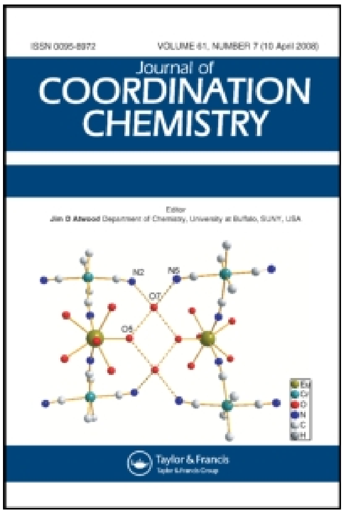

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A SHORT HYDROGEN BONDED COLUMNAR STRUCTURE: SYNTHESIS, SPECTROSCOPIC STUDIES AND X-RAY STRUCTURE OF A PALLADIUM(II) COMPLEX OF ALFA-FURIL DIOXIME

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A SHORT HYDROGEN BONDED COLUMNAR STRUCTURE: SYNTHESIS, SPECTROSCOPIC STUDIES AND X-RAY STRUCTURE OF A PALLADIUM(II) COMPLEX OF ALFA-FURIL DIOXIME

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Synthesis, spectroscopic studies and single crystal X-ray structure of $[Pd(Hafdo)_2]$, where H_2afdo is α-furilglyoxime, were carried out because of its potential columnar stack structure and the existence of a short intramolecular hydrogen bond. The compound crystallizes in the orthorhombic space group *Pnab* with $a = 6.930(3)$, $b = 14.286(2)$ and $c = 19.837(4)$ Å. The intensity data were collected on a CAD-4 diffractometer and the structure was refined to a final *R* value of 6.1%. The central metal atom in this inner complex has planar geometry and the oxime oxygen atoms are involved in a short intramolecular hydrogen bond with O---O distance of 2.583(4) Å. The complex molecules are stacked above one another along the crystallographic *a* axis with adjacent molecules rotated 90° with respect to each other. The Pd-Pd distance is 3.465(4) Å. The two oxygen atoms of the planar furane groups are separated by 2.686(4) Å and the furane rings are oriented at an angle of 46.7° with respect to each other. The columnar stack structure in this compound is similar to chelate structures exhibiting one-dimenisonal electrical conduction properties. The infrared spectra and the chemical shifts of the bridged proton of the title compound and several other metal complexes of α-amine oximes are reported. Efforts are made to correlate the O---O separation in these complexes with the infrared absorptions and with the values of ^1H nmr chemical shifts of the bridging proton.

INTRODUCTION

The oxime group is potentially ambidentate with possibilities of coordination through nitrogen and/or oxygen. The detailed crystal structures of many transition metal complexes of oximes, *vic*-dioximes (**Ia-Ic**), bidentate and tetradentate α-amine oximes (**II, IIIa-IIId**) are known from X-ray and neutron diffraction studies.[1-5] In most cases, coordination occurs through nitrogen atoms with a grossly planar arrangement around the central metal atom. The complexation is accompanied by the loss of one or two protons and the oxygen atoms are involved in a short intramolecular hydrogen bond having an O---O separation of around 2.4 Å. The trends of variation of the observed O-H distance with O---O separations have been studied and it has been suggested that the bridged hydrogen atom, at least in some of these complexes, is centered in an essentially symmetric potential.[6]

In addition to the above studies concerning short intramolecular hydrogen bonds, the metal-dioximates are of significant importance because several of these complexes, in which the adjacent planar molecules form columnar stacks such that there exists the possibility of direct metal-metal bonding, possess semiconducting properties.[7-10] For example, the chelate structures $[M(Hdmg)_2]$ and $[M(dpg)_2]X$ where dmg = dimethylglyoxime (**Ia**) and dpg = diphenylglyoxime (**Ib**), M = Ni(II),

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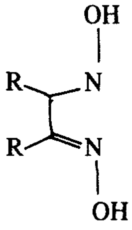
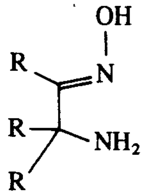


(I)



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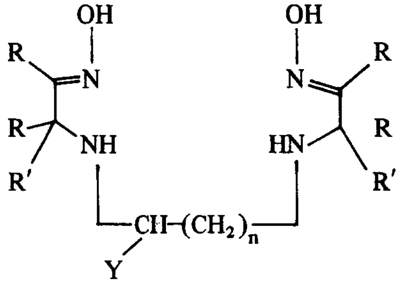

(III)

(**Ia**) H_2dmg; R = $-CH_3$
(**Ib**) H_2dpg; R = $-C_6H_5$
(**Ic**) H_2afdo; R = $-C_4H_4O$
(**II**) Hao; R = $-CH_3$

(**IIIa**) H_2enao; R′=R=CH_3; y=H; n=1
(**IIIb**) H_2pnao; R′=R=CH_3; y=H; n=2
(**IIIc**) H_2Mtenao; R′=R=CH_3; Y=CH_3; n=1
(**IIId**) H_2preh; R=CH_3; R′=None; y=H; n=2

Pd(II) or Pt(II) and X = Br^- or I^-, have columnar stack structures where the nature of metal-metal interactions have been a subject of many interesting investigations. In addition several *vic*-dioximates are widely used as analytical reagents for the spectrophotometric determination of metals.[11-12] One such compound recently reported is the *bis* complex of α-furil dioxime (**Ic**) used for the determination of rhenium(IV).[13] On the basis of the absence of Re=O stretches in the infrared spectrum of this compound, the presence of an intramolecular short hydrogen bond has been suggested to be present in it.

Because of the above importance of transition metal *vic*-dioximates, we have synthesized several complexes of α-furil dioxime, (H_2afdo) to investigate their solution and solid state chemistry, as a part of our continuing research program dealing with compounds exhibiting semi- and superconducting properties and short intramolecular hydrogen bonds. The ligand, α-furil dioxime, offers a rather interesting system since it has several donor sites available for coordination. It resembles dimethylglyoxime on one hand, while the oxygen atoms of the furane groups in the ligand, on the other hand, can adopt different orientations with respect to the metal atom. These structural variations can only be studied by complete three dimensional single-crystal X-ray analyses. This paper reports the ^{1}H-nmr and infrared spectroscopic data of several Ni(II) and Pd(II) complexes of α-amine dioximes and of α-furil dioxime. A complete crystal and molecular structure of *bis*(α-furildioximato)palladium(II) is reported and compared with some related structures. Some common features of the infrared spectra, which can play a diagnostic role for the identification of an intramolecular hydrogen bond in these and other similar complexes, are discussed.

EXPERIMENTAL

Chemicals and Solvents

All chemicals and solvents were obtained from Fluka AG and were used without further purification.

Spectroscopic and Analytical Measurements

Infrared spectra were obtained using a Perkin Elmer IR180 spectrophotometer and measured in KBr pellets. The ^{1}H nmr spectra were obtained using either a Varian

TABLE I

Results of IR and ^{1}H nmr spectroscopic measurements for alpha-amine oximes and alpha-furil dioxime complexes[a].

Compound	4000-3000 region		O-H-O bands	C=N band	N=O band	M-N band	O--O dist	Proton shift	Ref
$[Ni(Hpnao)]Cl$	3120 3230 3350 3440	2840 2980 3020	2360– 2400 1800	1600	1240 1100	540sbr 390– 410s.db 320w.br	2.409	18.5	3
$[Ni(Hao)_2]$	3130 3220 3260	2970 2920	2300 1800	1580	1250 1080	480w 410w 345– 370wbr	2.420	18.3	17
$[Ni(HMtenao)]ClO_4$	3230	2980 2960	1800	1580	1250 1090	485 420– 400sdb 365wbr	2.400	18.3	b
$[Ni(Henao)]ClO_4$	3150	2880 2980	2100 1750	1575	1220	540w 420wbr 350wbr	2.478		15
$[Pt(Hdmg)_2]$	3240 3320	2910 3000	2200 2300 1680	1530	1280 1080	520 410 320– 355wbr	2.62(2)		14
$[Pd(Hdmg)_2]$			2300 2400 1725	1552	1259 1091	510ss 390ss 345bs	2.63(1)		14
$[Cu(Hpreh)]NO_3$	3400	2920 2980	2360 2400 1760	1550	1270 1125	530sst 455sst 375– 300	2.49		36
$[Pd(Hafdo)_2]$	3120– 3140	2840 2920 2960	2200– 2400 1730	1575	1285 1070	540w 390m 315w	2.583(4)		c

[a] st=strong, m=medium, w=weak, br=broad, s=sharp, db=doublet. [b] M.S. Hussain, R.K. Murmann and E.O. Schlemper, unpublished work. [c] This work. Ir spectral data in cm^{-1}, distances in Å, chemical shifts in ppm.

T60 or a XL-200 nmr spectrometer in d_6-DMSO as solvent. The relevant infrared absorptions and the chemical shifts for the bridged protons relative to external TMS are reported in Table I. Elemental analyses were performed on a Carlo Erba (Italy) Elemental Analyzer.

Synthesis of the Complexes and Crystal Growth

The αamine oxime complexes for infrared spectroscopic studies were prepared using procedures reported earlier.[5,14-17] The [Pd(Hafdo)$_2$] complex was prepared by adding α-furil dioxime to a $PdCl_2$ solution in hot dilute HCl. The metal to ligand ratio was very close to 1:2 with the ligand being present in a slight excess. The resulting purple solution was filtered and allowed to evaporate at room temperature over a period of 3-4 days until dark maroon needle-shaped crystals appeared in the bottom of the container. The first crop of crystals was collected and the solution was further allowed to evaporate to obtain more product. The elemental analysis of the crystalline product is as follows: Calcd. for $PdC_{20}H_{14}N_4O_8$, [Pd(Hafdo)$_2$]: C, 44.10; N, 10.29; H, 2.59%. Found: C, 44.52; N, 10.19; H, 2.79%.

All other compounds used for the infrared studies were checked for their analytical purity and were dried before making their KBr pellets. The nmr spectra were measured within half an hour of preparing solutions. The detection of nmr signals for the bridged proton becomes very difficult if the solution is allowed to stay for a longer time. Most complexes are fairly stable in d-chloroform but their limited solubility in this solvent prohibits its extensive use. The solvent d_6-DMSO was found to be best for nmr studies of the bridged protons in these complexes.

Unit Cell and Space Group

A nearly equidimensional fragment 0.30 × 0.28 × 0.32 mm was cut from a naturally grown needle-shaped crystal of [Pd(Hafdo)$_2$]. The lattice parameters were calculated from a least-squares refinement of the setting angles of 25 reflections located by the automatic program SEARCH on the CAD4 diffractometer. All reflections used for calculation of the cell constants were in the 2θ range 21 to 37 degrees. The collected intensity data revealed systematic extinctions for $0kl$, $k+l$ odd, for $hk0$, k odd, and for $h0l$, h odd, indicating the space group *Pnab*, a nonstandard setting of *Pbcn* (No. 60). No cell of any other symmetry was found by Delauney Reduction with TRACERII.[18] The crystal data are: $PdC_{20}H_{14}N_4O_8$; $M = 544.7$ $a = 6.930(3)$, $b = 14.286(2)$, $c = 19.837(2)$ Å, $V = 1964$ Å^3, $F(000) = 1096$, d_{obs}. = 1.80 g cm^{-3}, $Z = 4$, $d_{calcd.} = 1.84$ g cm^{-3}, μ (Cu-K$_\alpha$) = 78.5 cm^{-1}. The density of the crystals was measured by flotation in a 1,3-dibromopropane-methylene chloride solution. The density of the solution was determined using a pycnometer.

Data Collection and Reduction

The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using the above crystal which was mounted in an arbitrary orientation on a glass fibre. The intensities of reflections with $2\theta < 60°$ in the quadrant hkl and $hk\bar{l}$ were measuresd using ZIGZAG method in $\mu - 2\theta$ scan mode and graphite monochromated Cu-K$_\alpha$ radiation. Each reflection was scanned for $(1.25 + 0.14 \tan\theta)°$ centered about the calculated Cu-K$_\alpha$ positions with the scan speed ranging from 2.01 to 5.03 degrees/min. Background counts were measured for half of the total scan time by extending the scan range 25% on either side of the scan limits. The intensities of three reference reflections were measured every 8000 s of X-ray exposure time and the crystal orientation was checked each 75 reflections. A total of 3466 reflections was measured. No systematic variation in the intensities of the standard reflections was observed over the entire period of data collection. The intensities were corrected for Lorentz and polarization affects and the symmetry-related and duplicate reflections were averaged to give 1459 unique reflections of which 1090 having $I > 3\sigma(I)$ were used in the refinement procedure. The agreement factor for data averaging was 0.009. Absorption correction were not considered necessary because the crystal was quite regular in shape.

Solution and Refinement of the Structure

The coordinates for the Pd atom were obtained from the Patterson peaks calculated using the SHELX76 package.[19] All other non-hydrogen atoms were located from successive Fourier and difference Fourier syntheses. A few cycles of isotropic refinement were followed by several cycles of anisotropic least-squares refinement of all non-hydrogen atoms. A difference fourier map at this stage yielded positions of all hydrogen atoms. In the final cycles, all non-hydrogen atoms were refined anisotropically while only positional parameters of the hydrogen atoms were refined with fixed isotropic temperature factors. The least-squares refinement of 188 variables led to the final $R = 0.061$ and $R_w = 0.072$ *with* $w = 9.9826/(\sigma^2 F_o + 0.000471F_o^2)$. The largest shift in any parameter was 0.11 times the estimated standard deviation of the corresponding parameter with the highest peak of 1.0 e/A^{-3} in the vicinity of palladium atom in the final difference Fourier map.

The full-matrix least-squares refinement was based on F_o, and the function minimized was $\Sigma w[\,|F_o| - |F_c|]^2$. Agreement factors are defined as $R = \Sigma[\,|F_o| - |F_c|]/\Sigma F_o$ and $R_w = [\Sigma w(\,|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. All calculations were carried out on the University of Petroleum and Minerals IBM 3033 computer using SHELX76. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann,[20] for H atoms from Stewart, Davidson and Simpson.[21] Anomalous dispersion corrections were taken from Cromer and Liberman.[22] The entire structure, including spherical absorption corrections, was also processed through the Structure Determination Package (SDP82) in the TEXRAY230 system,[23] which became available at the final stages of work on this compound. The results agreed well with those obtained from SHELX, as expected. The final atomic coordinates for heavy atoms and the positions for the hydrogen atoms along with B_{eq} values are listed in Table II. The anisotropic thermal parameters for non-hydrogen atoms and a listing of the observed and calculated structure factors are available as supplementary material from the Editor-in-Chief.

RESULTS AND DISCUSSION

Spectroscopic Studies

The infrared spectra in the region 4000–200 cm^{-1} and ^{1}H nmr chemical shifts of the bridged protons of the Ni(II), Pd(II) and Pt(II) chelates of several α-amine oximes are included in Table I along with those of the Pd(II) complex of α-furil dioxime. the empirical spectral assignments of the observed bands were made largely on the basis of a comparison with the spectra of the pure ligands[24–25] and with those of the transition metal glyoximates,[26] α-amine oximates[26] and of bisdimethylglyoximates.[27]

In the region 4000–3000 cm^{-1}, [Pd(Hafdo)$_2$] shows sharp bands at 3120 and 3140 cm^{-1} which may be assigned to the stretching vibrations of coordinated amines. Other complexes listed in Table I also exhibit similar absorptions from 3400–3200 cm^{-1}, in addition to the symmetric and asymmetric C-H stretches as bands of medium to strong

TABLE II
Positional and thermal parameters [Pd(Hafdo)$_2$][a].

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}(^{2})[b]
PD	0.5	0.5	0.5	3.09
N(1)	0.4932(5)	0.3619(5)	0.4928(3)	3.09
N(2)	0.5895(7)	0.4829(5)	0.4069(4)	3.96
C(1)	0.5481(7)	0.3286(4)	0.4362(5)	3.41
C(2)	0.5866(7)	0.3964(5)	0.3818(4)	3.67
O(1)	0.5057(6)	0.3096(6)	0.2851(4)	5.01
O(2)	0.6238(7)	0.5578(4)	0.3660(3)	3.77
O(3)	0.4512(5)	0.3115(5)	0.5479(3)	4.05
O(4)	0.6817(6)	0.1979(4)	0.3750(4)	5.01
C(3)	0.5752(8)	0.2258(6)	0.4264(5)	3.89
C(4)	0.6133(6)	0.3783(6)	0.3134(5)	3.03
C(5)	0.5515(9)	0.3032(5)	0.2211(6)	5.30
C(6)	0.7258(8)	0.4127(5)	0.2638(5)	4.14
C(7)	0.6909(8)	0.3643(5)	0.2038(5)	5.08
C(8)	0.5039(7)	0.1518(4)	0.4627(5)	4.82
C(9)	0.6843(9)	0.1015(5)	0.3763(6)	5.68
C(10)	0.5856(8)	0.0723(5)	0.4287(5)	4.89
OHO	0.464(6)	0.374(5)	0.588(3)	5.00
HC5	0.497(6)	0.278(5)	0.185(4)	5.00
HC6	0.829(7)	0.449(5)	0.281(4)	5.00
HC7	0.733(6)	0.359(4)	0.152(3)	5.00
HC8	0.502(7)	0.142(7)	0.504(4)	5.00
HC9	0.751(7)	0.087(6)	0.332(5)	5.00
HC10	0.559(8)	0.010(6)	0.468(6)	5.00

[a] Numbers given in parentheses in this and all subsequent tables are the estimated standard deviations in the last digit(s). [b] The B_{eq} values were calculated as $B_{eq} = 8\pi^2 U_{eq}$ where $U_{eq} = 1/3$ trace U.

intensities between 3000–2800 cm^{-1}. In the region 3000 to 1600 cm^{-1}, a broad absorption with a maximum falling near 2350 cm^{-1} and another around 1750 cm^{-1} were observed in the spectra of all complexes. Both bands, in general, are broad and of weak to medium intensity with the latter being more readily observed in all cases. The former may be assigned to the O--H--O stretching vibration whereas the latter may be attributed to the O--H--O in-plane deformation. In [Pd(Hafdo)$_2$], the band at 1730 cm^{-1} is strong and sharp. The two absorption bands can be used as diagnostic peaks for identification of an intramolecular hydrogen bond[30] in these chelate structures. In contrast to the above two bands, the presence of several narrow transmission bands superimposed on a broad continuous absorption in the region 1000–650 cm^{-1} and centered about 800 cm^{-1} is characteristic of a short hydrogen bond in dimeric cations of the type $[BHB]^+$ where B is a Lewis base.[31]

The O---O distance in [Pd(Hdmg)$_2$] is 2.626(4) Å and it exhibits O--H--O absorptions at 2340 and 1710 cm^{-1}.[14,28-29] In [Rh(Hpnao)Cl$_2$] the O---O distance is 2.474(7) Å and the O--H--O band is reported at 1792 cm^{-1} [26b]. The [Rh(H(ao)$_2$Cl$_2$] complex has an IR band at 1785 cm^1 for an O---O separation of 2.459(2) . Thus, an approximate correlation appears to exist between the O---O distance and the O--H--O bending vibration. A shift of about 50 cm^{-1} is observed for a change in the O---O distance from 2.4 Å to 2.6 Å . However, lack of sufficient data makes this apparent relationship between the shift and the O---O separation somewhat uncertain.

All compounds show strong absorptions centered around 1570, 1275 and 1090 cm^{-1} characteristic of C=N and N=O stretches assigned on a correlative basis with the spectra of the pure ligands. [Pd(Hdmg)$_2$] exhibits absorptions at 1552 cm^{-1} for C=N and at 1259 and 1091 cm^{-1} for N-O.[28-29] The N=O stretching frequencies are shifted (about 20 cm^{-1}) in the complex as compared with the free ligands while the effect on the C=N frequencies is much less pronounced. In all complexes the C=N and N=O bands are either broadened, shifted or split as compared with the spectra of the free ligands. The two absorptions near 500 and 400 cm^{-1} are assigned to metal-nitrogen stretchings in the complexes. No bands were detected in this region in the spectra of the pure ligands.

The nmr signals for the bridged proton in the bis-*vic*-dioximates are hard to detect in d_6-DMSO. In the α-amine oxime complexes the hydrogen-bonding proton appears at 18.3 p.p.m in [Ni(Hpnao)] and is shifted to 19.1 and 18.9 p.p.m in the oxidized products [Ni(pnao-6H)] and [Ni(pnao-7HNO$_2$)], respectively, suggesting a single minimum potential[32] for the hydrogen atom bridging oxygen atoms 2.41 Å apart. Because of the lack of enough nmr and structural results covering any significant range of O---O distances, the correlation between the ^{1}H nmr chemical shifts of the bridging protons and O---O separations is not unequivocal.

Molecular Packing and Structure

Molecular packing in the unit cell of [Pd(Hafdo)$_2$] viewed along the crystallographic *a* and *b* axes are illustrated in Figures 1 and 2. The Pd(II) atoms in the crystal lattice are

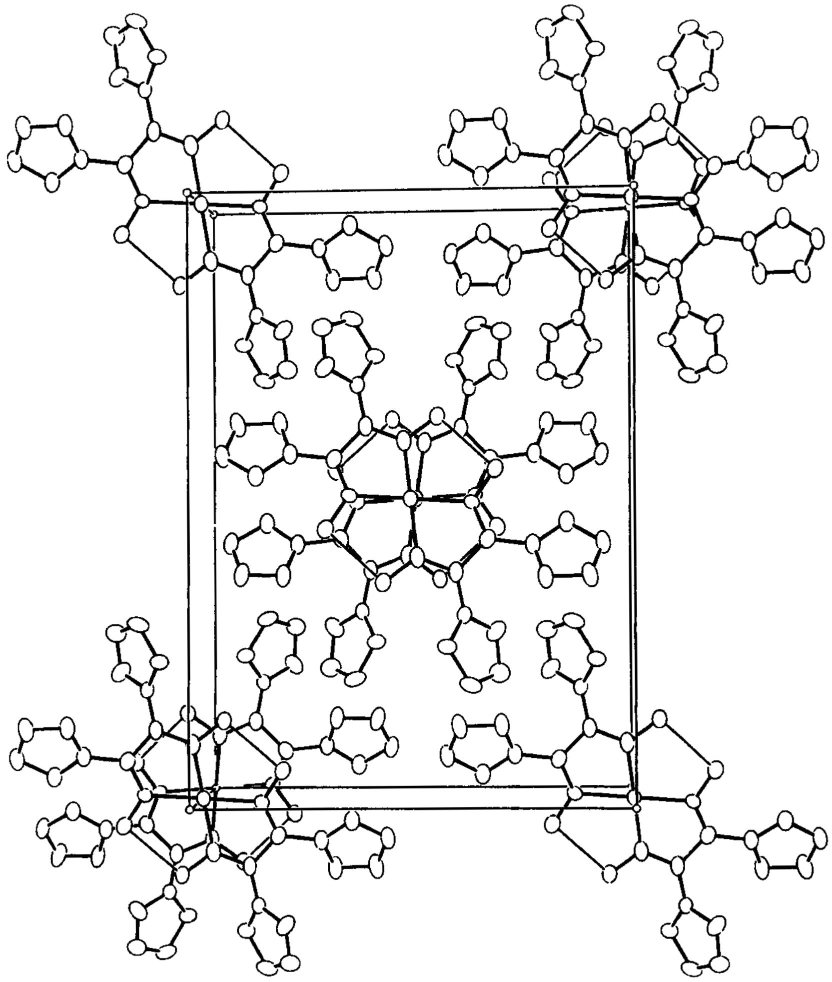

FIGURE 1 View of the unit cell showing the columnar stacking of [Pd(Hafdo)$_2$] viewed along the crystallographic *a* axis.

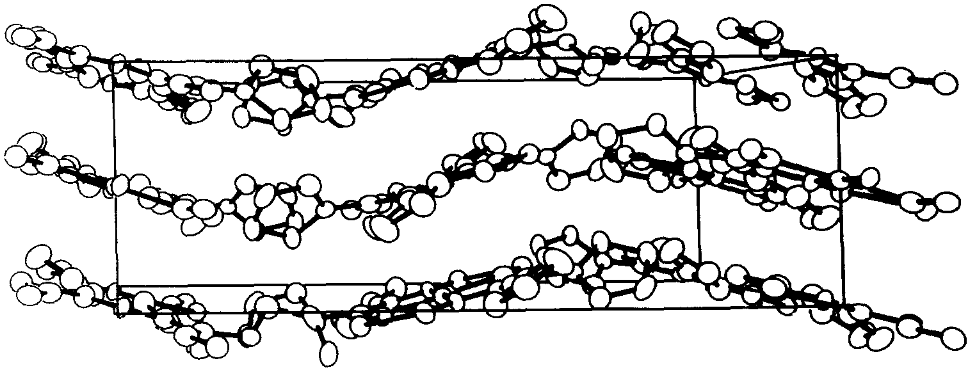

FIGURE 2 View along the *b* axis showing the layered structure of planar molecules in the unit cell.

3.465(4) Å apart which agrees with 3.459 Å determined previously[33] from the lattice constants. The planar [Pd(Hafdo)$_2$] molecules are stacked above one another along the *a* axis. Adjacent molecules in the stack are rotated by 90° with the palladium atoms forming an infinite linear chain along the needle axis of the crystal. The two ligands within each monomer are connected by short hydrogen bonds, conferring further rigidity to the planar molecule. The columnar stack structure in the present complex is similar to the structures of other vic-dioximates such as [Pd(Hdmg)$_2$], [Pt(Hdmg)$_2$], [Pd(dpg)$_2$], [Pd(dpg)$_2$]I and several other similar compounds[14,33-34] suggesting the existence of one-dimensional electrical conduction properties for the [Pd(Hafdo)$_2$] complex. The dark maroon color of the [Pd(Hafdo)$_2$] is also consistent with this possibility. None of the α-amine oximates exhibits a columnar structure and the palladium complexes (such as [Pd(Hpnao)]) are colorless. The molecular arrangement in the unit cell shows a layered structure which is depicted in Figure 2.

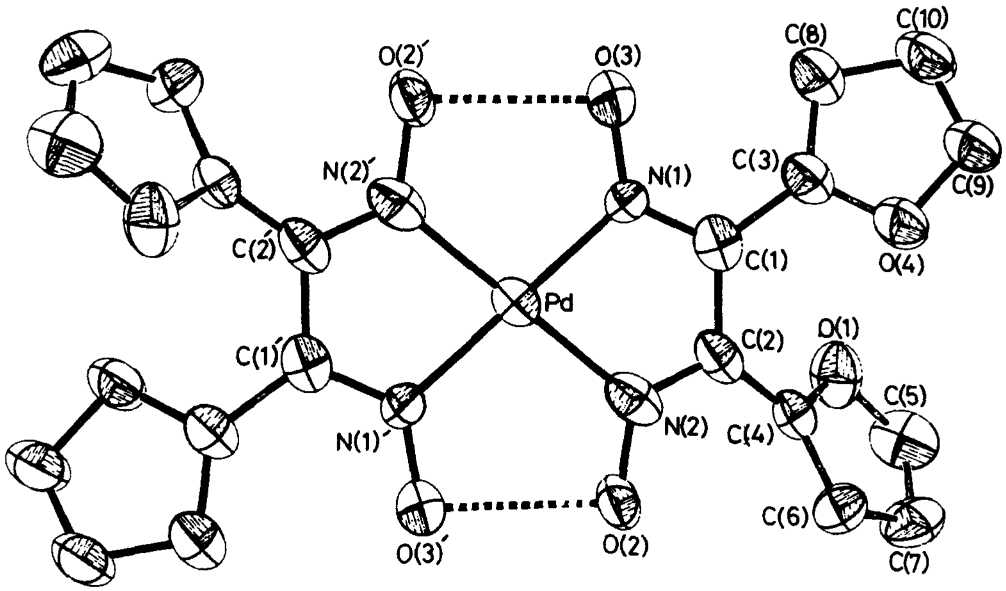

FIGURE 3 ORTEP diagram (45% probability ellipsoids) showing the relative orientation of the furane groups and labelling of atoms in [Pd(Hafdo)$_2$].

TABLE III
Bond lengths (Å) and angles (°) in [Pd(Hafdo)$_2$][a].

(a) Intramolecular Bonding Distances.			
Pd - N(1)	1.979(6)	Pd - N(2)	1.964(5)
N(1) - O(3)	1.341(5)	N(2) - O(2)	1.363(4)
N(1) - C(1)	1.277(6)	N(2) - C(2)	1.332(6)
C(1) - C(3)	1.494(6)	C(2) - C(4)	1.392(6)
C(3) - O(4)	1.320(6)	C(4) - O(1)	1.354(5)
C(3) - C(8)	1.371(7)	C(4) - C(6)	1.348(6)
C(9) — O(4)	1.378(6)	O(1) - C(5)	1.313(6)
C(9) - C(10)	1.313(7)	C(5) - C(7)	1.347(8)
C(8) - C(10)	1.437(7)	C(6) - C(7)	1.398(8)
C(1) - C(2)	1.474(7)		
(b) Intramolecular Bonding Angles.			
N(1)-Pd -N(2)	79.4(2)	N(1)-Pd-N(2)[b]	100.6(4)
C(1)-N(1)-Pd	115.3(3)	C(2)-N(2)-Pd	117.5(3)
O(3)-N(1)-Pd	118.8(3)	O(2)-N(2)-Pd	121.1(6)
O(3)-N(1)-C(1)	125.5(6)	O(2)-N(2)-C(2)	120.6(8)
C(2)-C(1)-C(3)	121.9(5)	C(1)-C(2)-C(4)	127.9(4)
C(2)-C(1)-N(1)	116.9(5)	C(4)-C(2)-N(2)	122.3(4)
C(3)-C(1)-N(1)	121.2(5)	C(1)-C(2)-N(2)	109.8(5)
C(1)-C(3)-O(4)	117.9(4)	C(2)-C(4)-O(1)	117.8(4)
C(1)-C(3)-C(8)	130.1(5)	C(2)-C(4)-C(6)	136.0(5)
O(4)-C(3)-C(8)	112.0(4)	O(1)-C(4)-C(6)	106.2(4)
O(4)-C(9)-C(10)	108.9(5)	O(1)-C(5)-C(7)	112.0(5)
C(9)-C(10)-C(8)	109.0(5)	C(5)-C(7)-C(6)	103.1(5)
C(10)-C(8)-C(3)	102.7(5)	C(7)-C(6)-C(4)	110.0(5)
(c) Non-Bonding Distances and Angles.		N(1)---N(2)[b]	3.034(5)
Pd --- Pd	3.465(4)	O(2) --- O(3)	2.583(4)
N(1) --- N(2)	2.517(4)	O(1) --- O(4)	2.686(4)
O(3) --- OHO	1.199(4)	O(2)---OHO	1.466(5)

[a]Chemically equivalent distances and angles are shown together. [b]Symmetry related positions.

The coordination geometry about the palladium(II) atom in [Pd(Hafdo)$_2$] is square planar, D_{2h}, as expected from the space group symmetry (Figure 3). The chelate bite angle (Table III) is 21.2° smaller than the non-bite angle. All atoms of the five-membered chelate ring as well as five-membered hydrogen bridged ring are coplanar (Table IV: planes 1 and 2) with a maximum deviation of −0.061 Å for any atom defining the plane. The above two rings are mutually coplanar resulting in an overall planar molecule. Both furane groups are planar as well (Table IV: planes 3 and 4) with one oriented at an angle of 46.7° to the other. The non-bonding distance between the furane oxygen atoms, O(1) and O(4) is 2.686(4) Å. These atoms are oriented opposite to each other but are not involved in any intra- or inter-molecular interactions. The alternative orientations of furane groups, with one or both oxygen atoms pointing towards the N-O bond, would have severe non-bonded interactions involving hydrogen atoms. The furane rings make dihedral angles of 39.5 and 18.9° with the five-membered chelate ring. The out-of-plane space requirements of the furane groups in [Pd(Hafdo)$_2$] appear to be similar to that of the methyl groups in [Pd(Hdmg)$_2$] allowing identical molecular planarity and stacking in the two structures. The furane rings, of course, will require more in-plane space as compared with methyl groups. The staggering of successive molecules by 90° results in the interlocking of furane rings (Figure 1) similar to that of the methyl groups in [Ni(Hdmg)$_2$],[7] which adds to the stability of the chain structure.

The overall distances and angles (Table III) are in good agreement with those observed in other similar complexes.[1,14] No significant difference is observed in chemically equivalent distances within the [Pd(Hafdo)$_2$] molecule itself. The Pd--Pd

TABLE IV
Least-squares planes and dihedral angles in [Pd(Hafdo)$_2$].

Plane 1:	Five-membered chelate ring. $-0.953x + 0.0453y - 0.2922z + 5.901 = 0$			
	Pd	0.016(1)	C(1)	−0.043(9)
	N(2)	−0.047(9)	N(1)	0.013(6)
	C(2)	−0.061(9)		
Plane 2:	Five-membered hydrogen bridged ring. $-0.9552x + 0.0134y - 0.2958z + 6.1757 = 0$			
	Pd	0.029(1)	N(2)	−0.025(11)
	O(2)	0.009(11)		
	O(1)†	0.019(10)	N(1)†	−0.033(8)
Plane 3:	Furane group (1). $-0.8143x - 0.0341y - 0.5794z + 8.2602 = 0$			
	C(3)	−0.007(8)	C(9)	0.013(9)
	C(8)	0.014(9)	O(4)	−0.003(9)
	C(10)	−0.017(8)		
Plane 4:	Furane group (II). $-0.6980x + 0.6777y - 0.2313z + 0.7468 = 0$			
	C(4)	−0.002(9)	C(5)	0.007(10)
	C(6)	0.006(9)	O(1)	−0.003(8)
	C(7)	−0.008(11)		

Dihedral Angles:

Plane I	Plane II	Angle (°)	Plane I	Plane II	Angle (°)
1	2	1.84	2	3	41.31
1	3	39.5	2	4	18.4
1	4	18.9	3	4	46.7

†Symmetry related atoms.

distances of 3.465(4) Å is similar to the corresponding distances of 3.517, 3.26 and 3.251 Å in [Pd(dpg)$_2$], [Pd(dpg)$_2$]I[32,33] and [Pd(Hdmg)$_2$],[14] all of which exhibit conduction properties. Studies to measure such properties on single crystals of [Pd(Hafdo)$_2$] are planned. The average N-O and C-N distancs of 1.353 and 1.306 Å are close to the average values of 1.35 and 1.30 Å found in most *vic*-dioximates.[1] In agreement with the usual observation, the N-O distance is not much different from 1.32–1.38 Å as observed in free dioximes[35] whereas the C-N length is longer than the values of 1.25–1.27 Å reported in free dioximes.

The 79.4(2)° chelate angle in the present complex is identical with the corresponding angle of 79.9(1)° in [Pd(Hdmg)$_2$] and is different from 80.6° observed in [Pd(Hpnao)] complex. The average CNO angle of 123.1° in the complex is about 11° more open than the free ligand value.

The intramolecular hydrogen bridged O---O distance of 2.583(4) Å is within the 2.59–2.67 Å range observed in *vic*-oximates of Pd(II), Pt(II) and Rh(II)[1] and is longer than of 2.474 Å observed in [Pd(Hpnao)].[5] With such an O---O separation the hydrogen atom would be situated unsymmetrically in the bridge, being closer to one of the two oxygen atoms. The bridged oxygen atoms have identical environment and neighbouring contacts, and neither is involved in any other hydrogen bonding. Because of the low precision in the location of hydrogen atoms from the X-ray data, no conclusions about the potential function can be drawn with any degree of reliability.

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