reduces its importance in controlling the rate of dissociation of the stibine.

As can be seen from the data in Table I, the change of the chelate diolefin from 1,5-cyclooctadiene to norbornadiene does not appreciably affect the kinetic behavior. There is a small increase in the reactivity which could be related to the different chelating properties of the two diolefins, but the discrimination between different entering amines remains practically the same. Changing the nature of the aromatic group R in the stibine (from *p*-tolyl to phenyl) does not influence the rate to any significant extent.

However, drastic changes are observed when triphenylphosphine or triphenylarsine is present instead of the stibine. The kinetics of the corresponding reactions are not reported, since the displacement of phosphine and arsine is too fast to be followed by our techniques. However, it could be seen that, whereas under the conditions used the displacement of phosphine was reversible, that of the arsine (and the stibine) was not. In the absence of data for the phosphine and arsine systems it would not be wise to suggest any special reason why the stibine bonded to Rh(I) promotes such a peculiar behavior. However, there might be some connection with the observation that equilibria of the type

$$[Rh(CO)L_2Cl] + L \rightleftharpoons [Rh(CO)L_3Cl]$$

leading to the formation of five-coordinated species are found[10] when L = SbR_3 but not when it is a phosphine or an arsine.

Experimental Section

The olefinic stibine complexes have been synthetized according to the method of Wilkinson[11] by treating $[(diolefin)RhX]_2$[12] in CH_2Cl_2 with the calculated amount of $Sb(p\text{-tolyl})_3$. After evaporating nearly all the solvent, the compounds were obtained by adding *n*-hexane.

$[(1,5\text{-cyclooctadiene})RhCl(SbR_3)]$ (R = *p*-tolyl) is a yellow compound. *Anal.* Calcd for $RhC_{29}ClH_{33}Sb$: C, 54.2; H, 5.1. Found: C, 54.9; H, 5.0.

$[(1,5\text{-cyclooctadiene})RhBr(SbR_3)]$ is an orange compound. *Anal.* Calcd for $RhBrC_{29}H_{33}Sb$: C, 50.7; H, 4.8. Found: C, 50.9; H, 4.8.

$[(norbornadiene)RhCl(SbR_3)]$ is a yellow compound. *Anal.* Calcd for $RhC_{28}ClH_{29}Sb$: C, 53.8; H, 4.6. Found: C, 54.0; H, 4.4.

The kinetics were followed spectrophotometrically. Known volumes of thermostated solutions of the complex and the reagent were mixed in the thermostated compartment of an Optica-CF4 double-beam recording spectrophotometer. The spectra changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region at known intervals. Once the spectrum changes were characterized and a suitable wavelength chosen to study the reaction, the kinetics were followed by setting the wavelength at the chosen value and recording the changes of optical density as a function of time.

Acknowledgment. We thank the Italian Council for Research (C.N.R., Rome) for financial support.

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[10] R. Ugo, F. Bonati, and S. Cenini, to be submitted for publication.

[11] M. A. Bennet and G. Wilkinson, *J. Chem. Soc.*, 1418 (1961).

[12] J. Chatt and L. M. Venanzi, *ibid.*, 4735 (1957).

The Crystal Structure and Molecular Conformation of Bis(N-*t*-butylsalicylaldiminato)palladium(II)[1]

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received February 24, 1968*

Abstract: A three-dimensional X-ray structure analysis of crystalline bis(N-*t*-butylsalicylaldiminato)palladium(II) leads to a centrosymmetric, but markedly "stepped," conformation for the molecule. The parallel mean planes of the salicylaldimine residues are separated by 1.72 Å and each plane is inclined 35.6° to the planar quasi-square coordination group. Conformational details of the *t*-butyl-substituted chelate rings, longer than normal values for some bond lengths, and shorter than usual nonbonding distances, are suggestive of pronounced steric strains within the molecule. The monoclinic unit cell of the crystal has $a = 19.38$, $b = 7.78$, $c = 14.71$ Å, $\beta = 108.8°$, and contains four molecules; calculated and measured densities are 1.45 and 1.44 g/cc, and the space group is C2/c. Reflections lying for the most part within the Cu $K\alpha$ limiting sphere were photographically recorded with Mo $K\alpha$ radiation; intensities were visually estimated. Structure determination utilized Patterson and Fourier syntheses, followed by anisotropic full-matrix least-squares refinement. A conventional R of 0.070 for the 1254 independent reflections was obtained.

The reasons for undertaking a structural investigation of the diamagnetic bis(N-*t*-butylsalicylaldiminato)palladium(II) chelate are best presented against the background provided by recent studies of the bis(N-alkylsalicylaldiminato) chelates of nickel(II). The Ni(II) complexes display a rather complicated magnetic behavior that is correlated with the existence of stereochemically distinctive, yet energetically comparable, diamagnetic and paramagnetic (triplet) species of each chelate.[4] In each of the several known crystal-

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[1] This investigation was supported in part by National Science Foundation Grant GP-6710X, by Public Health Research Grant 2-RO1-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

[2] National Science Foundation Predoctoral Trainee, 1965–1969.

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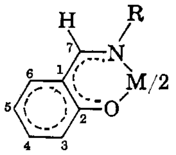
[4] See R. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964), for a comprehensive discussion with numerous references to pertinent earlier papers.

line structures,[5-7] a single stereochemically and magnetically pure species is utilized, but in solution the diamagnetic and paramagnetic forms exist in temperature-dependent equilibrium mixtures.[4] Paramagnetic species that may arise in a noncoordinating solvent by solute association, stable only at low temperatures, are not considered in this paper; attention is directed instead to the monomeric paramagnetic species that become assertive whenever the N-alkyl substituents, R in the diagram below, are branched-chain alkyls. Although the difference in the Gibbs (free) energy between chemically paired diamagnetic and paramagnetic monomers is somewhat sensitive to the choice of solvent and to substitution in the benzene ring of the salicylaldimine residue, the sign of ΔG is primarily determined by the choice of the N-alkyl substituent; the singly branched isopropyl and *sec*-butyl favor the diamagnetic species except at temperatures well above those accessible to direct measurement, whereas *t*-butyl substitution favors the paramagnetic species at all temperatures.[4]



The presumption that the observed variations in magnetic and thermodynamic properties of the monomeric Ni(II) chelates are sterically induced finds detailed support in the basic stereochemistries that are displayed by several of the pertinent species in known crystalline arrangements. In the diamagnetic form of a complex the central NiN_2O_2 coordination group is planar and quasi-square,[5,6] but in the paramagnetic form the coordination group is tetrahedral.[7] Tetrahedral coordination is compatible with at least approximate planarity of each half of the bis(salicylaldiminato)nickel(II) skeleton, the specific choice of N-alkyl substituent notwithstanding; planar quasi-square coordination, by contrast, is accompanied by a marked folding within each half of the basic skeleton when R is a singly branched alkyl and, presumably, by distortions that are so large as to destabilize the diamagnetic species when R is *t*-butyl.

Although diamagnetism in solution and in the crystal is retained by the bis(N-*t*-butylsalicylaldiminato)palladium(II) molecule, the ultraviolet spectrum given by this chelate is significantly different from that recorded for the chemically analogous Pd(II) chelates in which the alkyl substituent (R) is *n*-butyl or ethyl.[8] In the N-*n*-alkyl-substituted chelates the over-all configuration of the bis(salicylaldiminato)metal(II) skeleton is approximately planar, with modest departures therefrom in the six-membered chelate rings, but none in the central coordination group.[9] When the crystals used in the X-ray study now reported were supplied to us by Professor R. H. Holm, he pointed out that a similarly quasi-planar skeleton for the N-*t*-butyl-substituted chelate appeared to be sterically unattainable, and he posed the question whether the required conformational adjustments must include some departure from planarity in the PdN_2O_2 coordination group.[8] Our structure determination for the N-*t*-butyl-substituted chelate demonstrates that the palladium(II) atom does retain planar quasi-square coordination, but at the expense of especially large foldings in the chelate rings and other conformational strains that would seem to render this complex less stable than the isomeric N-*n*-butyl substituted chelate. It will be seen, moreover, that these conformational strains must be substantially larger in a diamagnetic, isostructural, N-*t*-butyl-substituted Ni(II) chelate.

Experimental Section

Monoclinic crystals of bis(N-*t*-butylsalicylaldiminato)palladium(II) have $a = 19.384 \pm 0.029$, $b = 7.777 \pm 0.010$, $c = 14.706 \pm 0.020$ Å, $\beta = 108.83 \pm 0.10°$, and a measured density of 1.444 g/cc; with a cell content of four formula weights the calculated density is 1.452 g/cc. Systematically absent X-ray spectra were those required by the space groups[10] C2/c and Cc. The choice of the centrosymmetric C2/c was supported by the negative results of sensitive tests for piezoelectricity and by all subsequent developments during structure determination.

Intensity data were visually estimated from two independent sets of equiinclination Weissenberg photographs that utilized Zr-filtered Mo Kα radiation and multiple-film techniques. Nine layers of Weissenberg data were collected from a crystal having the dimensions $0.325 \times 0.225 \times 0.100$ mm, with rotation about *b*, and an additional eight layers were recorded from a specimen of dimensions $0.350 \times 0.150 \times 0.113$ mm, with rotation about *c*. With a linear absorption coefficient[11] of 0.86 mm^{-1} for Mo Kα radiation and the experimental technique employed, the maximum variation of absorption in either specimen from the mean for the recorded reflections was approximately $\pm 6\%$; the corrections for variable absorption that would have given a small statistical improvement in the quality of the intensity data were not made. Intensities were reduced to relative squared amplitudes, $|F|^2$, by means of standard Lorentz and polarization factors. A total of 1254 independent reflections, comprising $\sim 60\%$ of those lying within the Cu Kα limiting sphere, were recorded as above background; this comparatively low yield of observable reflections was subsequently found to arise from the fact that half of the general (*hkl*) reflections carry no contributions from palladium atoms. Some 585 of the 1254 reflections were directly involved in the cross-correlation of the experimental data.

The wholly straightforward interpretation of the three-dimensional Patterson synthesis of the $|F|^2$ data placed the palladium atoms at the inversion centers specified by the fourfold positions,[10,12] 4d: $1/4, 1/4, 1/2$; $3/4, 1/4, 0$; $3/4, 3/4, 1/2$; $1/4, 3/4, 0$ of C2/c. The positions of the remaining atoms (apart from hydrogen) were then readily developed from Fourier difference syntheses. All such atoms were found in sets of general eightfold positions,[10] 8f: $\pm(x, y, z)$; $\pm(x, \bar{y}, 1/2 + z)$; $\pm(1/2 + x, 1/2 + y, z)$; $\pm(1/2 + x, 1/2 - y, 1/2 + z)$. Full-matrix least-squares refinement of the structure thus obtained was then pursued with use of a modified version of the Busing, *et al.*, program,[13] atomic form factors compiled by Cromer and Waber,[14] and corrections for the anomalous scattering of the palladium atom as given by Dauben and Templeton.[15] The function refined was $\Sigma w(|F_o| - |F_c|)^2$ wherein $w = (\sigma_{hkl})^{-2}$ is the weight assigned to each reflection (*hkl*). Refinement

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(5) (a) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, **21**, 546 (1966); (b) J. M. Stewart and E. C. Lingafelter, *ibid.*, 12, 842 (1959).

(6) E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(7) (a) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, 22, 780 (1967); (b) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *ibid.*, **17**, 1159 (1964).

(8) R. H. Holm, private communication, Sept 18, 1964.

(9) E. Frasson, C. Panattoni, and L. Sacconi, *Acta Cryst.*, **17**, 477 (1964).

(10) "International Tables for X-ray Crystallography. Vol. I. Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, p 101.

(11) "International Tables for X-Ray Crystallography. Vol. III. Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962, pp 166–167.

(12) The placement of 4 Pd in the positions,[10] 4c, equally compatible with the Patterson synthesis, leads (with a shift in origin) to the same crystalline arrangement.

(13) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge Tenn., 1962.

(14) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(15) C. H. Dauben and D. H. Templeton, *ibid.*, **8**, 841 (1955).

employing a modified Hughes weighting scheme based on the unscaled F_o data gave results that differed insignificantly from those obtained with unit weighting. The use of unit weighting and isotropic thermal parameters for all atoms except palladium gave a conventional unweighted residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.081.

Inasmuch as the palladium atoms were placed in an accurately face-centered array, the large majority of the observable reflections satisfied the face-centered criteria, *hkl* either all even or all odd. Examination revealed that in the generally satisfactory over-all correlation of the $|F_o|^2$ data these two most prominent classes of reflections were observationally bridged just 39 times. A single scale factor was assigned to all of the data in the initial stages of refinement, but it became increasingly evident that two slightly different scale factors were called for accordingly as the *hkl* were all odd or all even. During the latter stages of isotropic refinement and in two subsequent cycles of anisotropic refinement, the data from the even and odd layers along *b* were separately scaled; final values of the two scale factors differed from their average by 2.0%.

In the last cycle of anisotropic refinement, the average parameter shift was $0.02\sigma_p$ and the maximum shift was $0.08\sigma_p$, where σ_p is the estimated standard deviation of the parameter. The conventional weighted residual, $r = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, was 0.090, and the unweighted residual, R, was 0.070. The atomic coordinates and the anisotropic thermal parameters with accompanying estimated standard deviations are given in Tables I and II, respectively.[16, 17]

Table I. Atomic Coordinates in the Unit Cell of the Crystal

Atom type	Coordinates with standard deviations[a] 10^4x	10^4y	10^4z
Pd	2500	2500	5000
O	1563 (4)	1523 (11)	5029 (6)
N	3012 (5)	342 (12)	5719 (7)
C_1	2074 (6)	−29 (17)	6497 (9)
C_2	1498 (6)	815 (15)	5804 (9)
C_3	804 (7)	809 (19)	5936 (11)
C_4	708 (8)	21 (22)	6736 (12)
C_5	1284 (10)	−765 (21)	7449 (11)
C_6	1961 (8)	−823 (18)	7314 (10)
C_7	2776 (6)	−379 (16)	6349 (8)
C_8	3685 (6)	−461 (16)	5592 (9)
C_9	3782 (9)	−2391 (24)	5891 (15)
C_{10}	4374 (7)	587 (22)	6157 (12)
C_{11}	3580 (8)	−386 (21)	4475 (11)

[a] Figures in parentheses are the estimated standard deviations.

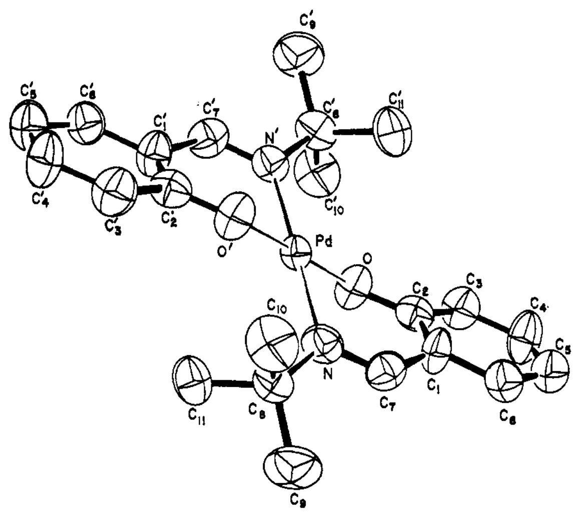

Figure 1. Model in perspective of the bis(N-*t*-butylsalicylaldiminato)palladium(II) molecule with each atom represented as an ellipsoid in conformity with the thermal parameters listed in Table II. In this view, chosen to minimize overlapping of the ellipsoids, the markedly stepped nature of the conformation is rather de-emphasized.

Discussion of Results

A model seen in perspective of the centrosymmetric framework of the bis(N-*t*-butylsalicylaldiminato)palladium(II) molecule, lacking only the hydrogen atoms, is illustrated in Figure 1; each atom is represented by an ellipsoid[18] having the shape, orientation, and relative size concomitant with the thermal parameters listed in Table II. Bond lengths and angles in the molecular skeleton are entered on the diagram of Figure 2 and are listed along with their estimated standard deviations in Tables III and IV; the short nonbonding separations between the methyl carbon atoms of a *t*-butyl substituent and contiguous atoms of the salicylaldimine residues in the same molecule also are listed in Table III.

Table II. Thermal Parameters of the Several Structural Classes of Atoms

Atom type	Thermal parameters,[a] Å² B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	2.3 (0.0)	3.8 (0.0)	2.9 (0.0)	0.2 (0.1)	0.7 (0.0)	0.1 (0.1)
O	2.7 (0.3)	5.2 (0.4)	3.8 (0.4)	0.0 (0.3)	0.7 (0.3)	0.9 (0.3)
N	3.4 (0.3)	4.0 (0.4)	3.6 (0.4)	0.8 (0.3)	0.8 (0.3)	0.2 (0.3)
C_1	3.8 (0.4)	5.3 (0.6)	3.3 (0.5)	0.2 (0.4)	1.2 (0.4)	0.9 (0.4)
C_2	3.3 (0.4)	3.6 (0.5)	4.0 (0.5)	−0.2 (0.3)	0.8 (0.4)	−0.5 (0.4)
C_3	3.5 (0.4)	6.1 (0.7)	5.7 (0.7)	−0.3 (0.5)	1.6 (0.5)	0.2 (0.6)
C_4	5.4 (0.7)	7.7 (0.9)	5.8 (0.8)	−0.5 (0.6)	3.4 (0.6)	0.8 (0.7)
C_5	7.4 (0.9)	6.1 (0.8)	4.4 (0.7)	−0.1 (0.7)	2.7 (0.6)	0.2 (0.6)
C_6	5.4 (0.6)	4.9 (0.6)	4.2 (0.6)	−0.2 (0.5)	1.8 (0.5)	−0.2 (0.5)
C_7	3.9 (0.5)	4.5 (0.5)	3.3 (0.5)	0.1 (0.4)	0.0 (0.4)	0.6 (0.4)
C_8	3.1 (0.4)	4.7 (0.5)	4.5 (0.6)	0.5 (0.4)	0.7 (0.4)	−0.2 (0.5)
C_9	6.3 (0.7)	5.3 (0.7)	9.7 (1.1)	2.5 (0.8)	3.0 (0.7)	1.2 (1.0)
C_{10}	3.3 (0.5)	7.8 (0.9)	6.7 (0.9)	−0.1 (0.5)	0.7 (0.5)	−0.4 (0.7)
C_{11}	4.8 (0.6)	6.7 (0.8)	5.2 (0.7)	0.4 (0.6)	2.6 (0.5)	−0.4 (0.6)

[a] Figures in parentheses are the estimated standard deviations.

The equations of the mean planes that partially characterize important subgroupings of atoms within the molecule specified by the coordinates of Table I are given in Table V, and the displacements from these

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(16) All computations were performed on a Control Data 1604 computer equipped with a Cal-Comp x–y plotter.

(17) A table of observed and calculated structure amplitudes has been deposited as Document No. 9967 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

(18) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

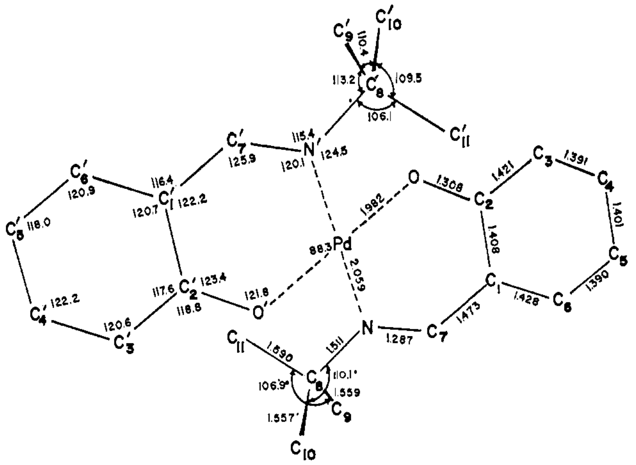

Figure 2. Diagram of the molecular skeleton giving bond distances and angles. The projection is normal to the mean planes of the salicylaldimine residues.

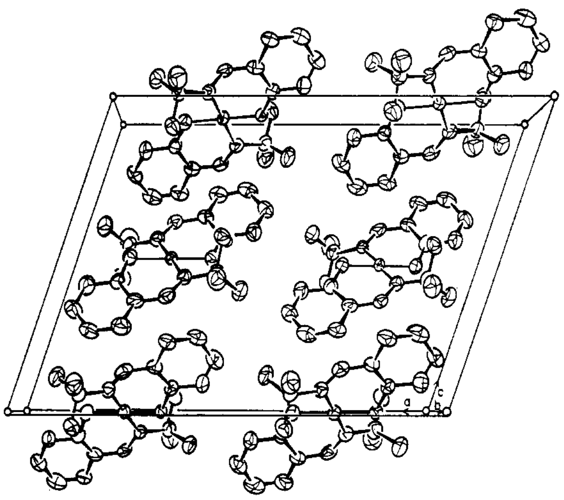

Figure 3. Model in perspective to illustrate the packing of the molecules in the crystalline arrangement. Molecular centers (palladium atoms) are in an accurately face-centered array.

Table III. Bond Lengths and Critical Nonbonding Distances (Å) in the Molecule[a,b]

Pd–O	1.982 (7)	C_5–C_6	1.390 (21)	C_8–C_{11}	1.590 (20)
Pd–N	2.059 (9)	C_6–C_1	1.428 (18)		
O–C_2	1.308 (14)	C_1–C_7	1.473 (17)	C_{10}–O'	3.056 (18)
C_1–C_2	1.408 (16)	C_7–N	1.287 (16)	C_{11}–O'	3.125 (18)
C_2–C_3	1.421 (16)	N–C_8	1.511 (14)	C_9–C_7	2.748 (20)
C_3–C_4	1.391 (21)	C_8–C_9	1.559 (20)	C_{10}–C_7	3.286 (19)
C_4–C_5	1.401 (23)	C_8–C_{10}	1.557 (18)	C_{11}–C_7	3.577 (20)

[a] Figures in parentheses are the estimated standard deviations. [b] Entries below the line in the third double column are the nonbonding separations.

Table IV. Intramolecular Bond Angles (Degrees)[a]

OPdN'	88.3 (0.4)	$C_4C_5C_6$	118.0 (1.3)	$PdNC_8$	124.5 (0.8)
OPdN	91.7 (0.4)	$C_5C_6C_1$	120.9 (1.3)	NC_8C_9	113.2 (1.1)
$PdOC_2$	121.8 (0.7)	$C_6C_1C_2$	120.7 (1.1)	NC_8C_{10}	110.1 (1.0)
OC_2C_1	123.4 (1.0)	$C_6C_1C_7$	116.4 (1.1)	NC_8C_{11}	106.6 (0.9)
OC_2C_3	118.8 (1.0)	$C_2C_1C_7$	122.2 (1.0)	$C_9C_8C_{10}$	110.4 (1.2)
$C_1C_2C_3$	117.6 (1.1)	C_1C_7N	125.9 (1.0)	$C_9C_8C_{11}$	106.9 (1.2)
$C_2C_3C_4$	120.6 (1.3)	C_7NPd	120.1 (0.8)	$C_{10}C_8C_{11}$	109.5 (1.2)
$C_3C_4C_5$	122.2 (1.3)	C_7NC_8	115.4 (1.0)		

[a] Figures in parentheses are the estimated standard deviations.

Table V. The Mean Planes of Some Characteristic Groupings of Atoms

Atomic groupings	Equation of mean plane[a,b]
I. Coordination group[c]	$0.170X - 0.455Y - 0.784Z = -6.590$
II. Salicylaldimine residue[c]	$-0.116X - 0.853Y - 0.509Z = -4.657$
III. Benzene ring skeleton[c]	$-0.075X - 0.861Y - 0.504Z = -4.643$
IV. Nitrogen sp² system[c]	$-0.375X - 0.585Y - 0.719Z = -7.112$

[a] X, Y, and Z are orthogonal coordinates measured (in Å) along a, b, and the normal to (001), respectively. [b] Angles (degrees) between the normals to pairs of planes are: I-II, 35.6; I-III, 35.0; I-IV, 33.8; II-III, 1.5; II-IV, 24.7; III-IV, 26.6°. [c] The atoms comprised in each grouping are Pd, N, N', O, O' in I; N, O, C_1-C_7 in II; C_1-C_6 in III; N, Pd, C_7, C_8 in IV.

mean planes of the atoms constituting the molecular framework are listed in Table VI. The model seen in perspective for the contents of the unit cell, Figure 3, is indicative of the easy intermolecular packing relations that generally prevail in the crystal.

The gross conformation of the molecular skeleton, apart from the methyl groups of the *t*-butyl substituents, is quite satisfactorily specified by citing the dihedral angle, 144.4°, between the plane of the PdN_2O_2 coordination group and either of the necessarily parallel mean planes of the two salicylaldimine residues (Tables V and VI); otherwise put, the perpendicular distance or "step" separating the mean planes of the salicylaldi-

Table VI. Atomic Displacements from Mean Planes of Table V

Atom	Displacement (Å) from mean plane[a] of—			
	I. Coordination group	II. Salicylaldimine residue	III. Benzene ring skeleton	IV. Nitrogen sp² system
Pd	0*	0.86	0.75	0.00*
O	0*	0.02*	−0.02	−1.10
N	0*	0.01*	−0.14	−0.01*
C_1	1.19	0.06*	−0.01*	−0.22
C_2	0.78	0.04*	0.01*	−0.83
C_3	1.17	−0.03*	−0.00*	−1.23
C_4	1.96	−0.06*	−0.01*	1.00
C_5	2.42	0.02*	0.02*	−0.35
C_6	2.00	0.04*	−0.01*	0.01
C_7	0.64	−0.11*	−0.24	0.01*
C_8	−0.67	−0.45	−0.66	0.01*
C_9	−1.00	−1.51	−1.74	−0.56
C_{10}	0.21	0.77	0.52	1.45
C_{11}	−2.06	−1.15	−1.37	−0.96

[a] Starred displacements are those of the atoms used in determining the least-squares mean plane.

mine residues is 1.72 Å with the palladium atom lying halfway between. The principal contribution to this stepped conformation of the molecular skeleton comes from a major folding of each six-membered chelate ring along an O–N edge of the coordination group.

The similarly stepped conformations of the bis(salicylaldiminato)metal(II) skeleton reported for the diamagnetic molecules in crystalline bis(N-isopropyl-3-ethylsalicylaldiminato)palladium(II)[19] and bis(N-isopropyl-3-methylsalicylaldiminato)nickel(II)[5a] are characterized by much smaller steps, 0.42 and 0.76 Å, respectively.[20] One must go to the stepped conformation observed for the bis(2,2′-dipyridyliminato)palladium(II) molecule in crystals[21] to find foldings within six-membered chelate rings that are comparable with those in the bis(N-*t*-butylsalicylaldiminato)palladium(II) chelate.

The recently reported stereochemical parameters of the bis(N-isopropyl-3-ethylsalicylaldiminato)palladium(II) molecule, derived from a very accurate determination of the crystalline structure,[19] are especially appropriate for direct comparison with the data of Tables II–VI.[22] We note first that the estimated standard deviations reported for the bond lengths in the N-isopropyl-substituted molecule[19] are quite generally only 20–25% as large as those of the corresponding parameters in the N-*t*-butyl-substituted species (Table III). The apparent increments in the several bond lengths (Figure 2) that attend replacement of isopropyl by *t*-butyl on the nitrogen atoms are (esd values are given in parentheses): Pd–O, −0.009 (0.007); O–C_2, −0.002 (0.014); C_2–C_1, −0.001 (0.016); C_1–C_7, 0.038 (0.017); C_7–N, 0.001 (0.016); N–Pd, 0.028 (0.009); N–C_8, 0.019 (0.014); averaged C–C in the benzene rings, 0.011 (0.019); averaged C_8–C in the N-alkyl substituents, 0.059 (0.020) Å. The apparent increments, all positive, that have objective significance are in the Pd–N bond, in the C–C bonds of the N-alkyl groups, and, just possibly, in the C_1–C_7 bond of the chelate ring.[23] The cumulative effect of the listed increments, both real and apparent, is to suggest that the N-*t*-butyl-substituted species carries enhanced strains concentrated in the region of the nitrogen atom and its *t*-butyl substituent.

Inasmuch as the packing contacts of the numerous N-alkyl hydrogen atoms with contiguous atoms of the salicylaldimine residues (and with one another) play a major role in determining the molecular conformation, it is unfortunate that the positions of the hydrogen atoms in the N-*t*-butyl-substituted molecule were not directly indicated in the final difference synthesis of the amplitude data. It is instructive, nonetheless, to compare the intramolecular nonbonding C···C and C···O separations listed in Table III with analogous data from the Braun and Lingafelter study[19] of the N-isopropyl-substituted species. The 2.75-Å separation between the chelate-ring carbon atom, C_7, and the methyl carbon atom, C_9, of the *t*-butyl group (Table III, Figures 1 and 2) is 0.13 Å shorter than the analogous separation involving a methyl carbon atom in the N-isopropyl-substituted molecule; further, the carbon–oxygen separations, $C_{10}\cdots O' = 3.06$ and $C_{11}\cdots O' = 3.13$ Å, that involve two methyl carbon atoms of the *t*-butyl group are both much shorter than the one short distance, 3,39 Å, of similar type found in the N-isopropyl derivative. It is clear that the presence of the additional carbon and hydrogen atoms in the *t*-butyl derivative requires a further tightening of the intramolecular packing and that quite specialized orientations of the three methyl groups around the C_8–C_9, C_8–C_{10}, and C_8–C_{11} bonds are needed to exclude H···H and H···O separations that would otherwise fall substantially below the respective van der Waals packing distances,[24] 2.40 and 2.60 Å.

If hydrogen atoms be placed in their expected positions on ring carbon atoms, and if the methyl groups of the *t*-butyl substituents be given their standard geometry, the most critical H···H contacts within the molecule become readily identifiable. Using the idealized parameters, the rotation of a C_9 methyl group about the C_9–C_8 bond would require the methyl hydrogen atom to pass in turn within 1.50 Å of the hydrogen atom attached to the C_7 carbon atom, a separation that is 0.90 Å less than the van der Waals diameter; such rotation would seem to occur infrequently, if at all. It is probable that the equilibrium orientation of the C_9 methyl group is nearly or exactly that which puts two of its hydrogen atoms equidistant from the hydrogen atom attached to C_7; even then the formally calculated H···H separation, 2.01 Å, is very small. Such fixing of the orientation of the C_9 methyl group strongly influences the orientations of the C_{10} and C_{11} methyl groups about the respective C_{10}–C_8 and C_{11}–C_8 bonds. Study of an accurately scaled model suggests that there is an essentially unique pattern for the coupled orientations of the three methyl groups that allows the two short H···O contacts and all other short H···H contacts (11 in number) in which each *t*-butyl group is concerned to be close to—perhaps in no case more than 0.20 Å shorter than—the respective van der Waals packing distances. Lacking direct experimental evidence on the matter, we refrain from elaborate description of this eminently reasonable, but still hypothetical, model for the positioning of the hydrogen atoms.

Referring now to the data given in Tables V and VI for the least-squares mean planes of four distinctive subgroupings of atoms in the structure, it is seen (Table V) that the plane I of the coordination group is tilted through angles ranging from 33.8 to 35.6° with respect to the other three planes; the concomitant large displacements of atoms not included in the coordination group from the plane I are listed in Table VI. It is further seen that the angle of tilt between the mean planes II and III of, respectively, the salicylaldimine residue and the benzene ring is only 1.5°, but that the displacements of such atoms as Pd, N, and C_7 from these planes differ substantially. The benzene ring is virtually planar, but the same cannot be said of either the remainder of the salicylaldimine residue or, much less,

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(19) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, **22**, 787 (1967).

(20) The preference of the 3-methyl-substituted Ni(II) chelate[5a] for diamagnetic planar coordination in the crystal while the corresponding 3-ethyl[7a] and 3-hydrogen[7b] chelates crystallize with paramagnetic tetrahedral coordination groups provides an unresolved problem.[5a]

(21) H. C. Freeman and M. R. Snow, *Acta Cryst.*, **18**, 843 (1965).

(22) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966), have critically reviewed the stereochemical data for other salicylaldiminato chelates. The averaged bond lengths in the salicylaldimine residue differ insignificantly from those reported in ref 19.

(23) To ensure that these observations were not attributable wholly or in part to faulty lattice constants, these latter were carefully redetermined using silicon as a standard.

(24) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

of the full chelate ring of which it is a part. The marked folding of each chelate ring about an N···O edge of the coordination group—surely the outstanding conformational feature of the molecular skeleton (*vide supra*)—is required to make room for the *t*-butyl group, but it cannot be a simple folding; a simultaneous requirement that is seen to be met (Table VI) is the retention of virtual planarity for the trigonal nitrogen sp^2 system comprising the nitrogen atom and the Pd, C_7, and (*t*-butyl) C_8 atoms directly bonded to it. Consequently, the mean plane IV of the nitrogen sp^2 system is tilted 26.6° from the plane of the benzene ring, the N, C_7, and C_8 atoms lie below the plane III by, respectively, 0.14, 0.24, and 0.66 Å, and the Pd atom is situated 0.75 Å above this plane.

The folding and, more particularly, the superimposed ruffling of the chelate ring implies some decrease in the stabilizing energy afforded by the delocalized π bonding. Such loss may, however, be partially compensated by the fact that folding and ruffling of the six-membered ring allows the bond angles therein to approach more nearly to the ideal values corresponding to the pattern of σ bonding.[25] We note by way of comparison that neither the marked folding observed for the six-membered acetylacetonatozirconium(IV) ring[26] nor the marked ruffling of the porphine skeleton that characterizes several metalloporphyrins[27] seems to require measurable increments in ring bond lengths relative to the corresponding quasi-planar conformations. The evidence cited earlier of cumulative bond strain in the molecular conformation reported herein, specifically in the Pd–N bonds and within the *t*-butyl substituents, is most directly attributable to the persistence of unduly tight-packing relations between the *t*-butyl groups and the salicylaldimine residues.

Substitution of nickel(II) for palladium(II) in the observed configuration would call for a decrease of ~0.14 Å in both the M–N and M–O complexing bond lengths[5a] with concomitant tightening of the critical intramolecular contacts between atoms of the *t*-butyl substituents and the salicylaldimine residues. Destabilization of this diamagnetic configuration relative to a paramagnetic tetrahedral configuration for the Ni(II) complex is thus all the more to be expected.

It is quite unlikely that the conformation of the molecule is significantly affected by the packing relations in the crystal. The one fairly short C···O distance between molecules, $C_9\cdots O'' = 3.47$ Å, is larger than the appropriate van der Waals separation,[24] 3.40 Å. Observed intermolecular separations between methyl carbon atoms and benzene ring carbon atoms, $C_9\cdots C_2'' = 3.57$, $C_9\cdots C_5'' = 3.61$, and $C_{11}\cdots C_6'' = 3.79$ Å, are just short enough to suggest that the positioning of the hydrogen atoms (or the C–H bonds) cannot be wholly ignored in the molecular packing. Other C···C separations of this type range upward from 3.86 Å.

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[25] The sum of the ideal values for the bond angles represented in the chelate ring falls ~30° short of the 720° required for a planar configuration. The sum of the observed values is 701.7°, compatible either with rather less ruffling and/or folding or, in a planar conformation, with less angular strain than if the ideal angles were preserved.

[26] J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, 2, 243 (1963).

[27] T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, **87**, 2305 (1965).