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Structures of *trans*-Bis[(phenylazo)acetaldoximato]platinum(II) and -palladium(II): A Case of Nonplanar Tetracoordination in a Bis Complex of Palladium(II)

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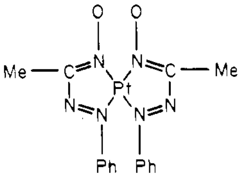
Arylazo oximes have the ability to furnish isomeric complexes with the heavier transition metals, and the structure and reactivity of such isomers are under study in these laboratories.[2-4] The reaction of K_2PtCl_4 with (phenylazo)acetaldoxime ($\mathrm{MeC({=}NOH)N{=}NPh}$, HL) in aqueous ethanol affords *cis*-PtL_2 (**1**), which has been fully characterized[3] X-ray crystallographically and otherwise. Under basic reaction conditions an isomer of **1**, previously[3] called the A isomer (A-PtL_2), results. The reaction of K_2PdCl_4 with HL under various reaction conditions yields only one isomer of the bis complex that was assumed[5] to be *trans*-PdL_2.



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Since the solution properties of PdL_2 and the A isomer of PtL_2 are grossly similar, the latter was assigned a trans structure. This admittedly inconclusive set of deductions had to be used since for long we were unable to grow sufficiently large single crystals of the A isomer of PtL_2 for X-ray work. Preliminary X-ray data with available crystals, however, showed that PdL_2 and A-PtL_2 are *not* isomorphous. This made the basis of our structural assignment for these species even more precarious.

After much trial and error we have now been able to obtain good crystals of A-PtL_2. The structure of this complex as well as that of PdL_2 has been accurately determined with the help of X-ray diffraction, and the results are reported here. The gross structures of both species are indeed trans planar, but the palladium complex displays a large and unusual distortion toward tetrahedrality.

Results and Discussion

Structure of *trans*-PtL_2. Discrete molecules are stacked parallel to the *b* axis at intervals of 3.956 Å. Each molecule is centrosymmetric (C_i). The metal atom and the eight other atoms forming the two chelate rings define an excellent plane of symmetry. The deviation of all atoms from the best plane is <0.08 Å. Each phenyl ring makes an angle of 43.8° with the above plane. A view of *trans*-PtL_2 is presented in Figure 1. Selected bond distances and bond angle data are collected in Tables I and II, respectively.

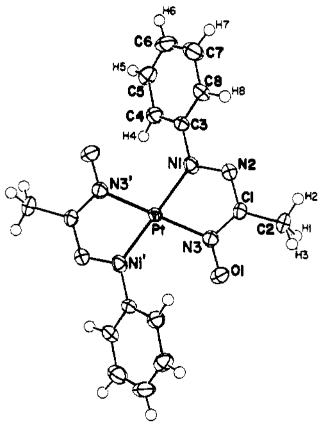

Figure 1. Molecular structure and atom-labeling scheme for *trans*-PtL_2. Non-hydrogen atoms are represented by their 50% probability ellipsoids. Hydrogen atoms are represented by circles of arbitrary radius.

Table I. Important Bond Distances (Å) and Their Estimated Standard Deviations for *trans*-PtL_2 and *trans*-PdL_2[a]

	distance			distance	
atoms	M = Pt	M = Pd	atoms	M = Pt	M = Pd
M-N(1)	2.020 (6)	2.033 (3)	C(1)-N(2)	1.338 (9)	1.352 (5)
M-N(3)	2.015 (6)	2.027 (3)	N(2)-N(1)	1.294 (9)	1.283 (4)
O(1)-N(3)	1.261 (8)	1.268 (4)	N(1)-C(3)	1.433 (9)	1.433 (5)
N(3)-C(1)	1.348 (9)	1.339 (5)	C(1)-C(2)	1.488 (10)	1.486 (6)

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

Table II. Important Bond Angles (deg) and Their Estimated Standard Deviations for *trans*-PtL_2 and *trans*-PdL_2[a]

	angle	
atoms	M = Pt	M = Pd
N(1)-M-N(1')	180	173.8 (2)
-N(3)	77.0 (2)	76.8 (1)
-N(3')	103.0 (2)	104.2 (1)
N(3)-M-N(3')	180	161.3 (2)
M-N(1)-N(2)	116.1 (5)	116.4 (2)
-C(3)	130.1 (5)	128.8 (2)
N(2)-N(1)-C(3)	113.8 (6)	114.7 (3)
N(1)-N(2)-C(1)	115.6 (6)	115.4 (3)
M-N(3)-O(1)	127.2 (5)	127.0 (3)
-C(1)	113.2 (5)	113.0 (2)
O(1)-N(3)-C(1)	119.6 (6)	118.9 (3)
N(2)-C(1)-N(3)	117.0 (6)	117.4 (3)
-C(2)	121.0 (7)	119.8 (4)
N(3)-C(1)-C(2)	121.7 (7)	122.8 (4)

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

In crystalline *cis*-PtL_2, loosely held (Pt–Pt = 3.151 Å) dimers of two nearly identical monomers are present.[3] Within a monomeric unit, each chelate ring is planar and the two rings are nearly coplanar. The molecules are more efficiently packed in the trans isomer ($d_{\mathrm{calcd}} = 2.12$ g $\mathrm{cm^{-3}}$) than in the cis isomer ($d_{\mathrm{calcd}} = 2.04$ g $\mathrm{cm^{-3}}$) of PtL_2.

Structure of *trans*-PdL_2. Molecules of PdL_2 (Figure 2) have C_2 symmetry. Discrete molecules are present in the crystal, and there is no sort of stacking. The shortest Pd–Pd distance is 6.636 Å. Each chelate ring is planar (all atoms are within 0.06 Å of the least-squares plane). The oxime oxygen and methyl carbon atoms also fall in this plane. The gross relative orientation of the two chelate rings is trans. However, a surprising feature of the *trans*-PdL_2 structure is a large de-

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[1] (a) Indian Association for the Cultivation of Science. (b) Texas A&M University.

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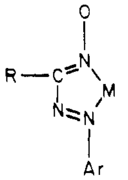
Table III. Selected Average Distances (Å) in Metal Arylazo Oximates[a]



compd	M-N(O)	M-N(Ar)	N-O	N(O)-C	(R)C-N	N=N	ref
HL (R = Me, Ar = Ph)			1.385 [1]	1.286 [2]	1.425 [1]	1.256 [2]	11
Cu(HL)(L) (R = Me, Ar = Ph)	1.987 [2]	1.997 [1]	1.347 [1]	1.307 [5]	1.398 [5]	1.285 [1]	8
$RuCl_2(HL)_2$ (R = Ph, Ar = Ph)	1.988 [2]	1.984 [5]	1.371 [2]	1.314 [8]	1.345 [24]	1.296 [5]	4
cis-PtL_2 (R = Me, Ar = Ph)	1.954 [6]	2.018 [7]	1.342 [19]	1.322 [2]	1.356 [6]	1.326 [5]	3

[a] Numbers in brackets are calculated as $[\Sigma_n \Delta^2{}_i/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the *i*th (of *n*) value from the arithmetic mean of the *n* values.

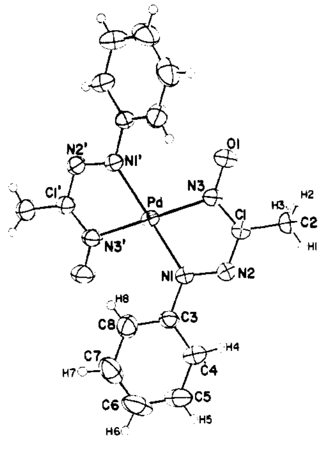


Figure 2. Molecular structure and atom-labeling scheme for *trans*-PdL_2. Non-hydrogen atoms are represented by their 50% probability ellipsoids, while hydrogen atoms are given as circles of arbitrary radius.

viation of the PdN_4 coordination sphere from planarity toward the tetrahedral configuration. The dihedral angle between the two planar chelate rings is 25.6°. The bond distances and angles within the chelate rings are very similar for the palladium and platinum complexes, as can be seen from the listings in Tables I and II.

The origin of the distortion in *trans*-PdL_2 and of the lack of it in *trans*-PtL_2 is unclear at present. Interplay of the following factors could be important: (i) stronger preference of platinum(II) for planar tetracoordination; (ii) gain in conjugation as the dihedral angle of the phenyl ring to the chelate ring decreases; (iii) increase in the steric repulsion between the phenyl ring and oxime oxygen of the adjacent ligand under conditions defined in (ii). The following observations are significant in this context: (a) the dihedral angle of the phenyl ring with the corresponding chelate ring is much smaller[6] (24.8°) in *trans*-PdL_2 than in *trans*-PtL_2; (b) in high-boiling solvents PtL_2 undergoes[7] an internal redox transformation in which an oximato oxygen atom migrates to the adjacent phenyl ring; (c) in tetrahedral[8] $Cu^I(HL)(L)$ the dihedral angle of the phenyl ring to the corresponding chelate ring is only ~1°.

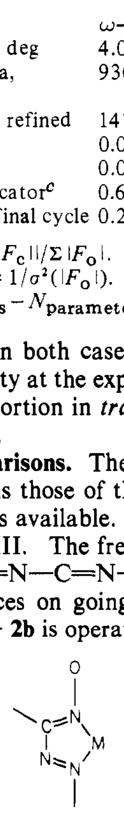
There have been several unsuccessful attempts in the past to utilize interligand steric crowding to introduce tetrahedral distortion in four-coordinate bis chelates of palladium(II). Good examples are certain salicylaldimines[9] and dipyrromethenes.[10] In both cases the metal coordination sphere retained planarity at the expense of intraligand bending. The tetrahedral distortion in *trans*-PdL_2 is unique and unprecedented for Pd^{II}.

Table IV. Selected Crystal Data, Data Collection Parameters, and Least-Squares Residuals for *trans*-ML_2 (M = Pt, Pd)

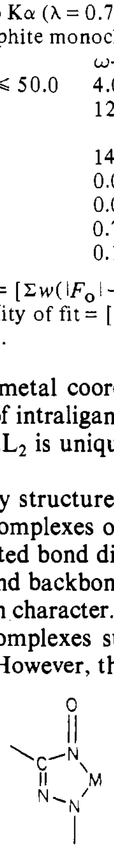
	M = Pt	M = Pd
formula	$PtC_{16}H_{16}N_6O_2$	$PdC_{16}H_{16}N_6O_2$
fw	519.4	430.7
space group	*I*2/*a*	*C*2/*c*
a, Å	20.033 (4)	20.679 (9)
b, Å	3.956 (1)	7.759 (3)
c, Å	20.578 (5)	11.405 (4)
β, deg	91.45 (2)	114.76 (3)
V, $Å^3$	1630 (1)	1662 (1)
Z	4	4
d_{calcd}, g/cm^3	2.12	1.72
cryst size, mm	0.30 × 0.09 × 0.05	0.35 × 0.25 × 0.15
μ(Mo Kα), cm^{-1}	90.8	11.2
data colln instrument	Syntex P$\bar{1}$	
radiation	Mo Kα (λ = 0.710 73 Å), graphite monochromated	
scan method	ω–2θ	ω–2θ
data colln range, deg	$4.0 \leq 2\theta \leq 50.0$	$4.0 \leq 2\theta \leq 60.0$
no. of unique data, $F_o{}^2 \geq 3\sigma(F_o{}^2)$	930	1272
no. of parameters refined	147	146
R^a	0.0166	0.0252
$R_w{}^b$	0.0226	0.0344
quality-of-fit indicator[c]	0.605	0.797
largest shift/esd, final cycle	0.21	0.17

[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 = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Other Comparisons. The X-ray structure of the free ligand,[11] as well as those of three complexes other than those reported here, is available. Selected bond distance data are given in Table III. The free-ligand backbone is nearly pure azo imine (–N=N—C=N—O) in character.[12] The changes in bond distances on going to complexes suggest that the resonance **2a** ↔ **2b** is operative. However, there are specific



2a



2b

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(6) In the equilibrium configuration within the crystal, the O(1)–C(8) distance is 2.94 Å. This is the shortest contact between the oximato oxygen and the phenyl ring.

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Table V. Positional and Isotropic Equivalent Thermal Parameters for *trans*-ML_2 (M = Pt, Pd)[a]

	M = Pt				M = Pd			
atom	*x*	*y*	*z*	*B*, Å^2	*x*	*y*	*z*	*B*, Å^2
M	0.000	0.000	0.000	2.054 (4)	0.000	0.21874 (5)	0.250	2.743 (6)
O(1)	−0.0509 (2)	0.362 (1)	0.1141 (2)	3.44 (8)	−0.1538 (1)	0.1380 (4)	0.1586 (2)	4.47 (6)
N(1)	−0.0876 (2)	−0.019 (1)	−0.0506 (2)	2.45 (8)	0.0010 (1)	0.2328 (4)	0.0728 (2)	2.82 (5)
N(2)	−0.1403 (2)	0.062 (1)	−0.0189 (2)	2.4 (1)	−0.0576 (1)	0.1972 (4)	−0.0241 (2)	3.14 (6)
N(3)	−0.0647 (2)	0.212 (1)	0.0614 (2)	2.50 (9)	−0.1032 (1)	0.1763 (4)	0.1280 (2)	3.09 (6)
C(1)	−0.1290 (3)	0.180 (2)	0.0413 (3)	2.4 (1)	−0.1130 (2)	0.1581 (5)	0.0049 (3)	3.09 (6)
C(2)	−0.1848 (3)	0.302 (2)	0.0815 (3)	3.7 (1)	−0.1815 (2)	0.0998 (6)	−0.0988 (3)	4.42 (9)
C(3)	−0.1013 (3)	−0.106 (1)	−0.1172 (3)	2.5 (1)	0.0576 (2)	0.2863 (5)	0.0398 (3)	2.96 (6)
C(4)	−0.0590 (3)	0.010 (2)	−0.1643 (3)	2.80 (9)	0.0570 (2)	0.2404 (5)	−0.0781 (3)	3.87 (8)
C(5)	−0.0746 (3)	−0.055 (1)	−0.2290 (3)	3.1 (1)	0.1125 (2)	0.2938 (7)	−0.1074 (4)	5.31 (9)
C(6)	−0.1311 (3)	−0.237 (2)	−0.2460 (3)	3.7 (1)	0.1660 (2)	0.3938 (6)	−0.0206 (4)	5.7 (1)
C(7)	−0.1732 (3)	−0.354 (2)	−0.1984 (3)	3.7 (1)	0.1663 (2)	0.4394 (6)	0.0949 (4)	5.0 (1)
C(8)	−0.1582 (3)	−0.289 (2)	−0.1336 (3)	2.9 (1)	0.1117 (2)	0.3858 (5)	0.1268 (3)	3.81 (8)
H(1)	−0.189 (5)	0.57 (2)	0.091 (5)	9 (3)*	−0.181 (2)	0.100 (5)	−0.170 (4)	5 (1)*
H(2)	−0.224 (3)	0.24 (2)	0.058 (3)	4 (1)*	−0.216 (2)	0.159 (7)	−0.090 (5)	8 (1)*
H(3)	−0.186 (3)	0.25 (2)	0.123 (3)	4 (2)*	−0.186 (2)	−0.020 (8)	−0.083 (4)	8 (1)*
H(4)	−0.021 (2)	0.16 (2)	−0.153 (2)	2 (1)*	0.022 (2)	0.154 (6)	−0.130 (3)	4.2 (9)*
H(5)	−0.050 (3)	0.04 (1)	−0.260 (3)	4 (2)*	0.113 (3)	0.270 (6)	−0.177 (5)	6 (1)*
H(6)	−0.137 (3)	−0.29 (2)	−0.285 (3)	4 (1)*	0.199 (3)	0.440 (7)	−0.033 (5)	10 (2)*
H(7)	−0.214 (4)	−0.44 (1)	−0.211 (4)	4 (2)*	0.198 (2)	0.505 (7)	0.158 (4)	6 (1)*
H(8)	−0.194 (3)	−0.36 (2)	−0.102 (3)	2 (1)*	0.111 (2)	0.423 (4)	0.195 (3)	3.5 (8)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + (ab\cos\gamma)\beta(1,2) + (ac\cos\beta)\beta(1,3) + (bc\cos\alpha)\beta(2,3)]$.

interactions characteristic of each metal, and it is not possible to rationalize all distance variations in Table III simply in terms of the varying contributions of **2a** and **2b**.

It is also notable that in both *trans*-PdL_2 and *trans*-PtL_2 the N–O distances (~1.26 Å) are short. While such short distances are not without precedent,[13] they are relatively rare. In oxime complexes N–O distances are usually[14] >1.3 Å, as shown in Table III. On going from *cis*-PtL_2 to *trans*-PtL_2, the N–O distance shortens but Pt–N(O) becomes longer.

Concluding Remarks. The present work vindicates our original proposal[3] that the A isomer of PtL_2 has the trans structure. In the PtL_2 compounds we thus have an authenic case of cis–trans isomerism. The other major result of this work is the discovery of the tetrahedral distortion of *trans*-PdL_2. The molecule is diamagnetic over the accessible range of temperature, and ^{1}H NMR spectra show no evidence of paramagnetic population. The chemical consequences of the proximity of the oximato oxygen atoms and phenyl rings in *trans*-bis(arylazo oximato)metal(II) are under study.[7]

Experimental Section

Preparation of Complexes and Crystals. Reported methods[3,5] were used to prepare A-PtL_2 and PdL_2. Crystals of A-PtL_2 were grown by slow diffusion of hexane into a dilute solution of the complex in chloroform. The crystals grow in the form of very thin, clustered needles. After many attempts a few crystals of suitable dimensions were obtained. Good crystals of PdL_2 were grown by slow diffusion of hexane into a dilute solution of the complex in benzene.

X-ray Structure Determinations. A summary of crystal characteristics, data collection parameters, and residuals from the least-squares refinements of both structures is given in Table IV. For each structure, measurements were taken by an automated diffractometer (Syntex P$\bar{1}$, with Mo Kα radiation) from a single crystal mounted at the end of a glass fiber. The determination of the unit-cell parameters and orientation matrix and the collection of intensity data by ω–2θ scans were conducted according to routine procedures.[15] For the crystal of *trans*-PtL_2, several azimuthal scans were made for reflections near $\chi = 90°$, for use in an empirical absorption correction.[16]

After data reduction and application of appropriate corrections,[17] each structure was solved and then refined with unique data having $F_o^2 \geq 3\sigma(F_o^2)$. For *trans*-$PtL_2$, the position of the platinum atom was derived from considerations of the unit-cell dimensions, the space group, and the chemical entity at hand. Development of the structure was followed by a convergent, full-matrix refinement with a data-to-parameter ratio of 6.3. All hydrogen atoms, found in a difference Fourier map, were refined, with isotropic thermal parameters, in the final cycle. A difference map following convergence had no peak more dense than 0.40 e/Å^3.

The structure of *trans*-PdL_2 was solved by direct methods and developed and refined by a sequence of alternating difference Fourier maps and least-squares cycles. All hydrogen atoms were located and then refined with isotropic thermal parameters. The final, convergent refinement involved a data-to-parameter ratio of 8.7. The largest difference peak following convergence had a density of 0.50 e/Å^3.

Least-squares residuals for both structures, as noted above, are given in Table IV. Positional and isotropic equivalent thermal parameters are listed in Table V.

There are no unusual crystallographic features in either structure. In the structure of *trans*-PtL_2, the molecules are stacked along the *y* axis, with the coordination plane of each one tilted 26° from perpendicularity to the axis. The Pt···Pt distance is the *b* lattice repeat, 3.956 (1) Å. In the structure of *trans*-PdL_2, the less anisotropic space-filling properties of the molecule do not effect significant directionality in either the internal packing or the external morphology of the crystal.

Acknowledgment. We thank Dr. Wenning Wang for assistance with the collection of X-ray data. Financial support from the Department of Science and Technology, New Delhi, India, and the Robert A. Welch Foundation (Grant No. A-494) is gratefully acknowledged.

Registry No. *trans*-PtL_2, 85027-38-9; *trans*-PdL_2, 63056-54-2.

Supplementary Material Available: Tables of observed and calculated structure factors, bond distances and bond angles, and anisotropic thermal parameters for both compounds (18 pages). Ordering information is given on any current masthead page.

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(17) For the structure of *trans*-PtL_2, crystallographic calculations were done on a VAX-11/780 computer in the Department of Chemistry at Texas A&M University, with programs from the Enraf-Nonius VAX-SCP package. For *trans*-PdL_2, a PDP-11/60 computer was used at B. A. Frenz and Associates, Inc., College Station, TX. Programs were from the SDP-PLUS package.