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Extending the coordination chemistry of cobalt with the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$: Synthesis of the first cobalt(III) derivatives

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ABSTRACT

The coordination chemistry of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards cobalt(II) and cobalt(III) centres has been explored using an electrospray ionisation mass spectrometry (ESI MS)-directed methodology. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $CoCl_2{\cdot}6H_2O$ in methanol gave a green-yellow suspension of the known adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$, and the $CoBr_2$ adduct could be similarly prepared. When *in situ*-generated $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$ is reacted with 8-hydroxyquinoline (HQ) and base, the initial product is the cobalt(II) adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ]^+$, which is then converted in air to the cobalt(III) adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$, isolated as its hexafluorophosphate salt. The corresponding picolinate (Pic) derivative $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Co(Pic)_2]^+$ was similarly prepared, however reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, $CoCl_2{\cdot}6H_2O$ and 8-(tosylamino)quinoline (HTQ) produced only the cobalt(II) adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoTQ]^+$. Reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, $CoCl_2{\cdot}6H_2O$ and dithiocarbamates gave cobalt(III) complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Co(S_2CNR_2)_2]^+$ [R = Et or $R_2 = (CH_2)_4$], and proceeded much more rapidly, consistent with the known ability of the dithiocarbamate ligand to stabilize cobalt in higher oxidation states. A study of the fragmentation of cobalt(III) adducts by positive-ion ESI mass spectrometry indicated that $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ fragments to form the radical cation $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^{\cdot+}$, which could also be generated by ESI MS analysis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in methanol–NaOH solution. In contrast, the corresponding indium(III) derivative $[Pt_2(\mu\text{-}S)_2(PPh_3)_4InQ_2]^+$, and the cobalt(III) dithiocarbamate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Co(S_2CN(CH_2)_4)_2]^+$ are much more reluctant to fragment under analogous conditions, and the differences are discussed in terms of cobalt(III) redox chemistry.

1. Introduction

The platinum(II) sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (and related complexes with alternative phosphine or arsine ligands) has been under investigation for many years. Such complexes display a rich chemistry on account of the electron-rich bridging sulfide ligands, which react with a diverse range of organic- and metal-based electrophiles [1–3]. A common theme in the chemistry of **1** is the formation of homo- and hetero-metallic sulfide-bridged aggregates, which are now known for the majority of main group and transition metals.

As part of ongoing investigations on the coordination chemistry of **1** we here report on a study of the coordination chemistry towards cobalt. Few cobalt derivatives of **1** are known, and all contain cobalt in the II oxidation state. The first example of a cobalt derivative was $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$ **2a** formed by reaction of **1** with anhydrous $CoCl_2$ in tetrahydrofuran; carbonylative desulfurisation of this complex eliminated the cobalt, forming $[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}S)]$ [4]. The only other examples of cobalt adducts are the diketonate complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoL]^+$, where $L = CH_3COCHCOCH_3$ (acac) or (2-thienyl)$COCHCOCF_3$ [5]. In our current investigations we wished to explore further the chemistry of **1** towards cobalt substrates, and in particular address the question of whether or not cobalt(III) complexes of **1** could be obtained. Due to the classical kinetic inertness of the low spin d^6 cobalt(III) centre, syntheses of substituted cobalt(III) complexes often conveniently proceed *via* a more labile cobalt(II) derivative [6], and the same approach was adopted in this work.

2. Results and discussion

2.1. Investigation of the cobalt(II) halide adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoX_2]$ (X = Cl or Br)

In this study, the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** was typically reacted with $CoCl_2{\cdot}6H_2O$ in methanol giving a green-yellow suspension, which was then reacted *in situ* with an additional ligand. In order to identify the green-yellow intermediate, in one experiment the solid was isolated and found to have properties consistent with the neutral cobalt(II) chloride adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$ **2a**. This has been previously synthesised by reaction

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of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with *anhydrous* $CoCl_2$ in tetrahydrofuran solvent, under argon [4]. In this original report it was suggested that the use of hydrated $CoCl_2$ would also give $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$, but it decomposes on formation. However, our observations in this work indicate that hydrated $CoCl_2$ can be used, at least in methanol solvent, without regard for the exclusion of air and moisture. Using the same method, the corresponding green bromide $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoBr_2]$ **2b** was prepared from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and hydrated cobalt(II) bromide. The cobalt–chloride and –bromide adducts are only sparingly soluble in methanol, but quite soluble in dichloromethane. Reaction of cobalt(II) thiocyanate with **1** resulted in the formation of a bright lime-green solid that was apparently insoluble in methanol and dichloromethane, which hampered attempts at characterising the compound.

The positive-ion ESI mass spectrum of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$ in acetonitrile–methanol solution shows $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl]^+$ at *m/z* 1597.120 (calculated 1597.140) resulting from ionisation by loss of a chloride ligand. Similar behaviour was shown by the bromide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoBr_2]$ which gave $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoBr]^+$ (*m/z* 1642.082, calculated *m/z* 1642.089). Neutral $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$ would be expected to be invisible to ESI MS analysis, and ionisation by chloride loss is the expected ionisation pathway based on the ESI MS behaviour of other neutral metal chloride coordination complexes [7]. Under soft fragmentation conditions (capillary exit voltage 50 V) additional minor peaks of a dication at *m/z* 1597.617 overlap with the isotope pattern for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl]^+$, and are assigned to the dimeric species $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl\}_2]^{2+}$ (calculated *m/z* 1597.640) which presumably contains chloride bridges and four-coordinate cobalt centres; a possible structure is given by **3**. Examination of the supernatant solution in a $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$-$CoCl_2$ reaction mixture showed some related species: $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Co_2Cl_2]^{2+}$ (*m/z* 846) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Co_2Cl_3]^+$ (*m/z* 1727) in addition to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl]^+$.

2.2. Synthesis of cobalt(III) adducts with N,N and N,O chelating ligands

The reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** towards $CoCl_2{\cdot}6H_2O$ and 8-hydroxyquinoline (HQ) was initially investigated. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** with one molar equivalent of $CoCl_2{\cdot}6H_2O$ in methanol quickly gave a greenish suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoCl_2]$ (*vide supra*). Upon addition of 2 mol equivalents of 8-hydroxyquinoline and excess trimethylamine base the solid dissolved to give an orange solution. This solution gradually darkened on stirring in air, giving (after several hours) a dark orange-brown solution that was shown to contain the cobalt(III) derivative $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ **4** by positive-ion ESI MS [observed *m/z* 1850.283, calculated 1850.262]. Precipitation of the product with excess NH_4PF_6 yielded $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]PF_6$ (**4**·PF_6) as a brown solid in 57% yield. It is worth noting that the use of a smaller amount of HQ (around 1.14 mol equivalents based on **1**) still leads to the isolation of pure $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]PF_6$ in 86% yield based on HQ used.

Monitoring of the above reaction on a smaller scale by ESI MS showed the initial orange solution to contain predominantly the cobalt(II) complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ]^+$ at *m/z* 1706.250 (calculated *m/z* 1706.217), with only a low intensity ion $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$. Over a period of several hours stirring in air $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ]^+$ slowly decreased in intensity and was replaced by $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ with concomitant darkening of the solution to a deep orange-brown; no other significant intensity species were observed. After stirring for 24 h, the formation of the cobalt(III) product was complete.

Crystallisation of **4**·PF_6 by vapour diffusion of diethyl ether into a dichloromethane solution yielded very dark brown, almost black, crystals suitable for an X-ray diffraction study. The crystals were of relatively poor quality but did provide a data set which reveals the main features. Fig. 1 shows the structure of the cation, while Table 1 gives selected bond lengths and angles. Refinement of the structure was complicated by apparent disorder of the two Q ligands (refer Section 4) and the quality of the data was not sufficient to resolve the disorder. The disorder in the ligands appears to involve partial occupancy with the opposite handed-ness about the C_2 axis (Fig. 2), with the O atom positions swapping.

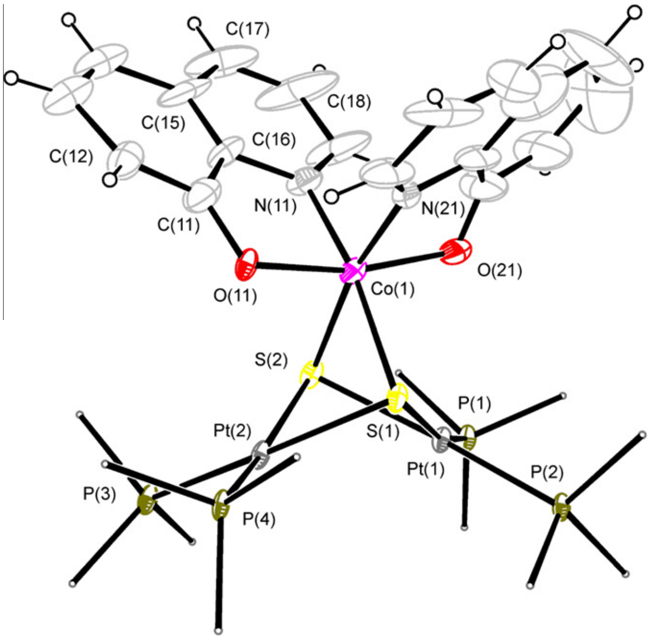

Fig. 1. Structure of the cation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]PF_6$ showing the atom numbering scheme. Only the *ipso* carbons of the PPh_3 ligands are shown as arbitrary small spheres.

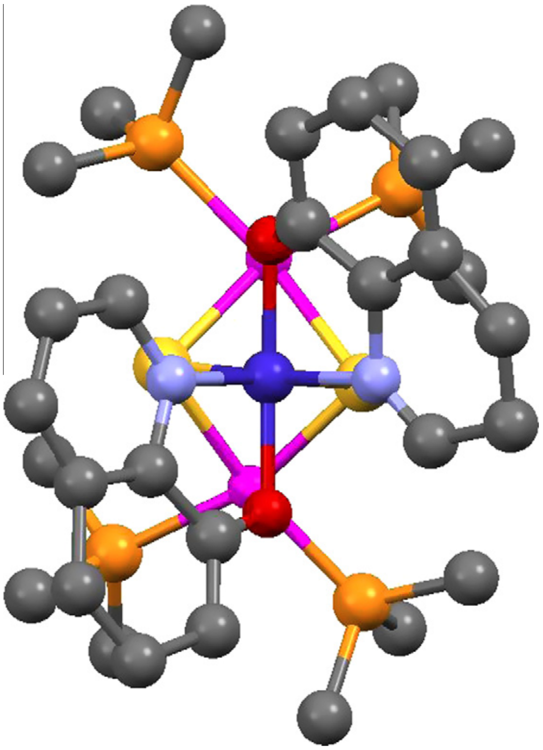

Fig. 2. A view of the core of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ cation looking down the approximate C_2 axis.