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LETTER

trans-Effect of dialkyl sulfide on a Pt(III)–Pt(III) bond. Synthesis, spectroscopy and X-ray crystal structure of $[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(SEt_2)_2]$

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Recent spectroscopic and structural studies on the $[Pt_2(P_2O_5H_2)_4(XY)]^{n-}$ system (XY = Cl_2, Br_2, I_2, CH_3I, $(SCN)_2$, $(C_3H_3N_2)_2$, $(NO_2)_2$, $(CH_3CN)_2$) established significant axial σ-electronic delocalization between the dσ(Pt) and σ(X)/σ(Y) orbitals [1]. The extent of charge-transfer mixing between the Pt–Pt and Pt–X/Pt–Y bonds can be correlated with the Pt–Pt distances where long Pt–Pt bonds are usually found with those axial ligands X and Y having strong σ-donor strengths [1, 2]. Herein is described the synthesis and X-ray structure of $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$, illustrating that are neutral Et_2S is an even better σ-donor to Pt(III) than are anionic ligands such as SCN^- and I^-. The photochemical reactions of $[Pt_2(P_2O_5H_2)_4]^{4-}$ with dialkyl sulfides have been described previously [3].

Experimental

$[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ was prepared by the literature method [4]. All reagents (analytical grade) for synthesis and spectroscopic measurements were obtained from Aldrich Co. Ltd. UV–Vis and ^{31}P NMR spectra were recorded on a Shimadzu UV-240 spectrophotometer and a Jeol model FX 90Q spectrometer (90 MHz), respectively.

$[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(SEt_2)_2]$

A methanolic solution (20 ml) containing $[Bu_4N]_4[Pt_2(P_2O_5H_2)_4]$ (0.5 g) and Et_2S (1 g) was treated with H_2O_2 (30%, 2 ml) at room temperature. After effervescence ceased, the solution was left to stand in air for 15 min. Addition of diethyl ether to the solution gave the orange product in high yield (> 80%). Crystals of $[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(SEt_2)_2]$ were obtained by vapor diffusion of diethyl ether into acetonitrile solution.

X-ray structure determination

The $[Bu_4N]_2[Pt_2(P_2O_5H_2)_4(SEt_2)_2]$ complex was recrystallized by diffusion of diethyl ether into acetonitrile. Crystal data: $M = 1623.25$, monoclinic, space group $P2_1/c$, $a = 11.240(2)$, $b = 12.700(3)$, $c = 22.101(6)$ Å, $\beta = 91.27(2)°$, $V = 3154(1)$ Å^3, $Z = 2$, $D_{calc} = 1.713$ g cm^{-3}, $F(000) = 1628$, crystal dimensions = 0.20 × 0.30 × 0.40 mm. The intensity data were measured on a CAD-4 diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å) using the $\omega/2\theta$ scan mode at 297 K with $2\theta_{max} = 50°$. Cell dimensions were obtained from 25 reflections with 2θ angle in the range of 19.28–23.82°. A total of 6142 reflections was measured and 3294 reflections were observed ($I > 2.0\sigma(I)$). Absorption corrections ($\mu = 48$ cm^{-1}) were made according to Ψ curves of 3 selected reflections. The minimum and maximum transmission factors are 0.73 and 1.0. The structure was solved by the Patterson method and refined by least-squares. Full matrix least-squares refinement on 334 parameters converged to yield agreement indices $R(F) = 0.055$, $R_w(F) = 0.053$ and $GOF = 2.74$. Table 1 lists the atomic coordinates of non-hydrogen atoms.

Results and discussion

As with other $[Pt_2(P_2O_5H_2)_4XY]^{n-}$ complexes [2a], oxidation of $[Pt_2(P_2O_5H_2)_4]^{4-}$ with H_2O_2 in the presence of excess Et_2S gave $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$. The ^{31}P NMR spectrum of $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ shows a pseudo triplet with $\delta = 25.1$ ppm (relative to H_3PO_4) and $J_1(\text{Pt–P}) = 2040$ Hz, which are characteristics of the $[Pt_2(P_2O_5H_2)_4XY]^{n-}$ system. Figure 1 shows the ORTEP plot of the complex anion with atom numbering. There are two cations and one complex anion in an asymmetric unit. The $[Bu_4N]^+$ ion is in a regular tetrahedral symmetry. The complex anion shown in Fig. 1 has a C_i molecular symmetry with i at the midpoint of the Pt–Pt bond. Four bridging diphosphite ligands are bonded to two Pt atoms in a rough C_{4v} symmetry with two axial Et_2S ligands *trans* to the Pt–Pt bond. The Pt–Pt–S(SEt_2) group is essentially linear (Pt–Pt–S = 173.41(14)°). As in the cases of other $[Pt_2(P_2O_5H_2)_4XY]^{n-}$ complexes [2], the PtP_4 units are

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TABLE 1. Atomic parameters x, y, z and B_{iso} (e.s.d.s refer to the last digit printed)

	x	y	z	B_{iso}
Pt	0.10848(6)	0.51001(5)	0.03022(3)	2.57(3)
S	0.2908(4)	0.5404(4)	0.0930(3)	5.0(3)
P1	0.0254(5)	0.4532(5)	0.1224(3)	5.8(3)
P2	0.0634(6)	0.6838(4)	0.0606(3)	6.3(4)
P3	0.2022(5)	0.5654(5)	−0.0590(3)	5.9(3)
P4	0.1629(6)	0.3351(5)	0.0037(4)	7.2(4)
O1	−0.1194(12)	0.4544(14)	0.1175(6)	8.3(11)
O2	−0.0771(12)	0.7074(12)	0.0524(7)	8.0(9)
O11	0.0627(16)	0.3440(12)	0.1411(8)	9.8(12)
O12	0.0517(13)	0.5337(14)	0.1750(5)	8.3(10)
O21	0.0766(14)	0.6990(12)	0.1293(7)	8.8(10)
O22	0.1349(14)	0.7669(10)	0.0227(10)	10.4(13)
O31	0.2313(14)	0.6833(11)	−0.0598(7)	8.1(9)
O32	0.3146(10)	0.4978(16)	−0.0727(6)	8.4(10)
O41	0.2898(12)	0.3315(12)	−0.0253(8)	8.5(10)
O42	0.1611(16)	0.2589(10)	0.0602(9)	10.6(11)
C1	0.3737(25)	0.4156(18)	0.1106(14)	11.8(20)
C2	0.4577(23)	0.4277(20)	0.1590(15)	11.9(20)
C3	0.4067(19)	0.6164(18)	0.0567(9)	6.5(13)
C4	0.442(3)	0.7087(18)	0.0845(15)	13.9(25)
N	0.1881(14)	0.0088(13)	0.1924(7)	5.9(9)
C11	0.1578(23)	−0.1033(19)	0.2209(12)	9.1(17)
C12	0.2452(22)	−0.1669(22)	0.2488(12)	9.5(18)
C13	0.216(3)	−0.2631(18)	0.2732(12)	9.5(18)
C14	0.305(3)	−0.3338(24)	0.2865(15)	13.6(24)
C21	0.206(3)	0.0888(21)	0.2444(14)	12.2(21)
C22	0.230(3)	0.1836(24)	0.2521(18)	17.1(30)
C23	0.255(4)	0.2423(24)	0.3014(16)	17.8(30)
C24	0.277(4)	0.329(3)	0.3085(19)	21.7(39)
C31	0.286(4)	0.016(3)	0.1424(14)	19.6(32)
C32	0.400(5)	0.068(4)	0.1232(24)	35.0(57)
C33	0.470(3)	0.051(3)	0.0856(12)	16.1(28)
C34	0.500(5)	0.148(3)	0.0538(18)	28.1(48)
C41	0.058(4)	0.0416(21)	0.1693(13)	16.6(31)
C42	−0.008(3)	−0.0146(23)	0.1200(12)	13.0(22)
C43	−0.107(3)	0.0430(22)	0.0925(13)	12.2(20)
C44	−0.171(3)	−0.014(3)	0.0507(11)	14.0(25)

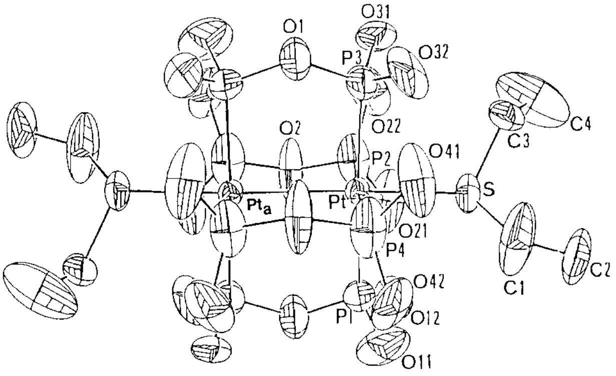

Fig. 1. ORTEP plot of $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ with atom numbering. Pt–Pt$_a$, 2.766(1); Pt–S, 2.479(5); Pt–P(1), 2.372(6); Pt–P(2), 2.365(5); Pt–P(3), 2.364(6); Pt–P(4), 2.381(6); P(3)–O(1), 1.629(14); P(3)–O(31), 1.533(15); P(3)–O(32), 1.563(15) Å. Pt$_a$–Pt–S, 173.41(14); Pt$_a$–Pt–P(1), 91.56(14); Pt$_a$–Pt–P(2), 91.75(15); Pt$_a$–Pt–P(3), 91.66(14); Pt$_a$–Pt–P(4), 91.39(16); S–Pt–P(1), 84.41(19); S–Pt–P(2), 82.85(20); S–Pt–P(3), 92.44(19); S–Pt–P(4), 93.96(20); P(1)–Pt–P(2), 87.09(25); P(1)–Pt–P(3), 176.71(20); P(1)–Pt–P(4), 92.0(3); Pt–S–C(1), 112.7(8); Pt–S–C(3), 115.2(7); Pt–P(1)–O(1), 110.6(6)°.

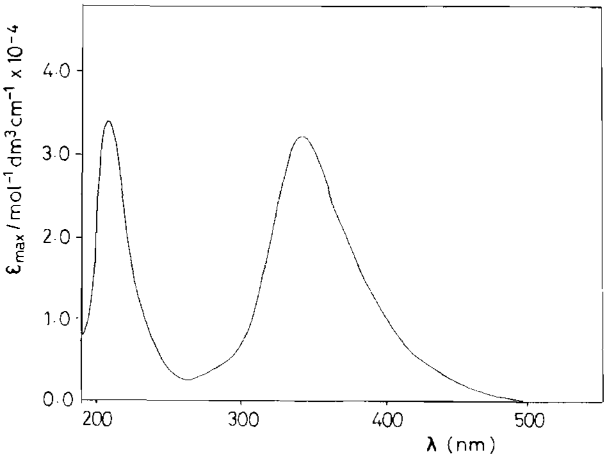

Fig. 2. UV–Vis absorption spectrum of $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ in acetonitrile at room temperature.

essentially planar (Pt–Pt–P angles, 91.39(16)–91.75(15)°). The most interesting structural feature is the Pt–Pt distance of 2.766(1) Å. This Pt–Pt distance is the longest reported for the $[Pt_2(P_2O_5H_2)_4XY]^{n-}$ system [1]. It is even longer than that for $[Pt_2(P_2O_5H_2)_4(SCN)_2]^{4-}$ and $[Pt_2(P_2O_5H_2)_4I_2]^{4-}$ where the respective Pt–Pt distances are 2.760(1) [2a] and 2.754–2.746(1) [2b] Å. This finding suggests that σ-electronic delocalization of the Pt(III)–Pt(III) with the Pt–SEt$_2$ bond is even more pronounced than that with Pt–SCN and Pt–I. The Pt–S(SEt$_2$) distance of 2.479(5) Å is comparable to that of 2.466(4) Å [2a] for Pt–S(SCN) in $[Pt_2(P_2O_5H_2)_4(SCN)_2]^{4-}$. Figure 2 shows the UV–Vis absorption spectrum of $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ in acetonitrile at room temperature. The intense band at 342 nm with $\epsilon_{max} = 3.2 \times 10^4$ mol^{-1} dm^3 cm^{-1} is undoubtedly due to the $\sigma(SEt_2) \rightarrow d\sigma^*(Pt)$ charge-transfer transition. This energy is also lower than that for the $\sigma(SCN) \rightarrow d\sigma^*(Pt)$ (337 nm) in $[Pt_2(P_2O_5H_2)_4(SCN)_2]^{4-}$ [2a] or $\sigma(I) \rightarrow d\sigma^*(Pt)$ (338 nm) in $[Pt_2(P_2O_5H_2)_4I_2]^{4-}$ [2b]. Thus the spectroscopic data correlate with the X-ray result that the energy of the $\sigma(SEt_2)$ orbital is even higher than that for the $\sigma(SCN^-)$ and $\sigma(I^-)$ orbitals.

Supplementary material

Full tables of bond lengths and angles, H-atom coordinates, thermal parameters and structure factors are available from Yu Wang (Taiwan).

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