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Palladium(II) complexes of N_2O_2 and N_2S_2 ligands: Syntheses and X-ray crystal structures

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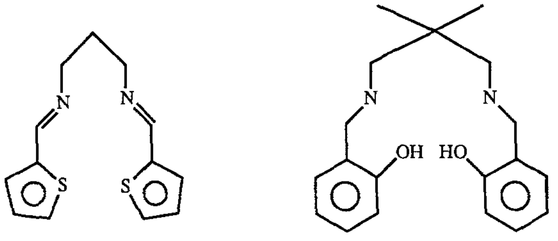
Palladium(II) complexes of an imine-thiophene ligand N,N′ bis(1-methylenethiophene)-1,3-diaminopropane and an amine-phenol ligand N,N′-bis(2-hydroxybenzyl)1,3-diamino-2,2-dimethylpropane were synthesized by reacting K_2PdCl_4 with alcoholic solutions of the ligands. X-ray structures of the complexes were determined using data from a CAD-4 Nonius diffractometer (Mo $K\alpha$ radiation). The structures were solved by conventional methods resulting in R factors of 0.044 and 0.061 using 1841 and 2241 independent reflections, respectively. Crystal data: Complex I, orthorhombic, space group $Pbca$, $a = 11.323(2)$, $b = 14.819(2)$, $c = 23.873(3)$ Å, $V = 4006(1)$ Å^3, $Z = 8$. Complex II: Space group $P2_1/c$, $a = 9.169(2)$, $b = 31.920(4)$, $c = 8.902(6)$, $\beta = 90.38(2)°$, $V = 2605(1)$ Å^3. $Z = 4$. Both complexes showed coordination of the ligands through the nitrogens only while the sulphur and the oxygen atoms were uncoordinated. Square planar coordination is completed by *cis* chloro ligands.

Introduction

We have been interested in the syntheses of new ligands for complexation of radioactive metals for the development of diagnostic and therapeutic radiopharmaceuticals (Pillai *et al.*, 1990a; Troutner *et al.*, 1991). We have earlier demonstrated that tetradentate amine-phenol ligands form complexes with ^{99}Tc readily (Pillai *et al.*, 1990b). We have now synthesized a new N_2S_2 ligand by condensing 1,3 propanediamine with thiophene carboxaldehyde. Palladium(II) complexes of the imine-thiophene ligand and an amine-phenol ligand synthesized earlier were prepared and characterized by X-ray crystallography. The ligands used in these studies are shown in Fig. 1.



Ligand I Ligand II

Fig. 1. Ligand I: N,N′bis (1-methylene thiophene)1,3 diaminopropane. Ligand II: N,N′-bis (2-hydroxybenzyl)1,3-diamino-2,2-dimethylpropane.

Experimental

Synthesis of ligand I

Twenty grams (0.178 mol) of 2-thiophene carboxaldehyde was dissolved in 200 ml of ethanol. 6.6 g (0.089 mole) of 1,3 propanediamine was added to this and refluxed for 24 h. Ethanol was removed by rotary evaporation which leaves a yellow oil. The compound could not be recrystallized. ^{1}H and ^{13}C nuclear magnetic

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resonance spectra did not show any peaks due to impurities. ^{1}H-NMR: (d)ppm 2.03–2.08 (p) 2H, 3.62–3.65 (t) 4H, 7.01–7.03 (t) 2H, 7.23–7.24 (d) 2H, 7.33–7.34 (d) 2H, 8.33(s) 2H. ^{13}C-NMR: (d)ppm 31.55, 58.45, 127.07, 128.39, 129.96, 142.28, 154.25. Synthesis and characterization of ligand II were reported earlier (Pillai *et al.*, 1990a).

Syntheses of complexes

Both complexes were prepared in parallel fashion by reacting an alcoholic solution of the ligand with aqueous K_2PdCl_4 at room temperature. Syntheses of complex I is discussed in detail below.

Complex I

One hundred seventy milligrams of the ligand was dissolved in 20 ml of absolute ethanol in a 50 ml round bottom flask. K_2PdCl_4 (206 mg) was dissolved in 10 ml of double distilled water and was slowly added to the ligand solution. The solution was kept stirring for 16 h and ethanol removed by rotary evaporation. The product was extracted into $CHCl_3$. The $CHCl_3$ was removed by rotary evaporation and the yellow residue was redissolved in CH_2Cl_2 by gentle heating. Yellow crystals appeared after 4–5 days at room temperature, and were collected and used for X-ray crystallography.

Complex II was prepared under identical conditions, except that the recrystallization was from ethanol.

Yields of the crystals were less than 20% in both cases. No attempts were made to maximize yields.

Data collection and refinement of X-ray structure

The procedure used for both complexes was essentially identical. The X-ray data were collected at 22(1)°C on an Enraf-Nonius CAD-4 automated diffractometer controlled by a digital PDP 11/34 computer using Mo $K\alpha$ radiation. Twenty-five reflections were located by automatic search of reciprocal space and recentered and lattice constants were obtained by least squares fit of those reflections. To check the instrument and crystal stability, the intensities of three standard reflections were recorded after every 7200 s of X-ray exposure and showed no significant decay or fluctuation. Orientation was checked after every 200 reflections with the use of the same standards, and all 25 original reflections were recentered when the measured deviations were significant. A summary of crystal data, data collection parameters and refinement results is given in Table 1.

Table 1. Crystal data, data collection parameters and refinement: results

	Complex I	Complex II
Formula	$PdC_{14}H_{16}N_2S_2Cl_4$	$PdC_{21}H_{32}N_2O_3Cl_2$
Formula wt	524.62	537.81
Space group	*Pbca*	$P2_{1/c}$
a(Å)	11.323(2)	9.169(2)
b(Å)	14.819(2)	31.920(2)
c(Å)	23.873(3)	8.902(6)
β(°)	—	90.38(2)
V(Å^3)	4006(1)	2605(1)
Z	8	4
Mo$K\alpha$(Å)	0.7107	0.7107
d_{cal} (g/cm^3)	1.740	1.371
Crystal size (mm)	0.15 × 0.25 × 0.33	0.20 × 0.22 × 0.30
μ cm^{-1}	13.8	9.30
Relative transmission factors	0.89–1.0	0.96–1.0
Scan method	θl-2θ	θ-2θ
2θ range (°)	2–46°	2–40°
Number of reflections measd	2610	3725
No. of independent reflections measd	2610	2407
No. of independent reflections ($I > 3\sigma(I)$)	1841	2241
No. of variables	208	272
$R(F)$	0.044	0.061
$Rw(F)$	0.065	0.072
Maximum shift/ error on last cycle	0.040	0.46

Results

Palladium complexes of two ligands were prepared. Ligand I is a Schiff base type ligand with N_2S_2 core for chelation while, ligand II is a reduced Schiff base ligand with N_2O_2 core. In both cases the crystal structure consists of mononuclear square planar complexes of Pd(II). In the complexes the ligand is coordinated to the metal only through the nitrogens and the square plane about Pd(II) is completed by chloride ions. The ORTEP diagrams of the complexes are given in Figures 2 and 3. Important bond lengths for complexes I and II are given in Tables 2 and 4. Tables 3 and 5 give

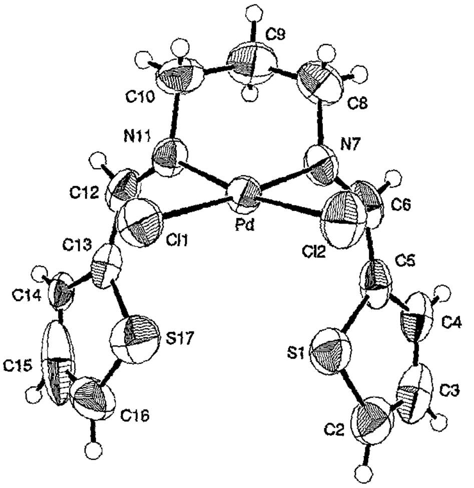

Fig. 2. ORTEP diagram of the Pd(II) complex of N,N'bis (1-methylene thiophene)1,3-diaminopropane.

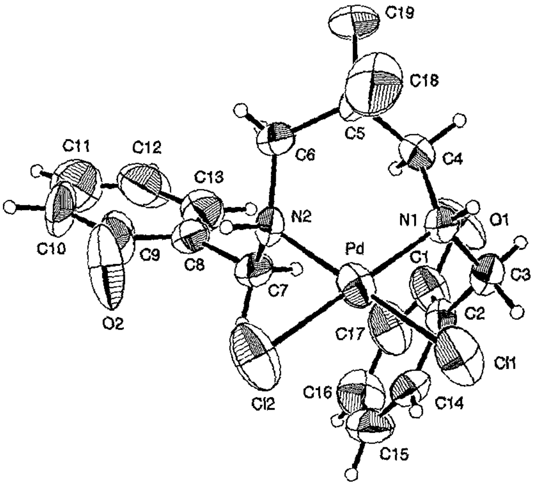

Fig. 3. ORTEP diagram of the Pd(II) complex of N,N'-bis (2-hydroxybenzyl)1,3-diamino-2,2-dimethylpropane.

bond angles. Positional parameters and their estimated standard deviations are given in Tables 6 and 7.

There are major differences in conformation of the six-membered Pd(II)-containing rings of the two complexes. In the case of the imine (N_2S_2) ligand, the ring is a good chair with N7, C8, C10, and N11 as the seat, defining within experimental error a perfect plane (Pd is 1.225(9) Å above the plane and C9 is −0.64(2) Å below the plane). For the amine (N_2O_2) complex the corresponding six-membered ring is a highly distorted boat. The "planar" portion (N1, C4, C6, N2) is highly puckered (average deviation from the plane (0.15(1) Å)) with Pd and C5 0.635(1) Å and 0.681(1) Å, respectively,

Table 2. Bond distances (Å) for complex I

PD—Cl(1)	2.299(2)	C(9)—C(10)	1.52(2)
Pd—Cl(2)	2.290(2)	C(10)—N(11)	1.47(1)
Pd—N(7)	1.995(7)	N(11)—C(12)	1.28(1)
Pd—N(11)	2.020(6)	C(12)—C(13)	1.40(1)
S(1)—C(2)	1.70(1)	C(13)—C(14)	1.58(1)
S(1)—C(5)	1.738(9)	C(13)—S(17)	1.696(9)
C(2)—C(3)	1.36(2)	C(14)—C(15)	1.32(2)
C(3)—C(4)	1.40(2)	C(15)—C(16)	1.38(2)
C(4)—C(5)	1.37(1)	C(16)—S(17)	1.66(1)
C(5)—C(6)	1.43(1)	C(18)—Cl(3)	1.88(2)
C(6)—N(7)	1.29(1)	C(18)—Cl(4)	1.68(2)
N(7)—C(8)	1.48(1)	Cl(3)—Cl(4)	2.98(1)
C(8)—C(9)	1.48(2)		

Table 3. Bond angles (°) for complex I

Cl(1)—Pd—Cl(2)	91.96(9)	N(7)—C(8)—C(9)	110.8(8)
Cl(1)—Pd—N(7)	175.4(2)	C(8)—C(9)—C(10)	116.8(8)
Cl(1)—Pd—N(11)	91.4(2)	C(9)—C(10)—N(11)	110.8(8)
Cl(2)—Pd—N(7)	89.6(2)	Pd—N(11)—C(10)	109.3(5)
Cl(2)—Pd—N(11)	170.4(2)	Pd—N(11)—C(12)	132.4(5)
N(7)—Pd—N(11)	86.4(3)	C(10)—N(11)—C(12)	118.3(7)
C(2)—S(1)—C(5)	90.3(5)	N(11)—C(12)—C(13)	129.7(7)
S(1)—C(2)—C(3)	113.9(9)	C(12)—C(13)—C(14)	120.6(7)
C(2)—C(3)—C(4)	111.5(9)	C(12)—C(13)—S(17)	126.9(7)
C(3)—C(4)—C(5)	113.3(9)	C(14)—C(13)—S(17)	112.4(6)
S(1)—C(5)—C(4)	110.9(7)	C(13)—C(14)—C(15)	102.9(8)
S(1)—C(5)—C(6)	124.8(7)	C(14)—C(15)—C(16)	121(1)
C(4)—C(5)—C(6)	124.1(9)	C(15)—C(16)—S(17)	113(1)
C(5)—C(6)—N(7)	129.3(8)	C(13)—S(17)—C(16)	91.4(6)
Pd—N(7)—C(6)	130.5(6)	Cl(3)—C(18)—Cl(4)	114(1)
Pd—N(7)—C(8)	112.3(6)		
C(6)—N(7)—C(8)	117.1(7)		

Table 4. Bond distances (Å) for Complex II

Pd—Cl(1)	2.313(2)	C(4)—C(5)	1.54(1)
Pd—Cl(2)	2.310(2)	C(5)—C(6)	1.54(1)
Pd—N(1)	2.047(5)	C(5)—C(18)	1.56(2)
Pd—N(2)	2.054(6)	C(5)—C(19)	1.55(1)
O(1)—Cl	1.371(9)	C(8)—C(9)	1.40(1)
O(2)—C(9)	1.34(1)	C(8)—C(13)	1.39(1)
N(1)—C(3)	1.500(9)	C(9)—C(10)	1.44(1)
N(1)—C(4)	1.488(9)	C(10)—C(11)	1.34(2)
N(2)—C(6)	1.48(1)	C(11)—C(12)	1.35(2)
N(2)—C(7)	1.519(9)	C(12)—C(13)	1.42(2)
C(1)—C(2)	1.396(9)	C(14)—C(15)	1.37(1)
C(1)—C(17)	1.38(1)	C(15)—C(16)	1.38(1)
C(2)—C(3)	1.498(9)	C(16)—C(17)	1.38(1)
C(2)—C(14)	1.38(1)		

Table 5. Bond angles (°) for Complex II

Cl(1)—Pd—Cl(2)	92.40(9)	N(4)—C(5)—C(18)	112.7(8)
Cl(1)—Pd—N(1)	87.2(2)	C(4)—C(5)—C(19)	105.7(9)
Cl(1)—Pd—N(2)	178.9(2)	C(6)—C(5)—C(18)	109.4(9)
Cl(2)—Pd—N(1)	178.7(2)	C(6)—C(5)—C(19)	106.3(8)
Cl(2)—Pd—N(2)	87.0(2)	C(18)—C(5)—C(19)	111(1)
N(1)—Pd—N(2)	93.5(2)	N(2)—C(6)—C(5)	117.0(7)
Pd—N(1)—C(3	115.0(4)	N(2)—C(7)—C(8)	111.9(6)
Pd—N(1)—C(4)	116.1(4)	C(7)—C(8)—C(9)	120.1(8)
C(3)—N(1)—C(4)	110.2(5)	C(7)—C(8)—C(13)	119.4(8)
Pd—N(2)—C(6)	118.4(5)	C(9)—C(8)—C(13)	120.4(8)
Pd—N(2)—C(7)	109.5(4)	O(2)—C(9)—C(8)	117.4(8)
C(6)—N(2)—C(7)	113.9(6)	O(2)—C(9)—C(10)	125(1)
O(1)—C(1)—C(2)	118.0(7)	C(9)—C(10)—C(11)	122(1)
O(1)—C(1)—C(17)	121.5(7)		

above the best plane. The dangling rings also have quite different orientations in the two complexes. For complex I they are related by a near mirror plane which bisects the Pd(II) coordination plane between the coordinated chlorides (Figure 2). Complex II has no such pseudo-symmetry.

For II there are two molecules of disordered ethanol per complex. Location of these disordered atoms was attempted but was only partially successful. As a result the location of hydrogen atoms was also incomplete. Neither the methyl nor the phenol hydrogen atoms could be placed with certainty and thus were not included. However the location and refinement of non-hydrogen atoms in the Pd(II) complex was easily accomplished. The amine groups are both hydrogen bonded, N1 intermolecularly to Cl(1) (N1 · · · Cl(1) = 3.370(8) Å, HN1 · · · Cl(1) = 2.54 Å, N1-HN1 · · · Cl(1), 153°) and N2 intramolecularly to O2 (N2 · · · O2 =

Table 6. Atomic parameters and B$_{\text{iso}}$ for complex I

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}[a] (Å^2)
Pd	0.11338(5)	0.23034(4)	0.12592(2)	3.20(3)
Cl(1)	0.2051(2)	0.2240(2)	0.2117(1)	4.6(1)
Cl(2)	0.2822(2)	0.2800(2)	0.0830(1)	5.2(1)
S1	0.1979(2)	0.0676(2)	0.042(1)	5.1(1)
C2	0.2216(9)	−0.0172(7)	0.0040(5)	5.7(5)
C3	0.156(1)	−0.0109(8)	−0.0512(5)	6.3(6)
C4	0.0858(8)	0.0670(7)	−0.0510(4)	4.6(5)
C5	0.0971(7)	0.1169(6)	−0.0032(4)	4.3(4)
C6	0.0286(8)	0.1960(7)	0.0090(4)	4.6(4)
N7	0.0263(6)	0.2443(5)	0.0538(3)	3.9(3)
C8	−0.0570(9)	0.3213(7)	0.0548(4)	5.8(5)
C9	−0.1543(9)	0.3047(8)	0.0953(5)	6.4(6)
C10	−0.1190(8)	0.2888(6)	0.1561(5)	5.1(5)
N11	−0.0460(5)	0.2075(5)	0.1612(3)	3.6(3)
C12	−0.0912(7)	0.1378(7)	0.1845(4)	4.2(4)
C13	−0.0437(8)	0.0511(6)	0.1919(4)	4.2(4)
C14	−0.1242(7)	−0.0294(6)	0.2121(4)	3.6(4)
C15	−0.050(2)	−0.098(1)	0.2128(5)	9.8(9)
C16	0.0648(13)	−0.0882(7)	0.1954(5)	7.0(7)
S17	0.0964(3)	0.0177(2)	0.1777(1)	6.6(1)
C18	0.980(2)	0.121(1)	0.3423(7)	15(1)
Cl3	0.9188(6)	0.0062(5)	0.3583(2)	15.1(4)
Cl4	1.0900(4)	0.1524(8)	0.3852(3)	19.6(7)

[a] Bis$_{\text{iso}}$ is the mean of the principal axes of the thermal ellipsoid.

Table 7. Atomic parameters and B_{iso} for complex II

Atom	x/a	y/b	z/c	$B_{iso}(Å^2)$
Pd	0.04882(8)	0.09262(2)	0.0726(1)	3.68(1)
Cl1	−0.0935(3)	0.05518(9)	−0.0957(4)	5.62(8)
Cl2	−0.1239(4)	0.1450(1)	0.0935(5)	7.30(9)
O1	0.5717(7)	0.0576(2)	−0.055(1)	6.6(2)
O2	0.133(1)	0.2126(3)	0.321(1)	9.5(3)
N1	0.1987(8)	0.0454(2)	0.0567(9)	3.0(2)
N2	0.172(1)	0.1259(2)	0.2251(9)	4.3(2)
C1	0.491(1)	0.0879(3)	−0.127(1)	4.8(3)
C2	0.3418(9)	0.0809(3)	−0.146(1)	2.9(2)
C3	0.2701(9)	0.0414(3)	−0.094(1)	3.4(2)
C4	0.310(1)	0.0434(3)	0.179(1)	4.8(3)
C5	0.254(2)	0.0551(4)	0.335(1)	6.9(4)
C6	0.240(2)	0.1029(3)	0.352(1)	6.2(3)
C7	0.276(1)	0.1546(3)	0.142(1)	4.0(2)
C8	0.356(1)	0.1831(3)	0.247(1)	4.6(3)
C9	0.279(2)	0.2127(3)	0.332(1)	6.5(3)
C10	0.364(2)	0.2405(4)	0.425(2)	8.5(4)
C11	0.509(2)	0.2395(5)	0.427(2)	9.7(5)
C12	0.582(2)	0.2108(4)	0.345(2)	8.9(4)
C13	0.507(1)	0.1820(4)	0.252(1)	6.3(3)
C14	0.262(1)	0.1115(3)	−0.218(1)	3.9(2)
C15	0.323(1)	0.1479(4)	−0.269(1)	5.1(3)
C16	0.470(1)	0.1546(4)	−0.248(2)	6.4(3)
C17	0.554(1)	0.1246(4)	−0.176(2)	5.9(3)
C18	0.106(2)	0.0340(5)	0.373(2)	10.4(5)
C19	0.375(2)	0.0414(5)	0.447(2)	11.5(5)
C20	−0.009(4)	0.293(1)	0.320(4)	10.0[a]
C21	−0.111(3)	0.2053(9)	0.689(3)	11.8[a]
C22	−0.085(3)	0.168(1)	0.612(4)	8.9[a]
C23	−0.003(4)	0.252(1)	0.060(4)	7.5[a]
C24	−0.018(4)	0.221(1)	−0.092(4)	11.1[a]
C25	−0.066(8)	0.162(3)	−0.26(1)	8.2[a]
C26	−0.234(7)	0.399(2)	0.005(8)	10.4[a]
C27	−0.104(5)	0.282(2)	0.312(6)	10.0[a]
C28	−0.124(6)	0.363(2)	0.027(6)	10.6[a]

[a] Refined with isotropic thermal parameter.

2.918(9) Å, HN2 · · · O2, 2.02 Å, N2-HN2 · · · O2, 124°). Apparently O1 is intermolecularly hydrogen bonded to Cl(1) (3.094(7) Å) but the hydrogen on O1 was not located.

Bond distances and angles in the complexes are quite normal. The Pd-N (amine) distances (ave. 2.051(4) Å) are slightly longer than the Pd—N (imine) distances (ave. 2.01(1) Å). In addition the Pd—Cl distances (ave. 2.295(5) Å) in the imine complex are shorter than those (ave. 2.312(2) Å) in the amine complex. However these values are well within normal Pd—N and Pd—Cl bond distance ranges. In a tetradentate amine oxime complex (Hussain and Schlemper, 1979) of Pd(II) with similar *cis* amine nitrogens, the Pd—N (amine) distance averaged 2.040(4) Å.

The complexes in both the cases were prepared at acidic pH (~5–6). The reason for non-coordination of the oxygen atoms or the sulphur atoms may be due to the lower pH, at which these atoms are less basic and deprotonation is more difficult. In the case of the phenolic OH of ligand II, complexation at pH 9 was tried; however the resultant palladium complex had very little solubility in most organic solvents, and crystals suitable for X-ray structure determination could not be obtained. When reaction was carried out at pH = 9 with a similar amine-phenol ligand with a four carbon diamine bridge, the resulting crystals contained a square Pd(II) complex with coordination of both the nitrogens and phenolic oxygens (Pillai and Schlemper, to be published).

For ligand I complexation was studied only at acidic pH since the sulphur atom would be capable of coordinating even at this lower pH. The non-coordination of sulphur in this case may result from steric limitations. If the sulphur were to coordinate five-membered rings would result and would be limited in flexibility because of multiple bonds. Reduced ligands of this type might give complexes with coordination of both nitrogen and sulphur atoms.

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