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Isomeric Bis[(phenylazo)acetaldoximato]platinum(II) Compounds

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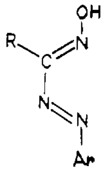
The reaction of (phenylazo)acetaldoxime, HL, with K_2PtCl_4 has been shown to yield complexes of composition PtL_2 in two isomeric forms, depending on reaction conditions. Under basic conditions deep green A, believed to be the trans isomer, is obtained, while under acidic conditions black B, the cis isomer, which has been X-ray crystallographically characterized, is obtained. Conditions for interconverting the A and B isomers have been defined. Both isomers have been characterized by measurements of molecular mass, mass spectra, electrochemistry, EPR spectra, and chemical reactivity. Isomer B both in the solid state and in solution is EPR active, and it is postulated that this may be due to traces of the *cis*-PtL_2^+ ion. In the crystal the asymmetric unit consists of two *cis*-PtL_2 molecules closely associated, though they separate when B is dissolved in chloroform (and, presumably, also in other solvents). The two independent, planar *cis*-PtL_2 units are essentially identical in structure with bond lengths and angles in accord with expected bond orders. The crystals belong to space group $P\bar{1}$, and the unit cell dimensions are as follows: a = 10.548 (5) Å, b = 16.341 (8) Å, c = 10.550 (6) Å, α = 98.02 (4)°, β = 106.28 (4)°, γ = 99.12 (4)°, V = 1691 (2) Å^3, Z = 4 (PtL_2).

Introduction

The anions, L^-, derived from arylazo oximes,[2,3] HL (**1**), are



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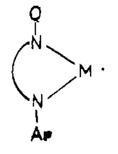

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excellent bidentate ligands and give rise to chelate rings of type **2**. The synthesis, structure, and reactivity of a number of metal arylazo oximates are reported by Chakravorty et al. In the presence of HL cobalt(II) is spontaneously oxidized to the meridional cobalt(III) complex[4,5] CoL_3. Rhodium(III) with a larger diameter yields both meridional and facial isomers.[6] The iron(II) analogue[7] FeL_3^- is presumably facial and can bind[8] other metal ions through oximato oxygen atoms: FeL_3Na, $(FeL_3)_2Mg$, $(FeL_3)_2Ni$, $(FeL_3)_2Cr^+$, etc. In $Ru^{III}X_2(HL)(L)$ the two X atoms (X = Cl, Br) are trans and the hydrogen-bonded (HL)(L) moiety is believed to span planar tetracoordination.[9] In species of the type $Ru^{II}X_2(HL)_2$, the X ligands are cis and there is X···H–L hydrogen bonding.[10] Copper(II) is readily reduced in the presence of HL, giving[11] $[Cu(HL)(L)]_2$, in which the copper(I) stereochemistry is distorted tetrahedral; dimerization occurs via hydrogen bonding (X-ray work[12]). Phosphines convert[13] the dimer to a reactive complex, $Cu(HL)(PR_3)_2$. Trinuclear copper(II) is known[14] in perchlorates of the spin-doublet ions $Cu_3L_3O^+$ and $Cu_3L_3(OH)^{2+}$.

Bis complexes of nickel (NiL_2) were reported years ago[15] (we have difficulties in reproducing the results). The palladium(II) chelates $Pd_2X_2L_2$, PdL_2, and PdLAz (Az = orthometalated azobenzene) and their reactions are well studied.[6,16-18] *The bis complex PdL_2 exists in only one form, which is believed to have trans stereochemistry.*[17]

In this work we are concerned with platinum(II) complexes of (phenylazo)acetaldoxime (**1**, R = Me, Ar = Ph). The structure of the ligand itself has been reported.[19] It has been found to react with K_2PtCl_4 to afford the bis complex, PtL_2, in two isomeric forms designated A and B. Both isomers are grossly diamagnetic in the solid state. The A isomer has the expected ^1H NMR spectrum and other properties, which are closely akin to those[17] of PdL_2. The B isomer displays relatively weak EPR signals both in the solid state and in solution; ^1H NMR signals are absent. It undergoes a reversible one-electron electrochemical oxidation near +0.4 V vs. SCE; the A isomer has no such oxidation response.

This paper reports a thorough study of isomers A and B in which their structures and properties have been clarified. There have previously been two preliminary reports[6,20] on the substance we now designate B. Since only this form was then known, it was assigned[20] a trans structure, since a cis structure in which two phenyl rings would be juxtaposed was expected to be relatively unstable. When the A isomer was discovered about 2 years later and found to be very similar to the only known form of PdL_2, which is almost certainly trans,[17] it was clear that the nature of the B isomer required further investigation. While isomer A has failed to yield any crystals suitable for X-ray crystallography, we remain confident that it is the trans isomer. Fortunately, isomer B has formed good crystals and its structure is now known.

Results and Discussion

Syntheses

The reaction of HL with K_2PtCl_4 yields A under basic conditions and B under acidic conditions. For example in a 50:50 water–dioxane mixture as solvent, A alone is formed

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Table I. Cyclic Voltammetric Data[a,b] in 90:10 Acetonitrile-Dichloromethane

isomer	$\bar{E}_p$ (ΔE_p), V
A[c]	−0.388 (0.087), −1.772 (0.075)
B[d]	+0.429 (0.062), −0.266 (0.057), −1.762 (0.085)

[a] Conditions: scan rate, 0.05 V s^{-1} at 298 K; working electrode, glassy carbon; supporting electrolyte, tetraethylammonium perchlorate. [b] Both isomers undergo irreversible oxidation at >1.1 V; the nature of this oxidation has not been investigated. [c] Two couples with low current (<1e) occur at $\bar{E}_p$ = −1.01 and −1.55 V; their origin is unknown. [d] Coulometric oxidation at +0.6 V shows 0.95 faradays/mol (average of five independent measurements).

when KOH is present in the reaction mixture while B alone is formed in the presence of $HClO_4$. If neither KOH nor $HClO_4$ is added, first A deposits and as the acidity of the solution increases (due to release of H^+ from HL) B also starts depositing. In the final stages nearly pure B is formed. When ethanol is used as the solvent, B alone is recovered when the reaction period is long (48 h). The role of the solvated proton or protic solvents in favoring the B isomer may be a cooperative template effect of the metal and the proton whereby two oximato functions are brought together in a cis position via hydrogen bonding in the course of the chelative reaction.

Interconversion of the Isomers

Both A → B and B → A transformations are achievable by heating but under very different reaction conditions. Photoirradiation of A and B at 254 or 350 nm leads to decomposition without isomerization. Studies at other wavelengths have not been made. In general the behavior of PtL_2 isomers in relation to interconversion appears to be quite different from that[21] of bis(glycinato)platinum(II) isomers.

A *to* B. When solutions of A are boiled in hydrocarbon or alcoholic solvents, B is produced. The extent of the conversion can be measured spectrophotometrically. One or more blue species (λ_{max} 620–640 nm) are also formed. On prolonged boiling B is progressively converted to the blue species, which are under investigation. The optimum periods of boiling (concentration of A ~10^{-4} M) for getting the maximum yield of B are as follows: ethanol, 1 h; *n*-butanol, 10 min; xylene, 30 min; toluene, 3 h. The conversion occurs more readily in alcohols than in hydrocarbons. In a given group, the higher the boiling point of the solvent, the shorter the time for optimum conversion. The advantage with alcohols may be in the proposed template effect of the proton mentioned above.

B *to* A. For this a solution of B in benzene is treated with hydrochloric acid in acetonitrile. Subsequent slow and careful addition of the reaction mixture to excess alkali yields A. Hydrogen chloride is known to open the arylazo oximate ring at the oximato end as will be discussed later. Reestablishment of the chelate ring under strongly alkaline conditions is attended by isomerization.

Some Selected Reactions

Electrochemical Reactions. The electrochemical responses of A and B were examined in 90:10 acetonitrile–dichloromethane mixtures at glassy carbon or platinum electrodes by using cyclic voltammetry and coulometry. The results are shown in Table I and Figure 1. The following symbols are used: E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; $\bar{E}_p$, average of E_{pc} and E_{pa}; $\Delta E_p = |E_{pc} - E_{pa}|$. The formal potentials are referenced to the saturated calomel electrode (SCE).

Two successive one-electron (from current height considerations) reduction responses are observed at negative potentials for both A and B. The electrons are believed to be added to the azoimine function as in the case of palladium arylazo oximates[17,18] and other azo complexes.[22] The reversible one-electron oxidative response of B near +0.4 V distinguishes B from A. The one-electron stoichiometry of couple 1 was established from current heights and coulometry (Table I).

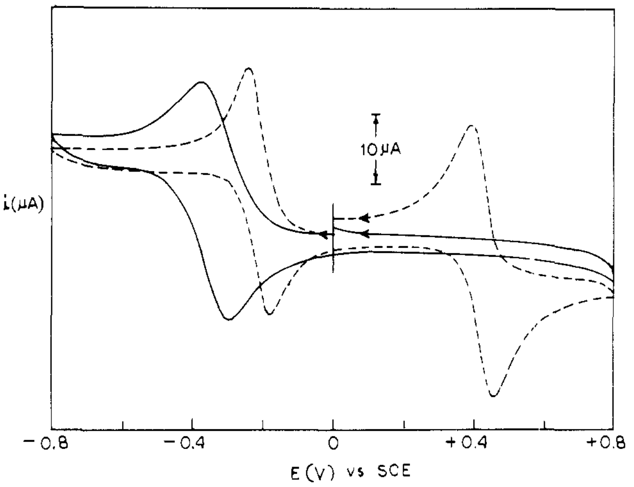
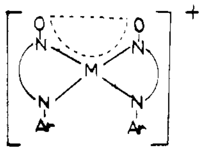


Figure 1. Cyclic voltammograms of PtL_2 in 10:90 dichloromethane–acetonitrile (0.1 M TEAP) at 298 K in the region +0.8 to −0.8 V: (—) isomer A; (---) isomer B.

$$B^+ + e^- \rightleftharpoons B \qquad (1)$$

We believe that in B^+ the metal is in an oxidized state, but EPR confirmation has not been practicable. The brown solution of B^+ is stable at least for 30 min under a dry dinitrogen atmosphere. When it is exposed to the atmosphere, a blue solution (λ_{max} 630 nm) of unknown nature, but possibly the same as the one observed in the A to B conversion, is formed. Since the B isomer is known to contain *cis*-PtL_2 (vide infra), a plausible, though speculative, explanation for the relative ease with which B (but not A) can be oxidized is that delocalization can occur over the cis-nitroxide system, as indicated in **3**, whereas no analogous possibility exists for the trans isomer, A.



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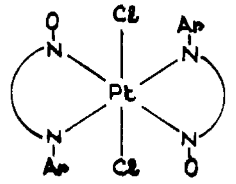
Oxidative Addition of Cl_2. Both A and B react with chlorine to afford the same PtL_2Cl_2 product (δ_{Me} 2.33). The Cl ligands appear from the infrared spectrum to be trans (ν_{PtCl} 324 cm^{-1}, and the remainder of the vibrational spectrum (500–4000 cm^{-1}) is more akin to that of A than that of B. It thus seems likely that PtL_2Cl_2 has a structure of type **4**. A cis → trans rearrangement of the PtL_2 moiety, therefore, occurs when Cl_2 reacts with B.



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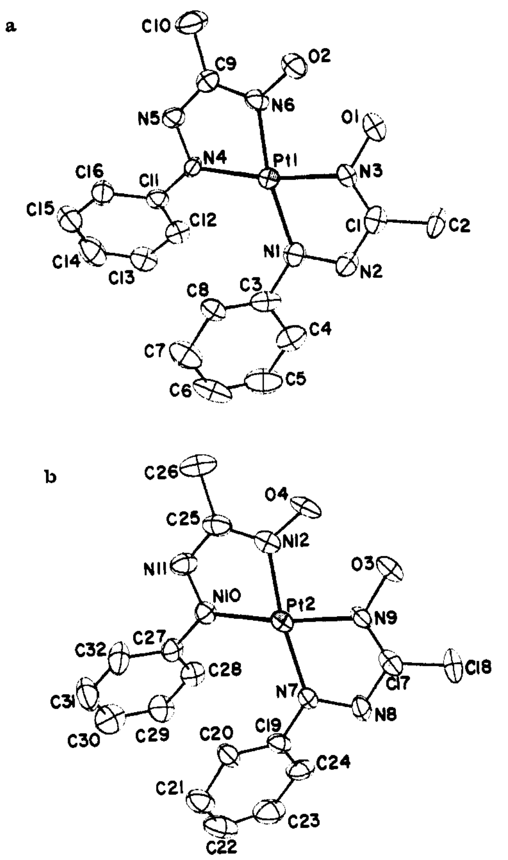
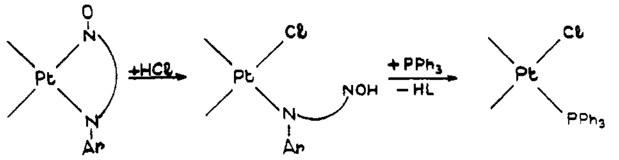


Figure 2. Atom-labeling scheme and 50% probability ellipsoids for (a) molecule 1 and (b) molecule 2.

Ligand Elimination. Both A and B react (the reaction of B is faster) with anhydrous hydrogen chloride in benzene medium, yielding a red solution. Addition of triphenylphosphine to the solution yields *cis*-$PtCl_2(PPh_3)_2$ (ν_{PtCl} 303, 280 cm^{-1}).

As in the case[17] of PdL_2, the oximato function in PtL_2 can be protonated and displaced by chloride (**5** → **6**). The



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phosphine then displaces the azo group, completing ligand elimination (**6** → **7**). On neutralization of the red solution (**6**) with aqueous alkali the original PtL_2 isomer is regenerated. The isomerization process (with A assumed to be trans) implicit in the conversion A → *cis*-$PtCl_2(PPh_3)_2$ occurs at the stage **6** → **7**. The previous report[20] that *trans*-$PtCl_2(PPh_3)_2$ results from B is in error.

Structural Results

As mentioned earlier, an X-ray determination of the crystal structure of A has not been carried out since suitable single crystals have not been obtained. Since the likelihood of A consisting simply of *trans*-PtL_2 molecules is very great, it did not seem worthwhile to make a special effort to obtain good crystals. Isomer B, however, readily afforded good crystals, and its structure has been established.

Crystalline isomer B contains *cis*-PtL_2 molecules, but these are arranged in an unexpected way. The crystallographic asymmetric unit consists of two crystallographically independent molecules, which have almost identical internal dimensions and are close enough to each other to constitute a kind of dimer. The structures of the two molecules are shown in Figure 2, and a stereoview of the dimer is shown in Figure 3. Average values of some important dimensions are listed in Table II.

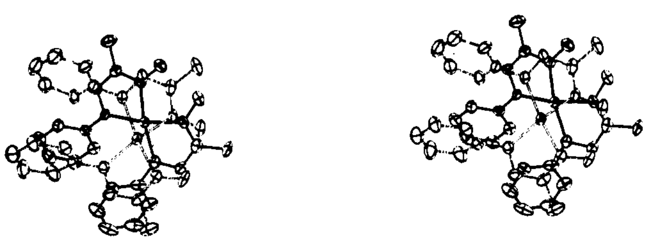


Figure 3. Stereoscopic view of the asymmetric unit. Molecule 1 has dark bonds. Molecule 2 has hollow bonds.

Table II. Selected Average Distances and Angles[a]

Distances, Å

	B	HL[19]
Pt-N(O)	1.954 [5]	
Pt-N(Ph)	2.018 [7]	
(Ph)N-N	1.326 [3]	1.256 [2]
N-O	1.34 [2]	1.385 [1]
(N)N-C(CH_3)	1.356 [6]	1.425 [1]
(O)N-C(CH_3)	1.322 [2]	1.286 [2]
C-CH_3	1.506 [9]	1.484 [3]
(Pt)N-C_6H_5	1.432 [5]	1.437 [3]

Angles, deg

(O)N-Pt-N(O)	95.3 [7]	Pt-N-C_6H_5	131.4 [6]
(Ph)N-Pt-N(Ph)	111 [2]	Pt-N-O	122.9 [5]
(O)N-Pt-N(Ph)	76.4 [3]		

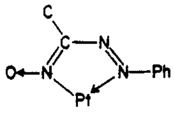
[a] Numbers in brackets are calculated as $[\overline{\Sigma}_n \Delta_i / n(n-1)]^{1/2}$, in which Δ_i is the deviation of the ith (of n) values from the arithmetic mean of the n values.

The platinum atoms are each coordinated by a planar arrangement of four nitrogen atoms. The two coordination planes (i.e., the mean planes of the four coordinated nitrogen atoms) in the loose dimer are nearly parallel, forming a dihedral angle of 16.4°. Each platinum atom is located slightly out of its coordination plane, by distances of 0.10 and 0.12 Å for Pt(1) and Pt(2), respectively. The directions of these displacements are such that the two platinum atoms approach each other.

The ligand backbone, comprising an N-N-C-N-O unit, is planar in each of the four crystallographically independent ligands, and the peripheral atoms C(Ph), C(Me), and O are nearly coplanar with their respective ligand backbones. The phenyl groups are tilted with respect to the coordination plane in each molecule. In molecule 1 each phenyl plane makes an angle of 38.4° with the coordination plane about Pt(1). The two aromatic rings are not parallel, however, but rather form a dihedral angle of 27.7°. In molecule 2 the two phenyl groups form dihedral angles of 50.3 and 51.5° with the four-membered platinum coordination shell; they make an angle of 12.1° to each other.

It is evident that steric interactions have a major influence on the geometry of this compound. The ligands are in a cisoid configuration, which places two phenyl groups in proximity. The effects of this can be seen in the (Ph)N-Pt-N(Ph) bond angles, which have an average value of 111 [2]°, and in the Pt-N-C(Ph) angles, which average to 131.4 [6]°. The distortion of the ligand arrangement gives the immediate coordination shell approximate C_{2v} symmetry, with the 2-fold axis bisecting the (Ph)N-Pt-N(Ph) bond angles. The average (O)N-Pt-N(O) angle is 95.3 [7]°, and the average chelate bite angle is 76.4 [3]°.

The electronic configuration of the ligand might be represented as a resonance hybrid with two major contributors, **8** and **9**. The bond lengths, as well as those in HL itself[19] for



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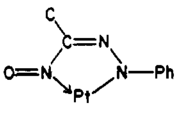

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comparison, are listed in Table II. For HL itself, the bond lengths are quite consistent with the electronic structure depicted in **1**, to which **8** is very similar. The bond lengths in B indicate that there has been a shift of electron density away from **8** toward **9**, though **8** seems, perhaps, still to predominate. The N–O bond distance (average value 1.34 [2] Å) is closer to a typical N–O single-bond distance (1.405 Å) than to the double-bond distance (1.206 Å). Also, the Pt–N(Ph) distances are systematically longer than the Pt–N(O) distances.

The fact that the platinum atoms are slightly out of their coordination planes, toward each other, with a Pt(1)–Pt(2) distance of 3.151 (1) Å, opens the possibility of a weakly bonding electronic interaction between them. This bonding is, of course, not to be compared with the strong single bonds, having distances of ca. 2.5 Å, found in some Pt^{III}–Pt^{III} molecules,[23] nor is it as strong as the bonding in some Pt^{II}–Pt^{II} compounds where distances below 3.0 Å are found.[24-26] An instructive comparison can be made with some of the stacked-planar platinum complexes.[27] Those that have a significant Pt–Pt interaction and are one-dimensional conductors have distances in the range 2.8–3.0 Å while $K_2Pt(CN)_4·3H_2O$, which is an insulator, has Pt–Pt distances of 3.48 Å. The present case is nearer to those that exhibit conductance and must, therefore, have significant metal–metal overlap.

There is a single short (<3.00 Å) noncovalent contact between the ligands of molecule 1 and those of molecule 2. This is a contact at 2.930 (10) Å between N(2) and O(4). This contact is not regarded as indicative of the presence of a hydrogen atom but is more likely the result of packing forces.

Physical Data

Molecular Mass. Osmometric molecular weights of A and B in chloroform solution (310.5 K) are 517 and 563, respectively (calcd 519). The mass spectrum of the B isomer was studied. The fragmentation pattern was complex, but loss of O and NO characteristic[17,28] of oxime complexes was observed. The molecular ion peak occurs at m/e = 519 (based on ^{195}Pt isotope). Other significant peaks are at m/e 504, 503, 489, and 357 corresponding to loss of CH_3, O, NO, and L, respectively.

Vibrational Spectra. Each isomer has its characteristic IR spectrum. Some characteristic vibrations are as follows: $\nu_{C=N}$, 1572 (A) and 1580 cm^{-1} (B); ν_{NO},[29] 1265 (A) and 1240 cm^{-1} (B). This indicates that the contribution of **8** may be somewhat more in A than in B. The two isomers are readily distinguished by two sharp bands: 1385 cm^{-1} (present in A but absent in B) and 835 cm^{-1} (present in B but absent in A).

Table III. Electronic Spectra[a] in Dichloromethane at 298 K

isomer	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
A	750 (3200), 675 (3000), 620 sh (2100), 570 (1700), 530 sh (1600), 460 sh (4000), 372 (17 100), 305 (3000)
B	1050 (6500), 960 sh (5600), 600 sh (900), 490 (3500), 380 (9600), 345 (9900), 305 (11 100)

[a] sh = shoulder.

Table IV. EPR Spectral Data of B

phase	temp, K	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle$	$A_{\parallel}$, G	$A_{\perp}$, G
toluene	300			1.976		
powder[a]	300	1.943	1.996	1.975[b]		
powder	77	1.946	1.988	1.974[b]	74	66

[a] Measurement at Q band; all other measurements are at X band. [b] $\langle g \rangle = {}^1/_3[2g_{\perp} + g_{\parallel}]$.

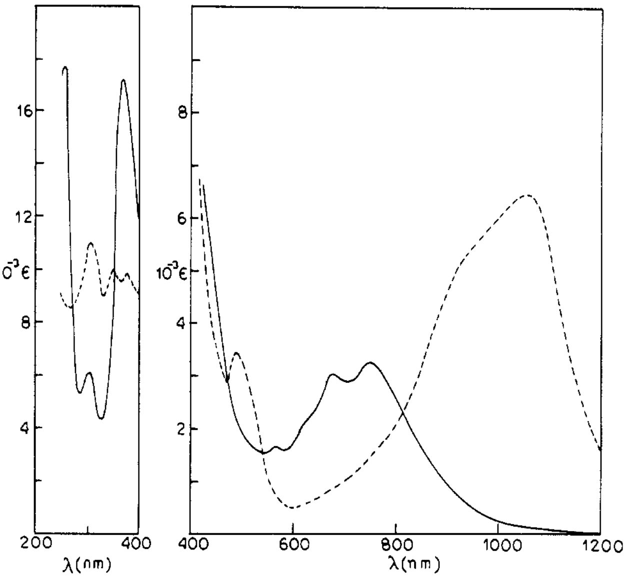

Figure 4. Visible–UV spectra of PtL_2 in dichloromethane: (—) isomer A; (- - -) isomer B.

Electronic Spectra. Both isomers are soluble in aromatic hydrocarbons and halocarbons. Solution colors are as follows: A, deep green; B, brownish yellow. Spectral data in dichloromethane are presented in Table III and Figure 4. The absorption in the visible and near-IR regions is believed to be due to a d (Pt) → π (azoimine) MLCT transition. The shift of bands to lower energy in going from A to B is consistent with their redox potentials, since in B both metal oxidation and ligand reduction, particularly the former, occur more readily than in A. The MLCT bands of PdL_2 are at higher energies[17] than those of PtL_2 (A). The ligand reduction potential[17] of PdL_2 is correspondingly more negative than that of A.

Magnetic Resonance. Both A and B are grossly diamagnetic in the solid state (Gouy method).

A has a normal ^1H NMR spectrum (δ_{Me} 2.33, $\delta_{aromatic}$ 7.56) in $CDCl_3$. The B isomer displays no ^1H signals. It appears to contain a small percentage of a paramagnetic species, e.g. B′: electron exchange between B and B′ could result in the observed ^1H NMR behavior. Attempts to determine the bulk solution paramagnetic susceptibility of B using Evans' method[30] failed. The signals (*tert*-butyl alcohol) from the solution of B in $CDCl_3$ and pure solvent were nonresolvable. A slight broadening was all that was observed. The percentage of B′ present is thus small.

B is EPR active in both powder and solution states. Spin counts have not been made, but the gain needed to observe

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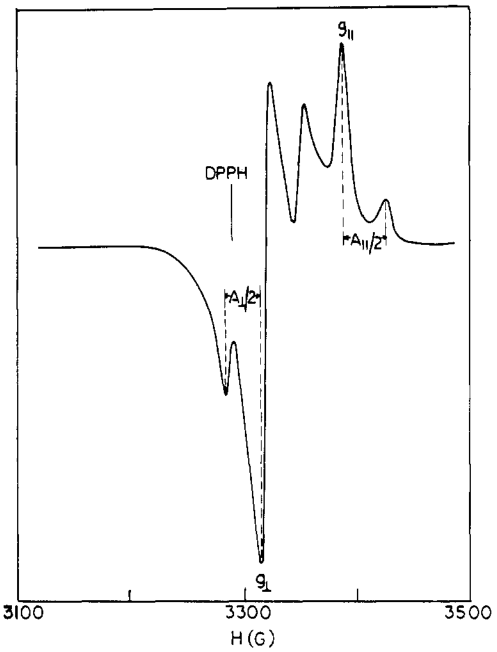

Figure 5. EPR spectrum of the B isomer (powder) of PtL_2 at 77 K.

reasonable spectral intensity is large (50 times that for the normal case), again showing that the contribution of B′ is small. EPR parameters are summarized in Table IV.

The powder spectra are axial. At 77 K five lines (Figure 5) are seen. The two major lines—$g_\parallel$ and $g_\perp$—represent molecules with nonmagnetic Pt isotopes. Hyperfine interaction with ^{195}Pt (33.7% abundance) is expected to give rise to two $g_\parallel$ and two $g_\perp$ satellites. Two of the satellites occurring between the major $g_\parallel$ and $g_\perp$ signals overlap with each other, accounting for the five lines. Lack of hyperfine structures in the solution spectrum indicates that the signs of $A_\parallel$ and $A_\perp$ are opposite. Since $g_\perp > g_\parallel$, B′ could be[31] a d^7 species having a tetragonal configuration [Pt(III)].

Concluding Remarks

The nature of the PtL_2 complexes, where HL is (phenylazo)acetaldoxime, is now largely clarified. Much indirect evidence indicates that isomer A is the trans isomer, and X-ray crystallography has shown directly that the B isomer is the cis isomer. The physicochemical properties of A and B can for the most part be readily understood in terms of these structures. However, isomer B presents two features that remain somewhat puzzling. One is the curious dimeric packing in the crystalline state. This is not an occurrence that was anticipated, nor is there any obvious reason for it.

The second aspect of B that has not been conclusively accounted for is the occurrence of an EPR-active impurity in both the solid compound and its solutions. On the evidence at hand, we think it is probable that the paramagnetic centers (B′) present in B are actually B^+ or a close relation thereof. The invariable presence of a small amount of paramagnetic "impurity" in a "pure" diamagnetic complex is known elsewhere.[32]

Experimental Section

Materials. K_2PtCl_4 was prepared by a reported method.[33] (Phenylazo)acetaldoxime was synthesized as before.[2,4] Acetonitrile for electrochemical studies was obtained by CaH_2 and P_4O_{10} treatments of the commercial solvent. Electrochemically pure dichloromethane was prepared from the commercial solvent by treatment of $NaHCO_3$ and anhydrous $CaCl_2$. Tetraethylammonium bromide was converted[34] to tetraethylammonium perchlorate (TEAP).

Table V. Crystal Data

formula	$PtC_{16}H_{16}N_6O_2$
space group	$P\bar{1}$
a, Å	10.548 (5)
b, Å	16.341 (8)
c, Å	10.550 (6)
α, deg	98.02 (4)
β, deg	106.28 (4)
γ, deg	99.12 (4)
V, Å^3	1691 (2)
d_{calcd}, g/cm^3	2.040
Z	4
fw	519.43
cryst size, mm	0.60 × 0.55 × 0.35
μ(Mo Kα), cm^{-1}	87.54
range of 2θ, deg	$0 < 2\theta \leqslant 52.5$; $+h, \pm k, \pm l$
no. of data, $F_o^2 > 3\sigma(F_o^2)$	4693
no. of variables	451
R^a	0.0349
$R_w{}^b$	0.0482
esd	1.108
largest shift^c	0.04

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Measurements. Molecular weights were determined by using a Knauer vapor pressure osmometer with benzil as calibrant. Mass spectra were recorded on a Hitachi RMS-4 spectrometer operating at 80 eV and by use of a direct-insertion probe at 493 K. IR spectra were obtained with Beckman IR-20A and IR-270M spectrophotometers. Electronic spectra were recorded with a Cary 17D or a Pye Unicam SP8-150 spectrophotometer. ^1H NMR data were collected with the help of a Varian T-60A spectrometer. EPR spectra were recorded with Varian E-104 (at X-band) and E-109 (at Q-band) spectrometers. The g values for powdered samples were evaluated by a published method.[35] Electrochemical measurements were carried out with Princeton Applied Research equipment as described elsewhere.[36] The glassy-carbon electrode was of PAR G0021 type. All measurements were carried out under a dinitrogen atmosphere and are uncorrected for junction potential.

Preparation of Complexes. Bis[(phenylazo)acetaldoximato]platinum(II), PtL_2. Isomer A. To an aqueous solution (20 mL) of K_2PtCl_4 (0.830 g, 2 mmol) was added dropwise with magnetic stirring a solution of (phenylazo)acetaldoxime (0.652 g, 4 mmol) in 30 mL of 0.5 N potassium hydroxide. Stirring was continued for 4 h. The black precipitate was thoroughly washed with water and then with ether. The crude product was chromatographed on a silica gel (60–120 mesh) column (1 cm × 50 cm) with benzene as the eluting agent. A yellow band consisting of unreacted ligand separated first and was rejected. The deep green band that followed was collected. The eluted solution was evaporated to dryness under vacuum, yielding pure compound. The product can be recrystallized from a dichloromethane–hexane mixture, giving dark, needle-shaped crystals. The yield was 0.52 g (50%). Anal. Calcd for $PtC_{16}H_{16}N_6O_2$: C, 36.99; H, 3.10; N, 16.18. Found: C, 37.34; H, 3.30; N, 15.93.

Isomer B. A solution containing K_2PtCl_4 (0.83 g, 2 mmol) in water (25 mL) was mixed with an ethanolic solution (30 mL) of (phenylazo)acetaldoxime (0.652 g, 4 mmol), and the mixture was stirred for 48 h. The deposited black solid was thoroughly washed with water (to remove K_2PtCl_4, KCl) and then with ethanol. After it was dried, the crude product was recrystallized from a chloroform–hexane mixture and black shining crystals resulted. The yield was 0.73 g (70%). Anal. Calcd for $PtC_{16}H_{16}N_6O_2$: C, 36.99; H, 3.10; N, 16.18. Found: C, 37.12; H, 3.08; N, 16.10.

Interconversions. (a) A → B. A solution of A (0.015 g, 0.029 mmol) in 30 mL of xylene was boiled for 30 min. The solvent was removed

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Table VI. Fractional Crystallographic Coordinates and Their Estimated Standard Deviations for *cis*-$Pt[N(O)C(CH_3)NN(C_6H_5)]_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pt1	0.24150 (3)	0.30344 (2)	0.44884 (3)	C8	0.2010 (9)	0.4088 (5)	0.1715 (8)
Pt2	0.18843 (3)	0.15726 (2)	0.19968 (3)	C9	0.0285 (8)	0.2308 (5)	0.5380 (8)
O1	0.4471 (6)	0.2284 (4)	0.6139 (6)	C10	−0.0504 (10)	0.1759 (6)	0.6018 (10)
O2	0.2169 (6)	0.1789 (4)	0.6153 (6)	C11	−0.0038 (8)	0.3962 (5)	0.3601 (7)
O3	0.4430 (6)	0.1180 (4)	0.3522 (6)	C12	0.0760 (8)	0.4752 (5)	0.3763 (8)
O4	0.4592 (6)	0.2184 (4)	0.1972 (6)	C13	0.0136 (10)	0.5398 (5)	0.3275 (9)
N1	0.3584 (7)	0.3729 (4)	0.3630 (7)	C14	−0.1241 (11)	0.5232 (6)	0.2684 (10)
N2	0.4881 (7)	0.3697 (5)	0.3968 (7)	C15	−0.2050 (10)	0.4434 (6)	0.2490 (9)
N3	0.4201 (7)	0.2808 (4)	0.5223 (6)	C16	−0.1436 (9)	0.3791 (6)	0.2938 (8)
N4	0.0560 (6)	0.3318 (4)	0.4175 (6)	C17	0.2514 (8)	0.0565 (5)	0.3962 (9)
N5	−0.0258 (6)	0.2871 (4)	0.4694 (6)	C18	0.3298 (10)	0.0112 (6)	0.4965 (10)
N6	0.1568 (7)	0.2307 (4)	0.5481 (6)	C19	−0.0834 (8)	0.0709 (5)	0.2358 (7)
N7	0.0596 (6)	0.0871 (4)	0.2724 (6)	C20	−0.1431 (8)	0.1397 (5)	0.2193 (8)
N8	0.1130 (7)	0.0425 (4)	0.3627 (7)	C21	−0.2892 (9)	0.1228 (7)	0.1831 (9)
N9	0.3070 (6)	0.1076 (4)	0.3306 (7)	C22	−0.3625 (9)	0.0431 (7)	0.1567 (10)
N10	0.0844 (7)	0.1959 (4)	0.0379 (6)	C23	−0.2983 (10)	−0.0241 (7)	0.1705 (10)
N11	0.1555 (7)	0.2405 (5)	−0.0234 (6)	C24	−0.1543 (9)	−0.0128 (6)	0.2107 (9)
N12	0.3307 (7)	0.2150 (4)	0.1371 (7)	C25	0.2904 (9)	0.2513 (6)	0.0328 (9)
C1	0.5196 (9)	0.3173 (6)	0.4837 (9)	C26	0.3882 (10)	0.3008 (7)	−0.0257 (10)
C2	0.6625 (9)	0.3047 (8)	0.5326 (11)	C27	−0.0580 (8)	0.1784 (5)	−0.0313 (7)
C3	0.3262 (9)	0.4291 (5)	0.2700 (8)	C28	−0.1267 (9)	0.0966 (5)	−0.0682 (8)
C4	0.4254 (10)	0.5015 (6)	0.2778 (9)	C29	−0.2673 (10)	0.0803 (6)	−0.1350 (9)
C5	0.3917 (12)	0.5524 (6)	0.1858 (10)	C30	−0.3348 (11)	0.1449 (7)	−0.1645 (10)
C6	0.2672 (13)	0.5334 (6)	0.0868 (9)	C31	−0.2596 (10)	0.2293 (6)	−0.1256 (12)
C7	0.1701 (11)	0.4621 (6)	0.0803 (9)	C32	−0.1209 (10)	0.2460 (5)	−0.0594 (10)

Table VIII. Interatomic Distances (Å) and Their Estimated Standard Deviations for *cis*-$Pt[N(O)C(CH_3)NN(C_6H_5)]_2$[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Pt1	Pt2	3.151 (1)	N5	C9	1.349 (11)	C11	C16	1.407 (12)
Pt1	N1	2.024 (7)	N6	C9	1.328 (11)	C12	C13	1.412 (12)
Pt1	N3	1.941 (7)	N7	N8	1.334 (9)	C13	C14	1.375 (14)
Pt1	N4	2.029 (6)	N7	C19	1.419 (10)	C14	C15	1.395 (15)
Pt1	N6	1.960 (7)	N8	C17	1.375 (11)	C15	C16	1.390 (13)
Pt2	N7	2.022 (7)	N9	C17	1.323 (11)	C17	C18	1.508 (12)
Pt2	N9	1.949 (7)	N10	N11	1.319 (10)	C19	C20	1.380 (12)
Pt2	N10	1.997 (6)	N10	C27	1.436 (10)	C19	C24	1.402 (12)
Pt2	N12	1.965 (7)	N11	C25	1.351 (12)	C20	C21	1.450 (13)
O1	N3	1.380 (9)	N12	C25	1.319 (12)	C21	C22	1.353 (15)
O2	N6	1.306 (8)	C1	C2	1.506 (13)	C22	C23	1.38 (2)
O3	N9	1.367 (8)	C3	C4	1.426 (13)	C23	C24	1.431 (13)
O4	N12	1.314 (9)	C3	C8	1.389 (13)	C25	C26	1.528 (13)
N1	N2	1.326 (10)	C4	C5	1.373 (15)	C27	C28	1.362 (11)
N1	C3	1.444 (11)	C5	C6	1.39 (2)	C27	C32	1.400 (12)
N2	C1	1.350 (12)	C6	C7	1.404 (15)	C28	C29	1.415 (13)
N3	C1	1.317 (12)	C7	C8	1.392 (12)	C29	C30	1.387 (14)
N4	N5	1.325 (9)	C9	C10	1.482 (12)	C30	C31	1.418 (14)
N4	C1	1.431 (10)	C11	C12	1.384 (11)	C31	C32	1.397 (14)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

under vacuum. The residue was dissolved in dichloromethane and was chromatographed on a silica gel (60–120 mesh) column (0.5 cm × 22.0 cm) with benzene as the solvent. The brownish yellow band of **B** was the first to be eluted out. Pure **B** was isolated by removing the solvent under vacuum. The yield was 0.005 g (33%).

(b) B → A. By the dissolution of concentrated hydrochloric acid in acetonitrile an acid of strength 0.01 N was prepared. To a benzene solution (15 mL) of **B** (15 mg, 0.029 mmol) was added 7.2 mL of the above acid (HCl:**B** = 2.5:1). The red solution thus produced was added dropwise to 14.5 mL of 0.01 N aqueous potassium hydroxide with stirring. The presence of excess base is essential for the conversion. (Dropwise addition of alkali to the red solution regenerates **B**.) After 2 h the green benzene layer was separated and then evaporated to dryness under vacuum to obtain pure **A**. The yield was 5.0 mg (33%).

Reaction of A and B. (a) With Dichlorine. Through a solution of **A** or **B** (30 mg, 0.038 mmol) in 20 mL of dry benzene was bubbled dichlorine. After a few bubbles had passed, the color of the solution suddenly changed to red. Addition of hexane (20 mL) produced dark-colored bis(arylacetaldoximato)dichloroplatinum(IV). The yield (0.034 g) is nearly quantitative.

(b) With Hydrogen Chloride and Triphenylphosphine. Through a solution of **A** or **B** (15 mg, 0.029 mmol) in dry benzene (20 mL) was bubbled anhydrous hydrogen chloride gas until the solution became red (for **A** and **B** 15 and 2 bubbles were respectively needed; the reaction with **B** is faster). Triphenylphosphine (15.4 mg) in 5 mL of benzene was then added to the above solution. When it was stirred, the solution became yellow and white crystals of *cis*-$PtCl_2(PPh_3)_2$ were deposited (yield 60%).

X-ray Crystallography. Data Collection. An opaque, green-black crystal of **B** of dimensions 0.60 × 0.55 × 0.35 mm was mounted at the end of a glass fiber and coated with a thin layer of epoxy cement. All geometric and intensity data were collected from this crystal, on an automatic four-circle diffractometer (Syntex $P\bar{1}$) equipped with a standard-focus Mo X-ray tube and a single-crystal graphite monochromator mounted in the perpendicular orientation.

The unit cell dimensions and the orientation of the crystal with respect to a goniometer reference frame were given by a least-squares fit to the angular positions of 15 accurately located reflections in the range 18° $< 2\theta <$ 30°.

The triclinic cell was checked for higher symmetry by a computerized comparison of the reduced cell to a table of all reduced-cell types.[37] As a further check on the lattice geometry as well as crystal quality, axial photographs were made for several direct-lattice axes.

Intensity data were collected for 6319 reflections in the range $0 < 2\theta <$ 52.5°, with a $2\theta-\omega$ scan motion. Three standard reflections

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Table IX. Bond Angles and Their Estimated Standard Deviations for *cis*-Pt{N(O)C(CH_3)NN(C_6H_5)}$_2$[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Pt2	Pt1	N1	86.1 (2)	Pt1	N6	O2	123.6 (6)	N4	C11	C12	119.3 (8)
Pt2	Pt1	N3	89.0 (2)	Pt1	N6	C9	117.3 (5)	N4	C11	C16	119.2 (7)
Pt2	Pt1	N4	101.5 (2)	O2	N6	C9	119.0 (7)	C12	C11	C16	121.4 (8)
Pt2	Pt1	N6	94.0 (2)	Pt2	N7	N8	116.9 (5)	C11	C12	C13	118.5 (8)
N1	Pt1	N3	75.6 (3)	Pt2	N7	C19	130.7 (5)	C12	C13	C14	119.4 (9)
N1	Pt1	N4	112.9 (3)	N8	N7	C19	112.3 (7)	C13	C14	C15	122.5 (9)
N1	Pt1	N6	170.2 (3)	N7	N8	C17	112.5 (7)	C14	C15	C16	118 (1)
N3	Pt1	N4	166.7 (3)	Pt2	N9	O3	123.7 (5)	C11	C16	C15	119.8 (9)
N3	Pt1	N6	94.6 (3)	Pt2	N9	C17	118.1 (6)	N8	C17	N9	115.9 (8)
N4	Pt1	N6	76.7 (3)	O3	N9	C17	118.1 (7)	N8	C17	C18	120.1 (8)
Pt1	Pt2	N7	88.4 (2)	Pt2	N10	N11	116.7 (5)	N9	C17	C18	123.9 (8)
Pt1	Pt2	N9	83.6 (2)	Pt2	N10	C27	130.6 (5)	N7	C19	C20	116.5 (8)
Pt1	Pt2	N10	106.8 (2)	N11	N10	C27	112.5 (6)	N7	C19	C24	118.7 (8)
Pt1	Pt2	N12	93.9 (2)	N10	N11	C25	113.6 (7)	C20	C19	C24	124.6 (8)
N7	Pt2	N9	76.6 (3)	Pt2	N12	O4	121.7 (6)	C19	C20	C21	116.2 (9)
N7	Pt2	N10	109.7 (3)	Pt2	N12	C25	116.4 (6)	C20	C21	C22	121 (1)
N7	Pt2	N12	172.1 (3)	O4	N12	C25	121.9 (8)	C21	C22	C23	120 (1)
N9	Pt2	N10	167.6 (3)	N2	C1	N3	116.0 (8)	C22	C23	C24	122 (1)
N9	Pt2	N12	96.0 (3)	N2	C1	C2	120.0 (9)	C19	C24	C23	115.4 (9)
N10	Pt2	N12	76.9 (3)	N3	C1	C2	123.9 (9)	N11	C25	N12	116.2 (8)
Pt1	N1	N2	117.3 (6)	N1	C3	C4	119.3 (9)	N11	C25	C26	120.8 (9)
Pt1	N1	C3	131.0 (6)	N1	C3	C8	118.7 (8)	N12	C25	C26	123.0 (9)
N2	N1	C3	111.7 (7)	C4	C3	C8	121.9 (8)	N10	C27	C28	118.7 (8)
N1	N2	C1	112.3 (8)	C3	C4	C5	117 (1)	N10	C27	C32	118.9 (8)
Pt1	N3	O1	122.7 (5)	C4	C5	C6	121 (1)	C28	C27	C32	122.4 (9)
Pt1	N3	C1	118.7 (6)	C5	C6	C7	120.5 (9)	C27	C28	C29	118.2 (8)
O1	N3	C1	118.6 (7)	C6	C7	C8	120 (1)	C28	C29	C30	121.8 (9)
Pt1	N4	N5	115.5 (5)	C3	C8	C7	119.0 (9)	C29	C30	C31	118 (1)
Pt1	N4	C11	133.3 (5)	N5	C9	N6	115.6 (8)	C30	C31	C32	120.2 (9)
N5	N4	C11	111.0 (6)	N5	C9	C10	121.1 (8)	C27	C32	C31	119.0 (9)
N4	N5	C9	114.7 (7)	N6	C9	C10	123.3 (8)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

were scanned after every 97 data measurements. No reduction was found in the intensities of the standard reflections throughout the 111-h period that the crystal was exposed to X-rays.

The usual Lorentz and polarization corrections were made to the measured intensities, and structure factors were derived. An empirical absorption correction[38] was based on azimuthal scans of nine reflections with goniometer positions near $\chi = 90°$. It was found that transmission decreased to below 50% of the maximum value, at some azimuthal settings, so the absorption correction was applied to all the data. After averaging of equivalent reflections, there remained 4693 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. These were used for structure solution and refinement.

Table V gives a summary of relevant crystal parameters.

Structure Solution and Refinement. Positions of the two platinum atoms in the asymmetric unit were derived from the top peaks of a Patterson map.[39] Two cycles of least-squares refinement of the parameters of these two atoms resulted in a standard R factor of ca. 16%. The remaining 48 atoms were located by two successive difference Fourier maps. The final refinement involved positional and anisotropic thermal parameters for 50 atoms, as well as an overall scale factor. These 451 parameters were fitted to 4693 data, and the final discrepancy indices were $R = 0.0349$ and $R_w = 0.0482$, with a quality-of-fit parameter of 1.108. (These quantities are defined at the end of Table V.) The largest relative shift of any parameter in the last cycle was 0.04 times the estimated standard deviation for that parameter. A difference Fourier map after convergence of the refinement showed no peaks of chemical significance; the only peak above 1 e/Å^3 was within 1 Å of atom Pt(1) and is assumed to be the result of series-termination effects.

Table VI gives the atomic coordinates and their estimated standard deviations for all atoms. Table VII (available as supplementary material) contains the anisotropic thermal parameters with esd's. Tables VIII and IX give the bond lengths and bond angles, respectively. Figure 2 shows the atom-labeling scheme and 50% probability ellipsoids for molecules 1 and 2, and Figure 3 is a stereoscopic view of the contents of the asymmetric unit. A table of least-squares planes and dihedral angles is available (Table X, supplementary material).

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Registry No. 4, 85080-91-7; A, 85027-38-9; B, 85027-39-0; *cis*-$PtCl_2(PPh_3)_2$, 15604-36-1; Cl_2, 7782-50-5.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table VII), least-squares planes and dihedral angles (Table X), and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(39) Crystallographic calculations were done by a PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX. Software was from the Enraf-Nonius Structure Determination Package.