-87-8.

Supplementary Material Available: Tables A–C, listing structure factor amplitudes, H atom positional parameters, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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Triamines of Cobalt(III). 5. Nuclear Magnetic Resonance Characterization of Diethylenetriaminecobalt(III) Complexes and the Structure of Meridional Bis(diethylenetriamine)cobalt(III) Nitrate Monohydrate

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The proton and carbon-13 magnetic resonance spectra of bis(diethylenetriamine)cobalt(III) ion (I) and triazido(diethylenetriamine)cobalt(III) (II) suggest that the tridentate ligand occupies the meridional position of the octahedra about the cobalt(III) metal centers. This configuration is confirmed by crystallographic analysis. The crystal and molecular structure of I was determined by three-dimensional x-ray analysis using monochromatic Mo Kα radiation. The compound is found to be monoclinic, with space group $P2_1/c$ whose unit cell data are $a = 8.766$ (4) Å, $b = 12.167$ (6) Å, $c = 18.669$ (8) Å, $\beta = 103.5$ (5)°, $Z = 4$, $d_{\mathrm{calcd}} = 2.047$ g cm^{-3}, and $d_{\mathrm{obsd}} = 2.04$ g cm^{-3}. The structure was solved by normal Patterson and Fourier methods and refined by conventional full-matrix least-squares techniques to a final discrepancy factor of 0.067. The maximum distortion of the octahedron is 5.6 (7)° from an ideal angle of 90°; and 9.3 (8)° from the expected 180° angle.

Introduction

In the bis(diethylenetriamine)cobalt(III) ion, the diethylenetriamine ligand may coordinate so as to generate three geometrical isomers: meridional, u-facial, and s-facial (Figure 1). These three have been isolated[1,2] and the crystal structures determined for compounds with the u-facial[3] and s-facial[4] configurations.

As part of a systematic study of cobalt(III) triamines, synthesis of *fac*- and *mer*-triazidodiethylenetriaminecobalt(III) ($\mathrm{Co(dien)(N_3)_3}$) was attempted by various means. The latter was easily prepared[5,6] while the former could be prepared only from the meridional isomer.[7] When attempts were made to prepare *fac*-$\mathrm{Co(dien)(N_3)_3}$ directly from cobalt nitrate, sodium azide, and diethylenetriamine, a large yield of what ultimately proved to be *mer*-$\mathrm{(Co(dien)_2)(NO_3)_3 \cdot H_2O}$ was produced, with little evidence for the formation of the other isomers of $\mathrm{(Co(dien)_2)^{3+}}$.

Experimental Section

Preparation of Racemic *mer*-$\mathbf{(Co(C_4H_{13}N_3)_2)(NO_3)_3 \cdot H_2O}$. Orange crystals of excellent quality were prepared by mixing 1 mol of cobalt nitrate hexahydrate with 1 mol of diethylenetriamine in water at room temperature (21 °C). This mixture was air oxidized for 1 h and filtered. A small amount of sodium azide had been added in an attempt to prepare the *fac*-$\mathrm{Co(dien)(N_3)_3}$; however, only the *mer*-$\mathrm{(Co(dien)_2)^{3+}}$ ion formed (and in greater yield than when azide was not present). The solution was treated with large amounts of methanol causing a crude yellow product to precipitate. Pure crystals were obtained by recrystallizing the crude product in water and air-drying after separation.

Spectroscopy. Proton magnetic resonance spectra were recorded with Varian A-60 and Varian XL-100 instruments at 60 and 100 MHz, respectively. All samples were dissolved in DMSO-d_6 with a concentration of ca. 5% by weight and run against internal TMS. PMR results are tabulated in Table I.

Carbon-13 resonance frequencies were measured on a Bruker HFX-90 NMR instrument operating in a Fourier transform mode using a Nicolet FT-1083 computer, 8K data table. $\mathrm{C_6H_6}$ was used as a spectrometer lock. All spectrometer operating parameters are identical for the two samples. All samples were run against internal TMS as standard.

X-Ray Data Collection. The compound prepared as above crystallized as parallelepipeds. A crystal measuring 0.18 × 0.33 × 0.10 mm was chosen from the recrystallized material and mounted with epoxy resin with the "*b*" axis of the crystal paralleling the glass capillary tube. Weissenberg and oscillation photographs indicated a monoclinic space group with systematic absences: (1) for the $0k0$ reflections, $k = 2n + 1$; (2) for the $h0l$ reflections, $l = 2n + 1$. These absences are characteristic of the assigned space group $P2_1/c$.

The crystal was transferred to a Syntex $P2_1$ automated diffractometer with a graphite monochromator for data collection, the details of which are summarized in Table II.

Solution and Refinement of the Structure. Standard Lorentz and polarization corrections were applied, and absorption corrections were made by the method of Coppens et al.[8a] The grid used for the absorption correction was 4 × 4 × 4 (parallel to *a*, *b*, *c*). Calculated