Sulfur dioxide gas detection by reversible η^1-SO_2–Pt bond formation as a novel application for periphery functionalised metallo-dendrimers‡

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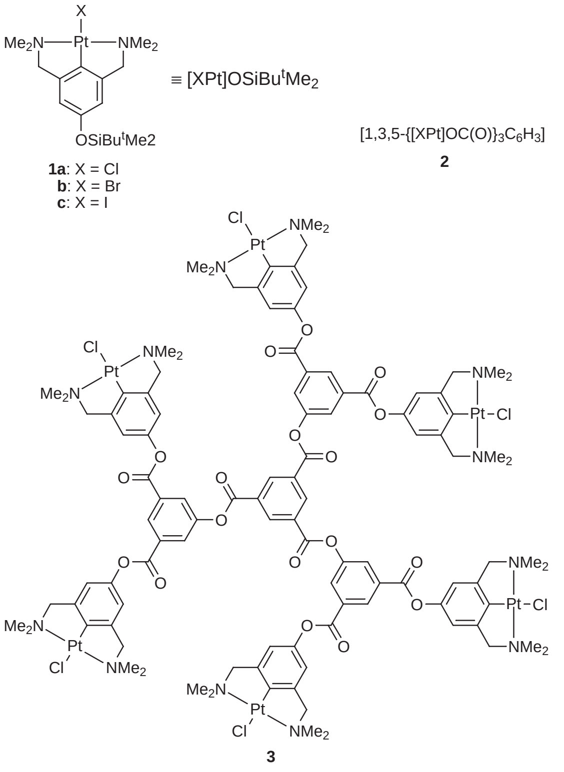
Multimetallics such as dendrimer 3 which are functionalised at their periphery with platinum(II) metal centres reversibly absorb SO_2 to yield macromolecules with significantly enhanced solubility characteristics and drastic colour changes; properties which make these compounds highly active sensors for milligram quantities of toxic SO_2 gas.

Since the first reports of synthetic dendrimers in the late 1970s, these compounds have been of widespread interest.[1] Several applications for this type of macromolecule have been realised owing to their unique properties, *e.g.* homogeneous catalysis,[2] as receptors for bioactive molecules[3] or in photophysical applications.[4] Herein we report the first example of transition-metal modified dendrimers which reversibly bind SO_2 and therefore have potential for use as molecular sensors for this toxic gas.

Platinum(II) complexes of type **1** (Scheme 1) have been shown to be suitable precursors for the synthesis of multimetallic systems. Using the methodology developed by Miller *et al.*[5] trimetallic compound **2** and dendrimer **3** containing platinum(II) functional units have been prepared from **1** (Scheme 1).[6,7] The characterisation of these materials, however, is hampered by their low solubility properties. In contrast to their carbosilane analogues,[2] dendrimers which contain aryl-ester core units have been calculated to be planar molecules.[6] This molecular geometry may be the reason for the low solubility of **2** and **3** in common organic solvents. From earlier experiments however, it has been shown that mononuclear platinum and nickel complexes containing the terdentate monoanionic diaminoaryl ligand [NCN$^-$ = {C_6H_2-$(CH_2NMe_2)_2$-2,6-R-4}$^-$] reversibly bind SO_2[8–10] and coordination of this ligand is known to greatly increase the solubility of the resulting five-coordinate platinum(II) compounds.[11] All these SO_2 adducts possess a generalised square pyramidal geometry around the metal centre.[12] A crystal structure determination of the SO_2 adduct of **1c** (**4**; Fig. 1) confirms that SO_2 is bound to Pt in a η^1-binding mode through sulfur and is positioned at the apex of a distorted square-pyramid, which best describes the geometry around the metal centre.§ No disorder arising from interactions with iodide have been found. It is noteworthy that in earlier studies,[13] SO_2 has been found to be bound to iodide, which is competitive to platinum in size and electronegativity.



Scheme 1 Mono- and multi-metallic platinum(II) complexes containing aryldiamine ligands

Thus, we have studied the effect of the presence of SO_2 on dendrimers which are functionalised with square planar platinum(II) metal centres. Compounds **2** and **3** react instantaneously when exposed to SO_2 (g) to form the corresponding SO_2 adducts **5** and **6**,¶ respectively (Scheme 2), both in the solid state and in solution (*e.g.* $CHCl_3$, toluene; max. solubility of **6** in $CHCl_3$: 2.5 mass%). Adduct formation is suggested by ^1H NMR spectroscopy, since the resonance signals of protons in close proximity to Pt undergo a characteristic down field shift [0.23 ppm for the CH_2N methylene protons and 0.16 ppm for the $N(CH_3)_2$ groups].[8] Owing to the change of the coordination number around the metal centre, the electronic spectrum shows two new absorption bands at *ca.* 350 and 400 nm (CH_2Cl_2 solution). The exact wavelengths of these bands depend on the metal-bound halogen atom, but are not significantly changed by different substituents on the aryl ring of the NCN ligand.[14] The band at higher frequency is quite strong with absorption coefficients > 20 000 dm^3 mol^{-1} cm^{-1}. In an atmosphere of SO_2, adduct formation of these new materials occurs quantita-

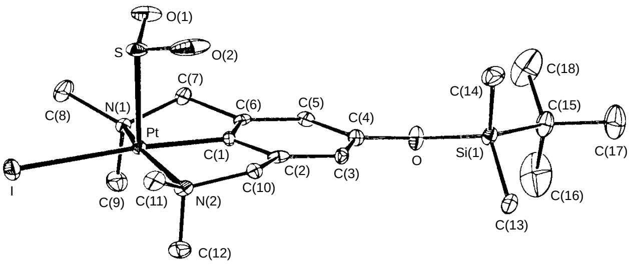
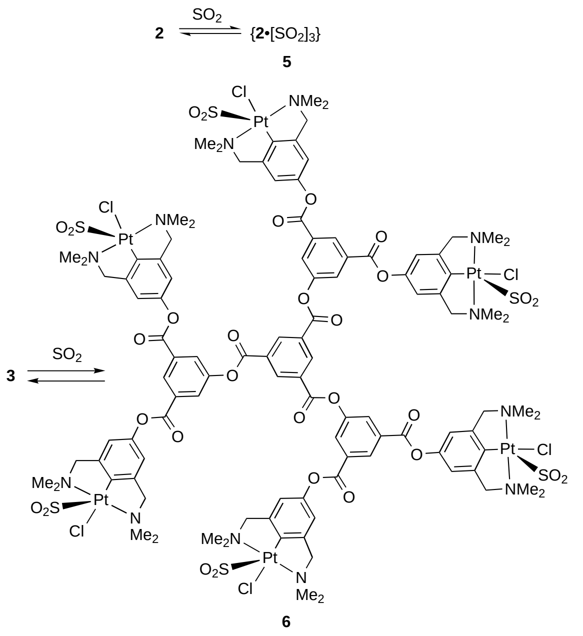


Fig. 1 ORTEP plot (50% probability level) of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°), Pt–I 2.7175(7), Pt–N(1) 2.112(4), Pt–N(2) 2.113(5), Pt–C(1) 1.946(6), Pt–S 2.4792(15), S–O(1) 1.443(4), S–O(2) 1.433(6); I–Pt–S 94.14(4), C(1)–Pt–S 91.44(18).



Scheme 2 Formation of the SO_2 adducts **5** and **6** from the corresponding multimetallic precursors upon addition of sulfur dioxide

tively both when the compounds are in the solid state or in solution. The reaction process can be followed visually and/or by UV–VIS spectroscopy, as a characteristic change from colourless to bright orange is noted. Traces of SO_2 are sufficient to observe this change. For example, with a CH_2Cl_2 solution of **2** which is exposed to SO_2, concentrations as low as 10 mg dm^{-3} (at a platinum/SO_2 molar ratio of 0.2) can be detected using UV–VIS spectroscopy. Similarly, when the atmosphere contains SO_2 (3 ± 0.5%), coating of a filter paper with **2** by 10 nmol mm^{-2} is already sufficient to detect a significant colour change. Obviously, higher sensitivity towards SO_2 can be achieved by increasing the concentration of the adsorbed dendrimer.‖

Desorption of SO_2 from adducts **5** and **6** can be achieved by a number of mild procedures, such as heating to 40 °C for several minutes or reducing the pressure to *ca.* 2.7 kPa (20 mm Hg). Both methods quantitatively regenerate **2** or **3**, respectively. Repetitive adsorption/desorption cycles have been performed without significant loss of material or activity.

In contrast to monomeric analogues or dendrimers containing flexible cores (*e.g.* carbosilanes or aminoalkanes), the organometallic trimer and dendrimer presented here possess a rigid disc-like molecular structure and therefore are probably better candidates for recovery *via* ultrafiltration technology.[15,**] Owing to the electronic characteristics of the NCN–metal unit,[16] the Pt–C bond in monomeric and dendritic compounds is resistant to insertion reactions of SO_2. In addition, this stability allows the construction of macromolecules starting from simple organometallic building blocks rather than from metal-free ligand precursors.[1,2] Such a methodology reduces the difficulties associated with quantitative end-group substitution.[6]

The organometallic compounds presented here are characterised by their high reactivity towards sulfur dioxide and even submillimolar quantities of this gas are indicated by a drastic colour change. Moreover, mild and selective methods are available to recycle the adducts to the SO_2 free compounds in order to regenerate the ‘detector’. In addition, these materials can be used in the solid state (pure or adsorbed onto an inert surface) or in dilute solution, a property which greatly broadens their potential application. An increase in sensitivity and/or efficiency may be possible with dendrimers of higher generation or by adjustment of the ligand array around the Pt metal centre, *e.g.* by changing the metal-bound halogen atom. Optimization of the properties of these dendrimers is a subject of current investigation in our laboratories.

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Notes and References

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§ *Crystal data* for **4**: $C_{18}H_{33}IN_2O_3PtSSi$, M_r = 707.61, orange, cut to shape crystal (0.15 × 0.30 × 0.30 mm), orthorhombic, space group $Pna2_1$ (no. 33), a = 11.7451(8), b = 17.3316(12), c = 11.8018(12) Å, U = 2402.4(3) Å^3, Z = 4, D_c = 1.9564(2) g cm^{-3}, $F(000)$ = 1360, μ(Mo-Kα) = 72.8 cm^{-1}, 8751 reflections measured, 4177 independent, R_{int} = 0.0274, (2.10 < θ < 27.50°, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.710 73 Å) on an Enraf-Nonius CAD4-T diffractometer on rotating anode. CCDC 182/779.

¶ *Selected data* for **6**: ^{1}H NMR ($CDCl_3$–SO_2), δ 9.26 (s, 3 H), 8.81 (s, 3 H), 8.32 (s, 6 H), 6.79 (s, 12 H), 4.24 (s, 24 H) 3.20 (s, 72 H); λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) (CH_2Cl_2–SO_2): 405 nm (sh, 11 000), 354 nm (42 000). According to stopped-flow measurements, the equilibrium between **3** and **6** is reached in less than 5 ms (UV–VIS) after addition of SO_2.

‖ Compare the threshold values which are presently in use: Central Europe (Zürich): 100 ng dm^{-3}; North America (Los Angeles): 520 ng dm^{-3}.

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