DALTON
FULL PAPER

Transformation of sulfur dioxide to sulfate at a palladium centre

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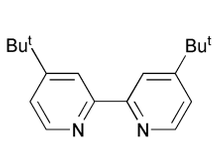
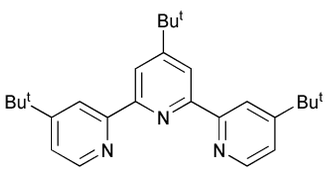
Reaction of 4,4′,4″-tri(*tert*-butyl)-2,2′:6′,2″-terpyridine (terpy*) with gaseous SO_2–O_2 mixtures and $[PdCl_2(MeCN)_2]$ followed by aqueous workup affords crystallographically characterised [PdCl(terpy*)]Cl and both *O*- and *S*-bound $[Pd(SO_3)(terpy*)]$. The former is also available from $[PdCl_2(MeCN)_n]$ ($n = 0$, 2) and terpy*; the latter from aerobic oxidation of $[Pd(dba)_2]$–terpy*–SO_2 mixtures (dba = dibenzylideneacetone). Oxidation of $[Pd(SO_3)(terpy*)]$ with O_2 (at 210 °C in $PhNO_2$) yields crystallographically characterised *O*-bound $[Pd(SO_4)(terpy*)]$. The crystal structures of two related compounds are also reported: [Pd(OAc)(terpy*)]Cl and $[PdCl_2(bipy*)]$.

Introduction

There is an increasing interest in reactions featuring "soft" transition metals in combination with ligands that are normally considered "hard".[1] One under-utilised substrate in this respect is sulfur dioxide and in particular its oxidation reactions. Sulfur dioxide is employed on industrial scale in aerobic, free radical-based, alkylsulfonic acid production from hydrocarbons.[2] Similarly, SO_2 is used as a promoter in heterogeneous platinum-catalysed alkane oxidations.[3] While the basic features of sulfur dioxide co-ordination chemistry have been well defined[4] there have been few homogeneous models of such SO_2 oxidation processes.[5] We report here our studies of SO_2 oxidation and hydrolysis reactions in the presence of palladium complexes of the ligands 4,4′-di(*tert*-butyl)-2,2′-bipyridine (bipy*) and 4,4′,4″-tri(*tert*-butyl)-2,2′:6′,2″-terpyridine (terpy*).



bipy*



terpy*

Results and discussion

SO_2 Activation studies

Bubbling mixtures of gaseous SO_2–O_2 through an acetonitrile solution of $[PdCl_2(MeCN)_2]$ in the presence of terpy* leads to the formation of a lemon yellow solution. Subsequent addition of aqueous methanol effected the production of up to three compounds. Under favourable conditions precipitation of single crystals occurred which were subsequently identified as the sulfite complex $[Pd(SO_3)(terpy*)]$ **1**/**1a** while on other occasions only [PdCl(terpy*)]Cl **2** was formed. The ratio of these species was found to be dependent of the reaction micro-conditions; minor variations in the SO_2–O_2 flow rates and other conditions had dramatic and variable effects on the **1**(**1a**) : **2** ratio. If the reaction was allowed to stand for extended periods then samples of $MeC(=O)NH_2$ were obtained through the hydrolysis of the acetonitrile solvent. This latter reaction appears to be catalysed by the **1**–**2** mixtures. Confirmation of the structures was initially complicated by the lack of convenient spectroscopic handles in the co-ordinated anions and by the tendency of anions to readily dissociate during positive ion mass spectrometry.

Literature reactions of palladium bipy/terpy complexes with SO_2 appear to be limited to the studies of Esmardi[6] (who prepared non-crystalline $[PdCl_2(SO_2)(terpy)]$, $[Pd(SO_4)(bipy)]$ and related species by reaction of $[Pd(H)Cl_2(CO)]^-$ with SO_2 followed by ligand addition). Proton NMR investigation of our reaction mixtures suggested only the presence of $[PdCl(terpy*)]^+$ cations after treatment with SO_2–O_2. This raises the possibility that the sulfite ligand in **1** arises from sulfurous acid generated by hydrolysis of SO_2 during crystallisation of the reaction mixture. This idea was tested by exposure of an acetonitrile solution of [PdCl(terpy*)]Cl to an aqueous solution of SO_2. The sulfite complex **1** is not prepared by this chemistry but a new species is formed; however, its high lability prevented its isolation. To overcome these problems we undertook a campaign of synthesis and crystallographic study to see if the electronic nature of the co-ordinated anion(s) in these species could be related in any way to the chemical shift of the diagnostic pyridyl protons in the co-ordinated terpy* and bipy* ligands.

Preparation of sulfite complexes

The non-reproducibility of our initial SO_2 studies led us to seek an alternative preparation of $[Pd(SO_3)(terpy*)]$ **1**(**1a**). Saturation of THF solutions $[Pd(dba)_2]$ (dba = dibenzylideneacetone) containing terpy* led to the formation **1** in low (30%), but reproducible, yield. It is possible that this reaction proceeds *via* a labile palladium SO_2 species that undergoes subsequent terpy* ligation and aerobic oxidation as under these anhydrous conditions no SO_2 hydrolysis is possible. Such behaviour would account for the variable yield of **1**(**1a**) in the initial studies using Pd^{II} precursors where the multiple Pd^0/Pd^{II} redox reactions required would be critically dependent on the local SO_2 and O_2 concentrations. Attempts to prepare complexes from SO_2 saturated $CDCl_3$ solutions containing $[Pd(dba)_2]$ and terpy* led only to very labile species. Complex **1**(**1a**) could be crystallised as a trihydrate from aqueous acetonitrile or as a solvate from $CDCl_3$. Both morphologies were subjected to X-ray analysis. The molecular structure of the chloroform-derived crystal is shown in Fig. 1, while selected bond distance and angle data

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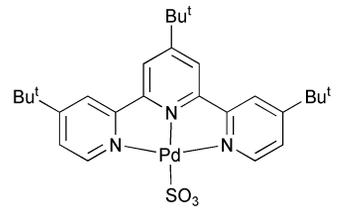
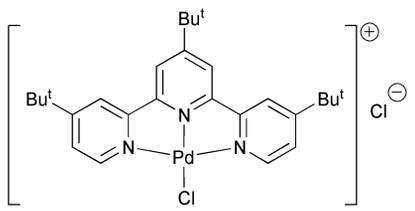


1 *S*-bound SO_3
1a *O*-bound SO_3



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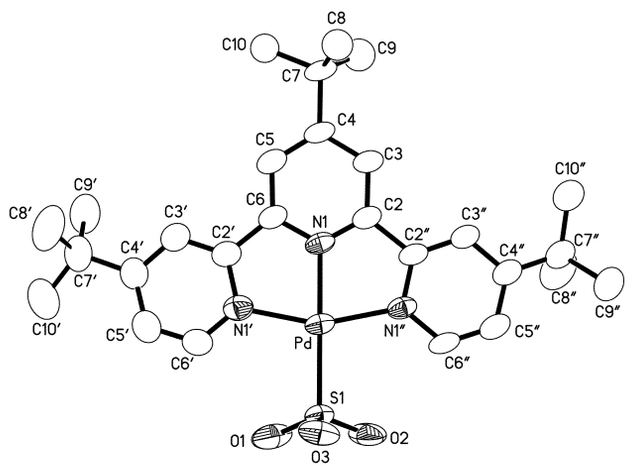


Fig. 1 Molecular structure of *S*-bound [Pd(SO_3)(terpy*)] **1** ($CDCl_3$ morphology). Hydrogen atoms are omitted for clarity as are hydrogen bonded and lattice $CDCl_3$. Only the major component of a disordered Bu^t fragment is shown.

is summarised in Table 1. Interestingly, the equivalent acetonitrile–water morphology shows disorder in the sulfite unit and 25% of the SO_3 units are *O*-bound. An ORTEP plot of *O*-bound [Pd(SO_3)(terpy*)] **1a** is shown in Fig. 2 with associated data presented in Table 1. Such linkage isomerism in palladium sulfite complexes does not appear to have been reported before; however this phenomenon has been noted in Pt(IV) complexes.[7] Previously crystallographically characterised palladium sulfite complexes appear to be limited to *cis*-Na_2[Pd(SO_3)$_2$(en)] which also contains an *S*-bound SO_3 (Pd–S, 2.269; S–O_{ave}, 1.484 A; O–S–O_{ave}, 108.5°).[8] The similarity of these values to **1** is consistent with its formulation as a sulfite rather than a sulfur trioxide complex. In particular, no evidence for the presence of any *O*-bound protons could be found in the residual electron density surrounding the SO_3 ligand. In the $CDCl_3$ morphology the terpy* ligand of **1** shows a "gull-wing" deformation. This distortion probably arises out of conflict between the terpy* bite angle [N(1′)–Pd–N(1″) = 158.7°] and the favoured 180° geometry of d^8 square planar complexes. In the $CDCl_3$ morphology a solvent molecule resides near the Pd centre, while three $CDCl_3$ molecules sit in a pyramidal fashion around the sulfite ligand and hydrogen bond to the *O*-atoms of the ligand. Similar hydrogen bonds (to water) are seen in the trihydrate morphology. In all these cases the O···H(D) contacts are in the range 2.03–2.11 Å. The ^{1}H solution NMR spectra of *S*- and *O*-bound **1** and **1a** are identical suggesting equilibration between the two forms on an NMR timescale. Such lability for

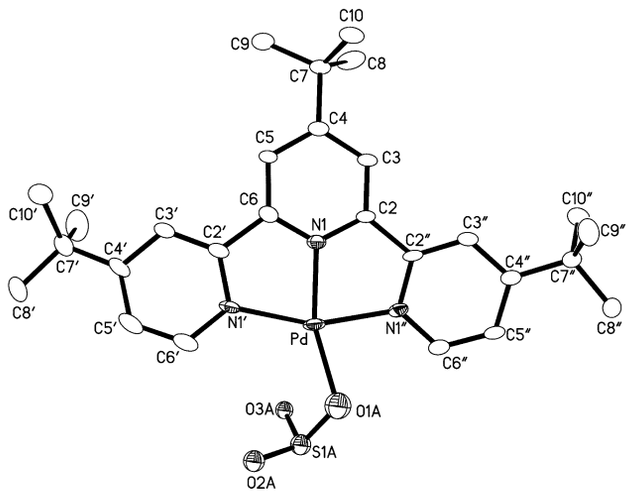


Fig. 2 Molecular structure of the *O*-bound component [Pd(SO_3)(terpy*)] **1a** (acetonitrile–water morphology). Hydrogen atoms are omitted for clarity as is lattice water.

the sulfite ligand may also be a contributing factor in the isolation of **1**(**1a**) in our SO_2 activation studies in aqueous acetonitrile. The [Pd(SO_3)(terpy*)] **1/1a** complex (either morphology) gave strong IR bands at 1260 cm^{-1} [ν(S=O)*asym*], 1133 cm^{-1} [δ(S=O)*sym*], 1100 cm^{-1} [δ(S=O)*sym*] and 983 cm^{-1} [ν(S–O), where the assignments have been made based on literature precedent.[6] Isolated **1a** also exhibited absorption bands due to lattice water [3488 cm^{-1}, ν(O–H); 1612 cm^{-1}, ν(H–O–H)].

At the onset of our studies few palladium complexes of bipy* and terpy* had been prepared. To allow NMR and structural comparisons with **1** two chloro and one acetate complexes were prepared. Direct reaction of $PdCl_2$ and the relevant ligand fashioned in moderate yields [PdCl(terpy*)]Cl **2** but was an acceptable route for the preparation [$PdCl_2$(bipy*)] **3**. Near quantitative yields of **2** are realised using [$PdCl_2(MeCN)_2$] as a soluble palladium source and during the course of our studies Osborn and co-workers reported an essentially identical procedure using [$PdCl_2(PhCN)_2$].[9] Both complexes **2** and **3** could be crystallised and their molecular structures are shown

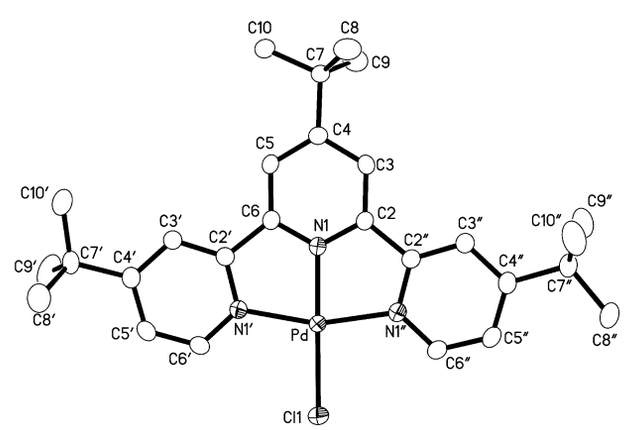


Fig. 3 Molecular structure of [PdCl(terpy*)]Cl **2**. Hydrogen atoms and the chloride counter anion are omitted for clarity.

in Figs. 3 and 4 respectively. The co-ordination geometries displayed by **2**–**3** are largely unaffected by the electron rich *tert*-butyl substituted ligands. For example, the Pd–Cl distances are very similar to those in the unsubstantiated complexes: [Pd-Cl(terpy)]Cl (2.134 Å)[10] and [$PdCl_2$(bipy)] (2.276, 2.319 Å).[11] Reaction of $Pd(OAc)_2$ with terpy* led to clean formation of the acetate; in this case the product readily crystallised as [Pd(OAc)(terpy*)]Cl **4** from dichloromethane–hexane. The halogenated solvent is apparently the source of the outer-sphere counter ion. The molecular structure of [Pd(OAc)(terpy*)]Cl **4**

Table 1 Selected intramolecular distance (Å) and angle (°) data for complexes **1**–**2** and **4**–**6**

	[Pd(*S*-SO_3)-(terpy*)] **1**	[Pd(*O*-SO_3)-(terpy*)] **1a**	[PdCl-(terpy*)]Cl **2**	[Pd(OAc)-(terpy*)]Cl **4**	[Pd(SO_4)-(terpy*)] **5**	[($NHSO_2Ar$)-(terpy*)] **6**[a]
Pd–N(1)	2.008(4)	1.986(4)	1.929(2)	1.928(2)	1.918(4)	1.935(6)
Pd–N(1′)	2.069(5)	2.083(4)	2.030(2)	2.012(2)	2.207(5)	2.023(7)
Pd–N(1″)	2.075(5)	2.085(4)	2.020(2)	2.009(2)	2.018(5)	2.022(7)
Pd–Cl	—	—	2.2980(7)	—	—	—
Pd–S	2.2457(13)	2.267(2)*b*	—	—	—	—
Pd–O	—	2.03(2)	—	2.0448(15)	2.001(4)	—
Pd–N(4)	—	—	—	—	—	2.027(7)
S–O	1.448(4)	1.483(4)[b]	—	—	1.425(5)	1.431(8)
	1.456(5)	1.52(2)			1.453(5)	1.445(7)
	1.457(4)	1.498(5)[b]			1.474(5)	
		1.50(2)			1.530(4)	
		1.536(15)[b]				
		1.33(5)				
N(1)–Pd–X	176.84(11) (X = S)	170.98(10) (X = S)	178.02(8) (X = Cl(1))	175.23(7) (X = O(1))	173.1(2) (X = O(1))	176.4(3) (X = N(4))
		161.8(5) (X = O(1A)				
N(1′)–Pd–X	101.10(13) (X = S)	96.74(10) (X = S)	100.07(7) (X = Cl(1))	96.83(6) (X = O(1))	106.6(2) (X = O(1))	96.5(3) (X = N(4))
		117.8(5) (X = O(1A))				
N(1″)–Pd–X	101.34(12) (X = S)	104.47(10) (X = S)	98.26(7) (X = Cl(1))	100.99(6) (X = O(1))	91.9(2) (X = O(1))	101.9(3) (X = N(4))
		83.3(5) (X = O(1A))				
N(1)–Pd–N(1′)	79.0(2)	79.29(14)	80.59(10)	81.41(7)	80.2(2)	81.0(3)
N(1)–Pd–N(1″)	78.7(2)	79.40(14)	81.01(10)	80.82(7)	81.3(2)	80.5(3)
N(1′)–Pd–N(1″)	157.5(2)	158.68(14)	161.53(10)	162.18(6)	161.5(2)	161.5(3)
Pd–X–S	—	118.2(9) (X = O(1A)	—	—	123.4(2) (X = O(1))	117.1(4) (X = N(4))
O–S–O	111.2(3)	111.8(3)[b]	—	—	113.0(3)	119.0(5)
	109.8(3)	109.9(7)[b]			110.9(3)	
	110.4(3)	110.4(7)[b]			111.6(3)	
		111(2)			107.7(3)	
		99(2)			108.1(2)	
		104.8(9)			105.2(3)	

[a] From ref. 9 which uses a different atomic numbering scheme translated here as N(2) = N(1), N(1) = N(1′), N(3) = N(1″), with N(4) being the sulfonamido nitrogen. [b] *S*-bound component in crystal.

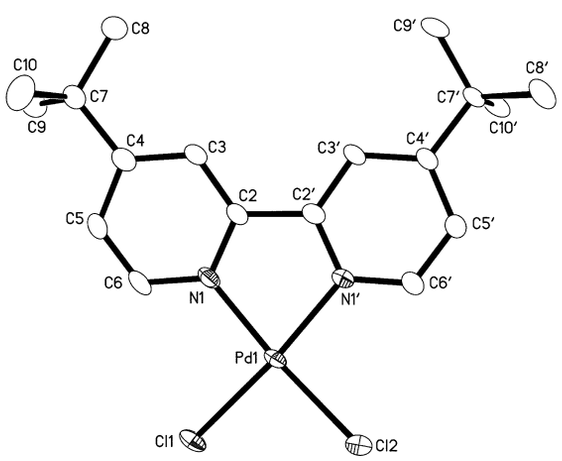


Fig. 4 Molecular structure of [$PdCl_2$(bipy*)] **3**. Selected bond distances and angles Pd1–N1 2.015(3), Pd1–N1′ 2.022(3), Pd1–Cl1 2.2763(9), Pd1–Cl2 2.2834(9) Å; N1–Pd1–N1′ 79.59(10), N1–Pd1–Cl1 95.36(8), N1′–Pd1–Cl1 174.56(7) N1–Pd1–Cl2 174.02(7) N1′–Pd1–Cl2 95.31(7), Cl1–Pd1–Cl2 89.84(3)°. Hydrogen atoms are omitted for clarity.

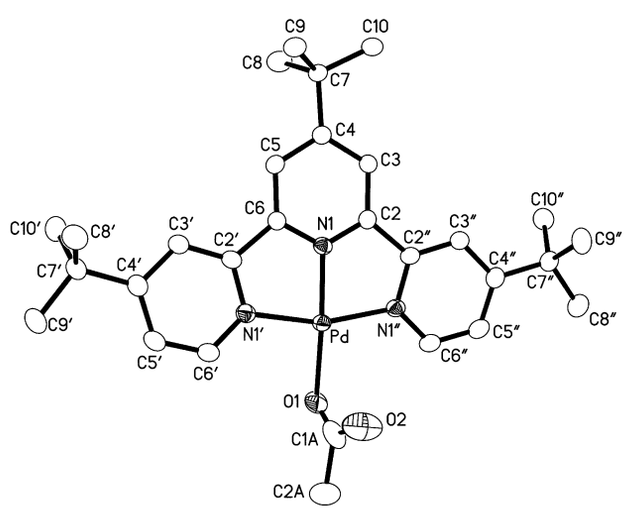
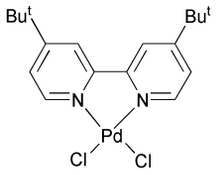


Fig. 5 Molecular structure of [Pd(OAc)(terpy*)]Cl **4**. Hydrogen atoms and the chloride counter anion are omitted for clarity.

is shown in Fig. 5 while selected bond distance and angle data appear in Table 1. When dissolved in dichloromethane crystallographically pure **4** gives rise to two sets of exchanging signals in its ^{1}H NMR spectrum. This feature appears to be due to facile exchange between [Pd(OAc)(terpy*)]Cl **4** and [PdCl(terpy*)]OAc resulting in a 1 : 1 mixture of these two species in solution.

Aerobic oxidation of [Pd(SO_3)(terpy*)] 1 to [Pd(SO_4)(terpy*)] 5

Because of the HSAB (Hard–Soft–Acid–Base) miss-matching of the sulfate ligand and palladium centre we were keen to explore the preparation of [Pd(SO_4)(terpy*)] **5** *via* aerobic



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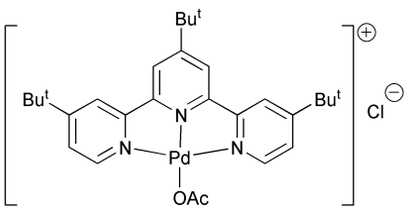

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oxidation. When d_5-$PhNO_2$ solutions of [Pd(SO_3)(terpy*)] were heated to 210 °C under an oxygen atmosphere ^{1}H NMR spectroscopy indicated smooth formation of a single new species. This species could be easily isolated and characterised crystallographically as the sulfate complex **5**. The preparation could also be obtained on a preparative scale, although in this case it was necessary to bubble oxygen gas through the refluxing solution. Attempts to carry out the transformation of [Pd(SO_3)-(terpy*)] **1** to [Pd(SO_4)(terpy*)] **5** aerobically in chlorobenzene at 135 °C led to only traces of the product being formed. The isolated [Pd(SO_4)(terpy*)] **5** complex shows a number of characteristic IR bands typical for S–O vibrational frequencies. Bands at 1259, 1134, 981 cm^{-1} were assigned to *ν*(S=O)*asym*, *δ*(S=O)*sym* and *ν*(S–O) stretches based on the limited literature precedent.[6] Two very strong peaks are observed at 1522 and 1345cm^{-1} in the sulfate complex **5** which are not present in the IR spectrum of the sulfite **1**. However, we cannot assign these peaks as there are few appropriate examples with fully assigned IR data. As the IR spectra did not allow unambiguous assignment of the bonding mode of the sulfate ligand an X-ray study was undertaken. The structure of **5** is shown in Fig. 6, while a

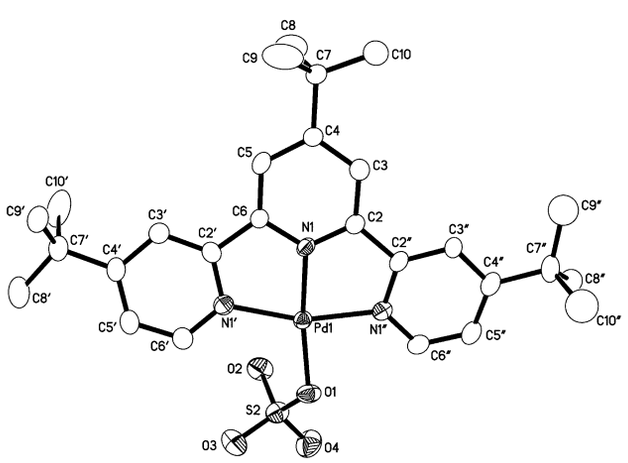
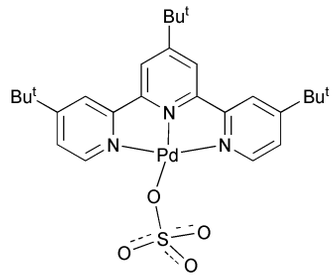


Fig. 6 Molecular structure of [Pd(SO_4)(terpy*)] **5**. Hydrogen atoms are omitted for clarity. Only the major component of a disordered Bu^t fragment is shown.

summary of the useful bond distance and angle data is given in Table 1. Based on inspection of the Cambridge Crystallographic Database,[12] no structures of palladium(II) sulfate complexes are available, only some solution species are known.[13] The sulfate in **5** adopts an η^1 bonding mode with an Pd–O distance of 2.001(4) Å and a Pd–O–S angle of 123.4(2)°. The structure of **5** is clearly closely related to that of Osborn's sulfonamido complex **6** which shows a Pd–N distance of 2.027(7) Å and a Pd–N–S angle of 117.1(4)°.[9] Aside from



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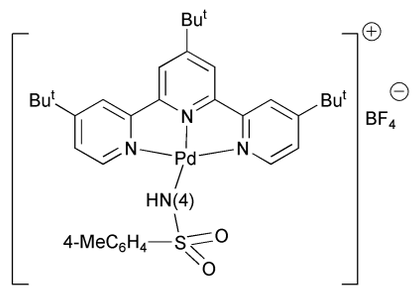

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this only a handful of η^1-SO_4 complexes of platinum have been reported.[14]

All other attempts to prepare complex **5** by alternative routes were unsuccessful. For example, no coordination of terpy* with $PdSO_4$ was observed even under forcing conditions. Ligand substitution reactions of [PdCl(terpy*)]Cl **2** with Li_2SO_4 or 2 M H_2SO_4 were unsuccessful. Use of more forcing conditions using concentrated H_2SO_4 with [PdCl(terpy*)]Cl **2** resulted in the protonation of terpy* and precipitation of palladium black, while reactions of [Pd(SO_3)(terpy*)] **1** with 30% H_2O_2 or chloride abstraction from **2** with $AgPF_6$ followed by addition of various sulfate sources both led to uncharacterisable materials.

Spectroscopic comparison of 1–6

The *ortho* protons of the bipy* and terpy* ligands give characteristic doublets in their ^{1}H NMR spectra in the range 10.01–8.71 ppm. The values for compounds **1**–**6** are summarised in Table 2. The nature of the anion bound to the metal centre clearly affects the metal's electronic demand on the terpy* ligand. This effect gives a clue to why the chloride species appears to be predominantly isolated during the course of these experiments. Using ^{1}H NMR spectroscopy the chloride anion can be seen to place a much lower electronic demand (effective inductive electron withdrawal from the terpy*) *via* the palladium centre, than the corresponding sulfite and sulfate. This strongly suggests that in solution the sulfite and sulfate groups are rather labile. The viability of such ionisation processes is further demonstrated by the chloride–acetate exchange demonstrated by [Pd(OAc)(terpy*)]Cl **4** in solution. The lability of the sulfite and sulfate ligands in **1**/**1a**/**3** leads to a higher frequency shift in the $H_{6',6''}$ protons of the terpy* ligand due to the greater contribution of the [Pd(terpy*)]$^{2+}$ cation. The lability of the sulfite and sulfate groups also leads to preferred isolation of [PdCl(terpy*)]Cl **2** under the majority of reaction conditions.

Conclusions

We have been able to demonstrate the sequential oxidation of sulfur dioxide to sulfate at a palladium centre *via* an intermediate *S*- or *O*-bound sulfite complex [Pd(SO_3)(terpy*)] **1**/**1a**. The oxidation of the latter only proceeds under forcing aerobic conditions and provides a rare example of a crystallographically characterised palladium η^1-sulfate complex, [Pd(SO_4)(terpy*)]

Table 2 Selected ^{1}H NMR data[a] for complexes **1**–**2** and **4**–**6**

δ (*J*/Hz)	[Pd(SO_3)(terpy*)] **1**	[PdCl(terpy*)]Cl **2**	[Pd(OAc)(terpy*)]Cl **4**[b]	[Pd(SO_4)(terpy*)] **5**	[Pd($NHSO_2Ar$)(terpy*)]BF_4 **6**[c]
$H_{6'/6''}$	10.01 (6.0)	8.76 (6.0)	8.71 (broad d)	9.27 (6.0)	8.14 (6.0)
$H_{3/5}$	7.97	9.04	8.68	8.14	8.28
$H_{3'/3''}$	7.93 (1.0)	9.01 (2.0)	8.54	8.09 (1.0)	8.28
$H_{5'/5''}$	7.62 (6.0, 1.0)	7.58 (6.0, 2.0)	7.88 (6.0, 2.0)	7.61 (6.0, 1.0)	7.54 (6.0, 2.0)

[a] In $CDCl_3$ at ambient temperature. [b] 1 : 1 mixture with **2**. [c] From ref. 9.

5. The nature of the bound ligand, X, in [PdX(terpy*)] complexes engenders dramatic shifts in the proton chemical shifts of the $H_{6',6''}$ terpyridyl protons when these are labile (SO_3^{2-} and SO_4^{2-}).

Experimental

General

THF was distilled from sodium benzophenone ketyl under an argon atmosphere, hexane was dried over Na wire, dichloromethane was distilled from CaH_2, petrol refers to the fraction boiling at 40–60 °C unless otherwise stated. Proton and ^{13}C NMR spectra were recorded on the Bruker AM400, AV400, DRX500, and JEOL GX270 machines at ambient as stated. IR spectra were recorded on a Perkin-Elmer FTIR 1600 spectrometer. Mass spectra were recorded using either FAB or ES ionisation mode on a VG micromass 70E or AIMS902 at the University of Nottingham, or by ES at the EPSRC service, University of Swansea. Mixtures of bipy* and terpy* were prepared by a literature method.[15] The mixture was absorbed onto silica gel and was heated in a Kugelrohr oven at 160 °C (0.3 mmHg) until all the bipy* had sublimed, leaving terpy* adsorbed onto the silica surface. The terpy* was recovered by dichloromethane extraction. The following compounds were prepared by literature methods: [$PdCl_2(MeCN)_2$],[16] [Pd($dba)_2$].[17]

Preparations

[Pd(SO_3)(terpy*)] 1/1a or [PdCl(terpy*)]Cl 2 initial method. Crystalline [$PdCl_2(MeCN)_2$] (250 mg; 0.96 mmol) was dissolved up into acetonitrile (15 ml) at room temperature and stirred vigorously for 10 min to give a bright orange solution. The reaction mixture was flushed with O_2 (50 ml min^{-1})–SO_2 (100 ml min^{-1}) bubbling directly into the solution. Solid terpy* (100 mg; 0.25 mmol) was added in one portion to give a suspension, after 10 min the ligand had fully dissolved. The remaining terpy* (233 mg; 0.58 mmol) was added and the reaction mixture was left stirring under O_2–SO_2 gas flow at room temperature. The gas flow was stopped after 2 h and the reaction mixture flushed with O_2 to remove SO_2 gas. Water (20 ml) and methanol (2 ml) were added to the reaction mixture and the yellow solution was left to stand (48 h). Five nominally identical repetitions led to the isolation of [Pd(SO_3)(terpy*)] **1/1a** (53–68%, as a trihydrate **1/1a** that could be recrystallised from $CDCl_3$ as **1**, runs 1–2); [PdCl(terpy*)]Cl **2** (95%, run 3–4); MeC(=O)NH_2 (formed continuously, >2 g isolated typically, run 5).

[Pd(SO_3)(terpy*)] 1 alternative method. Solid [Pd($dba)_2$] (143 mg; 0.25 mmol) (dba = dibenzylideneacetone) and terpy* (100 mg; 0.25 mmol) were dissolved in dry THF (5 ml) under an argon atmosphere. The resulting dark red solution was stirred at room temperature under a constant stream of SO_2 gas (80 ml min^{-1}) bubbling through the solution (2 h) after which the solution had turned yellow. A very pale green precipitate was filtered off yielding [Pd(SO_3)(terpy*)] **1** 40 mg (30%) with identical properties to that prepared above.

[PdCl(terpy*)]Cl 2 alternative methods. Solid [$PdCl_2$(Me$CN)_2$] (100 mg; 0.39 mmol) was suspended in dry THF (15 ml), followed by the addition of terpy* (155 mg; 0.39 mmol) in one portion. The reaction mixture was refluxed for (48 h) after which time TLC indicated only trace amounts of terpy*. The reaction mixture was allowed to cool to room temperature and an orange precipitate which formed was filtered off, dried under high vacuum to yield 197 mg (93%). Alternatively, $PdCl_2$ (220 mg; 1.12 mmol) in water (20 ml) was boiled with terpy* (500 mg; 1.2 mmol) for 3 h and the resulting brown precipitate purified by trituration with diethyl ether, then ethyl acetate to yield orange microcrystals (233 mg; 32%).

[Pd(SO_3)(terpy*)] 1/1a. Mp > 240 °C (dec., from aq. MeCN). Anal. Calc. for $C_{27}H_{35}N_3O_3PdS\cdot 3H_2O$: C, 50.5; H, 6.4; N, 6.5%. Found: C, 50.1; H, 6.1; N, 6.5%. δ_H (400 MHz, $CDCl_3$): 10.01 (d, 2 H, *J* = 6.0, $H_{6'/6''}$); 7.97 (s, 2 H, $H_{3/5}$); 7.93 (d, 2 H, *J* = 1.0, $H_{3'/3''}$); 7.62 (dd, 2 H, *J* = 6.0, 1.0, $H_{5'/5''}$); 1.55 (s, 9 H, Bu^t); 1.42 (s, 18 H, Bu^t). δ_c (67.80 MHz, $CDCl_3$): 167.0, 165.0, 155.6, 155.1, 152.6, 125.0, 119.5, 118.7, 36.2 (Bu^t), 35.7 (Bu^t), 30.7 (Bu^t), 30.3 (Bu^t). ν_{max} (KBr disc)/cm^{-1} 3488s (included H_2O), 3049m, 2960s (C–H), 2870m, 2360s, 2342, 1612s, x1560w (C=C), 1542w, 1475m (C=C), 1426m, 1365w, 1260m ν(S=O)$_{asym}$, 1133s δ(S=O) $_{sym}$, 1100s δ(S=O)$_{sym}$, 983s (S–O), 898.2m ν (S–O), 858w, 743w, 668m, 638s, 612m. MS: *m*/*z* (ES+) 588 (M^+, 20%); 610 (MNa^+, 100%) [Found (HRMS): MNa^+ 610.1344, $C_{27}H_{35}NaSPdN_3O_3$ requires 610.1332].

[PdCl(terpy*)]Cl 2. Mp > 240 °C (dec., from $CDCl_3$). Anal. Calc. for $C_{27}H_{35}N_3Cl_2Pd\cdot 2.5CDCl_3$: C, 40.6; H, 4.1; N, 4.9%. Found: C, 40.9; H, 4.4; N, 4.6%. δ_H (400 MHz, $CDCl_3$); 9.04 (s, 2 H, $H_{3/5}$); 9.01 (d, 2 H, *J* = 2.0, $H_{3'/3''}$); 8.76 (d, 2 H, *J* = 6.0, $H_{6'/6''}$); 7.58 (dd, 2 H, *J* = 6.0, 2.0, $H_{5'/5''}$); 1.63 (s, 9 H; Bu^t); 1.53 (s, 18 H; Bu^t). δ_c (67.8 MHz, $CDCl_3$) 170.0, 168.3, 158.0, 154.5, 152.0, 124.5, 123.9, 123.0, 37.7 (Bu^t), 36.5 (Bu^t), 30.8 (Bu^t), 30.4 (Bu^t). ν_{max} (KBr disc)/cm^{-1} 3422m (included water), 2965s (C–H), 1614s, 1561m (C=C), 1469m (C=C), 1413m, 1368w, 1261m, 1178w, 1022w, 920w, 872m, 735w, 608w. MS: *m*/*z* (ES+) 542 (M^+, 100%).

Acetamide, MeC(=O)NH_2. Acetamide was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. The crystals that separated from the aqueous acetonitrile–methanol mixture showed the following data: rhombohedral form space group *R*3*c*; *a* 11.526, *c* 13.589 Å (CCDC code: ACEMIDO1).

[$PdCl_2$(bipy*)] 3. Palladium dichloride (220 mg, 1.12 mmol) in water (20 ml) was boiled with bipy* (300 mg, 1.12 mmol). After heating for 30 min further portions of water (5 ml) and ethanol (2.5 ml) were added to improve solubility. The reaction was left to reflux for 50 h, yielding the crude product as a black crude suspension. The crude solid was stirred vigorously in dichloromethane for 1 h resulting in a yellow solution and fine black precipitate (Pd^0). The precipitated metal was filtered off through Celite, and the filtrate was removed under reduced pressure to yield a yellow solid. The solid was taken up in the minimum volume of dichloromethane and recrystallisation was achieved by addition of hexane and cooling in the freezer to yield fine orange needles (332 mg; 67%). Mp >193 °C (dec.). Anal. Calc. for $C_{27}H_{35}N_3Cl_2Pd$: C, 48.5; H, 5.3; N, 6.3%. Found: C, 48.00; H, 5.3; N, 6.3%. δ_H (400 MHz, $CDCl_3$): 9.30 (d, 2 H, *J* = 6.0, $H_{6/6'}$); 7.89 (d, 2 H, *J* = 2.0, $H_{3/3'}$); 7.52 (dd, 2 H,

J = 6.0, 2.0, $H_{5/5'}$); 1.46 (s, 18 H; Bu^t). δ_c (67.8 MHz, $CDCl_3$) 165.1, 156.1, 150.4, 123.9, 119.3, 35.8 (Bu^t), 30.3 (Bu^t). ν_{max} (KBr disc)/cm^{-1} 3434s, 2973s (C–H), 1614s, 1543w, 1472m (C=C), 1414m, 1251m, 1092w, 902w, 882w, 853s. MS: *m*/*z* (ES+) 432 ($M^+ - Cl + MeCN$, 100%).

[Pd(OAc)(terpy*)]Cl 4. Palladium acetate (100 mg; 0.45 mmol) was added in one portion to acetonitrile (3 ml) under nitrogen supply at 20 °C and was stirred for 5 min, followed by addition of terpy* (180 mg; 0.45 mmol). The reaction mixture was heated to reflux for 10 min, after which time not all the terpy* had dissolved, the reaction mixture was allowed to cool and dichloromethane (3 ml) was added. The terpy* dissolved immediately and the reaction was allowed to stir at 20 °C for 15 h. The crude reaction mixture was filtered through a small plug of Celite, washing with dichloromethane (2 x 10 ml). The organic washings were reduced under vacuum to give an orange coloured solid. The solid was taken up in dichloromethane (1 ml) and was layered with hexane (3 ml). Upon standing pale yellow crystals formed which were filtered and dried under high vacuum to yield **4** (75 mg; 30%). Mp >230 °C (dec., from CH_2Cl_2). δ_H (400 MHz, DMSO, 298 K) 8.78 (br s, 4H; OAc + Cl); 8.72 (br s, 2H; Cl); 8.69 (br s, 2H; Cl); 8.56 (d, 2H, J_{HH} = 6.0 Hz; OAc); 8.13 (d, 2H, J_{HH} = 6.0 Hz, OAc); 7.85 (d, 2H, J_{HH} = 6.0 Hz; OAc) *overlapped by* 7.85 (br s, 2H; Cl); 2.03 (s, 3H; CH_3CO_2); 1.54 (s, 9H; Bu^t); 1.45 (s, 18H; Bu^t); δ_H (400 MHz, DMSO, 373 K) 8.71 (*apparent* d, 2H, J = 2.0); 8.68 (br s, 2H); 8.54 (br s, 2H); 7.88 (dd, 2H, J = 6.0, 2.0, $H_{5'/5''}$); 1.84 (br s, 3H; CH_3CO_2); 1.57 (s, 9H; Bu^t); 1.47 (s, 18H; Bu^t). δ_c (100 MHz, DMSO, 373 K) 167.5, 166.7, 157.7, 154.1, 151.1, 124.7, 122.6, 121.4, 36.7 (^{t}Bu), 35.7 (^{t}Bu), 29.9 (^{t}Bu), 29.5 (^{t}Bu). ν(solid state)/ cm^{-1} 2958w; 1613vs (C–O), 1556w; 1480s, 1425m, 1401m, 1367s, 1326s, 1300w, 1264s, 1023m, 916s, 856m. MS: *m*/*z* (ES+) 544 (terpy*PdCl^{37}, 100%); 542 (terpy*PdCl^{35}, 100%); 507 (terpy*Pd, 70%) [Found (HRMS): ($M^+ - Cl$) 566.2005, $C_{29}H_{38}N_3O_2Pd$ requires 566.1999].

[Pd(SO$_4$)(terpy*)] 5. A d^5-nitrobenzene solution (2.5 ml) of [Pd(SO_3)(terpy*)] **1** (50 mg; 0.085 mmol) was heated to 100 °C in for 3 h under a constant stream of oxygen. Proton NMR spectroscopy of the reaction mixture showed the formation of new signals atributed to **5** as well as those of **1**. The reaction mixture was left heating for a further 10 h under O_2 at 210 °C after which time ^{1}H NMR spectroscopy indicated **5** was the major product but traces of **1** remained. The new species **5** was isolated by removing all the d^5-nitrobenzene solvent and liquid/liquid diffusion (dichloromethane–hexane) to yield large orange shaped wedges and small yellow crystals (**1**). X-Ray characterisation of the orange crystals showed formation of the desired sulfate species. Repetition of the experiment but with O_2 bubbling directly through the $PhNO_2$ solution lead to clean formation of **5** (93% isolated yield) after 12 h. Lower boiling solvents were ineffective. Mp >240 °C (dec., from CH_2Cl_2–hexane). δ_H (400 MHz, $CDCl_3$): 9.27 (d, 2 H, J = 6.0, $H_{6'/6''}$); 8.14 (s, 2 H, $H_{3/5}$); 8.09 (d, 2 H, J = 1.0, $H_{3'/3''}$); 7.61 (dd, 2 H, J = 6.0, 1.0, $H_{5'/5''}$); 1.60 (s, 9 H; Bu^t); 1.44 (s, 18 H; Bu^t). δ_c (67.8 MHz, $CDCl_3$); 169.2, 167.9, 158.3, 154.1, 134.6, 129.3, 123.5, 122.6, 37.7 (Bu^t), 36.4 (Bu^t), 30.6 (Bu^t), 30.3 (Bu^t). ν_{max} (KBr disc)/ cm^{-1} 3422s, 2961s (C–H), 2360s, 2342s, 1612s, 1560w (C=C), 1522vs, 1474m (C=C), 1425w, 1367w, 1345vs, 1259m $\nu(S{=}O)_{asym}$, 1134 $\delta(S{=}O)_{sym}$, 1020w, 981vs (S–O), 850w, 797w, 712m, 680w, 668w, 638m, 609w. MS: *m*/*z* (ES+) 628 (MNa^+, 2%); 542 (Pd(MeCN)(terpy*), 40%); 524 (NaPd(terpy*), 100%) [Found (HRMS): ($M^+ - SO_4$) 507.1864, $C_{27}H_{35}N_3Pd$ requires 507.1866].

X-Ray crystallography

Crystals of **1**/**1a** were grown from aqueous MeCN solutions saturated with SO_2–O_2 (Daresbury) or from $CDCl_3$ solutions (**1**, Nottingham); **2** and **3** were grown from $CDCl_3$ solutions, **4** and **5** were grown by CH_2Cl_2–hexane solutions.

All crystals were mounted in a perfluoropolyether oil film mounted on a dual stage fibre and flash frozen to 150 K using an Oxford Cryosystem open-flow nitrogen cryostat.[18] The trihydrate morphology of compound **1a** was collected on Station 9.8[19] at the Daresbury Synchrotron Radiation Source, using a Bruker SMART CCD area detector diffractometer and silicon monochromated radiation (λ = 0.6890 Å). Data for all other compounds were collected on a SMART1000 CCD area detector diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). SAINT v6.01 (v6.02a for compound **4**)[20] was used to integrate the data and apply the Lorentz and polarisation corrections. Crystal data and details of the data collection and refinement are given in Table 3. The data were corrected for absorption using semi-empirical methods[21] for all structures (including that of compound **1a** where SADABS was also used to apply a beam decay correction) except for **4** where numerical methods were used.[22]

The structures were solved by direct methods using SHELXS-97[23] for all structures except **1** where SIR92[24] was used. The structures were refined on F^2 using full-matrix least squares (SHELXL-97). Unless otherwise stated, all fully occupied non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were placed in geometrically calculated positions except those of the water molecules in compounds **1a** and **2** and those of the MeCN in compound **4** which were located by difference Fourier synthesis. Geometrically placed hydrogen atoms were refined as part of a riding model with the hydrogen atoms assigned isotropic adps 1.2 times the parent atom U_{eq}, except for the methyl hydrogen atoms where it was 1.5 times, the water hydrogen atoms were refined with restraints and the MeCN hydrogen atoms were refined as a rigid rotating group. Suitable geometric restraints were applied to all disorder models. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 25.

In compound **1** 4.5 molecules of $CHCl_3$ per asymmetric unit were incorporated in the structure, one of which was modelled with the three Cl atoms each over three sites with occupancies 0.5:0.3:0.2. One Bu^t group also showed disorder and was modelled over two sites with occupancies 0.6:0.4. In compound **1a** the SO_3 is disordered with 75% *S*-bound to the palladium and 25% *O*-bound to the palladium.

Dichloromethane is included at three sites in compound **2**, one site fully occupied, one site modelled as half occupied and a third as a quarter occupied, with one Cl atom modelled over two sites with occupancies 0.15 and 0.10, the latter refined with an isotropic adp.

A molecule of CH_2Cl_2 incorporated in the structure of compound **5** showed disorder and was modelled with the two Cl atoms over two sites with occupancies 0.60 and 0.40. The three methyl C atoms of one tBu group were also modelled over two sites with occupancies 0.55 and 0.45. The Flack parameter (0.00(4)) for complex **5** (space group $P2_12_12_1$) establishes that the correct axial directions have been chosen.

CCDC reference numbers 186002 (**1**), 186163 (**1**/**1a**), 186001 (**2**), 186003 (**3**), 186000 (**4**) and 186004 (**5**).

See http://www.rsc.org/suppdata/dt/b2/b205548a/ for crystallographic data in CIF or other electronic format.

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Table 3 Crystallographic data, details of data collection and refinement for **1–5**

	[Pd(SO$_3$)(terpy*)] **1**	[Pd(SO$_3$)(terpy*)] **1a**	[PdCl(terpy*)]Cl **2**	[PdCl$_2$(bipy*)] **3**	[Pd(OAc)(terpy*)]Cl **4**	[Pd(SO$_4$)(terpy*)] **5**
Molecular formula	$C_{31.5}H_{39.5}Cl_{13.5}N_3O_3PdS$	$C_{27}H_{39}N_3O_6PdS$	$C_{28.75}H_{40.5}Cl_{5.5}N_3OPd$	$C_{18}H_{24}Cl_2N_2Pd$	$C_{31}H_{41}ClN_4O_2Pd$	$C_{29}H_{39}Cl_4N_3O_4PdS$
M	1125.20	640.07	745.52	445.69	643.53	773.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group (standard setting)	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$ ($P2_1/c$)	$P2_12_12_1$
a/Å	11.2719(10)	13.790(5)	15.9261(13)	7.3555(9)	11.0537(9)	10.1352(5)
b/Å	20.494(2)	19.148(6)	13.1424(11)	19.140(2)	22.089(2)	13.5105(6)
c/Å	20.230(2)	10.992(4)	17.6773(14)	12.969(2)	12.7592(11)	24.505(1)
β/°	96.222(2)	95.117(8)	112.388(2)	96.666(2)	100.132(1)	—
V/Å^3	4646(1)	2891(2)	3421.1(8)	1813.5(7)	3066.8(8)	33355.5(5)
Z	4	4	4	4	4	4
Absorption coefficient/mm^{-1}	1.26	0.76	1.00	1.32	0.73	0.97
Crystal size/mm	0.43 × 0.14 × 0.12	0.44 × 0.02 × 0.02	0.40 × 0.27 × 0.24	0.50 × 0.12 × 0.11	0.30 × 0.28 × 0.12	0.32 × 0.10 × 0.07
T/K	150	150	150	150	150	150
Reflections collected	42063	14916	18584	11373	26915	21680
Independent reflections (R_{int})	11484 (0.043)	5445 (0.055)	8213 (0.025)	4323 (0.043)	7342 (0.032)	7773 (0.037)
Data/parameters	11178/497	5445/386	7861/390	4193/208	7156/354	7743/364
wR_2 (obs. and all data)	0.184 and 0.208	0.0709 and 0.1563	0.112 and 0.117	0.1082 and 0.1129	0.0639 and 0.0681	0.131 and 0.139
R_1 (obs. and all data)	0.0663 and 0.1123	0.0593 and 0.1490	0.0390 and 0.0467	0.0427 and 0.0513	0.0278 and 0.0358	0.0536 and 0.0643

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