Syntheses and Crystal Structures of Three Palladium(II) Complexes with Isonitrosobenzoylacetoneimine Ligand

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Three palladium (II) complexes with the isonitrosobenzoylacetoneimine (HIBI) ligand, Pd(p-$CH_3C_6H_4IBI$)$_2$ (1), Pd(C_6H_5IBI)$_2$ (2) and Pd_2Cl_2($C_6H_5CH_2IBI$)$_2$·$CHCl_3$ (3), were prepared and characterized by IR, Raman and X-ray diffraction studies. The geometries around the palladium atoms in the complexes 1 and 2 are distorted *trans*-PdN_4 square planes, and the Schiff base ligands $RIBI^-$ are coordinated through their oximo-nitrogen atoms and imino-nitrogen atoms. The week Pd···H—C agostic interactions [Pd···H = 0.2764 nm] complete the hexacoordinate environment around palladium in the complex 1. The octahedral deformation of the classical square planar environment of the Pd atom is due to the week Pd···O(1b) interactions [Pd—O(1b) = 0.3157(9) nm] in the complex 2. The complex 3 is a first example of binuclear complex with isonitrosoketoimine ligands, in which one of oximo groups is coordinated through oximo-nitrogen and oximo-oxygen atoms.

Keywords isonitrosobenzoylacetoneimine, crystal structure, palladium complex, spectroscopy

Introduction

Isonitrosoketones and related ligands such as nitrosophenoles are used as analytical reagents.[1] Complexes of cobalt metals[2,3] with isonitrosoketoneimines are relevant to the chemistry and biochemistry of the vitamin B_{12} coenzymes. Isonitroso(oximino) group of those ligands can coordinate through either oxygen and/or nitrogen atoms giving rise to several geometrical isomers.[4-6] This has prompted us to investigate the structure and overall coordination modes of these complexes.[7-9] Here we describe three palladium(II) complexes with the isonitrosobenzoylacetoneimine (HIBI) ligand.

Experimental

C, H and N were analyzed using an EA 1110 CHNS Elemental Analyzer. IR spectra were recorded on a Perkin-Elmer FT-IR Fourier transform IR spectrometer by use of KBr discs. Raman spectra were obtained on a Nicolet Raman 910 Fourier transform laser-Raman spectrometer. UV-vis spectra in the $CHCl_3$ were obtained on a Perkin-Elmer λ9 UV/vis/near-IR spectrometer.

Syntheses

The general procedure for the preparation of title complexes is as follows. Isonitrosobenzoylacetone (1.0 mmol) and amine (1.0 mmol) in 15 mL of methyl alcohol were stirred for 4 h. NaOH (1.0 mol/L) was added to the solution until pH = 7.5 and then $PdCl_2$ (0.5 mmol) was added and stirred for 10 h. The resulting solution was evaporated under vacuum, and the compounds were filtered off, washed with small amounts of methyl alcohol, and recrystallized from chloroform-methyl alcohol (1:1, *V*/*V*) mixture to give the crystals suitable for X-ray structural analysis.

Pd(p-$CH_3C_6H_4IBI$)$_2$ (1) Orange-red complex. UV-vis ($CHCl_3$) λ_{max}: 265 (π-π^*), 341, 418 (MLCT)

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nm; IR (KBr) ν: 1686, 1672 (C = O), 1555 (C = NO), 1099 (N—O), 601, 586 (Pd—N) cm^{-1}; Raman ν: 1645 (C = O), 1554 (C = NO), 1168 (N—O), 590 (Pd—N) cm^{-1}. Anal. calcd for $C_{34}H_{30}N_4O_4Pd$: C 61.40, H 4.55, N 8.43; found C 62.31, H 4.32, N 8.23.

$Pd(C_6H_5IBI)_2$ (**2**) Orange-red complex. UV-vis ($CHCl_3$) λ_{max}: 269 (π-π^*), 347, 417 (MLCT) nm; IR (KBr) ν: 1643 (C = O), 1560 (C = NO), 1126 (N—O), 601, 568 (Pd—N) cm^{-1}; Raman ν: 1641 (C = O), 1554 (C = NO), 616, 589 (Pd—N) cm^{-1}. Anal. calcd for $C_{32}H_{26}N_4O_4Pd$: C 60.34, H 4.11, N 8.80; found C 60.82, H 3.98, N 8.35.

$Pd_2Cl_2(C_6H_5CH_2IBI)_2 \cdot CHCl_3$ (**3**) Olive-green complex. UV-vis ($CHCl_3$) λ_{max}: 260 (π-π^*), 335, 417 (MLCT) cm^{-1}; IR (KBr) ν: 1665 (C = O), 1138, 1113 (N—O), 612, 596 (Pd—N) cm^{-1}; Raman ν: 1670 (C = O), 1568 (C = NO), 1110 (N—O), 630, 600 (Pd—N) cm^{-1}. Anal. calcd for $C_{35}H_{31}Cl_5N_4O_4Pd_2$: C 43.71, H 3.25, N 5.83; found C 43.98, H 3.12, N 5.63.

X-Ray structure determination

X-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometrer for crystals **1** and **3**, and on a Rigaku AFC5R diffractometrer for crystal **2** at room temperature with graphite-monochromated Mo Kα radiation (λ = 0.071069 nm), using ω-2θ scan mode. All data were corrected for Lp factors and Ψ absorption. The structures were solved by the direct methods, and refined by least squares. All hydrogen atoms were located by difference Fourier maps and geometrical calculations (U_{iso} 0.0008 nm^2). Their coordinates and thermal parameters were fixed during structure refinement. All calculations were performed on a Pentium PC computer, using SHELXL 97 program system.[10] Details of crystal parameters, data collection and structure refinement are given in Table 1.

The selected bond distances and angles of title complexes are listed in Tables 2 and 3, respectively.

Table 1 Crystallographic data and refinement details for complexes **1**, **2** and **3**

Complex	**1**	**2**	**3**
Formula	$C_{34}H_{30}N_4O_4Pd$	$C_{32}H_{26}N_4O_4Pd$	$C_{35}H_{31}Cl_5N_4O_4Pd_2$
Formula weight	665.02	636.97	961.69
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (nm)	1.1064(2)	0.6306(1)	1.5234(3)
b (nm)	1.3112(3)	1.7560(4)	1.2389(2)
c (nm)	1.1366(2)	1.2712(3)	2.0932(4)
β (°)	114.96(3)	100.64(3)	102.80(3)
V (nm^3)	1.4949(5)	1.3834(5)	3.852(1)
Z	2	2	4
D_{cal} ($Mg \cdot m^{-3}$)	1.477	1.529	1.658
μ (mm^{-1})	0.666	0.716	1.323
F(000)	680	648	1921
Crystal dimensions (mm)	0.40 × 0.30 × 0.15	0.40 × 0.40 × 0.25	0.30 × 0.15 × 0.10
Independent reflections	2914	2633	6747
Observed reflections [$I > 2\sigma(I)$]	2285	1778	3589
Variables	197	187	452
R/wR	0.0459/0.1486	0.0906/0.2273	0.0681/0.1488
S	1.036	1.004	0.925
Residual electron density ($e \cdot nm^{-3}$)	870 (−613)	1971 (−1914)	1087 (−753)

Table 2 Selected bond distances (nm) and bond angles (°) for complexes **1** and **2**

Complex **1**		Complex **2**	
Pd(1)—N(1)	0.2048(3)	Pd(1)—N(1)	0.2033(7)
Pd(1)—N(2)	0.2054(4)	Pd(1)—N(2)	0.2058(6)
O(1)—C(1)	0.1226(6)	O(1)—C(1)	0.123(1)
O(2)—N(1)	0.1266(5)	O(2)—N(1)	0.1276(8)
N(1)—C(2)	0.1338(5)	N(1)—C(2)	0.132(1)
N(2)—C(11)	0.1443(6)	N(2)—C(11)	0.144(1)
N(2)—C(3)	0.1314(5)	N(2)—C(3)	0.129(1)
C(2)—C(3)	0.1436(6)	C(2)—C(3)	0.142(1)
N(1)-Pd(1)-N(2)	79.2(1)	N(1)-Pd(1)-N(2)	79.0(2)
O(2)-N(1)-Pd(1)	124.4(3)	O(2)-N(1)-Pd(1)	124.4(5)
C(2)-N(1)-Pd(1)	114.2(3)	C(2)-N(1)-Pd(1)	114.4(5)
C(3)-N(2)-Pd(1)	113.8(3)	C(3)-N(2)-Pd(1)	112.6(5)
C(11)-N(2)-Pd(1)	126.0(3)	C(11)-N(2)-Pd(1)	126.6(5)
O(2)-N(1)-C(2)	121.3(4)	O(2)-N(1)-C(2)	121.1(7)
C(3)-N(2)-C(11)	120.1(4)	C(3)-N(2)-C(11)	120.8(6)
N(1)-C(2)-C(3)	115.3(3)	N(1)-C(2)-C(3)	115.0(7)
N(2)-C(3)-C(2)	117.5(4)	N(2)-C(3)-C(2)	119.1(7)
O(1)-C(1)-C(2)	118.0(4)	O(1)-C(1)-C(2)	118.8(7)

Table 3 Selected bond distances (nm) and bond angles (°) for complex **3**

Pd(1)—N(1)	0.1978(8)	Pd(1)—N(2)	0.2038(7)
Pd(1)—Cl(1)	0.2287(3)	Pd(1)—Cl(2)	0.2322(3)
Pd(2)—N(3)	0.1963(8)	Pd(2)—N(4)	0.2011(8)
Pd(2)—O(2)	0.2051(7)	Pd(2)—Cl(2)	0.2352(3)
O(1)—C(1)	0.123(1)	O(2)—N(1)	0.1313(9)
O(3)—C(18)	0.124(1)	O(4)—N(3)	0.1249(9)
N(1)—C(2)	0.130(1)	N(2)—C(3)	0.129(1)
N(2)—C(11)	0.147(1)	N(3)—C(19)	0.133(1)
N(4)—C(20)	0.127(1)	N(4)—C(28)	0.150(1)
C(2)—C(3)	0.144(1)	C(19)—C(20)	0.143(1)
N(1)-Pd(1)-N(2)	79.7(3)	N(1)-Pd(1)-Cl(1)	175.6(2)
N(2)-Pd(1)-Cl(1)	96.3(3)	N(1)-Pd(1)-Cl(2)	93.9(2)
N(2)-Pd(1)-Cl(2)	172.6(2)	Cl(1)-Pd(1)-Cl(2)	90.3(1)
N(3)-Pd(2)-N(4)	79.9(4)	N(3)-Pd(2)-O(2)	171.7(3)
N(4)-Pd(2)-O(2)	92.8(3)	N(3)-Pd(2)-Cl(2)	95.2(3)
N(4)-Pd(2)-Cl(2)	173.8(3)	O(2)-Pd(2)-Cl(2)	92.4(2)
Pd(1)-Cl(2)-Pd(2)	101.7(1)	N(1)-O(2)-Pd(2)	122.6(6)
C(2)-N(1)-O(2)	118.4(8)	C(2)-N(1)-Pd(1)	114.7(7)
O(2)-N(1)-Pd(1)	126.8(6)	C(3)-N(2)-C(11)	121.2(9)
C(3)-N(2)-Pd(1)	113.5(7)	C(11)-N(2)-Pd(1)	125.3(7)
O(4)-N(3)-C(19)	122.1(9)	O(4)-N(3)-Pd(2)	123.0(7)
C(19)-N(3)-Pd(2)	114.8(7)	C(20)-N(4)-C(28)	124.0(9)
C(20)-N(4)-Pd(2)	114.3(7)	C(28)-N(4)-Pd(2)	121.5(6)

Results and discussion

Structures of **1** *and* **2**

The structures of the complexes **1** and **2** have a crystallographic center and Pd(II) situated on the center at (0, 0, 0). The molecular structure of complex **1** is shown in Fig. 1, atoms labeled with "a" being related by the center of inversion. Two oximo-nitrogen atoms and two imino-nitrogen atoms of the Schiff base ligands $RIBI^-$ form a distorted *trans*-PdN_4 square plane. The bond lengths of Pd(1)—N(1) and Pd(1)—N(2) are 0.2048 (3) and 0.2054 (4) nm for **1** (R = *p*-$CH_3C_6H_4$), 0.2033(7) and 0.2058(6) nm for **2** (R = C_6H_5), respectively. These bond lengths are in good agreement with the corresponding ones in complexes of $PdCl(C_6H_5IAI)$-$(C_6H_5NH_2)$[8] and $Pd(C_6H_5CH_2IEAI)_2$.[9] The bond angles of N(1)-Pd(1)-N(2) are 79.2(1)° for **1** and 79.0(2)° for **2**, respectively.

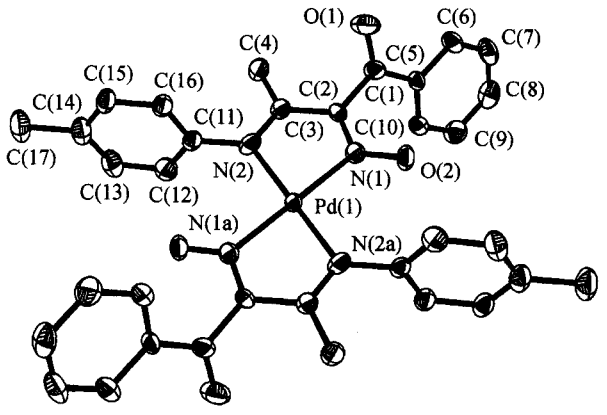

Fig. 1 Molecular Structure of $Pd(p\text{-}CH_3C_6H_4IBI)_2$.

It is noteworthy that short contacts of 0.2764 nm exist between H(6b) at C(6b) and Pd(1), between H(6c) at C(6c) and Pd(1) in complex **1** [symmetry codes: (b) $0.5-x$, $-0.5+y$, $0.5-z$; (c) $-0.5+x$, $0.5-y$, $-0.5+z$]. This value is less than the sum of the van der Waals radii [$r(H)=0.12$ nm, $r(Pd)=0.19$ nm], indicating some metal-hydrogen interaction and thus these hydrogen atoms occupy the fifth and the sixth coordination sites around the palladium atoms (Fig. 2) [C(6)—H(6) 0.1027 nm, H(6b)···Pd(1)—N(1) 85.4(2)°, H(6b)···Pd(1)—N(2) 79.7(2)°]. Week C—H···Pd and C—H···M agostic bonds have been reported in other cases.[11-14] Pd···H(imine) lengths are 0.284 and 0.294 nm in complex $PdCl_2(C_6H_{14}N_2O_2)$.[11] Pd···H(methyl) length is 0.27 nm in complex $PdCl_2(C_7H_{16}N_2O_2)$.[12]

The Pd(1) atom is hexacoordinate in complex **2**, as can be seen from the projection of the structure down the *c*-axis (Fig. 3). In the axial positions, two carbonyl O (1b) [symmetry code: (b) $1+x$, y, z] atoms from neighboring ligands $C_6H_5IBI^-$ complete the coordination to form a distorted octahedral environment with a Pd(1)···O(1b) distance of 0.3157(9) nm. The chains of molecules are formed by these Pd···O forces along *a* axis. It has been reported that M···O distances [0.2953 nm for $Ni(C_8H_{13}N_3O_3)_2$,[15] 0.3226 nm for $Pd(C_8H_{13}N_3O_3)_2$[15]] are long enough for the energies of M···O interactions to be considered comparable to the energies of normal chemical bonds.[15] At the same time, these distances are short enough for effective interactions between the magnetic orbital of different molecules via the intermediate metal ion.[15]

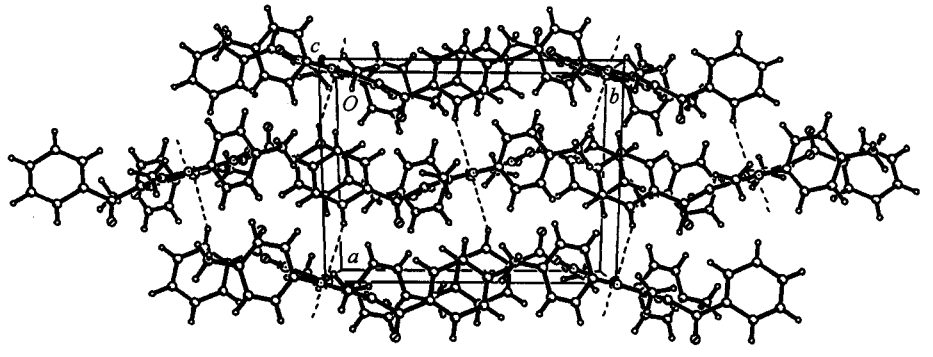

Fig. 2 Packing diagram of **1** showing Pd···H forces as broken lines.

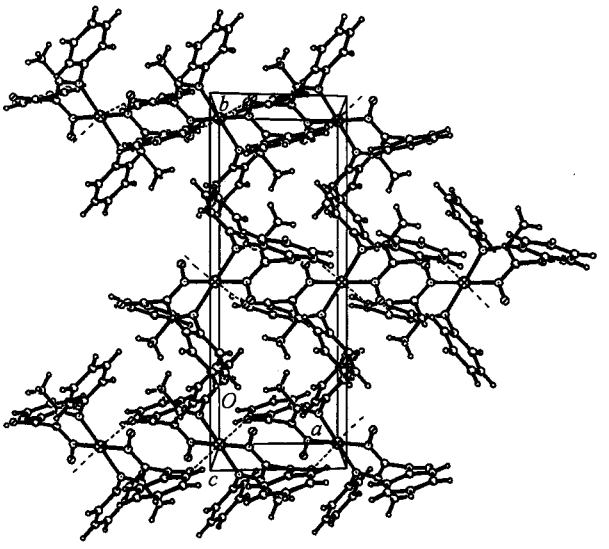

Fig. 3 Packing diagram viewed down the *c*-axis for **2**.

Structure of **3**

Complex **3** consists of a $Pd_2Cl_2(C_6H_5CH_2IBI)_2$ molecule and a lattice $CHCl_3$ molecule. As illustrated in Fig. 4, Pd(1) atom is coordinated by two nitrogen atoms from a ligand $C_6H_5CH_2IBI^-$ and two Cl^- anions, forming a *cis*-square-planar arrangement. At the same time, O(2) atom of oximo group of the $C_6H_5CH_2IBI^-$ and Cl(2), oximo-nitrogen atom and imino-nitrogen atom from the other ligand $C_6H_5CH_2IBI^-$ coordinate to Pd(2), forming the other square-planar arrangement. The two square-planars are bridged by the Cl(2) and N(1)—O(2), forming a binuclear structure. To our knowledge, the title complex is the first example of binuclear metal complex with isonitroso-β-diketoimine ligands, in which the oximo group of one ligand $C_6H_5CH_2IBI^-$ is coordinated through oximo-nitrogen and oximo-oxygen, and the oximo group of the other ligand $C_6H_5CH_2IBI^-$ is coordinated through oximo-nitrogen. The bond lengths of Pd(1)—N(1) and Pd(1)—N(2) are 0.1978(8) and 0.2038(7) nm; the bond lengths of Pd(2)—N(3) and Pd(2)—N(4) are 0.1963(8) and 0.2011(8) nm, respectively. These bond lengths of Pd—N(oximo) are much less than the corresponding ones in complexes **1**, **2**, $PdCl(C_6H_5I\text{-}AI)(C_6H_5NH_2)$[8] and $Pd(C_6H_5CH_2IEAI)_2$.[9] The Pd—Cl(terminal) of 0.2287(3) nm is less than Pd—Cl(bridging) of 0.2322(3) and 0.2352(3) nm. The Pd···Pd distance is 0.3642(1) nm. The bond angles of N(1)-Pd(1)-N(2) and N(3)-Pd(2)-N(4) are 79.7(3)° and 79.9(4)°, respectively. These bond angles are in good agreement with the corresponding ones in **1** and **2**.

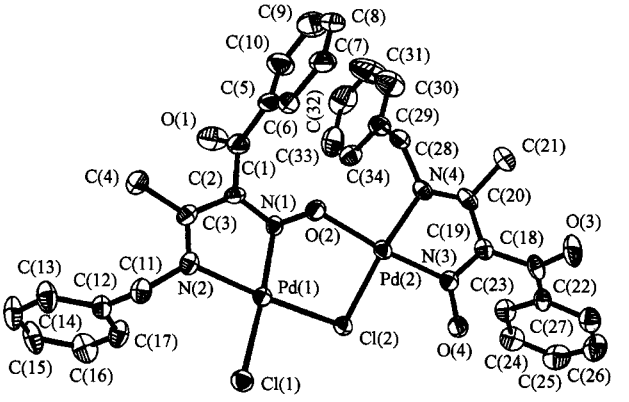

Fig. 4 Molecular structure of $Pd_2Cl_2(C_6H_5CH_2IBI)_2$.

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