Platinum-mediated monohydration of SO₂

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The monohydration of SO₂ has been achieved in solution mediated by a platinum-aquo complex. Benzamidate ligands play a key role along the process, acting as versatile proton shuttles. Finally, the platinum center allows the stabilization of benzimidic acid and a hydrogensulphite anion, the disfavored tautomers of benzamide and sulphonate, respectively.

Hydration of SO₂ is a reaction that has long attracted considerable attention and whose study, at the experimental and theoretical level, has been subject of increasing interest in recent years.^{1,2,3} Although sulphur dioxide is substantially soluble in water,⁴ the SO₂ molecule itself does not react with water but forms hydrated sulphur dioxide adducts.^{3,5} The interaction between the two molecules is mainly established between the lone pair orbital of the electron donor (H₂O) and the empty π* orbital of the acceptor (SO₂) so that the dative bond is perpendicular to the SO₂ plane.^{6,7}

In the gas phase, the SO₂ molecule has the tendency to be surrounded by more than one water molecule, forming hydrated gaseous adducts SO₂·(H₂O)_n (*n* = 1-3) whose structures have been studied by microwave and infrared spectroscopy.^{8,9,10} The structures and relative energies of SO₂·(H₂O)_n (*n* = 1-6) clusters have also been studied by quantum chemical calculations.^{11,12} The reaction shown in scheme 1, eq 1 has been theoretically studied and the results reported show that the participation of several water molecules reduces the reaction barrier of the hydrolysis of SO₂, although the resulting H₂SO₃·(OH₂)_{n-1} (*n*=1-5) adducts are thermodynamically unstable with regard to SO₂·(OH₂)_n ones.^{11,12,13,14,15,16}

In aqueous media, sulphur dioxide solutions own acidic character. They mainly contain solvated SO₂, but also minor concentrations of sulphurous acid (H₂SO_{3(aq)}) and of anions as hydrogensulphite (SO₃H⁻), its tautomer sulphonate (HSO₃⁻), and sulphite (SO₃²⁻) (scheme 1, eqs 2-4).^{1,14,15} However, it has not been possible to isolate and characterize sulphurous acid in aqueous solution because under standard conditions the H₂SO₃ molecule is also thermodynamically unstable with regard to the dissociation products SO₂ and H₂O.

Scheme 1. Selected reactions describing the behaviour of sulphur dioxide towards water under different conditions.

In this manuscript we wish to communicate the reaction between an anionic aqua-platinum(II) complex with sulphur

dioxide, which proceeds via a formal insertion of the latter molecule into the Pt-O bond.

We have prepared the platinum(II) aquo-complex **1** (scheme 2) by using convenient, high-yield procedures (†ESI). As established by X-ray diffraction methods (figure 1), the H₂O ligand in this complex is σ-coordinated to Pt and forms two strong hydrogen bonds to the neighbouring benzamidate ligands, with average hydrogen bond C=O...H-O distances of 1.82(2) Å. Concomitantly, the C-N and C-O interatomic distances are in-between the usual values for single and double bonds, evidencing π-delocalization along the N-C-O peptidic bond (tables S1 and S2).

Scheme 2. Synthesis of [NBu₄][*trans*-Pt(HNCOPh)₂Cl(OH₂)] (**1**).

This bonding pattern is highly interesting and results in the H₂O molecule being tightly bound in the metal coordination sphere. The strength of the involved hydrogen-bonds has been estimated in 14.2 kcal/mol each by DFT calculations (figures S8, S9 and table S3). In keeping with this estimate, the H₂O molecule in **1** is not readily replaced by other neutral ligands as pyridine. Nevertheless, rapid H/D exchange takes place at room temperature with external D₂O, as established by NMR spectroscopy.

Figure 1. Thermal ellipsoid of the complex anion found in the crystal lattice of **1**. Selected bond lengths (Å) and angles (°): Pt-N1 2.0098(16), Pt-N2 2.0061(16), Pt-O3 2.0424(14), Pt-Cl 2.2859(5), O1-H1O 0.81(2), O1-H2O 0.84(2), O1...H2O 1.81(2), O2...H1O 1.83(2), O3-H1O 0.81(2), O3-H2O 0.84(2), N1-Pt-N2 178.48, N1-Pt-O3 90.61, N1-Pt-N2 178.46(6), N2-Pt-O 89.66(6) N1-Pt-Cl 89.00(5), N2-Pt-Cl 90.73(5), Cl-Pt-O3 179.46(6).

Compound **1** reacts with SO₂ at low temperature affording complex **2** (scheme 3), which forms as the result of SO₂ insertion into the Pt-OH₂ bond keeping a strictly one-to-one

ratio between the SO₂ and the OH₂ molecules, in a reaction mediated by the platinum bis-benzamidate moiety.

Scheme 3. Synthesis of [NBu₄][*trans*-Pt(HNC(OH)Ph)₂Cl(SO₃)] (**2**).

The X-ray diffraction structure of complex **2** reveals a number of interesting features. Most notably, **2** can be described as the result of the full splitting of the water molecule coordinated to platinum in **1**. Thus two coordinated benzimidic acid units are formed via proton transfer, whereas the coordinated SO₂ formally adds the remaining oxide to render a sulphite ligand, which is also stabilized by a hydrogen bonding with the acid proton of one of the N-donor ligands. The C-N and C-O bonds distances in the latter are intermediate between single and double bonds, in agreement with a π -electron density delocalization along the N-C-O bond system, although less marked than in **1** (tables S1 and S2). The S-coordinated sulphite anion shows three different S-O bond distances. Thus the terminal S-O bonds are between 1.46 and 1.49 Å, whereas the S-O bond taking part in the hydrogen bond is slightly longer (1.5113(13) Å). The halfway hydrogen atom placed between two oxygens of the S- and N2- ligands lowers their anionic character and affords an ambivalent description, as a sulphite-benzimidic acid and also as a hydrogensulphite-benzamidate system. Remarkably both the benzimidic acid and the hydrogensulphite anion are disfavoured tautomers with regard to benzamide and sulphonate respectively. The O2...O3 distance (2.444(2) Å) is

Figure 2. Thermal ellipsoid of the complex anion found in the crystal lattice of **2**. Selected bond lengths (Å) and angles (°): Pt-N1 2.0249(15), Pt-N2 2.0352(16), Pt-S 2.2441(4), Pt-Cl 2.4064(4), S-O3 1.5113(13), S-O4 1.4659(14), S-O5 1.4825(14), O1-H1O 0.86(3), O2...H2O 1.10(4), O3...H2O 1.35(4), N1-Pt-N2 177.79(6), N1-Pt-S 85.00(5), N2-Pt-S 95.40(5), N2-Pt-Cl 84.13(5), S-Pt-Cl 176.91(2), O3-S-O4 109.82(8), O4-S-O5 111.47(9), O3-S-O5 107.50(8).

one of the shortest distances found in such kind of structural situation, comparable to that found in the solvated protons H₅O₂⁺ [2.419 Å] or H₇O₃⁺ [2.439 Å] trapped in crown ether molecules.^{17,18} It is worth noting that the hydrogen atoms have been found in the electron density map and the O...H2O distances have been freely refined. Both distances are long to be considered ordinary O-H bonds, but lay in the shortest end of the range of O...H hydrogen-bonding distances (1.1 - 2.3 Å and above).¹⁹ Besides the structure shows two additional hydrogen-bond interactions (H1N...O5 = 1.97(3) and H1O...Cl 2.10(3) Å) that contribute to the overall stability of the molecule.

Structural characterization in solid state of the hydrogensulphite anion is unusual. Indeed, even if it is the dominating monoanion in aqueous sulphite solutions,^{20,21} it has never been isolated in a solid salt since, on attempts to crystallize its salts from aqueous solutions, it undergoes the condensation reaction resulting in the disulphite anion (scheme 1, eq 5). In contrast to this, its tautomer sulphonate, [HSO₃]⁻, which presents a S-H bond, has been isolated and characterized as rubidium and caesium salts.^{21,22} Interestingly, complexes containing the hydrogensulphite ligand have been postulated or described in the literature but they are less frequent than those with alkyl-sulphite ligands.^{23,24,25,26,27} Focusing on metallic compounds, for example, hydrogensulphite-metal complexes have been postulated (but not observed) in the reactions of complexes [Pt(Ph₂PCH=CHPh₂)(CH₂CN)(OH)] and [Pt(Ph₂PCH=CHPh₂)(CF₃)(OH)] with SO₂,²⁶ and observed in

Scheme 4. DFT calculated mechanism for the reaction of **1** and SO_2 , in dichlorometane solution (abridged version). The numbers indicate relative H and G values in kcal/mol.

the reaction of $[\text{Pd}(\text{bipy})(\text{C}_6\text{F}_5)(\text{OH})]$ with SO_2 in tetrahydrofuran, in which solely IR characterization is included.²³ Structural data are available for the ruthenium complexes $[\text{Ru}(\text{C}_5\text{Me}_5)(\text{CO})_2(\text{SO}_2\text{OH})]$ ²⁴ and $[\text{Ru}(\text{bipy})_2(\text{py})(\text{SO}_2\text{OH})]$,²⁵ but only the former has been obtained by a reaction with SO_2 . Metal-sulphite compounds are more frequent in the literature.

Exploring the PES of complex **2** in solution by DFT methods suggest a very rich dynamic behaviour. Several minima of comparable stability have been found, mainly differing in the orientation of the benzimidic acid ligands (figure S15). Two of them (**2A-DFT** and **2B-DFT**) are virtually isoenergetic. According to the calculations, the structure closely related to **2** (**2A-DFT**) shows a mobile hydrogen atom connecting the S-donor and one of the N donor ligands, via an $\text{O}\cdots\text{H}\cdots\text{O}$ system, which requires less than 2 Kcal/mol to bounce from one O atom to the other (figure S14). Complementarily, the AIM analysis performed on **2A-DFT** supports the existence of several hydrogen bonds stabilizing the structure, consistent with the structural data obtained (figures S12, S13, and table S3).

In agreement with the presence of the hydrogensulphite ligand, the IR spectrum shows a broad signal of medium intensity at 1012 cm^{-1} . Besides, signals at 1636 and 1575 cm^{-1} corresponding to the delocalized N-C-O bond system are observed (figure S2). Interestingly, the ^1H NMR spectrum of **2** in CD_2Cl_2 shows fast fluxional behaviour, even at 173 K . At 233 K two broad signals of similar intensities at 15.08 and 8.17 ppm are observed, that can be assigned to the H-O and the H-N respectively. A typical set of signals attributable to two equivalent (in the NMR timescale) phenyl rings (figures S5-S7) is also observed. These data strongly suggest fast dynamic exchange processes that involve rotation of the benzimidic acid ligands, whereby hydrogen-bonds are broken and formed in **2**. The calculated energy barriers for these processes are below 7 kcal/mol (figure S15), in good agreement with the spectroscopic observations.

The formation of the hydrogensulphite derivative **2** has been modelled by DFT calculations (scheme 4; for a complete profile, see figure S16). Starting material **1A-DFT** presents several nucleophilic spots, which are likely to interact with the acidic S atom of sulphur dioxide. The most favoured adduct is the one showing a Pt-S interaction. Nevertheless the energy difference among the different possible adducts is small, which

suggests that adduct formation is a dynamic reversible process. The key step of the reaction is the SO_2 insertion into the Pt-O bond via **TS1-DFT**, which presents a free energy barrier of 24.8 Kcal/mol. This process gives rise to an intermediate that can be regarded as the result of the interaction of a sulphurous acid molecule with an unsaturated 14-valence electron platinum (II) fragment. Finally, one of the benzamidate ligands abstracts a proton, giving rise to the final product **2A-DFT**. This study provides a detailed picture of the reaction and highlights the influential participation of the benzamidate ligands in the whole process, as they act as intramolecular proton-transfer agents and finally stabilize the resulting product.

In summary, the H_2O molecule in the Pt(II) aquo-complex **1** is caged in an ambiphilic cavity made by an acidic center (the metal) and two basic sites (the benzamidate ligands). This platinum complex is able to capture one SO_2 molecule, promoting its controlled monohydration that eventually affords the hydrogensulphite metal compound **2**. All along this process the benzamidate ligands behave not as spectator ligands but play a key role acting as versatile and efficient proton shuttles where required.

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