Oxidation of a Pt$_2$(μ-SO$_2$) Moiety to μ-SO$_3$ and the Crystal Structure of [Pt$_2$(μ-SO$_3$)(μ-SO$_2$)(C$_8$H$_{12}$)$_2$] †

David H. Farrar* and Ravi R. Gukathasan
Department of Chemistry, Lash Miller Chemical Laboratories, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Bis(cyclo-octa-1,5-diene)platinum(o) as a solid has been found to react immediately with SO$_2$ giving [Pt$_2$(μ-SO$_2$)$_2$(C$_8$H$_{12}$)$_2$], (1). N.m.r. spectroscopy reveals that the two C$_8$H$_{12}$ ligands in the dimer (1) have three co-ordinated olefinic groups with the remaining one not co-ordinated. The presence of μ-SO$_2$ ligands is consistent with the i.r. spectrum. Solutions of complex (1) are oxidized slowly by atmospheric O$_2$ to give the novel μ-SO$_3$ complex [Pt$_2$(μ-SO$_3$)(μ-SO$_2$)(C$_8$H$_{12}$)$_2$], (2). Complex (2) was characterized by single-crystal X-ray crystallography and consists of two distorted square-planar platinum(II) fragments held together by a bridging SO$_2^{2-}$ anion and a bridging SO$_3^{2-}$ anion. The bond parameters at both Pt atoms indicate a square-planar co-ordination geometry and a value of 20.1° is calculated for the dihedral angle between the two square-planar fragments. The μ-SO$_2$ ligand is σ-bonded to both Pt atoms through the S atom while the μ-SO$_3$ ligand is σ-bonded to one Pt atom by the S atom and to the other metal *via* an O atom. The two Pt, the two S, and the O atoms form a puckered five-membered ring.

The oxidation of sulphur dioxide to sulphur trioxide is a primary step in the conversation of sulphur to sulphuric acid.[1] The catalyst currently used to effect this oxidation is supported vanadium pentoxide[2,3] although platinum-based catalysts were used in the past. Recently, the sulphur–sulphur dioxide–sulphur trioxide–sulphuric acid cycle has attracted attention as a result of more stringent pollution controls.[1] We report in this paper the room-temperature air oxidation of an SO$_2$ ligand bridged between two Pt atoms to a bridging SO$_3$ ligand. There are several examples of the oxidation by O$_2$ of an SO$_2$ ligand bound to one platinum group metal giving sulphato (SO$_4^{2-}$) complexes.[4] The first step in this type of reaction is believed to be displacement of the SO$_2$ ligand by the O$_2$ ligand, followed by electrophilic attack by an SO$_2$ molecule on co-ordinated O$_2$. Despite the numerous studies on the SO$_2$ ligand,[4] to our knowledge the air oxidation to SO$_3$ has never been reported and this is the first reported complex containing a μ-SO$_3$ ligand.

Results

While studying[5] the reactions of platinum cluster complexes and SO$_2$ we observed that solid samples of [Pt(C$_8$H$_{12}$)$_2$] (C$_8$H$_{12}$ = cyclo-octa-1,5-diene) react immediately with SO$_2$ to give an orange compound, later formulated as [Pt$_2$(μ-SO$_2$)$_2$-(C$_8$H$_{12}$)$_2$], (1). All attempts to obtain single crystals of (1) for an X-ray crystal structure determination have failed. Complex (1) reacts slowly with O$_2$ to give one product which has been characterized by X-ray crystallography as [Pt$_2$(μ-SO$_3$)(μ-SO$_2$)(C$_8$H$_{12}$)$_2$], (2). Reaction of (1) and *m*-chloroperbenzoic acid also resulted in formation of complex (2), together with some decomposition; (1) does not react with Me$_3$NO to give (2).

Crystals of (2) are built up from discrete molecules and a perspective view of the molecule together with the atom numbering scheme is given in the Figure. Selected intramolecular distances are presented in Table 1. The shortest

Table 1. Selected bond distances (Å) and angles (°) for complex (2)

Pt(1)–S(1)	2.327(8)	Pt(2)–S(1)	2.279(8)
Pt(1)–S(2)	2.290(8)	Pt(2)–O(23)	2.06(2)
Pt(1)–C(1)	2.31(8)	Pt(2)–C(9)	2.18(3)
Pt(1)–C(2)	2.25(3)	Pt(2)–C(10)	2.06(3)
Pt(1)–C(5)	2.29(3)	Pt(2)–C(13)	2.29(3)
Pt(1)–C(6)	2.27(3)	Pt(2)–C(14)	2.27(3)
S(1)–O(11)	1.45(2)	S(2)–O(21)	1.43(2)
S(1)–O(12)	1.47(2)	S(2)–O(22)	1.43(2)
		S(2)–O(23)	1.54(2)
S(1)–Pt(1)–S(2)	88.7(3)	S(1)–Pt(2)–O(23)	90.0(5)
S(1)–Pt(1)–C(5)	91.3(8)	S(1)–Pt(2)–C(9)	94.7(8)
S(1)–Pt(1)–C(6)	92.2(7)	S(1)–Pt(2)–C(10)	92.5(9)
S(2)–Pt(1)–C(1)	93.6(8)	O(23)–Pt(2)–C(13)	90.6(9)
S(2)–Pt(1)–C(2)	93.7(8)	O(23)–Pt(2)–C(14)	89.3(8)
Pt(1)–S(1)–Pt(2)	109.5(3)	Pt(1)–S(2)–O(21)	106.5(9)
Pt(1)–S(1)–O(11)	106.3(8)	Pt(1)–S(2)–O(22)	114.2(10)
Pt(1)–S(1)–O(12)	107.4(9)	Pt(1)–S(2)–O(23)	108.1(8)
Pt(2)–S(1)–O(11)	109.3(9)	O(21)–S(2)–O(22)	114(1)
Pt(2)–S(1)–O(12)	109.4(9)	O(21)–S(2)–O(23)	108(1)
O(11)–S(1)–O(12)	115(1)	O(22)–S(2)–O(23)	106(1)
S(2)–O(23)–Pt(2)	115(1)		

contact between the molecules is 2.36 Å involving H(61) [bonded to C(6)] and H(101′) at ($\frac{1}{2}$ − x, −y, $\frac{1}{2}$ − z). Complex (2) can be described as two distorted square-planar platinum(II) fragments held together by a bridging SO$_2^{2-}$ anion and a bridging SO$_3^{2-}$ anion. The Pt(1) inner co-ordination sphere contains S(1), S(2), and the cyclo-octa-1,5-diene ligand C atoms C(1), C(2), C(5), and C(6). The olefinic C atoms are symmetrically displaced about a plane defined by Pt(1), S(1), and S(2). A similar inner co-ordination sphere exists at Pt(2) defined by S(1), O(23), and C(9), C(10), C(13), and C(14). The angles subtended at both Pt atoms are consistent with a square-planar co-ordination geometry. The S(1)–Pt(1)–S(2) angle is 88.7(3)° and S(1)–Pt(2)–O(23) is 90.0(5)°. A value of 20.1° was calculated for the dihedral angle between the two square-planar fragments.

The two Pt, the two S, and O(23) atoms form a puckered five-membered ring. Atom O(23) is 0.74(2) Å below a plane defined

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Table 2. N.m.r. spectroscopic data[a]

Complex		$\delta(^{13}C)^{b}/$ p.p.m.	$^{1}J(^{195}Pt-^{13}C)$ Hz	$^{3}J(^{195}Pt-^{13}C)^{c}$	$\delta(^{1}H)$	$^{2}J(^{195}Pt-^{1}H)/Hz$
(1)	a	87.6 (0.63)	154	17	5.43	d
	b	96.4 (0.55)	187	36	4.98	105
	c	111.0 (0.59)	55	10	6.86	50
	d	105.8 (0.59)	44	20	5.71	39
	e	110.5 (0.59)	45	26	5.51	d
	f	105.7 (0.59)	50	33	5.45	d
	g, h	128.7 (2.8)	e	e	5.56	e
(2)		93.5	228			
		113.2	83			
		113.7	47			
		114.8	60			

[a] Letters correspond to the positions shown for complex (1). The ^{1}H and ^{13}C resonances have been related by a heteronuclear two-dimensional shift correlation n.m.r. experiment. [b] The ^{13}C relaxation times T_1, in seconds, are given in parentheses below the chemical shifts. [c] May be $^{4}J(^{195}Pt-Pt-^{13}C)$. [d] Not resolved due to overlap. [e] Not observed.
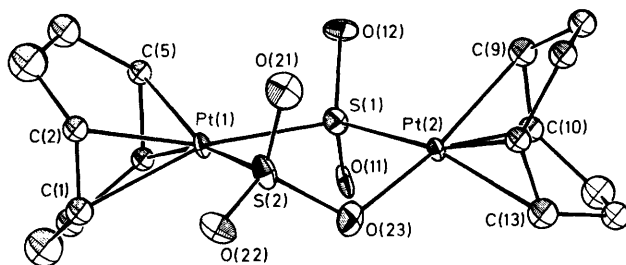

Figure. An ORTEP diagram of complex (2) with hydrogen atoms omitted. The thermal ellipsoids are represented by 30% probability contours

by Pt(1), Pt(2), S(1), and S(2). All angles subtended at both S atoms are in accord with tetrahedral SO_2^{2-} and SO_3^{2-} anions. The μ-SO$_2$ ligand is σ-bonded to both Pt atoms through S(1), while the μ-SO$_3$ ligand is σ-bonded to Pt(1) by S(2) and to Pt(2) via O(23). The Pt(1)–S(2) and Pt(2)–S(1) distances, 2.290(8) and 2.279(8) Å, are not significantly different nor do they differ from the Pt–S values reported[6] for the complex [Pt$_3$(μ-SO$_2$)$_3$-(PPh$_3$)$_3$] of 2.271(5), 2.279(4), and 2.275(4) Å. The Pt(1)–S(1) distance, 2.327(8) Å, does differ significantly from the other values; the reason for this difference is not clear. The S–O distances in the μ-SO$_2$ ligand are normal.[6] The exo-S–O distances in the μ-SO$_3$ ligand are both 1.43(2) Å which also is the value reported for the SO$_3$ molecule.[7] The S(2)–O(23) distance, 1.54(2) Å, is longer than the two exo distances although it is shorter than a S–O single bond length of 1.70 Å, calculated using covalent radii.[8]

The Pt–C distances for the olefinic C atoms trans to a S atom are equivalent [average 2.28(2) Å] while the two C atoms trans to O(23) have an average Pt–C distance of 2.12(8) Å. This is consistent with the relative trans influence of oxygen versus sulphur ligands.[9] All parameters associated with the C$_8$H$_{12}$ fragments are normal.[10]

The ^{13}C n.m.r. spectrum of complex (2) at 25 °C contains only four resonances in the olefinic region and thus a fluxional process
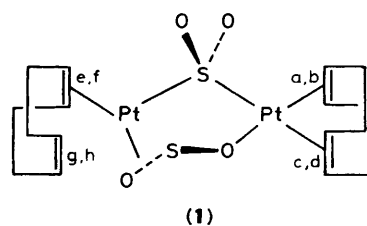
must exist which equates the carbon atoms in each of the four olefin groups. Of the four values, presented in Table 2, one is decidedly upfield of the remaining three and exhibits a much larger $^{195}Pt-^{13}C$ coupling constant. This resonance is assigned to the carbon atoms labelled C(9) and C(10) which are trans to oxygen and more strongly bound to platinum.

Complex (1) is assigned the structure shown on the basis of spectroscopic and analytical data. While this structure is usual, it does fit all the data we have been able to obtain. Elemental analysis gives the empirical formula Pt(SO$_2$)(C$_8$H$_{12}$). The i.r. spectrum of (1) has v(SO$_2$) bands at 1 177, 1 043, and 997 cm^{-1} suggesting the presence of a μ-SO$_2$ ligand[5] and possibly an η^2,μ-SO$_2$ ligand.[11]

The ^{13}C n.m.r. spectrum of complex (1) has seven resonances due to olefinic carbon atoms and the assignment of these peaks is indicated in Table 2. The observation of $^{195}Pt-Pt-^{13}C$ inner satellites confirms the dimeric nature of the complex. As in the case of (2), the upfield signals with large $^{1}J(^{195}Pt-^{13}C)$ values are ascribed to the carbon atoms which are trans to an oxygen atom. The remaining two olefinic carbon atoms in the C$_8$H$_{12}$ ligand have been identified by two-dimensional n.m.r. experiments.[12] A heteronuclear two-dimensional shift correlation spectrum of the ^{1}H and ^{13}C resonances has allowed us to correlate the ^{1}H and ^{13}C data as presented in Table 2. It was then shown, using $^{1}H-^{195}Pt$ heteronuclear two-dimensional shift correlation, that the ^{1}H signals from the H atoms bonded to the C atoms labelled a—d are coupled to the same Pt atom. Resonances c—f are assumed to be trans to S atoms based on the similarity with the chemical shifts observed for complex (2).

The remaining signal at 128.7 p.p.m. is very close to the position observed for the olefinic groups in the cyclo-octa-1,5-diene molecule. The peak integrates as two C atoms and we have assigned this resonance to an unco-ordinated olefin in a C_8H_{12} ligand. The possibility that this signal could arise from free cyclo-octa-1,5-diene has been eliminated as the relaxation time T_1 for peak (g, h) is 2.8 s whereas the corresponding value for cyclo-octa-1,5-diene was found to be 15 s. The solid-state ^{13}C n.m.r. spectrum of complex (1) has broad unresolved peaks at approximately the same chemical shifts as those found in the solution spectrum and thus no major change occurs when samples of (1) are dissolved. In the absence of magic angle spinning the entire spectrum collapses which again suggests that the peak labelled (g, h) is related to a 'dangling' cyclo-octa-1,5-diene ligand and not an occluded molecule.

Discussion

Solid samples of $Pt(C_8H_{12})_2$ react immediately with SO_2 giving $[Pt_2(\mu\text{-}SO_2)_2(C_8H_{12})_2]$, (1). N.m.r. spectroscopy was used to determine the bonding modes of the C_8H_{12} ligands. The presence of a $\mu\text{-}SO_2$ ligand is consistent with the i.r. spectrum although it is not entirely clear whether the second SO_2 ligand is $\eta^2\text{-}SO$ bound to one metal atom and $\sigma\text{-}O$ bound to the other (as shown) or a $\sigma\text{-}S/\sigma\text{-}O$ bridge with an *exo* S=O. There is one example in the literature of the former[11] whereas the latter has not been observed. Solutions of complex (1) are oxidized slowly by atmospheric O_2 to give the novel $\mu\text{-}SO_3$ complex $[Pt_2(\mu\text{-}SO_3)(\mu\text{-}SO_2)(C_8H_{12})_2]$, (2). Hydrogen is not evolved in the air oxidation and solutions of (1) are found to convert cleanly into (2) under an atmosphere of dry oxygen, thus precluding reaction with H_2O or an HO radical initiated oxidation of SO_2.[13]

Bridging SO_2 ligands are usually quite stable chemically[4,14] and thus the reasons as to why a $\mu\text{-}SO_2$ ligand in (1) is easily oxidized are of interest. The oxidation of SO_2 ligands to SO_4 in mononuclear complexes is known.[14,15] There is one example of the complete oxidation of the $\mu\text{-}SO_2$ ligand in $[\{Fe(SMe)(CO)_2(PMe_3)\}_2SO_2]$ giving $[Fe(SMe)(CO)_2(PMe_3)]_2[SO_4]$.[16] Air oxidation where only one O atom is transferred has been reported for the $\eta^2\text{-}S_2$ ligand in $[Mn(C_5H_5)(CO)_5(S_2)]$ resulting in $[Mn(C_5H_5)(CO)_5(S_2O)]$.[17] To our knowledge, this is the first observation of the oxidation of a $\mu\text{-}SO_2$ ligand to a $\mu\text{-}SO_3$ ligand. While the exact nature of the $\mu\text{-}SO_2$ ligand in complex (1) prior to reaction with O_2 is not known, if our assignment as $\eta\text{-}SO$ bound to one metal atom and $\sigma\text{-}O$ bound to the other is correct, then molecular models indicate some ring strain is present. The observation of six separate resonances for co-ordinated olefinic C atoms in the ^{13}C n.m.r. spectrum of (1) at room temperature shows that the complex is fairly rigid and does not possess a mirror plane. This is in contrast to complex (2) where at the same temperature fluxionality associated with inverting the five-membered ring results in the C_8H_{12} ligands having pseudo-mirror symmetry. One possibility is that release of strain energy is partly responsible for the facile nature of the reaction. The oxidation is formally changing a trigonal planar platinum(o) centre in (1) to a square-planar platinum(II) centre in (2) with co-ordination of the 'dangling' olefin, assuming that our structural assignment of (1) is correct. The complex $[\{Mo(CO)_2(PPh_3)(py)(\mu\text{-}SO_2)\}_2]$ (py = pyridine) has two $\mu\text{-}SO_2$ ligands co-ordinated to one metal through a S=O π bond and a second metal *via* the remaining O atom forming a six-membered ring, and the complex is very stable.[11]

Normal '$(\sigma\text{-}S)\text{-}\mu\text{-}SO_2$' ligands do not undergo further oxidation when treated with an excess of *m*-chloroperbenzoic acid.[18,19] The reaction of the $\mu\text{-}SO_2$ ligand in the complex $[Pt_2(\mu\text{-}SO_2)(CO)_2(PBu^t_2Ph)_2]$ with Me_3NO results in removal of the SO_2 ligand as $Me_3NO\cdot SO_2$.[19] In contrast, complex (1) does not react with Me_3NO.

Experimental

Synthesis of $[Pt_2(\mu\text{-}SO_2)_2(C_8H_{12})_2]$, (1).—A solid sample of $[Pt(C_8H_{12})_2]$ (0.30 g, 0.729 mmol) was exposed to an atmosphere of SO_2 resulting in an immediate colour change to a dark purple solid. The free C_8H_{12} was removed by washing with hexanes. This solid was then dissolved in $CHCl_3$, an insoluble fraction was removed by filtration, and the orange product was obtained by precipitation with hexanes, filtered off, and dried at reduced pressure. Yield 83%. I.r. (Nujol mull) $v(S\text{-}O)$ 1 177m, 1 043s, and 997m (sh) cm^{-1} (Found: C, 26.0; H, 3.2; O, 8.6; S, 8.6. Calc. for $C_{16}H_{24}O_4Pt_2S_2$: C, 26.1; H, 3.3; O, 8.7; S, 8.7%).

Synthesis of $[Pt_2(\mu\text{-}SO_3)(\mu\text{-}SO_2)(C_8H_{12})_2]$, (2).—Complex (1) (0.25 g, 0.34 mmol) was dissolved in $CHCl_3$ (25 cm^3) and the solution was stirred under an oxygen atmosphere for 48 h at 23 °C. The solvent was removed at reduced pressure and the resulting yellow solid was recrystallized from CH_2Cl_2—hexanes mixtures. Yield 95%. I.r. (Nujol mull) $v(S\text{-}O)$ 1 214s, 1 154s, 1 086s, 1 020s, 998m, 847s, and 652s cm^{-1}.

Crystallography.—*Crystal data for* (2). $C_{16}H_{24}O_5Pt_2S_2$, $M = 750.67$, orthorhombic, $a = 12.117(2)$, $b = 24.158(4)$, $c = 12.126(1)$ Å, $U = 3 549.8$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710 69$ Å), space group $Pbca$,[22] $Z = 8$, $D_c = 2.81$ g cm^{-3}, yellow plates, crystal dimensions $0.012 \times 0.011 \times 0.005$ cm, crystal faces $\{111\}$, $\{100\}$, $\mu(\text{Mo-}K_\alpha) = 161.6$ cm^{-1}, $F(000) = 3 104$.

Data collection and processing. Enraf–Nonius CAD4 diffractometer, graphite-monochromated Mo-K_α radiation. θ—2θ mode with scan width $0.80 + 0.35 \tan \theta$, scan speed 0.5—10.0° min^{-1}. 3 118 Unique reflections measured ($1 < 2\theta < 50°$, $+h$, $+k$, $+l$). Gaussian absorption correction[23] with a $12 \times 10 \times 6$ grid (transmission coefficients varied from 0.285 to 0.406); no decomposition observed; the recorded intensities were corrected for Lorentz and polarization effects.[23] 1 225 Unique data with $I > 3\sigma(I)$. All calculations were performed using the Enraf–Nonius Structure Determination Package running on a DEC PDP-11/23 computer.

Structure analysis and refinement. The positional co-ordinates for the Pt atoms were obtained from a three-dimensional Patterson synthesis. A series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining 31 non-hydrogen atoms. Hydrogen atoms were located and included in subsequent calculations with idealized positional co-ordinates (either sp^2 or sp^3 geometries and a C–H bond distance of 1.0 Å) but not refined. After several cycles of full-matrix least-squares refinement on F the model converged at $R = \Sigma||F_c| - |F_o|/\Sigma|F_o|| = 0.0474$ and $R' = [\Sigma w(|F_c| - |F_o|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.0510$ (1 225 observations and 146 variables; Pt, S, and O atoms refined with anisotropic thermal parameters and all C atoms refined isotropically). In the final cycle no shift exceeded 0.02 of its standard deviation. A total difference Fourier synthesis calculated from the final structure factors

Table 3. Positional parameters for the non-H atoms of complex (2)

Atom	x	y	z
Pt(1)	0.093 43(9)	0.139 38(4)	0.596 7(1)
Pt(2)	0.330 19(9)	0.119 07(4)	0.400 1(1)
S(1)	0.206 3(7)	0.074 6(3)	0.510 4(6)
S(2)	0.178 8(7)	0.207 2(3)	0.496 1(7)
O(11)	0.265(2)	0.046 1(7)	0.598(2)
O(12)	0.135(2)	0.039 1(8)	0.442(2)
O(21)	0.130(2)	0.206 3(8)	0.389(2)
O(22)	0.178(2)	0.260 4(8)	0.547(2)
O(23)	0.301(1)	0.191 7(8)	0.484(2)
C(1)	0.023(3)	0.201(1)	0.725(3)
C(2)	−0.049(2)	0.194(1)	0.645(2)
C(3)	−0.152(3)	0.163(2)	0.650(3)
C(4)	−0.142(3)	0.100(1)	0.645(3)
C(5)	−0.030(2)	0.072(1)	0.645(2)
C(6)	0.045(2)	0.079(1)	0.731(2)
C(7)	0.023(3)	0.111(1)	0.838(3)
C(8)	0.017(3)	0.171(2)	0.830(3)
C(9)	0.337(3)	0.053(1)	0.277(3)
C(10)	0.410(3)	0.047(1)	0.361(2)
C(11)	0.529(3)	0.053(1)	0.359(3)
C(12)	0.566(3)	0.105(1)	0.315(3)
C(13)	0.492(3)	0.154(1)	0.331(3)
C(14)	0.405(3)	0.169(1)	0.260(2)
C(15)	0.380(3)	0.139(1)	0.153(2)
C(16)	0.373(3)	0.077(1)	0.164(2)

Estimated standard deviations in the least significant figure(s) are given in parentheses.

contained no features of chemical significance with the highest peak, of electron density 1.65 e Å^{-3}, between atoms O(22) and H(13) at fractional co-ordinates (0.144, 0.322, 0.603). The error in an observation of unit weight is 1.11. Final positional parameters for the non-H atoms are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Reaction of Complex (1) *and* m-*Chloroperbenzoic Acid.*—Complex (1) (0.30 g, 0.04 mmol) and *m*-chloroperbenzoic acid (0.01 g, 0.06 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 24 h at 23 °C. The solvent was removed at reduced pressure and an ^{1}H n.m.r. spectrum of the brown residue, dissolved in CDCl$_3$, indicated that conversion into complex (2) had occurred, together with some decomposition.

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