Crystal Structures of Palladium Complexes of 6-Oxa-3,9-dithiabicyclo[9,4,0]-pentadeca-1(11),12,14-triene (L), *cis*-X₂LPd(II) (X = NO₃, SCN)

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Recently, there has been a considerable interest in platinum group metal complexes of thioxa-donor macrocycles because of their unusual properties.¹ As an extension of our studies involving mixed-donor cyclic^{2a} and acyclic^{2b} ligands incorporating thioxa mixed-donors, we became interested in exploring their coordination chemistry of platinum group metal ions. The S₂O-donor macrocycle of the title complexes, 6-oxa-3,9-dithiabicyclo[9,4,0]pentadeca-1(11),12,14-triene (L) was found to form a stable complex with Ir(I), Rh(I) and Ru(II).¹ L has proven to be an excellent sensor for an Ag(I) ion-selective electrode.³ However, there is no report on the complexation with Pd(II) ion. Herein, we describe the preparations and crystal structures of Pd(II) complexes with L.

The ligand (L) was prepared according to the literature method.⁴ The non-crystalline dichlorate-type complex of the title compounds was prepared by reaction of L and K₂PdCl₄ in CH₂Cl₂/water. The title compounds (Fig. 1) were readily obtained by reactions between the starting dichlorate-type complex and AgNO₃ for **I** or KSCN for **II** in acetonitrile. The crystals of **I** and **II** suitable for X-ray determination were obtained by recrystallization from diethyl ether and acetonitrile, respectively.

The crystal and experimental data are given in Table 1. The structures were solved by direct methods and refined with anisotropic temperature factors for non-hydrogen atoms. All hydrogen atoms were located from difference Fourier maps and

were not refined. The atomic coordinates for non-hydrogen atoms are listed in Table 2. The selected bond lengths and bond angles are summarized in Table 3. The molecular structure and the atomic numbering are given in Fig. 2.

As shown in Figs. 2(a) and 2(b), each Pd atom in both structures lies at the center, surrounded by a distorted square planar array of two sulfur atoms and two unidentate anions in a *cis*-stereochemistry. In the endodentate conformers, O1 atoms are oriented toward Pd atoms and lie above the S₂PdX₂ coordination plane at Pd...O1 distances of 3.032(4) Å for **I** and 2.998(5) Å for **II**, which are rather long but are less than the sum

Fig. 1 Chemical structures for **I** and **II**.

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Table 1 Crystal and experimental data for **I** and **II**

	I	II
Formula	C ₁₂ H ₁₆ N ₂ O ₇ PdS ₂	C ₁₄ H ₁₆ N ₂ OPdS ₄
Formula weight	470.79	462.93
Temperature	293(2)K	298(2)K
Crystal color	orange	purple
Crystal description	plate	block
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>Z</i>	2	2
<i>a</i>	7.9069(16) Å	9.2019(7) Å
<i>b</i>	8.2172(16) Å	9.8553(7) Å
<i>c</i>	14.019(3) Å	9.8611(7) Å
α	102.59(3)°	96.0700(10)°
β	90.72(3)°	101.1320(10)°
γ	108.03(3)°	101.2560(10)°
<i>V</i>	842.1(3) Å ³	850.96(11) Å ³
<i>D_x</i>	1.857 g/cm ³	1.807 g/cm ³
<i>2</i> θ _{max}	56.54°	56.60°
<i>R</i>	0.029	0.0397
<i>wR</i>	0.0723	0.1067
No. of reflections used	3779[>2 σ (<i>I</i>)]	3884[>2 σ (<i>I</i>)]
Diffractometer	Bruker SMART	Bruker SMART
	CCD system	CCD system
Structure determination	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **I** and **II**

	x	y	z	U_{eq}
Compound I				
Pd	4535(1)	2043(1)	2104(1)	36(1)
S(1)	6920(1)	4508(1)	2202(1)	39(1)
S(2)	5770(1)	47(1)	2437(1)	50(1)
O(1)	7049(4)	1190(5)	606(2)	54(1)
O(1')	8691(7)	1873(8)	1085(4)	46(2)
C(1)	7683(4)	2405(4)	4040(2)	48(1)
C(2)	7076(5)	1981(6)	4914(3)	67(1)
C(3)	6835(6)	3240(8)	5671(3)	85(1)
C(4)	7179(6)	4950(7)	5580(3)	82(1)
C(5)	7817(5)	5411(5)	4732(2)	62(1)
C(6)	8072(4)	4148(4)	3960(2)	45(1)
C(7)	8787(4)	4685(4)	3045(2)	48(1)
C(8)	7867(4)	4350(4)	1022(2)	48(1)
C(9)	8235(8)	2699(6)	600(3)	89(2)
C(10)	7832(7)	-135(5)	806(3)	79(1)
C(11)	6310(5)	-1128(5)	1292(3)	74(1)
C(12)	7883(4)	1019(4)	3204(3)	55(1)
N(1)	1411(3)	-441(4)	2566(3)	60(1)
N(2)	3035(3)	4426(4)	1419(2)	49(1)
O(2)	2213(3)	-87(3)	1821(2)	61(1)
O(3)	2029(4)	450(5)	3392(2)	83(1)
O(4)	0(4)	-1669(4)	2421(3)	97(1)
O(5)	2890(3)	3571(3)	2061(2)	61(1)
O(6)	3882(4)	4181(5)	712(2)	81(1)
O(7)	2296(4)	5606(4)	1525(2)	75(1)
Compound II				
Pd	4739(1)	1629(1)	3854(1)	36(1)
S(1)	4355(1)	1569(1)	1432(1)	45(1)
S(2)	2328(1)	1581(1)	4258(1)	41(1)
O(1)	3687(6)	4189(5)	3073(5)	61(2)
O(1')	2487(13)	3718(10)	2149(11)	69(3)
C(1)	950(4)	-437(4)	1984(4)	43(1)
C(2)	278(4)	-1694(5)	2355(5)	61(1)
C(3)	367(6)	-2959(5)	1673(6)	74(2)
C(4)	1140(6)	-2984(5)	621(6)	69(1)
C(5)	1820(5)	-1753(4)	233(4)	54(1)
C(6)	1726(4)	-470(4)	907(4)	43(1)
C(7)	2423(5)	851(4)	424(4)	51(1)
C(8)	4665(5)	3390(5)	1162(4)	60(1)
C(9)	3571(9)	4207(6)	1580(8)	93(2)
C(10)	2436(10)	4254(6)	3553(8)	102(2)
C(11)	2211(6)	3399(5)	4614(5)	64(1)
C(12)	788(4)	918(5)	2721(4)	57(1)
S(3)	5745(1)	1841(1)	6247(1)	50(1)
S(4)	7254(1)	1519(1)	3767(1)	59(1)
C(13)	4420(5)	2092(5)	7114(4)	59(1)
C(14)	7962(5)	3094(5)	3429(5)	59(1)
N(1)	3555(6)	2307(7)	7764(4)	93(2)
N(2)	8500(6)	4156(5)	3145(7)	95(2)

Table 3 Selected bond lengths ($\text{\AA}$), bond angles ($^\circ$) and torsion angles ($^\circ$) for **I** and **II**

Compound I			
Pd-O(2)	2.069(2)	Pd-S(2)	2.2757(9)
Pd-O(5)	2.077(2)	Pd-S(1)	2.2769(11)
O(2)-Pd-O(5)	86.00(10)	O(2)-Pd-S(1)	170.69(7)
O(2)-Pd-S(2)	83.37(8)	O(5)-Pd-S(1)	88.09(8)
O(5)-Pd-S(2)	163.81(7)	S(2)-Pd-S(1)	103.88(3)
Compound II			
Pd-S(2)	2.3215(9)	Pd-S(1)	2.3393(9)
Pd-S(3)	2.3329(9)	Pd-S(4)	2.3556(10)
S(2)-Pd-S(3)	90.88(3)	S(2)-Pd-S(4)	171.02(4)
S(2)-Pd-S(1)	102.77(3)	S(3)-Pd-S(4)	81.28(4)
S(3)-Pd-S(1)	165.96(4)	S(1)-Pd-S(4)	85.34(4)

Fig. 2 Perspective views of (a) **I** and (b) **II** with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The H atoms have been omitted for clarity.

of the van der Waals radii.⁵

In **I**, Pd atom lies 0.045(1) $\text{\AA}$ above the mean plane defined by two oxygen atoms from each unidentate nitrate ion and two sulfur atoms. The Pd-S bond distances compare well with those found in other Pd (II) complexes (2.245 – 2.282 $\text{\AA}$) of macrocyclic thioethers.^{1b,2a} In **II**, the Pd atom locates at 0.004(1) $\text{\AA}$ above the mean plane consisting of two thiocyanate ligands and two sulfur atoms of L. The Pd-S1 or Pd-S2 bond lengths of **II** are somewhat longer (by 0.05 $\text{\AA}$) than those of **I**.

In Fig. 2, each complex shows different intermolecular interactions. For example, in **I**, the weak face-to-face aromatic stacking with the distance of 3.726 $\text{\AA}$ is observed. In **II**, however, there is an imposed inversion symmetry and the Pd atom is surrounded by a distorted pseudo-square-pyramidal array of two S atoms from one L, two S atoms from two SCN⁻ ions and one S atom from an adjacent SCN⁻ ion.

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