The First Mononuclear Pt^{III} Complex. Molecular Structures of $(NBu_4)[Pt^{III}(C_6Cl_5)_4]$ and of Its Parent Compound $(NBu_4)_2[Pt^{II}(C_6Cl_5)_4]\cdot 2CH_2Cl_2$

Rafael Usón,*[a] Juan Forniés,[a] Milagros Tomás,[a] Babil Menjón,[a] Karlheinz Sünkel,[b] and Robert Bau[b]

[a] *Department of Inorganic Chemistry, University of Zaragoza, Zaragoza, Spain*

[b] *Department of Chemistry, University of Southern California, Los Angeles, California, U.S.A.*

$(NBu_4)[Pt^{III}(C_6Cl_5)_4]$, fully characterized by crystallographic, spectral, and magnetic measurements has been isolated by oxidation with halogens or $TlCl_3$ of the parent compound $(NBu_4)_2[Pt^{II}(C_6Cl_5)_4]$, which has also been analysed by *X*-ray crystallography.

Several bi- or poly-nuclear complexes containing platinum formally in the Pt^{III} oxidation state have been characterized.[1] All of them have Pt–Pt bonds. The preparation of $Pt(NH_3)_2(SCN)_2I$, which according to its e.s.r. spectrum could be a Pt^{III} compound, has been claimed.[2]

Now we report the preparation and structural characterization of the first well authenticated monomeric Pt^{III} 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 Pt^{II} complex $(NBu_4)_2[Pt(C_6Cl_5)_4]$ can be oxidized to a stable M^{III} complex. Thus, if Cl_2 or Br_2 (in CCl_4 solution) was added to the colourless dichloromethane solution of the Pt^{II} complex, the instantaneous development of a deep-blue colour was observed and a blue Pt^{III} complex, formed according to equation (1), was isolated in 90% yield.

$$(NBu_4)_2[Pt(C_6Cl_5)_4] + 1/2\ X_2 \longrightarrow (NBu_4)[Pt(C_6Cl_5)_4] + NBu_4X \qquad (1)$$

The same Pt^{III} compound was obtained by treating the Pt^{II} 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 Pt^{III} complex is only slightly soluble), gave blue $(NBu_4)[Pt(C_6Cl_5)_4]$ (60% yield). With $TlCl_3$ [equation (2)], a blue solution was formed and the TlCl precipitated. Partial evaporation of the solution allowed separation of some of the Pt^{III} complex (52% yield) from the co-soluble $(NBu_4)[TlCl_4]$ complex.

$$(NBu_4)_2[Pt(C_6Cl_5)_4] + 3/2\ TlCl_3 \longrightarrow (NBu_4)[Pt(C_6Cl_5)_4] + (NBu_4)[TlCl_4] + 1/2\ TlCl \qquad (2)$$

At room temperature $(NBu_4)[Pt(C_6Cl_5)_4]$ 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 ($\Lambda_M = 125\ \Omega^{-1}\,cm^2\,mol^{-1}$).[4] The i.r. spectrum of the compound (Nujol) shows the absorptions due to C_6Cl_5 shifted 10—15 cm^{-1} towards higher energies relative to the corresponding ones of the Pt^{II} parent complex $(NBu_4)_2[Pt(C_6Cl_5)_4]$. A single absorption at 830 cm^{-1} (X-sensitive mode[5]) along with another at 602 cm^{-1} [assignable to ν(Pt–C)[6]] are in agreement with the square-planar

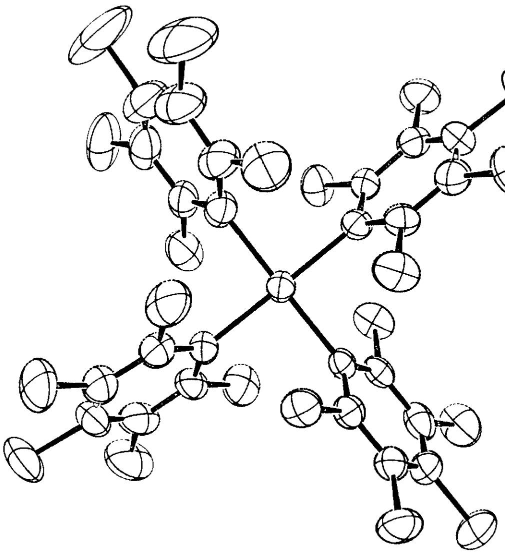

Figure 1. The molecular geometry of the $[Pt(C_6Cl_5)_4]^-$ anion in the Pt^{III} complex $(NBu_4)[Pt(C_6Cl_5)_4]$. Average Pt–C, C–C, and C–Cl distances in the anion are 2.094(8), 1.388(12), and 1.725(9) Å, respectively.

symmetry of the anion (D_{4h}, E_u mode). The Pt^{III} compound is paramagnetic: two independent magnetic susceptibility measurements[7] yield μ_{eff} 2.4—2.5 μ_B 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 $[Pt(C_6Cl_5)_4]^-$ anion.

The crystal structures of both $(NBu_4)[Pt(C_6Cl_5)_4]$ (Figure 1)† and its parent complex $(NBu_4)_2[Pt(C_6Cl_5)_4]\cdot 2CH_2Cl_2$ (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 $(NBu_4)[Pt(C_6Cl_5)_4]$, Pt–C 2.094(8), C–C 1.388(12), C–Cl 1.725(9) Å; for $(NBu_4)_2[Pt(C_6Cl_5)_4]$, 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_6Cl_5 rings and the central PtC_4 square plane) are essentially the same: 63.0° for the dark-blue Pt^{III} anion, $[Pt(C_6Cl_5)_4]^-$ (Figure 1), and 63.1° for the pale yellow (nearly colourless) Pt^{II} precursor, $[Pt(C_6Cl_5)_4]^{2-}$ (Figure 2). The $[Pt(C_6Cl_5)_4]^-$ anions in the crystal structure of $(NBu_4)[Pt(C_6Cl_5)_4$ are widely separated and show no evidence for the presence of Pt · · · Pt stacking interactions (the closest Pt · · · Pt distance is 9.7 Å).

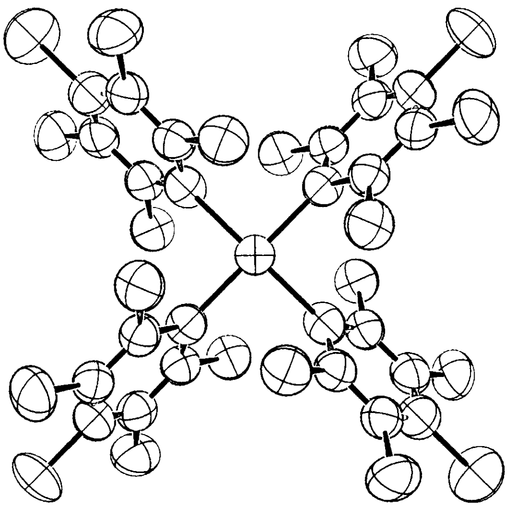

Figure 2. The molecular geometry of the $[Pt(C_6Cl_5)_4]^{2-}$ anion in the Pt^{II} complex $(NBu_4)_2[Pt(C_6Cl_5)_4]\cdot 2CH_2Cl_2$. Note that this is essentially identical to that of the Pt^{III} complex shown in Figure 1. Average Pt–C, C–C, and C–Cl distances in this anioin are 2.086(14), 1.393(16), and 1.731(12) Å, respectively.

Both the dark blue (almost black) crystals and the solutions of $(NBu_4)[Pt(C_6Cl_5)_4]$ show notable stability, which is probably unique to the C_6Cl_5 ligand since oxidation with halogens of other $[Pt^{II}X_4]^{2-}$ precursors did not lead to similar Pt^{III} complexes. A steric shielding of the Pt^{III} atom by the bulky C_6Cl_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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† *Crystal data* for $(NBu_4)[Pt(C_6Cl_5)_4]$, $C_{40}H_{36}Cl_{20}NPt$, M = 1434.88, triclinic, space group $P\bar{1}$ (No. 2), a = 9.747(8), b = 16.170(8), c = 17.675(8) Å, α = 104.95(3), β = 92.09(5), γ = 77.67(5)°, U = 2629(2) Å^3, D_c = 1.79 g cm^{-3}, Z = 2. X-Ray data were collected on a Nicolet/Syntex $P2_1$ diffractometer using Mo-K_α radiation. The structure was solved by standard heavy-atom techniques and refined to a final R factor of 3.3% for 4786 reflections. $(NBu_4)_2[Pt(C_6Cl_5)_4]\cdot 2CH_2Cl_2$, $C_{58}H_{76}Cl_{24}N_2Pt$, M = 1847.22, tetragonal, space group $P4/nnc$ (No. 126), $a = b$ = 14.407(6), c = 19.929(8) Å, U = 4135(3) Å^3, D_c = 1.49 g cm^{-3}, Z = 2. X-Ray data were collected as in the previous case, and the structure refined to a final R factor of 4.6% for 951 reflections. The structure determination of this compound was complicated by disorder effects, not only in the n-butyl groups of the cations but also in the CH_2Cl_2 molecules of crystallization. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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