The First Mononuclear PtIII Complex. Molecular Structures of (NBu4)[PtIII(C6Cl5)4] and of Its Parent Compound (NBu4)2[PtII(C6Cl5)4]-2CH2Cl2

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(NBu4)[PtIII(C6Cl5)4], fully characterized by crystallographic, spectral, and magnetic measurements has been isolated by oxidation with halogens or TICl3 of the parent compound (NBu4)2[PtII(C6Cl5)4], which has also been analysed by X-ray crystallography.

Several bi- or poly-nuclear complexes containing platinum formally in the PtIII oxidation state have been characterized.1 All of them have Pt–Pt bonds. The preparation of Pt(NH3)2(SCN)2, which according to its e.s.r. spectrum could be a PtIII compound, has been claimed.2 Now we report the preparation and structural characterization of the first well authenticated monomeric PtIII complex. A systematic study of the reactions between halogens and a series of anionic mono- or bi-nuclear pentafluoro- or pentachloro-phenyl derivatives of Pd or Pt, recently described by some of us,3 has revealed that only the PtIII complex (NBu4)2[Pt(C6Cl5)4] can be oxidized to a stable MIII complex. Thus, if Cl2 or Br2 (in CCl4 solution) was added to the colourless dichloromethane solution of the PtII complex, the instantaneous development of a deep-blue colour was observed and a blue PtIII complex, formed according to equation (1), was isolated in 90% yield.

(NBu4)2[Pt(C6Cl5)4] + 1/2 X2 → (NBu4)[Pt(C6Cl5)4] + NBu4X (1)

The same PtIII compound was obtained by treating the PtII precursor with iodine or thallium(III) chloride, albeit in lower yields. With iodine a brown solution was formed, which after evaporation to dryness and extraction with chloroform (in which the PtIII complex is only slightly soluble), gave blue (NBu4)[Pt(C6Cl5)4] (60% yield). With TICl3 [equation (2)], a blue solution was formed and the TICl precipitated. Partial evaporation of the solution allowed separation of some of the PtIII complex (52% yield) from the co-soluble (NBu4)[TICl4] complex.

(NBu4)2[Pt(C6Cl5)4] + 3/2 TICl3 →
(NBu4)[Pt(C6Cl5)4] + (NBu4)[TICl4] + 1/2 TICl (2)

At room temperature (NBu4)[Pt(C6Cl5)4] is air- and moisture-stable, both as a solid and in solution. It melts (with decomposition) at 210 °C. In acetone solution it behaves as a 1 : 1 electrolyte (A∞ = 125 Ω-1 cm2 mol-1).4 The i.r. spectrum of the compound (Nujol) shows the absorptions due to C6Cl5 shifted 10—15 cm-1 towards higher energies relative to the corresponding ones of the PtII parent complex (NBu4)2[Pt(C6Cl5)4]. A single absorption at 830 cm-1 (X-sensitive mode5) along with another at 602 cm-1 [assignable to v(Pt–C)6] are in agreement with the square-planar
Figure 1. The molecular geometry of the $[\text{Pt}(\text{C}_6\text{Cl}_5)_2]$ anion in the Pt$^{III}$ complex (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$. Average Pt-C, C-C, and C-Cl distances in the anion are 2.094(8), 1.388(12), and 1.725(9) Å, respectively.

symmetry of the anion ($D_{sh}$, $E_{sh}$ mode). The Pt$^{III}$ compound is paramagnetic: two independent magnetic susceptibility measurements yield $\mu_B$ 2.4–2.5 μμ at low temperature ($T = 6–80$ K), consistent with a spin 1/2 system with a large orbital contribution. This observation is also consistent with a d$^7$ electronic configuration for the $[\text{Pt}(\text{C}_6\text{Cl}_5)_2]$ anion.

The crystal structures of both (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$] (Figure 1)* and its parent complex (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$]2CH$_2$Cl$_2$ (Figure 2)† show virtually identical square-planar geometries. The average Pt-C, C-C, and C-Cl distances, and interatomic angles of the two anions, all agree within experimental error. {For (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$], Pt–C 2.094(8), C–C 1.388(12), C–Cl 1.725(9) Å; for (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$]2CH$_2$Cl$_2$, Pt–C 2.086(14), C–C 1.393(16), C–Cl 1.731(12) Å.} Even the average tilt angles (i.e., the angles between the C$_6$Cl$_5$ rings and the central PtC$_6$ square plane) are essentially the same: 63.0° for the dark-blue Pt$^{III}$ anion, $[\text{Pt}(\text{C}_6\text{Cl}_5)_2]^{-}$ (Figure 1), and 63.1° for the pale yellow (nearly colourless) Pt$^{II}$ precursor, $[\text{Pt}(\text{C}_6\text{Cl}_5)_2]^2-$ (Figure 2). The $[\text{Pt}(\text{C}_6\text{Cl}_5)_2]^{-}$ anions in the crystal structure of (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$] are widely separated and show no evidence for the presence of Pt···Pt stacking interactions (the closest Pt···Pt distance is 9.7 Å).

Both the dark blue (almost black) crystals and the solutions of (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_2$] show notable stability, which is probably unique to the C$_6$Cl$_5$ ligand since oxidation with halogens of other $[\text{PtX}_4]^2-$ precursors did not lead to similar Pt$^{III}$ complexes. A steric shielding of the Pt$^{III}$ atom by the bulky C$_6$Cl$_5$ ligands cannot be invoked since the geometries of the Pt$^{II}$ and Pt$^{III}$ complexes are virtually identical. However, a steric barrier could be responsible for the lack of any observable dimerisation and therefore for the paramagnetic behaviour of the complex.

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References


7 F. Palacio, unpublished results; K. Sünkel and C. A. Reed, unpublished results.