

Synthesis and crystal structure of a new water-soluble sulfur-containing palladacyclic diaqua complex

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Abstract

A new water-soluble sulfur-containing palladacyclic diaqua complex $[(SC)Pd^{II}(H_2O)_2]_2(SO_4)$ $\{[1]_2(SO_4)$, $SC = C_6H_4-2-(CH_2S^tBu)\}$ was synthesized from a reaction of Ag_2SO_4 with a water-insoluble palladacyclic dichloro complex $[(SC)Pd^{II}(\mu-Cl)]_2$ (**2**) in water. Water-solubility of $[1]_2(SO_4)$ at pH 7 at 25 °C is 9.4 mg/mL. NH_4PF_6 was added to the solution of $[1]_2(SO_4)$ in water to give $[1](PF_6)$. The structures of $[1](PF_6)$ and **2** were unequivocally determined by X-ray analysis.

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1. Introduction

The chemistry of water-soluble organometallic aqua complexes is presently undergoing very rapid growth because they can be used as water-soluble catalysts for many types of reactions in water to avoid the use of volatile organic solvents [1–3]. Among many water-soluble organometallic aqua complexes, palladacyclic aqua complexes have merited special attention because they prove to be extremely active catalysts for a variety of C–C bond formation reactions including Suzuki coupling of aryl bromides with aryl boronic acids [4]. Palladacyclic aqua complexes are divided into two types: palladacyclic mono aqua complexes with one or two palladacyclic plane(s) and palladacyclic diaqua complexes with one palladacyclic plane as shown in Chart 1 [4a,5]. Although there are many examples of palladacyclic mono aqua complexes (Chart 2) [6–11], there are only a few examples of water-soluble palladacyclic

diaqua complexes (Chart 3) [10b]. So far, synthesis and structures of water-soluble sulfur-containing palladacyclic diaqua complexes have yet to be reported.

We report herein the first example of synthesis and crystal structure of a new water-soluble sulfur-containing palladacyclic diaqua complex $[(SC)Pd^{II}(H_2O)_2]_2(SO_4)$ $\{[1]_2(SO_4)$, $SC = C_6H_4-2-(CH_2S^tBu)$, Chart 3, which was synthesized from the reaction of a water-insoluble palladacyclic dichloro complex $[(SC)Pd^{II}(\mu-Cl)]_2$ (**2**) with Ag_2SO_4 in water.

2. Experimental

2.1. Materials and methods

All experiments were carried out under an Ar atmosphere by using standard schlenk techniques. D_2O (99.9% D) was purchased from Cambridge Isotope Laboratories. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore; Milli-RO 5 plus and Q plus). 1H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer at 25 °C. The 1H NMR experiments in D_2O were performed by dissolving the samples in D_2O in an

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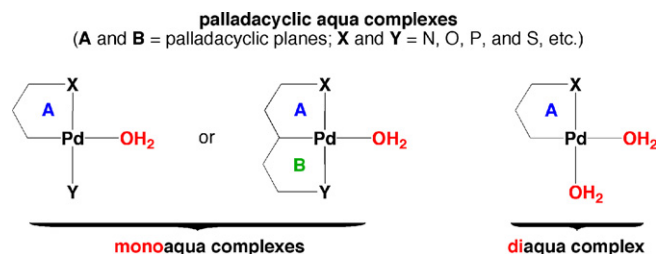


Chart 1. Palladacyclic aqua complexes (A and B = palladacyclic planes; X and Y = N, O, P, and S, etc.).

palladacyclic diaqua complexes whose structures were determined by X-ray analysis

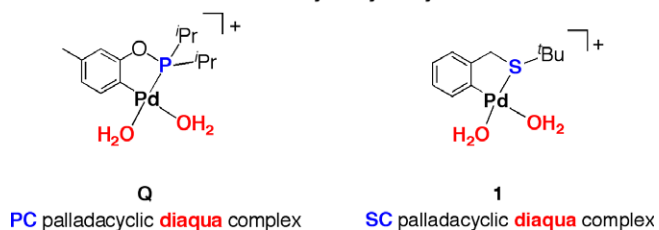


Chart 3. Palladacyclic diaqua complexes whose structures were determined by X-ray analysis.

palladacyclic mono-aqua complexes whose structures were determined by X-ray analysis

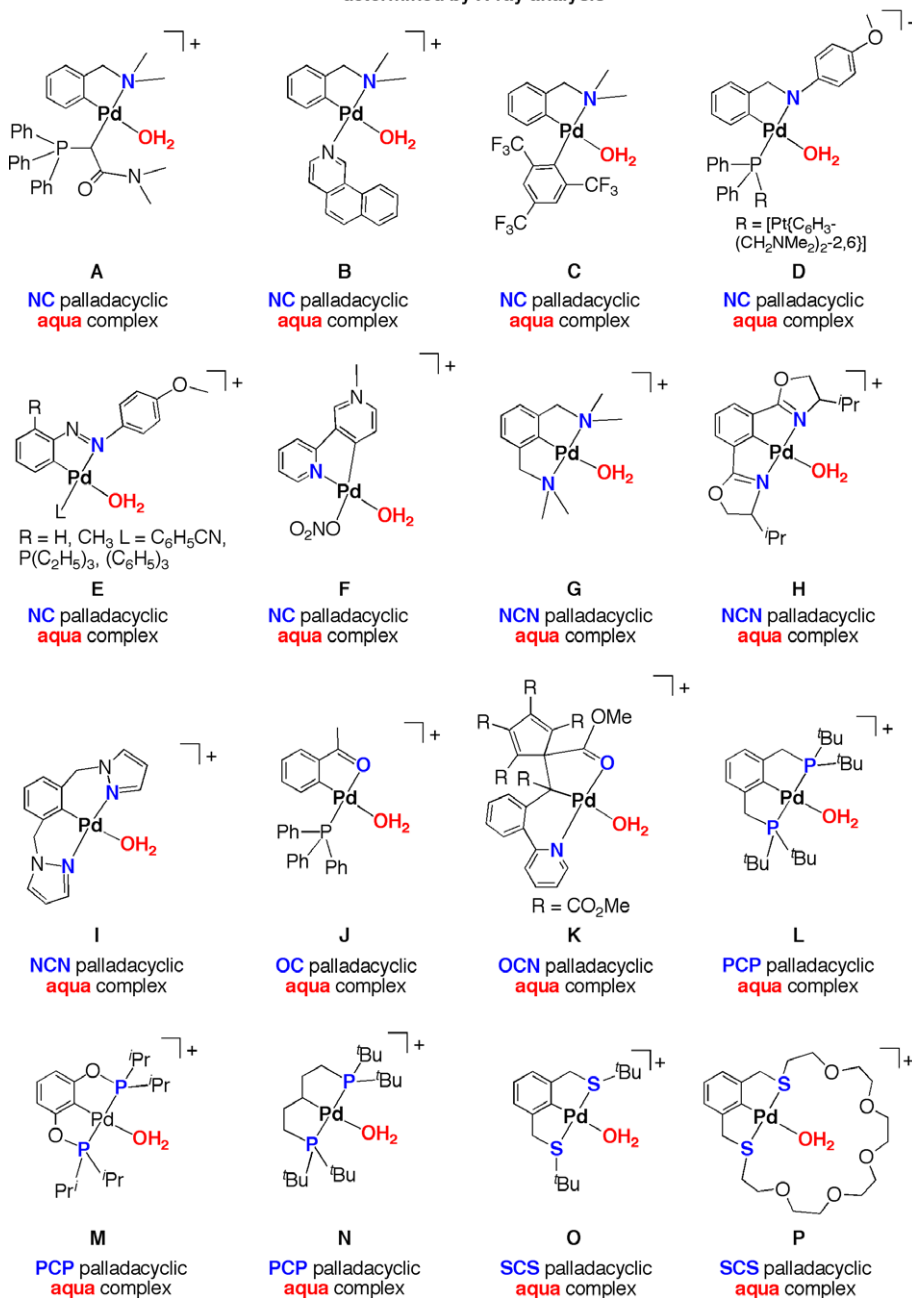


Chart 2. Palladacyclic mono-aqua complexes whose structures were determined by X-ray analysis.

NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt (TSP, as the reference with the methyl proton and carbon resonance set at 0.00 ppm) dissolved in D_2O (10 mM). The SC palladacyclic dichloro complex $[(SC)Pd^{II}(\mu-Cl)_2]$ (**2**) was prepared by the method described in the literature [12].

2.2. pH adjustment

In a pH range of 6–13, pH values of the solutions were determined by a pH meter (TOA, HM-18E) equipped with a glass electrode (TOA; GS-5015C). To determine the exact pH values, the 1H NMR experiments were performed by dissolving the samples in H_2O in an NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt (TSP, 500 mM, as the reference with the methyl proton resonance set at 0.00 ppm) dissolved in D_2O (for deuterium lock). Values of pD were corrected by adding 0.4 to the observed values [13].

2.3. Spectral measurements

The pK_a value of the palladacyclic diaqua complex $[1]_2(SO_4)$ was determined from the change in UV–Vis spectra using a Hewlett–Packard 8453 diode array spectrophotometer at various pH. The pH of the solution was adjusted by using 0.1 M NaOH/ H_2O without buffer for $[1]_2(SO_4)$.

2.4. Synthesis of $[(SC)Pd^{II}(H_2O)_2]_2(SO_4)$ $\{[1]_2(SO_4)\}$

The SC palladacyclic dichloro complex **2** (321 mg, 0.50 mmol) reacts with Ag_2SO_4 (780 mg, 2.5 mmol) in H_2O /acetone (250 mL, H_2O : acetone = 1:4) to afford the SC palladacyclic diaqua complex $[1]_2(SO_4)$, which was dried in vacuo (yield: 67% based on **2**). 1H NMR (300 MHz, in D_2O , referenced to TSP): δ 1.43 (s, 9H, $C(CH_3)_3$), 3.94 (d, $^2J_{H,H} = 17.1$ Hz, 1H, $C(H)H$), 4.28 (d, $^2J_{H,H} = 16.8$ Hz, 1H, $C(H)H$), 6.80–6.95 (m, 4H, aromatic). ESI-MS (in H_2O /acetone), m/z 401.2: $[1-(H_2O)_2 + \{(CH_3)_2CO\}_2]^+$ ($I = 100\%$ in the range of m/z 100–2000). Anal. Calc. for $C_{20}H_{25}O_6Pd_2S_3$: C, 37.56; H, 4.87%. Found: C, 37.10; H, 4.48%. Addition of NH_4PF_6 into the aqueous solution of $[1]_2(SO_4)$ gave a powder of $[1](PF_6)$.

2.5. X-ray crystallographic analysis

Yellow crystals of $[1](PF_6)$ and **2** used in X-ray structure analysis were obtained by layering CH_2Cl_2 solution of $[1](PF_6)$ or **2** with hexane. Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the

teXsan crystallographic software package of Molecular Structure Corporation.

3. Results and discussion

3.1. Synthesis and characterization of palladacyclic diaqua complex

The water-soluble palladacyclic diaqua complex $[1]_2(SO_4)$ was prepared by the reactions of Ag_2SO_4 with the corresponding water-insoluble palladacyclic dichloro complex **2** as shown in Eq. (1). Complex $[1]_2(SO_4)$ is highly soluble in water. The solubility of $[1]_2(SO_4)$ in water at pH 7 at 25 °C is 9.4 mg/mL.

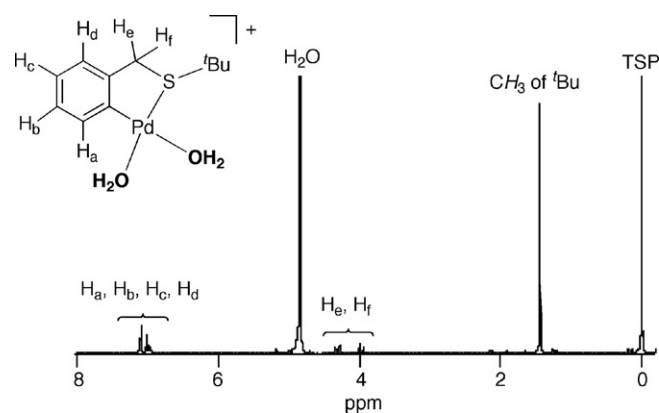
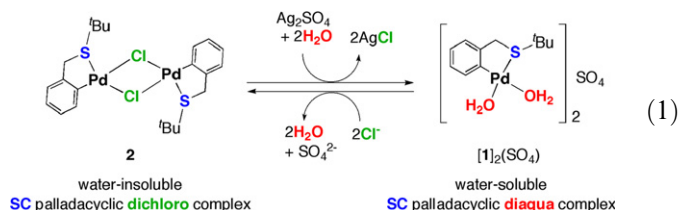


Fig. 1. 1H NMR spectrum of water-soluble $[1]_2(SO_4)$ in D_2O at 25 °C. TSP: the reference with the methyl proton resonance set at 0.00 ppm.

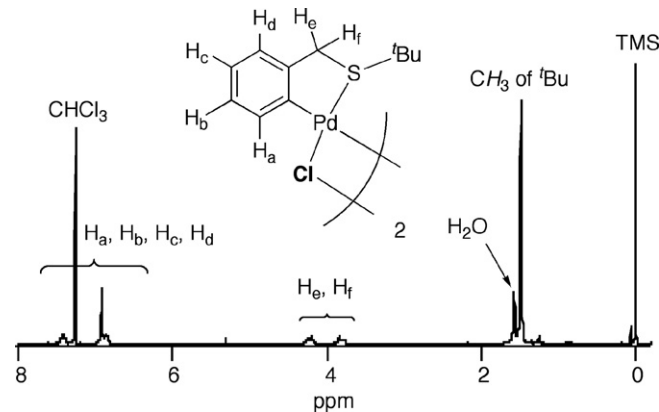


Fig. 2. 1H NMR spectrum of water-insoluble **2** in $CDCl_3$ at 25 °C. TMS: the reference with the methyl proton resonance set at 0.00 ppm.

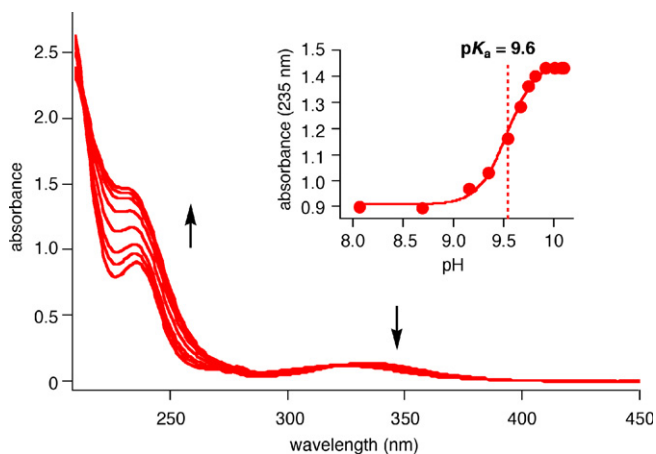


Fig. 3. pH-dependent UV-Vis spectra of $[1]_2(\text{SO}_4)$ (4.7×10^{-5} M) in a pH range of about 8–10. The inset gives a plot of absorbance ($\lambda = 235$ nm) vs. pH. Experiments were performed by the titration of $[1]_2(\text{SO}_4)$ with 0.1 M NaOH/H₂O at 25 °C.

Table 1
Crystallographic data and processing parameters for $[1](\text{PF}_6)$ and **2**

Compound	$[1](\text{PF}_6)$	2
Empirical formula	C ₁₁ H ₁₉ F ₆ O ₂ PPdS	C ₁₁ H ₁₅ ClPdS
Fw	466.69	321.15
Crystal color	Yellow	Yellow
Crystal dimensions (mm)	0.15 × 0.15 × 0.05	0.02 × 0.15 × 0.02
Crystal system	Monoclinic	Monoclinic
<i>a</i> (Å)	12.564(4)	8.192(1)
<i>b</i> (Å)	6.057(2)	5.8615(5)
<i>c</i> (Å)	22.313(8)	25.457(3)
β (°)	94.805(4)	101.099(6)
<i>V</i> (Å ³)	1691(1)	1199.5(2)
Space group (No.)	<i>P</i> ₂ / <i>c</i> (14)	<i>P</i> ₂ / <i>n</i> (14)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.832	1.778
<i>F</i> (000)	928	640
μ (Mo K α) (cm ⁻¹)	13.75	19.03
Radiation (λ , Å)	0.7107	0.7107
Temperature (°C)	-50	-50
$2\theta_{\text{max}}$ (°)	55	55
Absolute correction method	Numerical	Empirical
Number of reflections observed	3838	2747
(all, $2\theta < 54.97^\circ$)		
Number of parameters	199	127
<i>R</i> ^a	0.086	0.055
<i>wR</i> ^b	0.138	0.069
<i>R</i> ₁ ^c	0.050	0.035
Goodness-of-fit indicator (<i>S</i>) ^d	1.11	0.95
Maximum shift/error in final cycle	0.000	0.000
Maximum peak in final diff map (e Å ⁻³)	1.10	1.06
Minimum peak in final diff map (e Å ⁻³)	-0.78	-0.84

$$^a R = \sum (F_o^2 - F_c^2) / \sum F_o^2$$

$$^b wR = [\sum (F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$$

$$^c R_1 = \sum \|F_o^2 - F_c^2\| / \sum |F_o| \text{ for } I > 2.0\sigma(I) \text{ data.}$$

$$^d \text{Goodness of fit indicator, } S = [\sum (|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} \text{ (} N_o = \text{number of observations, } N_v = \text{number of variables).}$$

Fig. 1 shows ¹H NMR spectrum of the water-soluble complex $[1]_2(\text{SO}_4)$ in D₂O. The sharp signal of methyl protons of *t*-butyl group in $[1]_2(\text{SO}_4)$ was observed at 1.43 ppm. Fig. 2 shows ¹H NMR spectrum of the water-insoluble complex **2** in CDCl₃.

UV titration experiments revealed that the p*K*_a value of the diaqua complex $[1]_2(\text{SO}_4)$ was 9.6 as shown in Fig. 3. At this pH, complex **1** was deprotonated to form the corresponding dihydroxo complex.

3.2. Structures of the palladacyclic diaqua and dichloro complexes

NH₄PF₆ was added to the solutions of $[1]_2(\text{SO}_4)$ in water to give a powder of the palladacyclic diaqua complex

Table 2
Selected bond lengths (l/Å) and angles (ϕ /°) of $[1](\text{PF}_6)$ and **2**

$[1](\text{PF}_6)$		2	
<i>Bond distances</i> (Å)		<i>Bond distances</i> (Å)	
Pd1–C1	1.981(5)	Pd1–C1	1.995(3)
Pd1–O1	2.194(4)	Pd1–C11	2.3676(9)
Pd1–O2	2.090(5)	Pd1–Cl1*	2.4508(8)
Pd1–S1	2.266(2)	Pd1–S1	2.2631(9)
C1–C2	1.385(7)	C1–C2	1.390(4)
C1–C6	1.406(7)	C1–C6	1.405(4)
C6–C7	1.492(8)	C6–C7	1.500(5)
C7–S1	1.812(5)	C7–S1	1.812(3)
<i>Bond angles</i> (ϕ /°)		<i>Bond angles</i> (ϕ /°)	
Pd1–C1–C2	122.8(4)	Pd1–C1–C2	123.3(2)
Pd1–C1–C6	118.5(4)	Pd1–C1–C6	118.8(2)
Pd1–S1–C7	98.6(2)	Pd1–S1–C7	100.5(1)
C1–Pd1–O1	177.1(2)	C1–Pd1–Cl1	96.01(9)
C1–Pd1–O2	94.7(2)	C1–Pd1–S1	85.80(9)
C1–Pd1–S1	85.4(1)	C1–Pd1–Cl1*	178.9(1)
O1–Pd1–O2	86.2(3)	Cl1–Pd1–Cl1*	84.50(3)
O1–Pd1–S1	94.1(2)	Cl1–Pd1–S1	178.16(3)
O2–Pd1–S1	172.3(2)	Cl1*–Pd1–S1	93.71(3)
C1–C6–C7	119.0(4)	C1–C6–C7	119.9(3)
C6–C7–S1	110.3(4)	C6–C7–S1	110.7(2)
		Pd1–C1–C2	123.3(2)
		Pd1–C1–C6	118.8(2)
		Pd1–S1–C7	100.5(1)

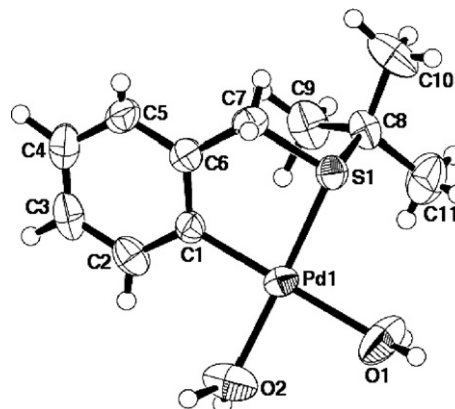


Fig. 4. ORTEP drawing of $[1](\text{PF}_6)$. The anion (PF_6) is omitted for clarity.

[1](PF₆), which was collected by filtration. Yellow crystals of [1](PF₆) used in X-ray structure analysis were obtained by layering CH₂Cl₂ solution of [1](PF₆) with hexane. Yellow crystals of **2** used in the X-ray structure analysis were obtained by layering CH₂Cl₂ solutions of **2** with hexane. Crystal data, data collection parameters, and structure refinement for [1](PF₆) and **2** are listed in Table 1. Selected bond lengths and angles for [1](PF₆) and **2** are listed in Table 2. ORTEP drawings of [1](PF₆) and **2** are shown in Figs. 4 and 5, respectively.

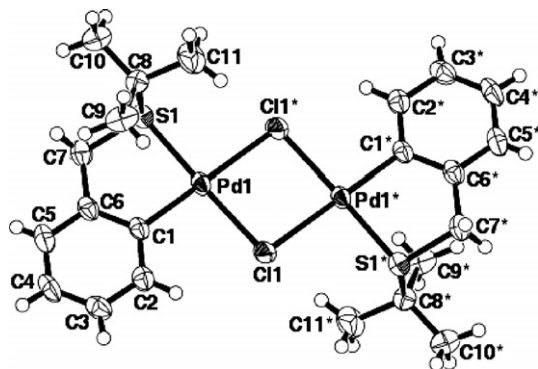


Fig. 5. ORTEP drawing of **2**.

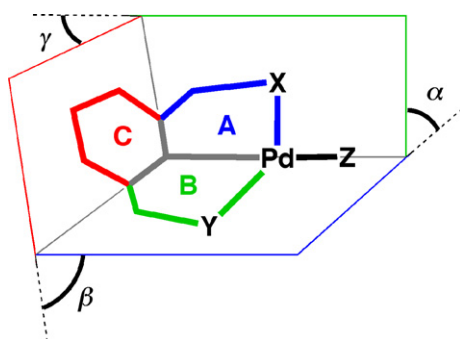


Fig. 6. Dihedral angles (α , β , and γ) between least-square planes of the palladacycles (A and B) and a least-square plane of the benzene ring (C). X, Y, and Z = S, or H₂O.

Fig. 4 shows the ORTEP drawing of [1](PF₆). Complex **1** adopts a square-planar coordination geometry with the Pd atom. The Pd–O1 bond length of [1](PF₆) is 2.194(4) Å, which is close to the Pd–O1 bond length observed in the palladacyclic diaqua complex **Q** {2.172(6) Å} previously determined by X-ray analysis [10b]. The distances between Pd–O1 and Pd–O2 of **1** in the solid state are not equivalent. The distance of Pd1–O1 {2.194(4) Å} trans to the C ligand is longer than that of Pd1–O2 {2.090(5) Å} trans to the S ligand. This indicates that the C ligand has a greater trans influence than the S ligand.

The dihedral angles γ (Fig. 6) between the planes of benzene ring (C) and the planes of palladacycle (A) in **1** and **O** are significantly larger than those of **Q** and **M** as shown in Table 3. The dihedral angle (γ) between the planes of the palladacyclic plane (A) and the planes of benzene ring (C) in **1**, **O**, **Q**, and **M** are 18.7(2), 16.7(1), 2.2(2), and 3.3(1)°, respectively.

4. Conclusions

We have synthesized and characterized a new water-soluble sulfur-containing palladacyclic diaqua complex [1]₂(SO₄) prepared by the reaction of water-insoluble palladacyclic dichloro complex **2** with silver salt (AgSO₄) in water. UV titration experiments revealed that the practical pK_a value of the aqua complex [1]₂(SO₄) was 9.6. The structure of [1](PF₆) was unequivocally determined by X-ray analysis.

5. Supplementary material

Crystallographic data for [1](PF₆) and **2** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-266120 and 266123, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

Table 3

Dihedral angles (α , β , and γ) between least-square planes of the palladacycles (A or B) and least-square plane of the benzene rings (C) of SC, SCS, PC, and PCP palladacyclic aqua complexes

	1	O⁺	Q⁺	M⁺
α^a	–	14.0(1)	–	7.66(4)
β^a	–	13.2(1)	–	4.4(1)
γ^a	18.7(2)	16.7(1)	2.2(2)	3.3(1)

^aSee Charts 2 and 3.

^a Dihedral angles are defined in Fig. 6.

Acknowledgements

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