

Note

Structures of $\text{Pt}_2(\text{CH}_3)_4(\text{S}(\text{CH}_3)_2)_2$ and $[\text{PtPh}_2(\text{S}(\text{CH}_3)_2)]_n$ ($n = 2, 3$)

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Received 27 August 2001; received in revised form 20 September 2001; accepted 27 September 2001

Abstract

$\text{Pt}_2(\text{CH}_3)_4(\text{S}(\text{CH}_3)_2)_2$ (**1**) and $[\text{PtPh}_2(\text{S}(\text{CH}_3)_2)]_n$ (**2**) are widely used precursor compounds to a variety of organoplatinum compounds. Both compounds were formulated as $\text{Pt}_2\text{R}_4(\text{S}(\text{CH}_3)_2)_2$ previously. Our investigation by single-crystal X-ray diffraction analyses revealed that compound **1** indeed exists as dinuclear compound in the solid state but compound **2** displays both a trinuclear cyclic structure and a dinuclear structure with the trinuclear structure being the dominant crystal form in the solid state. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclic trinuclear structures; Cyclic dinuclear structures; Organoplatinum compounds

1. Introduction

The title compound $\text{Pt}_2(\text{CH}_3)_4(\text{S}(\text{CH}_3)_2)_2$ (**1**) reported first by Scott and Puddephatt [1] is one of the most widely used starting materials for the syntheses of a variety of dimethylplatinum(II) derivative complexes and platinum(II) catalysts [2]. The proposed dinuclear formula of **1** is based on the analogues of **1**, $\text{Pt}_2(\text{CH}_3)_4(\text{SR}_2)_2$, R = Et, *n*-Pr, *i*-Pr, reported by Vrieze and coworkers [3]. Cotton and coworkers reported the crystal structure of $\text{Pt}_2(\text{CH}_3)_4(\text{S}(\text{C}_2\text{H}_5)_2)_2$ in 1986, which confirmed the proposed dinuclear structure [4]. Diarylplatinum(II) analogues of **1** formulated as $\text{Pt}_2\text{Ar}_4(\text{SR}_2)_2$, Ar = Ph, *p*-tolyl; R = Et, *n*-Pr or *i*-Pr were reported by Steele and Vrieze in 1977 [5]. Recently, a new analogue of **1**, formulated as $\text{Pt}_2\text{Ph}_4(\text{S}(\text{CH}_3)_2)_2$ (**2**) was reported by Rashidi et al. [6], which has also been demonstrated to be a robust starting material for the syntheses of diphenylplatinum(II) derivative complexes. During our investigation of new luminescent platinum(II) compounds, both **1** and **2** were used as the starting materials. From one of our syntheses, a small amount of unreacted compound **2** crystallized with the product and its structure was determined serendipitously by single-crystal X-ray diffraction. To our surprise, the crystal structure of **2** does not have the dinuclear structure as implied by the

previously reported formula. Instead, it displays a cyclic trinuclear structure with the formula of $\text{Pt}_3\text{Ph}_6(\text{S}(\text{CH}_3)_2)_3$. Because compounds **1** and **2** are important starting materials for various organoplatinum compounds and their previously proposed dinuclear structures have been implicated in some reaction pathways or mechanisms of organoplatinum(II) compounds, we believe that it is worth well to revisit the structures of **1** and **2**. We re-examined the crystals of **2** obtained from bulk syntheses. In addition to the trinuclear species, which is a dominating product, a dinuclear form of **2** was also identified. The crystal structure of **1** was also investigated by single-crystal X-ray diffraction analysis, which confirmed that compound **1** indeed has the dinuclear structure as proposed by Scott and Puddephatt. The details of the crystal structures of **1** and **2** are presented herein.

2. Experimental

Compounds **1** and **2** were synthesized according to literature procedures [6b,7]. ¹H-NMR spectroscopic data confirmed that compound **1** is the same compound as reported previously. Crystals of **1** were obtained from CH_3CN –hexane solution while crystals of **2** were obtained from CH_2Cl_2 –hexane solution. Two types of crystals of **2** were observed, long needle-like thin-plates **2a** (> 90%) and block crystals **2b** (< 10%), both of which were subjected to X-ray diffraction analysis.

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$^1\text{H-NMR}$ for **2a** (CD_2Cl_2 , 298 K, δ , ppm): 2.13 (s, 3H, S-CH₃, $^3J_{\text{Pt-H}} = 24$ Hz), 6.78 (m, 1H, Ph), 6.93 (m, 2H, Ph), 7.38 (dd, 2H, Ph, $^3J_{\text{Pt-H}} = 71$ Hz). $^1\text{H-NMR}$ for **2b** (CD_2Cl_2 , 298 K, δ , ppm): 2.38 (s, 3H, S-CH₃, $^3J_{\text{Pt-H}} = 18$ Hz), 6.84 (m, 1H, Ph), 6.98 (m, 2H, Ph), 7.36 (d, 2H, Ph, $^3J_{\text{Pt-H}}$ could not be determined.). $^1\text{H-NMR}$ spectra were taken in Bruker 300 MHz and Bruker 400 MHz (variable temperature spectra) spectrometers.

3. X-ray diffraction analyses

All crystals were mounted on glass fibers. The data were collected in a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo-K $_{\alpha}$ radiation, operating at 50 kV and 30 mA at 296 K. The hemisphere data collection ranging over 2θ is 5.10–56.6° for all compounds. No significant decay was observed during the data collection for **1** and **2a**. Compound **2b** decays rapidly during data collection. As a result, only 39% of the hemisphere data were collected for **2b**. Data were processed in a Pentium PC using the Bruker AXS Windows NT SHELXTL software package (version 5.10) [8]. Neutral atom scattering factors were taken from Cromer and Waber [9]. Empirical absorption corrections were applied for all crystals. Crystals of **1** belong to the triclinic space group $P\bar{1}$ and **2a** and **2b** belong to the monoclinic space group $P2_1/c$. The struc-

ture of **1** was solved by Patterson methods and the structures of **2a** and **2b** were solved by direct methods. All non-hydrogen atoms for **1** and **2a** were refined anisotropically. For compounds **2a** and **2b** there were two CH_2Cl_2 solvent molecules per complex. Due to the limitation of data, all non-hydrogen atoms but one carbon atom in **2b** were refined anisotropically. All positions of hydrogen atoms were calculated. The crystal data are summarized in Table 1.

4. Results and discussion

There are two independent molecules of **1** in the unit cell, both of which have a crystallographically imposed inversion center. The structure of one of the independent molecules of **1** is shown in Fig. 1 along with important bond lengths and angles. The Pt(II) center in **1** has a typical square-planar geometry with normal Pt–S and Pt–C bond lengths. The dimethylsulfido ligand functions as a bridging ligand to two Pt(II) centers. The Pt–Pt separation distance in **1** is 3.615(1) Å, comparable to the Pt–Pt distance (3.610(1) Å) in $\text{Pt}_2(\text{CH}_3)_4(\text{S}(\text{C}_2\text{H}_5)_2)_2$ [4]. The structure of **1** is consistent with the proposed dinuclear structure by Scott and Puddephatt [1] and the dinuclear structures of $\text{Pt}_2(\text{CH}_3)_4(\text{SR}_2)_2$, R = *n*-Pr, *i*-Pr by Vrieze and coworkers [3].

Table 1
Crystallographic data and structure refinement parameters for compounds **1**, **2a** and **2b**

Compound	1	2a	2b
Empirical formula	$\text{C}_8\text{H}_{24}\text{Pt}_2\text{S}_2$	$\text{C}_{42}\text{H}_{48}\text{Pt}_3\text{S}_3 \cdot 2\text{CH}_2\text{Cl}_2$	$\text{C}_{28}\text{H}_{32}\text{Pt}_2\text{S}_2 \cdot 2\text{CH}_2\text{Cl}_2$
Formula weight	127.68	1404.10	992.68
Temperature (K)	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
<i>a</i> (Å)	9.0640(16)	14.104(5)	9.211(9)
<i>b</i> (Å)	9.6611(17)	26.176(8)	16.021(15)
<i>c</i> (Å)	10.0750(18)	14.206(4)	11.894(11)
α (°)	105.171(3)	90	90
β (°)	99.849(3)	113.817(5)	105.13(2)
γ (°)	110.814(3)	90	90
<i>V</i> (Å ³)	761.1(2)	4798(3)	1694(3)
<i>Z</i>	2	4	2
<i>D</i> _{calc} (g cm ⁻³)	2.507	1.944	1.946
μ (cm ⁻¹)	185.98	91.08	87.05
$2\theta_{\text{max}}$ (°)	56.6	56.6	56.4
Reflections measured	5426	34 217	3127
Reflections used	3456	11 235	1627
Parameters	111	473	185
Final <i>R</i> [$I > 2\sigma(I)$]	$R_1 = 0.0535$, $wR_2 = 0.1416$	$R_1^a = 0.0475$, $wR_2^b = 0.0579$	$R_1^a = 0.0314$, $wR_2^b = 0.0386$
<i>R</i> (all data)	$R_1 = 0.0643$, $wR_2 = 0.1466$	$R_1 = 0.1444$, $wR_2 = 0.0726$	$R_1 = 0.0812$, $wR_2 = 0.0452$
Goodness-of-fit on F^2	0.978	0.876	0.820

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w[(F_o^2 - F_c^2)^2] / \sum w(F_o^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

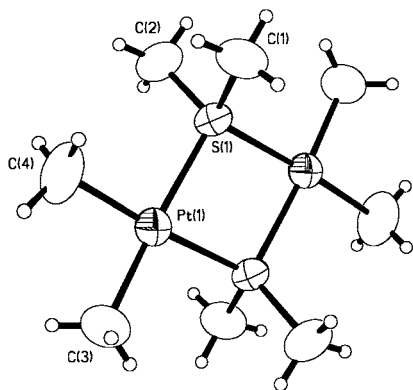


Fig. 1. A diagram showing the molecular structure of **1** with 50% thermal ellipsoids and labeling schemes. Important bond lengths (Å) and bond angles (°): Pt(1)–C(3), 2.019(12); Pt(1)–C(4), 2.032(14); Pt(1)–S(1), 2.354(3); C(3)–Pt(1)–S(1), 175.9(5); C(4)–Pt(1)–S(1A), 174.9(5).

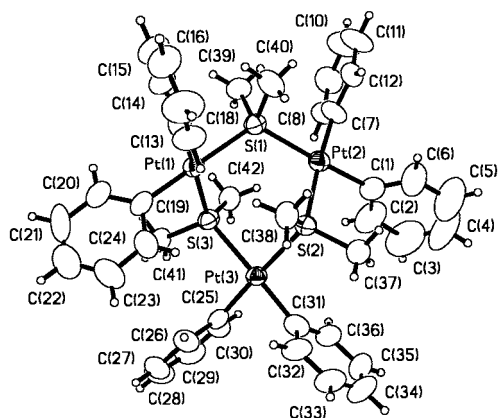


Fig. 2. A diagram showing the molecular structure of **2a** with 50% thermal ellipsoids and labeling schemes. Important bond lengths (Å) and bond angles (°): Pt(1)–C(13), 2.006(8); Pt(1)–C(19), 1.991(10); Pt(1)–S(1), 2.372(2); Pt(1)–S(3), 2.386(2); C(19)–Pt(1)–S(1), 177.9(3); C(13)–Pt(1)–S(3), 172.6(3); Pt(2)–C(1), 2.014(10); Pt(2)–C(7), 2.012(9); Pt(2)–S(2), 2.387(2); Pt(2)–S(1), 2.388(2); C(7)–Pt(2)–S(2), 175.2(3); C(1)–Pt(2)–S(1), 176.8(3); Pt(3)–C(25), 1.987(8); Pt(3)–C(31), 2.010(10); Pt(3)–S(3), 2.389(2); Pt(3)–S(2), 2.392(2); C(25)–Pt(3)–S(2), 175.9(3); C(31)–Pt(3)–S(3), 177.5(2).

Compound **2** displays two distinct crystal forms in the solid state, thin plates **2a** and blocks **2b**, with **2a** being the major form (>90%). We carried out the crystallization of **2** several times and observed consistently that **2a** is the dominating form. The structure of **2a** is shown in Fig. 2 along with important bond lengths and angles. Compound **2a** has a cyclic trinuclear structure with three Pt(II) centers bridged by three dimethylsulfido ligands. The Pt–S bond lengths are comparable with those of **1**, but the Pt–C bond lengths are somewhat shorter than those of **1**. The (Pt–S)₃ six-membered ring is puckered. The dihedral angles between the Pt(1) and Pt(2) planes, Pt(1) and Pt(3) planes, and Pt(2) and Pt(3) planes are 71.1, 55.2 and 65.3°, respectively. The Pt–Pt separation distances in **2a**

range from 3.999(1) to 4.095(1) Å, which are much longer than those of **1**. The Pt–S–Pt angles in **2a** ranging from 113.78(9) to 118.66(9)° are about 16° bigger in average than those of **1** (100.06(11) and 100.55(10)°). In 1971, Wilkinson and coworkers reported the trinuclear complex Pt₃(CH₂Si(CH₃)₃)₆–(S(CH₃)₂)₃ which was assumed to have a cyclic structure [10] similar to that of **2a**. The fact that compound **1** adopts a dinuclear structure while **2a** and Pt₃(CH₂Si(CH₃)₃)₆(S(CH₃)₂)₃ adopt a cyclic trinuclear structure could be explained by steric factors — the relatively steric bulky phenyl and trimethylsilylmethyl ligands favor the trinuclear cyclic structure. Nonetheless, the dinuclear form **2b** was also observed for compound **2**, albeit being a minor form. The structure of **2b** as shown in Fig. 3 resembles that of **1**. The Pt–Pt separation distance, 3.662(1) Å of **2b** is, however, considerably longer than that of **1**. For comparison, selected average bond lengths and angles of **1**, **2a**, **2b** and Cotton's structure Pt₂(CH₃)₄(S(C₂H₅)₂)₂ are listed in Table 2. We examined the solution behavior of compounds **2a** and **2b** in solution by ¹H-NMR spectroscopy. The solution for ¹H-NMR study was obtained by dissolving hand-picked crystals of **2a** and **2b** separately in CD₂Cl₂. At ambient temperature, **2a** and **2b** display distinct spectra and no interconversion was observed. We also examined the ¹H-NMR spectrum of **2a** over the temperature range of –100 to 25 °C, which showed that only one species is present in solution and that there is no evidence to support the presence of exchange between a dinuclear species and a trinuclear species. Compounds **2a** and **2b** react with CDCl₃. Therefore no reliable NMR data can be obtained to elucidate the relative stability of **2a** and **2b** in CDCl₃. It is very likely that the cyclic trinuclear structure may also be the dominating form for previously reported diarylplatinum analogues of **2** by Steele and Vrieze [5].

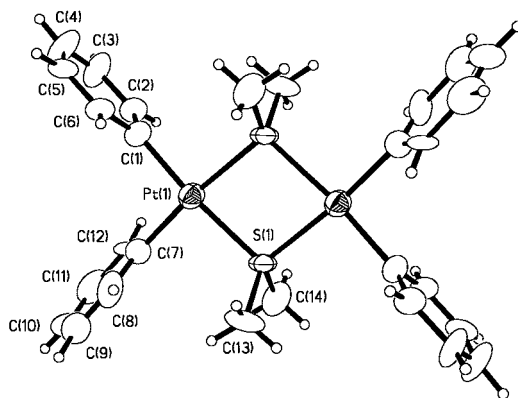


Fig. 3. A diagram showing the molecular structure of **2b** with 50% thermal ellipsoids and labeling schemes. Important bond lengths (Å) and bond angles (°): Pt(1)–C(3), 2.014(12); Pt(1)–C(7), 2.038(15); Pt(1)–S(1), 2.377(4); Pt(1)–S(1A), 2.388(4); C(1)–Pt(1)–S(1), 173.8(4); C(7)–Pt(1)–S(1A), 173.5(3).

Table 2
Selected bond lengths (Å) and bond angles (°)

Compound	Pt...Pt (Å)	Pt–S (Å)	Pt–C (Å)	Pt–S–Pt (°)
Pt ₂ (CH ₃) ₄ (S(C ₂ H ₅) ₂) ₂ (Ref. [4])	3.610(1)	2.354(1)	2.062(10)	100.1(1)
Pt ₂ (CH ₃) ₄ (S(CH ₃) ₂) ₂ (1)	3.615(1)	2.354(3)	2.025(12)	100.3(1)
Pt ₂ Ph ₄ (S(CH ₃) ₂) ₂ (2b)	3.662(1)	2.383(4)	2.026(14)	100.45(13)
Pt ₃ Ph ₆ (S(CH ₃) ₂) ₃ (2a)	4.052(1)	2.385(2)	2.003(9)	116.31(9)

In summary, single-crystal X-ray diffraction analyses established that compound **1** has a dinuclear structure as proposed previously, and compound **2** displays both the cyclic dinuclear structure and the cyclic trinuclear structure with the trinuclear structure being the dominating form when recrystallization was carried out using CH₂Cl₂.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 169172, 169173 and 171425 for compounds **1**, **2a** and **2b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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