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Iron(III) complexes of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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ABSTRACT

Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ and 2 mol equivalents of picolinic acid (HPic) or 8-hydroxyquinoline (HQ) and trimethylamine base gives iron(III) adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FePic_2]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FeQ_2]^+$, isolated as hexafluorophosphate salts; these complexes are the first isolated iron(III) derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. The X-ray structure of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FePic_2]PF_6$ shows the presence of a rare distorted trigonal prismatic coordination geometry while magnetic measurements confirm the presence of high-spin iron(III) centres in the complexes.

The dinuclear platinum(II) sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** has a well-established coordination chemistry as a metalloligand, whereby the electron-rich bridging sulfide ligands can coordinate to a wide range of metal centres, predominantly from the *p*- and *d*-blocks [1,2]. In recent years, we have been using the technique of electrospray ionisation mass spectrometry (ESI MS) [3] to probe the coordination chemistry of **1**, leading to the observation and subsequent isolation and characterisation of a wide range of new metalloligand complexes thereof [4]. With regard to the 3*d* metals, $\{Pt_2S_2\}$ metalloligand coordination chemistry has largely been confined to the somewhat softer, later metals, e.g. nickel [5], copper [6] and zinc [7]. The chemistry of iron adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is, to date, restricted to the mass spectrometric detection of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Fe(acac)OR]^+$ [$acac = CH_3C(O)CHC(O)CH_3$; R = Me or Et] adducts formed from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $Fe(acac)_3$ in ROH solvent [8]; these species have not yet been isolated on a macroscopic scale. Our recent observations that cobalt(III) adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ can be generated *in situ* by air oxidation of precursor $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$-cobalt(II) adducts [9] suggested that a similar methodology might be successful in the synthesis of new iron(III) adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. Our preliminary studies in this area are reported herein.

The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with iron(II) ammonium sulfate $[(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O]$ in methanol (in air) gave a brown suspension, which was not further characterised. Addition of 2 mol equivalents of 8-hydroxyquinoline (HQ) in small portions, followed by excess aqueous trimethylamine, resulted in a dark brown solution which when analysed by ESI MS showed a dominant ion assigned as $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FeQ_2]^+$. The product $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FeQ_2]PF_6$ **2** was isolated from the reaction mixture in 45% yield as a dark green-black solid by addition of excess NH_4PF_6 [10]. The corresponding reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$, picolinic acid (HPic) and aqueous trimethylamine gave the picolinate analogue $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FePic_2]PF_6$ **3** as a dark brown solid in 54% yield [11]. Iron complexes of the ligands pic^- [12–14] and Q^- [15] are well-established in the literature, with picolinate complexes being of particular interest for their role in catalysed oxidations of organic substrates [12,16–19].

When the reactions were monitored by ESI MS no evidence of intermediate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$-iron(II) adducts was observed, indicating rapid oxidation to iron(III) occurs. This contrasts with the cobalt system [9], where intermediate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$-cobalt(II) adducts were observed to smoothly convert to cobalt(III) adducts by air oxidation. The ESI mass spectra of the isolated complexes **2** and **3** in CH_2Cl_2-CH_3OH solution were investigated. For both complexes, the parent cation was observed as essentially the only species, at *m/z* 1847.33 [calculated 1847.26] for **2**, and *m/z* 1803.29 [calculated 1803.22] for **3**, when capillary exit voltages of 150 V were used. When spectra were recorded using higher capillary exit voltages (e.g. > 180 V) which promotes fragmentation, the radical cation $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^{\bullet+}$ at *m/z* 1502.26 was observed. The same behaviour was recently observed for cobalt(III) adducts [9], and indicates the presence of an internal redox process, generating a coordinated (reduced) metal(II) centre, which is then more easily fragmented, giving the cation $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^{\bullet+}$. Comparison of spectra of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FeQ_2]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ recorded under the same conditions showed the cobalt complex to have the greater tendency to form $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^{\bullet+}$; at a capillary exit voltage of 180 V, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^{\bullet+}$ was a minor fragment for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FeQ_2]^+$, but the base peak for the analogous cobalt complex. At very high capillary exit voltages (e.g. 240 V), significant

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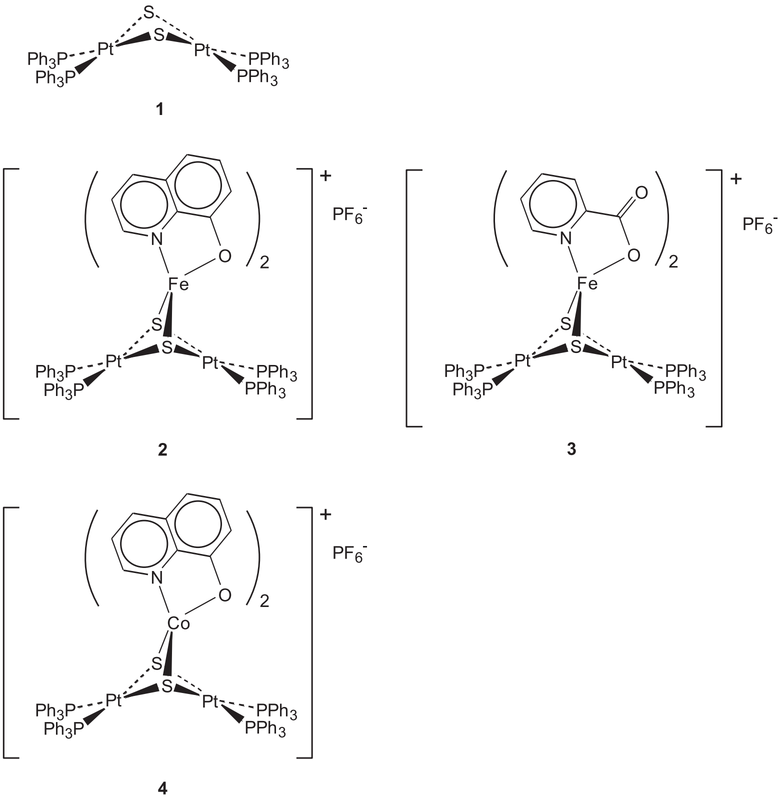

Scheme 1. Structures of platinum complexes described herein.

loss of PPh_3 ligands occurred, giving the ions $[Pt_2(\mu\text{-}S)_2(PPh_3)_3]^{\bullet+}$ (m/z 1240.18) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_2]^{\bullet+}$ (m/z 978.09).

$^{31}P\{^1H\}$ NMR spectra were unable to be recorded on these compounds, as a result of significant line broadening induced by the paramagnetic iron(III) centre. The UV-visible spectrum of a green dichloromethane solution of **2** showed absorptions at *ca* 590, 460 and 370 nm, while an orange-brown solution of complex **3** showed a broad absorption <500 nm. The IR spectrum of **2** was consistent with the complex, showing absorptions from aryl rings, together with a strong PF_6^- band at 840 cm^{-1}. Complex **3** showed the same bands together with medium intensity C=O bands from the picolinate ligand at 1666 and 1652 cm^{-1}.

In order to fully characterise the binding of the iron(III) centre to the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ metalloligand and provide comparisons with related complexes an X-ray structure determination was carried out on complex **3** [20]. The complex crystallises as dark yellow (almost black) block-like crystals on diffusion of diethyl ether into a dichloromethane solution. There are 8 molecules of the complex and associated PF_6^- anions and 16 molecules of dichloromethane of crystallisation in the unit cell of the primitive, centrosymmetric, orthorhombic space group Pbca (Scheme 1).

The core of the cation is illustrated in Fig. 1, together with selected bond lengths and angles. The complex contains a six-coordinate iron(III) centre coordinated to the bidentate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ metalloligand, and two chelating, monoanionic picolinate anions bonded through the pyridine nitrogen and the carboxylate oxygen. Fig. 2(a) shows the coordination sphere around iron, looking down the S···S vector, together with a view of the Pt_2S_2 core. The corresponding views of the cobalt(III) quinolinate complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ **4** (Q=anion of 8-hydroxyquinoline) are shown for comparison in Fig. 2(b).

The coordination around the iron has a geometry between that of an octahedron and a trigonal prism, and is in contrast to the almost regular octahedral geometry of the cobalt complex **4** (Fig. 2). Although the coordination geometry of iron(III) centres is typically octahedral, or slightly distorted octahedral, for example the iron(III) picolinate complex $[FePic_3]\cdot0.5$pyridine (CSD refcode WODKOP)[12], a small number of complexes have been reported where the coordination is closer to trigonal prismatic [21]. A good comparative example is that of the high-spin iron(III) dithiocarbamate complex $[Fe(S_2CN^nBu_2)_3]$

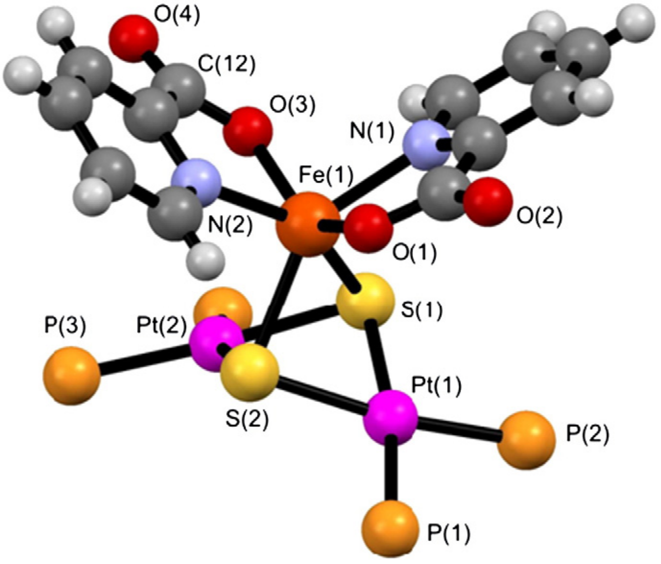

Fig. 1. Core of the cation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4FePic_2]PF_6$ **3** showing the partial atom numbering scheme. All triphenylphosphine carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(2) 2.2840(17), Pt(1)–P(1) 2.3113(18), Pt(2)–P(3) 2.2768(18), Pt(2)–P(4) 2.2876(18), Pt(1)–S(1) 2.3329(18), Pt(1)–S(2) 2.3641(16), Pt(2)–S(1) 2.3490(16), Pt(2)–S(2) 2.3596(17), Fe(1)–O(3) 1.981(5), Fe(1)–O(1) 1.991(5), Fe(1)–N(1) 2.190(6), Fe(1)–N(2) 2.207(7), Fe(1)–S(2) 2.444(2), Fe(1)–S(1) 2.489(2). P(2)–Pt(1)–P(1) 99.28(6), P(3)–Pt(2)–P(4) 99.78(6), S(1)–Pt(1)–S(2) 79.29(6), S(1)–Pt(2)–S(2) 79.05(6), S(1)–Fe(1)–S(2) 74.82(6), O(1)–Fe(1)–N(1) 75.3(2), O(3)–Fe(1)–N(2) 75.2(2), O(1)–Fe(1)–O(3) 134.7(2), N(1)–Fe(1)–N(2) 123.6(2).