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Crystal and Molecular Structure of $(PPh_3)_2Pt(OSNH)_2$; *Cis*-bis(thionyl imide-O)bis(triphenylphosphine)platinum(II)

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The major product of the reaction of tetrakis(triphenylphosphine)platinum(0) and tetrasulfurtetranitride in acetone has been determined to be $(Ph_3P)_2PtS_2N_2O_2H_2$ *from single crystal X-ray diffraction data. Space group,* $P\bar{1}$; $a = 10.082(3)$, $b = 10.258(3)$, $c = 17.812(6)$ Å, $\alpha = 86.05(3)^\circ$, $\beta = 81.02(3)^\circ$, $\gamma = 72.45(3)^\circ$; $D_{calc} = 1.637\ g\ cm^{-1}$ *for* $Z = 2$.

Introduction

The major product (94% yield) of the reaction of tetrakis(triphenylphosphine)platinum(0) and tetrasulfur tetraimide in acetone [1] showed an elemental analysis for Pt, S, P, N, C, and H which totaled 4.49% less than 100%. Mass spectroscopy, UV and IR analysis [2] did not allow complete identification of the material which was first assumed to be $(Ph_3P)_2PtS_2N_2H_2$. We have determined the crystal and molecular structure of this product and have identified the product as $(Ph_3P)_2PtS_2N_2O_2H_2$ with the first crystallographic identification of the OSNH species.

Experimental

A crystal (0.07 × 0.15 × 0.20 mm) was mounted on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were determined by least squares fit to the $2\theta, \omega$, and χ settings for twelve independent reflections (Table I). Data were measured at −120 °C using molybdenum (graphite monochromatized) radiation, a θ–2θ scan with speed of 2.0–29.3° min^{-1} depending upon the intensity of a 2 sec prescan and a 2θ scan range of $(1.6 + 0.692 \tan\theta)^\circ$ starting the scan from 0.8° below the calculated $K\alpha_1$ position. Background measurements were made at each end of the scan range for a time period equal to ¼ of the scan time with crystal and counter stationary. Reflections were measured in ½ of the sphere to $2\theta_{max} = 45^\circ$. Three standard reflections were measured after every 100 reflections and their intensities showed deviations of less than 4% during the course of data collection. 4082 independent reflections were considered observed $[I > 3\sigma(I)]$ and were used in solution and refinement after correction for background, Lorentz and polarization effects. Absorption corrections were made (transmission factors, 0.69–0.78).

TABLE I. Crystal Data.

Formula	$C_{36}H_{33}N_2O_{2.5}P_2PtS_2$
M WT	854.9
Space group	$P\bar{1}$
Systematic absences	none
$a = 10.082(3)$ Å	
$b = 10.258(3)$ Å	
$c = 17.812(6)$ Å	
$\alpha = 86.05(3)^\circ$	
$\beta = 81.02(3)^\circ$	
$\gamma = 72.45(3)^\circ$	
$V = 1734.4$ Å^3	
$D_{calc} = 1.637\ g\ cm^{-1}$	
$D_{meas} = 1.628\ g\ cm^{-1}$	
$Z = 2$	
$\mu(MoK_\alpha) = 48.85\ cm^{-1}$	
$F(000) = 846$	

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TABLE II. Atomic Coordinates.

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
Pt	0.12348(7)	0.08352(6)	0.28246(3)
P(1)	0.0148(4)	0.2230(4)	0.1903(2)
P(2)	0.0893(4)	0.2446(4)	0.3700(2)
S(1)	0.2488(7)	−0.1687(7)	0.1683(4)
S(2)	0.3636(6)	−0.1159(6)	0.3604(3)
O(1)	0.150(1)	−0.081(1)	0.2059(6)
O(2)	0.226(2)	−0.068(1)	0.3555(7)
N(3)	0.464(2)	−0.049(2)	0.3210(9)
N(4)	0.398(2)	−0.171(2)	0.1643(11)
Ring 11			
C(111)	0.135(1)	0.232(1)	0.104(2)
C(112)	0.085(2)	0.312(2)	0.0424(9)
C(113)	0.176(2)	0.324(2)	−0.0225(9)
C(114)	0.316(2)	0.256(2)	−0.0285(8)
C(115)	0.366(2)	0.174(2)	0.0337(9)
C(116)	0.276(2)	0.164(2)	0.0989(8)
Ring 12			
C(121)	−0.116(2)	0.150(1)	0.1642(8)
C(122)	−0.222(2)	0.135(2)	0.2217(9)
C(123)	−0.325(2)	0.080(2)	0.2053(9)
C(124)	−0.318(2)	0.038(2)	0.1327(11)
C(125)	−0.214(2)	0.049(2)	0.0778(10)
C(126)	−0.113(2)	0.109(2)	0.0901(9)
Ring 13			
C(131)	−0.078(2)	0.405(1)	0.2031(7)
C(132)	0.002(2)	0.497(2)	0.2034(8)
C(133)	−0.064(2)	0.635(2)	0.2142(8)
C(134)	−0.206(2)	0.685(2)	0.2222(9)
C(135)	−0.286(2)	0.596(2)	0.2198(8)
C(136)	−0.224(2)	0.460(1)	0.2114(8)
Ring 21			
C(211)	−0.099(1)	0.328(1)	0.3928(7)
C(212)	−0.162(2)	0.470(2)	0.3946(8)
C(213)	−0.308(2)	0.518(2)	0.4092(8)
C(214)	−0.390(2)	0.427(3)	0.4244(9)
C(215)	−0.326(2)	0.288(2)	0.4242(10)
C(216)	−0.185(2)	0.243(2)	0.4081(9)
Ring 22			
C(221)	0.146(2)	0.185(1)	0.4630(7)
C(222)	0.054(2)	0.170(2)	0.5274(8)
C(223)	0.102(2)	0.137(2)	0.5970(10)
C(224)	0.238(2)	0.110(2)	0.6018(8)
C(225)	0.335(2)	0.125(2)	0.5383(9)
C(226)	0.286(2)	0.159(2)	0.4692(8)
Ring 23			
C(231)	0.186(2)	0.367(2)	0.3432(8)
C(232)	0.293(2)	0.340(2)	0.2821(9)
C(233)	0.372(2)	0.429(2)	0.2608(10)
C(234)	0.349(2)	0.544(2)	0.2998(12)
C(235)	0.244(2)	0.570(2)	0.3632(12)

TABLE II. *(continued)*

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
C(236)	0.164(2)	0.482(2)	0.3838(10)
O(101)	0.486(7)	0.516(6)	0.955(4)
O(102)	0.578(7)	0.428(7)	0.990(4)
H(112)	−0.021	0.364	0.040
H(113)	0.118	0.400	−0.065
H(114)	0.396	0.256	−0.073
H(115)	0.457	0.130	0.026
H(116)	0.329	0.106	0.139
H(122)	−0.251	0.171	0.272
H(123)	−0.407	0.084	0.254
H(124)	−0.391	0.002	0.126
H(125)	−0.207	0.001	0.025
H(126)	−0.032	0.118	0.051
H(132)	0.092	0.460	0.197
H(133)	−0.001	0.679	0.208
H(134)	−0.262	0.787	0.229
H(135)	−0.379	0.625	0.222
H(136)	−0.253	0.392	0.212
H(212)	−0.101	0.520	0.389
H(213)	−0.340	0.627	0.411
H(214)	−0.488	0.473	0.430
H(215)	−0.375	0.213	0.433
H(216)	−0.514	0.162	0.403
H(222)	−0.038	0.200	0.526
H(223)	0.026	0.129	0.631
H(224)	0.281	0.093	0.644
H(225)	0.428	0.107	0.542
H(226)	0.346	0.190	0.428
H(232)	0.302	0.264	0.264
H(233)	0.448	0.395	0.214
H(234)	0.410	0.624	0.286
H(235)	0.227	0.647	0.387
H(236)	0.088	0.501	0.427

Atomic coordinates were determined by heavy atom techniques with hydrogens of the phenyl groups being located from a difference Fourier synthesis during the final stages. Three cycles of least-squares refinement [function minimized, $\Sigma(|F_o|-|F_c|)^2$] of positional parameters and anisotropic thermal parameters for nonhydrogen atoms and the scale factor gave final R = 4.8% [$R = (\Sigma||F_o|-|F_c||/\Sigma|F_o|) \times 100$]. Unit weights were used throughout [3]. Hydrogen isotropic thermal parameters were set to U = 3.8. In the final refinement, scattering factors for Pt, P and S [4] were corrected for anomalous dispersion [5]. The hydrogens attached to nitrogen could not be located definitively (see discussion). Two 0.25 occupancy oxygen atoms comprising one half molecule of water, were present in the cell and were stable to refinement (O(101) and O(102)).

TABLE III. Thermal Parameters in the Form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Atom	$10^3\ U_{11}$	$10^3\ U_{22}$	$10^3\ U_{33}$	$10^3\ U_{12}$	$10^3\ U_{13}$	$10^3\ U_{23}$
Pt	40(0.8)	27(0.8)	20(0.8)	−5(0.3)	−6(0.3)	−1(0.2)
P(1)	34(2)	30(2)	20(2)	−6(2)	−7(2)	−1(2)
P(2)	38(2)	30(2)	18(2)	−8(2)	−3(2)	−1(2)
S(1)	96(5)	85(4)	71(4)	−22(4)	−12(4)	0(3)
S(2)	70(4)	65(3)	54(3)	−27(3)	−17(3)	2(2)
O(1)	72(8)	26(6)	29(6)	0(6)	−19(6)	−7(5)
O(2)	100(12)	34(7)	54(8)	−8(7)	−17(8)	8(6)
N(3)	49(10)	96(13)	64(10)	−46(10)	−1(8)	21(9)
N(4)	40(9)	99(14)	100(15)	−9(9)	6(9)	−4(12)
C(111)	28(9)	36(9)	21(8)	−4(7)	−2(7)	−1(7)
C(112)	35(10)	50(11)	29(9)	−2(8)	−11(8)	10(8)
C(113)	72(14)	43(10)	24(9)	−10(10)	−7(9)	6(8)
C(114)	44(11)	46(10)	24(9)	−18(9)	18(8)	−16(8)
C(115)	28(9)	63(11)	39(10)	−9(8)	−9(8)	−21(9)
C(116)	42(10)	49(10)	20(9)	−16(8)	−6(8)	−8(7)
C(121)	30(9)	22(8)	31(8)	3(7)	−8(7)	6(6)
C(122)	54(11)	33(10)	31(9)	−12(9)	−9(8)	2(7)
C(123)	53(11)	21(8)	46(10)	−8(8)	−15(9)	4(7)
C(124)	52(11)	29(10)	66(12)	−13(8)	−17(10)	−6(9)
C(125)	65(14)	50(11)	50(12)	−12(10)	−18(11)	−15(9)
C(126)	42(11)	58(11)	37(9)	−14(9)	−10(8)	−12(8)
C(131)	37(10)	33(9)	14(7)	−16(8)	−7(6)	−2(6)
C(132)	59(11)	44(10)	23(8)	−10(9)	−25(8)	18(7)
C(133)	80(15)	34(10)	32(9)	−21(10)	−22(9)	−12(7)
C(134)	76(14)	26(9)	32(9)	7(9)	−11(9)	−7(7)
C(135)	55(12)	58(14)	20(8)	−5(11)	5(8)	4(8)
C(136)	56(12)	35(10)	12(7)	−9(8)	0(7)	2(6)
C(211)	26(8)	40(9)	17(7)	−5(7)	8(6)	−10(6)
C(212)	34(10)	43(10)	24(8)	4(8)	−7(7)	3(7)
C(213)	65(14)	60(12)	23(8)	21(11)	−8(8)	−8(8)
C(214)	42(11)	130(21)	17(9)	2(13)	6(7)	−27(10)
C(215)	47(14)	77(13)	42(11)	−25(11)	4(10)	−14(10)
C(216)	45(12)	75(13)	31(9)	−28(10)	8(8)	−11(9)
C(221)	42(10)	28(8)	16(7)	−13(7)	−5(7)	−9(6)
C(222)	44(11)	45(10)	27(8)	−22(8)	−9(8)	11(7)
C(223)	52(13)	52(11)	36(11)	−3(9)	−11(9)	0(8)
C(224)	80(14)	28(9)	24(8)	0(9)	−20(8)	3(6)
C(225)	40(11)	49(11)	43(10)	1(9)	−17(9)	−8(8)
C(226)	41(11)	46(10)	36(8)	−22(9)	−3(8)	1(7)
C(231)	27(9)	40(10)	20(8)	−8(7)	−5(7)	−2(7)
C(232)	43(11)	35(9)	46(10)	−16(8)	−11(9)	10(8)
C(233)	52(12)	61(12)	40(11)	−18(10)	21(9)	7(10)
C(234)	50(12)	54(12)	84(14)	−40(10)	−2(11)	19(11)
C(235)	61(13)	38(10)	85(14)	−23(10)	−15(11)	−2(10)
C(236)	48(11)	39(10)	48(11)	−20(9)	−6(9)	−4(8)

Discussion

$(Ph_3P)_2Pt(OSNH)_2$ exists as a square planar complex with a *cis* arrangement of ligands (Fig. 1). Examination of the packing of molecules in the cell (Fig. 2) reveals no significant interaction between molecules. The 0.5 molecule of water located in the cell is 3.8 Å from all other atoms. Therefore the details of the $(Ph_3P)_2Pt(OSNH)_2$ cluster may be considered uninfluenced by intermolecular packing.

The triphenylphosphine groups show normal angles and distances (Table IV based on the atomic coordinates of Table II). The P(1)–Pt–P(2) angle of 98.0(1)° reflects the influence of the bulk of the triphenylphosphine ligands *cis* to each other upon ideal square planar geometry. Each triphenylphosphine ligand is *trans* to an OSNH coordinated to plati-

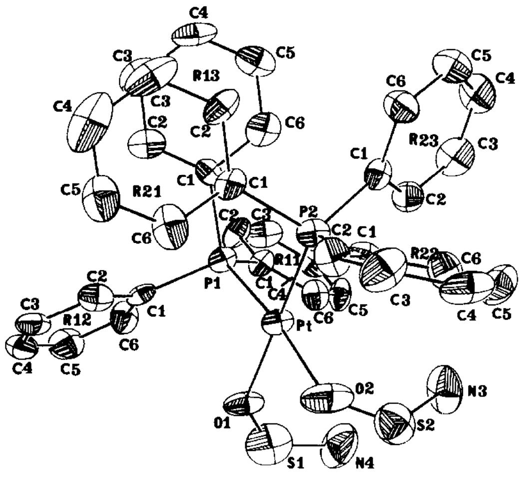

Fig. 1. Perspective view of the molecular structure of $(Ph_3P)_2Pt(OSNH)_2$.

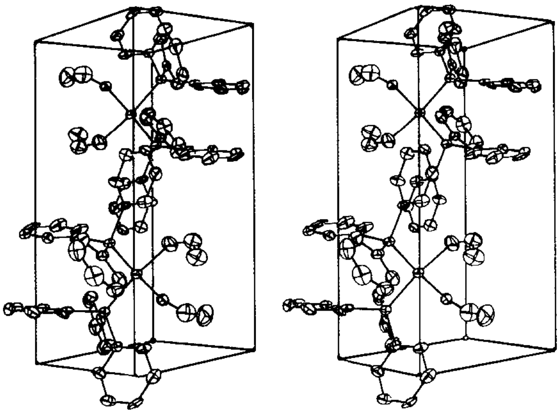

Fig. 2. Stereo view of the packing of molecules in the cell.

TABLE IV. Bond Distances (Å) and Angles (°).

Pt–P(1)	2.288(4)	P(1)–Pt–P(2)	98.0(1)
Pt–P(2)	2.264(4)	P(1)–Pt–O(1)	85.1(3)
Pt–O(1)	2.173(11)	P(1)–Pt–O(2)	171.1(4)
Pt–O(2)	2.088(12)	P(2)–Pt–O(1)	175.2(3)
O(1)–S(1)	1.26(1)	P(2)–Pt–O(2)	90.8(4)
O(2)–S(2)	1.34(2)	O(1)–Pt–O(2)	86.0(4)
S(1)–N(4)	1.48(2)	Pt–O(1)–S(1)	138.1(10)
S(2)–N(3)	1.45(2)	Pt–O(2)–S(2)	129.5(9)
P(1)–C(111)	1.82(1)	O(1)–S(1)–N(4)	121.9(12)
P(1)–C(121)	1.84(2)	O(2)–S(2)–N(3)	122.0(9)
P(1)–C(131)	1.84(1)		
P(2)–C(211)	1.83(1)		
P(2)–C(221)	1.84(1)		
P(2)–C(231)	1.80(2)		

num *via* oxygen. The presence of the OSNH species was unexpected. While the gas phase reaction of NH_3 with thionyl chloride has long been known to produce thionyl imide and ammonium chloride [6] and the IR [7], microwave [8], ultraviolet [9] and photoelectron spectra [10] of the species have been reported, the moiety has not previously been identified in a single crystal X-ray study. The structure shows some divergence between the two OSNH ligands; particularly O–S bond lengths, 1.26(1) and 1.34(2) Å and Pt–O–S angles, 138.1(10) and 129.5(9)°. Better agreement is shown by S–N bond lengths, 1.48(2) and 1.45(2) Å and O–S–N angles, 121.9(12) and 122.0(9)°. These S–O distances (av. 1.30 Å) and S–N distances (av. 1.46 Å) are shorter than those determined by microwave spectroscopy [8] for *cis* thionyl imide (1.451(5) and 1.512(5) Å respectively). The angle at sulfur is 120.4(5)° from microwave spectroscopy and 121.9° average in the X-ray structure.

The O–S and S–N bond lengths are also short compared to those observed in other structure determinations. A S–N triple bond distance of 1.45 Å is observed in NSF [11]. Sulfur–nitrogen bond lengths of 1.485–1.550 Å were observed in $R_2As_2 \cdot S_2N_4$ (R = phenyl or mesityl) [12]; 1.453 Å in $S_5N_5^+AlCl_4^-$ [13] and 1.493 Å in $S_4N_3^+NO_3^-$ [14].

The S–O bond (av. 1.30 Å) may be compared with distances of 1.43–1.45 Å observed in sulfur dioxide, sulfur trioxide and the sulfate ion [15]. Shorter S–O distances of 1.22–1.41 Å have been reported in 2-O-(*p*-bromobenzenesulfonyl)-1,4-3,6-dianhydro-D-gluticol-5-nitrate [16] and 1.34–1.39 Å in tosyl-1-prolyl-1-hydroxyproline monohydrate [17].

There are no close intermolecular contacts between the two OSNH species. With the exception of N(3)–N(4), 3.37(3) Å and O(1)–O(2), 2.90(2) Å, all other distances are greater than 3.5 Å. A final difference Fourier synthesis showed electron density peaks which might be interpreted as protons attached to nitrogen and hydrogen bonded to the oxygen of the same ligand, OSNH. Such hydrogen bonding has been observed in the planar *cis* OSNH species [7]. However the positions were unstable to refinement and are not reported. Failure to determine these positions however leaves unanswered many questions about the structure; indeed the possibility that the ligands are OSNH and HOSN as opposed to $(OSNH)_2$ cannot be eliminated. The thiazyl S-hydroxide species, HOSN, has been reported [10] but not observed in the solid state by X-ray techniques. The OSN^- ion has been isolated as the sodium salt, which gave a red colored solution in water, not dissimilar from that observed for an aqueous solution of the thiazyl S-hydroxide [18].

A list of calculated and observed structure factors is available on request.

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