## Inorganica Chimica Acta


trans-Effect of dialkyl sulfide on a $\mathrm{Pt}(\mathrm{III})-\mathrm{Pt}(\mathrm{III})$ bond. Synthesis, spectroscopy and X-ray crystal structure of $\left[\mathrm{Bu}_{4} \mathrm{~N}_{2}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]\right.$

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(Received September 13, 1991)

Recent spectroscopic and structural studies on the $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}(\mathrm{XY})\right]^{n-}$ system (XY= $\mathrm{Cl}_{2}, \mathrm{Br}_{2}, \mathrm{I}_{2}, \mathrm{CH}_{3} \mathrm{I}$, $\left.(\mathrm{SCN})_{2},\left(\mathrm{C}_{3} \mathrm{H}_{3} \mathrm{~N}_{2}\right)_{2},\left(\mathrm{NO}_{2}\right)_{2},\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2}\right)$ established significant axial $\sigma$-electronic delocalization between the $\mathrm{d} \sigma(\mathrm{Pt})$ and $\sigma(\mathrm{X}) / \sigma(\mathrm{Y})$ orbitals [1]. The extent of chargetransfer mixing between the $\mathrm{Pt}-\mathrm{Pt}$ and $\mathrm{Pt}-\mathrm{X} / \mathrm{Pt}-\mathrm{Y}$ bonds can be correlated with the $\mathrm{Pt}-\mathrm{Pt}$ distances where long $\mathrm{Pt}-\mathrm{Pt}$ bonds are usually found with those axial ligands X and Y having strong $\sigma$-donor strengths [1, 2]. Herein is described the synthesis and X -ray structure of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]^{2-}$, illustrating that are neutral $\mathrm{Et}_{2} \mathrm{~S}$ is an even better $\sigma$-donor to $\mathrm{Pt}(\mathrm{III})$ than are anionic ligands such as $\mathrm{SCN}^{-}$and $\mathrm{I}^{-}$. The photochemical reactions of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\right]^{4-}$ with dialkyl sulfides have been described previously [3].

## Experimental

$\left[\mathrm{Bu}_{4} \mathrm{~N}\right]_{4}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\right]$ 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 ${ }^{31} \mathrm{P}$ NMR spectra were recorded on a Shimadzu UV-240 spectrophotometer and a Jeol model FX 90Q spectrometer ( 90 MHz ), respectively.

[^0]$\left[\mathrm{Bu}_{4} \mathrm{NH}_{2}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]\right.$
A methanolic solution ( 20 ml ) containing $\left[\mathrm{Bu}_{4} \mathrm{~N}_{4}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\right](0.5 \mathrm{~g})\right.$ and $\mathrm{Et}_{2} \mathrm{~S}(1 \mathrm{~g})$ was treated with $\mathrm{H}_{2} \mathrm{O}_{2}(30 \%, 2 \mathrm{ml})$ 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 $\left[\mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]$ were obtained by vapor diffusion of diethyl ether into acetonitrile solution.

## $X$-ray structure determination

The $\left[\mathrm{Bu}_{4} \mathrm{~N}\right]_{2}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]$ complex was recrystallized by diffusion of diethyl ether into acetonitrile. Crystal data: $M=1623.25$, monoclinic, space group $P 2_{1} / c, a=11.240(2), \quad b=12.700(3), c=22.101(6) \AA$, $\beta=91.27(2)^{\circ}, V=3154(1) \AA^{3}, Z=2, D_{\text {calc }}=1.713 \mathrm{~g} \mathrm{~cm}^{-3}$, $F(000)=1628$, crystal dimensions $=0.20 \times 0.30 \times 0.40$ mm . The intensity data were measured on a CAD-4 diffractometer using Mo $K \alpha$ radiation ( $\lambda=0.7107 \AA$ ) using the $\omega / 2 \theta$ scan mode at 297 K with $2 \theta_{\text {max }}=50^{\circ}$. Cell dimensions were obtained from 25 reflections with $2 \theta$ angle in the range of $19.28-23.82^{\circ}$. A total of 6142 reflections was measured and 3294 reflections were observed ( $I>2.0 \sigma(I)$ ). Absorption corrections ( $\mu=48$ $\mathrm{cm}^{-1}$ ) were made according to $\Psi$ 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 $R(F)=0.055$, $R_{\mathrm{w}}(F)=0.053$ and $G O F=2.74$. Table 1 lists the atomic coordinates of non-hydrogen atoms.

## Results and discussion

As with other $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{XY}\right]^{n-}$ complexes [2a], oxidation of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\right]^{4-}$ with $\mathrm{H}_{2} \mathrm{O}_{2}$ in the presence of excess $\mathrm{Et}_{2} \mathrm{~S}$ gave $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]^{2-}$. The ${ }^{31} \mathrm{P}$ NMR spectrum of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]^{2-}$ shows a pseudo triplet with $\delta=25.1 \mathrm{ppm}$ (relative to $\mathrm{H}_{3} \mathrm{PO}_{4}$ ) and $J_{1}(\mathrm{Pt}-\mathrm{P})=2040 \mathrm{~Hz}$, which are characteristics of the $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{XY}\right]^{n-}$ 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 $\left[\mathrm{Bu}_{4} \mathrm{~N}\right]^{+}$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 $\mathrm{Pt}-\mathrm{Pt}$ bond. Four bridging diphosphite ligands are bonded to two Pt atoms in a rough $C_{4 v}$ symmetry with two axial $\mathrm{Et}_{2} \mathrm{~S}$ ligands trans to the $\mathrm{Pt}-\mathrm{Pt}$ bond. The $\mathrm{Pt}-\mathrm{Pt}-\mathrm{S}\left(\mathrm{SEt}_{2}\right)$ group is essentially linear ( $\left.\mathrm{Pt}-\mathrm{Pt}-\mathrm{S}=173.41(14)^{\circ}\right)$. As in the cases of other $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{XY}\right]^{n-}$ complexes [2], the $\mathrm{PtP}_{4}$ units are

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

|  | $x$ | $y$ | $z$ | $B_{\text {iso }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 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) |
| Ol | -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) | $9.8(12)$ |
| O 12 | $0.0517(13)$ | $0.5337(14)$ | 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) |
| 032 | $0.3146(10)$ | 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) |
| C 23 | 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) |

essentially planar (Pt-Pt-P angles, 91.39(16)$\left.91.75(15)^{\circ}\right)$. The most interesting structural feature is the $\mathrm{Pt}-\mathrm{Pt}$ distance of 2.766 (1) $\AA$. This $\mathrm{Pt}-\mathrm{Pt}$ distance is the longest reported for the $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{XY}\right]^{n-}$ system [1]. It is even longer than that for $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}(\mathrm{SCN})_{2}\right]^{4-}$ and $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{I}_{2}\right]^{4-}$ where the respective $\mathrm{Pt}-\mathrm{Pt}$ distances are $2.760(1)$ [2a] and $2.754-2.746(1)[2 \mathrm{~b}] \AA$. This finding suggests that $\sigma$ electronic delocalization of the $\mathrm{Pt}(\mathrm{III})-\mathrm{Pt}(\mathrm{III})$ with the $\mathrm{Pt}-\mathrm{SEt}_{2}$ bond is even more pronounced than that with $\mathrm{Pt}-\mathrm{SCN}$ and $\mathrm{Pt}-\mathrm{I}$. The $\mathrm{Pt}-\mathrm{S}\left(\mathrm{SEt}_{2}\right)$ distance of $2.479(5)$ $\AA$ is comparable to that of $2.466(4) \AA$ [2a] for $\mathrm{Pt}-\mathrm{S}(\mathrm{SCN})$ in $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}(\mathrm{SCN})_{2}\right]^{4-}$. Figure 2 shows the UV-Vis absorption spectrum of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]^{2-}$ in acetonitrile at room temperature. The intense band at 342 nm with $\epsilon_{\max }=3.2 \times 10^{4} \mathrm{~mol}^{-1} \mathrm{dm}^{3} \mathrm{~cm}^{-1}$ is un-


Fig. 1. ORTEP plot of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]^{2-}$ with atom numbering. $\mathrm{Pt}_{\mathrm{P}} \mathrm{Pt}_{\mathrm{a}}, 2.766(1) ; \mathrm{Pt}-\mathrm{S}, 2.479(5) ; \mathrm{Pt}-\mathrm{P}(1), 2.372(6) ; \mathrm{Pt}-\mathrm{P}(2)$, 2.365(5); $\mathrm{Pt}-\mathrm{P}(3), ~ 2.364(6) ; \mathrm{Pt}-\mathrm{P}(4), 2.381(6) ; \mathrm{P}(3)-\mathrm{O}(1)$ $1.629(14) ; \mathrm{P}(3)-\mathrm{O}(31), 1.533(15) ; \mathrm{P}(3)-\mathrm{O}(32), 1.563(15) \AA$. $\mathrm{Pt}_{\mathrm{a}}-\mathrm{Pt}-\mathrm{S}, \quad 173.41(14) ; \quad \mathrm{Pt}_{\mathrm{a}}-\mathrm{Pt}-\mathrm{P}(1), \quad 91.56(14) ; \quad \mathrm{Pt}_{\mathrm{a}}-\mathrm{Pt}-\mathrm{P}(2)$, 91.75(15); $\quad \mathrm{Pt}_{\mathrm{a}}-\mathrm{Pt}-\mathrm{P}(3), \quad 91.66(14) ; \quad \mathrm{Pt}_{\mathrm{a}}-\mathrm{Pt}-\mathrm{P}(4), \quad 91.39(16) ;$ 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); $\mathrm{P}(1)-\mathrm{Pt}-\mathrm{P}(4), 92.0(3) ; \mathrm{Pt}-\mathrm{S}-\mathrm{C}(1), 112.7(8) ; \mathrm{Pt}-\mathrm{S}-\mathrm{C}(3)$, 115.2(7); $\mathrm{Pt}-\mathrm{P}(1)-\mathrm{O}(1), 110.6(6)^{\circ}$.


Fig. 2. UV-Vis absorption spectrum of $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\left(\mathrm{SEt}_{2}\right)_{2}\right]^{2-}$ in acetonitrile at room temperature.
doubtedly due to the $\sigma\left(\mathrm{SEt}_{2}\right) \rightarrow \mathrm{d} \sigma^{*}(\mathrm{Pt})$ charge-transfer transition. This energy is also lower than that for the $\sigma(\mathrm{SCN}) \rightarrow \mathrm{d} \sigma^{*}(\mathrm{Pt})(337 \mathrm{~nm})$ in $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}(\mathrm{SCN})_{2}\right]^{4-}$ $[2 \mathrm{a}]$ or $\sigma(\mathrm{I}) \rightarrow \mathrm{d} \sigma^{*}(\mathrm{Pt})(338 \mathrm{~nm})$ in $\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{I}_{2}\right]^{4-}$ [2b]. Thus the spectroscopic data correlate with the X -ray result that the energy of the o( $\mathrm{SEt}_{2}$ ) orbital is even higher than that for the $\sigma\left(\mathrm{SCN}^{-}\right)$and $\sigma\left(\mathrm{I}^{-}\right)$ orbitals.

## Supplementary material

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

## Acknowledgements

Financial support from the University of Hong Kong, the Croucher Foundation and the National Research Council of Taiwan is gratefully acknowledged.

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