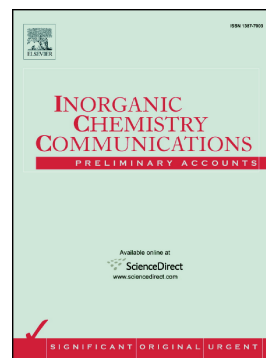


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Unprecedented pentanuclear mixed-valence Pt^(II)-Pt^(IV) complex anion in Q₂[Pt₅Cl₂₀] salts (Q = TBA, PPN)

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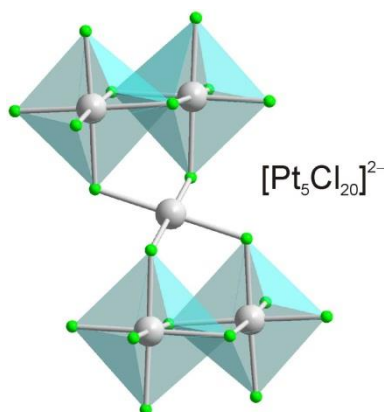
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Abstract Red crystals of [TBA]₂[Pt₅Cl₂₀] were obtained by reacting [TBA]₂[PtCl₆] with an excess of AlCl₃ at room temperature in CH₂Cl₂. The salt [PPN]₂[Pt₅Cl₂₀] containing the same anion was prepared by reaction of platinum tetrachloride with a small excess of [PPN]Cl in 1,2-dichloroethane at room temperature. Single crystal X-Ray diffraction studies confirmed that both species contained the mixed-valence [Pt₅Cl₂₀]²⁻ anion with two dinuclear platinum^(IV) Pt₂Cl₁₀ fragments organized around a central square planar platinum^(II) in a chair arrangement.

Keywords: platinum^(IV); mixed-valence; chlorido-complexes; X-ray diffraction studies;



Graphical abstract

Highlights

A mixed-valence $[\text{Pt}_5\text{Cl}_{20}]^{2-}$ anion has been crystallographically studied.

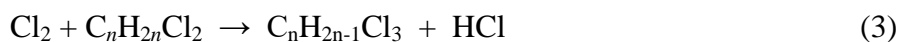
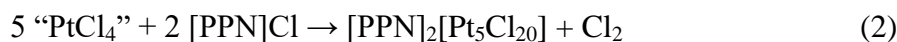
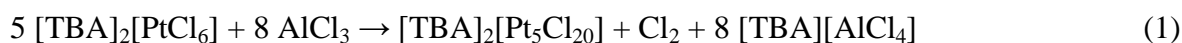
Two different salts have been prepared, having TBA or PPN as a cation.

Two different synthetic routes are presented.

The chemistry of platinum^(IV) complexes presents interesting aspects concerning their redox properties, that makes these systems suitable for catalytic [1] and biological [2] applications. In the field of anticancer metal complexes, many examples are described where platinum^(IV) derivatives act as efficient and selective prodrugs[2,3]: they are sufficiently inert to limit side reactions with nucleophiles in physiological media, but, once in the hypoxic tumoral tissues, they can be easily reduced to generate the active platinum^(II) species. Finding reliable synthetic procedures affording platinum^(IV) compounds and studying their reactivity are therefore primary tasks. The majority of the reported platinum^(IV) complexes are prepared by oxidation of the corresponding platinum^(II) species [4] (for instance with halogen, X_2 or synthetic equivalent like PhICl_2 , with hydrogen peroxide, H_2O_2 , or even with O_2), nevertheless salts containing chlorido-complex anions of platinum(IV) are commercially available and could be alternative precursors. In this communication we report the preparation of an unprecedented pentanuclear mixed-valence $\text{Pt}^{(IV)}\text{-Pt}^{(II)}$ chloridocomplex anion.

Salts containing dinuclear chlorido-complex anions of platinum^(IV), $\text{Q}[\text{Pt}_2\text{Cl}_9]$ [5] ($\text{Q} =$ tetrabutylammonium, TBA^+ , and bis-triphenylphosphineiminium, PPN^+) and $\text{Q}_2[\text{Pt}_2\text{Cl}_{10}]$ [5,6] ($\text{Q} =$ TBA^+ , PPN^+ , and triphenylcarbenium, CPh_3^+) have been reported in the literature. They were obtained by reacting $[\text{TBA}]_2[\text{PtCl}_6]$ or $[\text{PPN}]_2[\text{PtCl}_6]$ with AlCl_3 as chloride scavenger [5] according to a procedure developed for the synthesis of noble metal halocarbonyls [7] or from the treatment of platinum tetrachloride, $[\text{PtCl}_4]$, with QCl [5,6]. The reactions were carried out in SOCl_2 [5] or chlorinated hydrocarbons (CH_2Cl_2 , $1,2\text{-C}_2\text{H}_4\text{Cl}_2$, $1,1,2,2\text{-C}_2\text{H}_2\text{Cl}_4$) [5,6]. $[\text{TBA}][\text{Pt}_2\text{Cl}_9]$ contains the dinuclear $[\text{Pt}_2\text{Cl}_9]^-$ anion where the two platinum atoms are connected by three bridging chlorides with a geometry corresponding to two face-sharing PtCl_6 octahedra [5]. In the derivative $[\text{PPN}]_2[\text{Pt}_2\text{Cl}_{10}] \cdot \text{C}_7\text{H}_8$, the centrosymmetric dinuclear anions are formed by two edge-sharing PtCl_6 octahedra [5].

In this paper we report that the mixed valence pentanuclear $\text{Pt}^{(II)}\text{-Pt}^{(IV)}$ $[\text{Pt}_5\text{Cl}_{20}]^{2-}$ anion formed either reacting $[\text{TBA}]_2[\text{PtCl}_6]$ with AlCl_3 or treating $[\text{PtCl}_4]$ with $[\text{PPN}]\text{Cl}$ (Eqs 1 and 2) in chlorinated hydrocarbons and nice single crystals grew when the reaction mixtures were kept without stirring at room temperature for a relatively long time.



In the equations Cl_2 appears as a product to justify the partial reduction of platinum^(IV) to platinum^(II). These reactions, supposed to be endoergonic and displaced to the left, can be favoured if Cl_2 is removed, for instance by reaction with the solvent (Eq 3, $n = 1, 2$). Actually, the reduction was not observed when the preparation was carried out in SOCl_2 [5], probably because this solvent is not a good halogen trap.

Since the reductive elimination of chlorine by the $\text{Pt}^{(\text{IV})}$ complexes can be photo-assisted [8], we repeated the reaction of $[\text{TBA}]_2[\text{PtCl}_6]$ with AlCl_3 (in 1,2-DCE) both in the light and in the dark, always observing the formation of the scarcely soluble $[\text{TBA}]_2[\text{Pt}_5\text{Cl}_{20}]$, and demonstrating that light was not involved in this case. The process seems to be temperature-dependent, since, when the reactions were carried out in CH_2Cl_2 at -30°C , $\text{Q}[\text{Pt}_2\text{Cl}_9]$ salts [5] containing only platinum^(IV) centres precipitated out. It is possible that the scarce solubility of $\text{Q}[\text{Pt}_2\text{Cl}_9]$ at low temperature inhibits its evolution to $\text{Q}_2[\text{Pt}_5\text{Cl}_{20}]$.

The structure of the centrosymmetric anion $[\text{Pt}_5\text{Cl}_{20}]^{2-}$ is shown in Fig.1. The inversion centre coincides with the position of the Pt3 atom. Pt1 and Pt2 atoms are octahedrally coordinated sharing the edge Cl1...Cl2. Pt3 is instead in a square planar coordination sharing the vertices Cl3 and Cl7 with the octahedra of Pt1 and Pt2. Pt3 coordination plane (Cl3, Cl7, Cl3', Cl7') makes a dihedral angle of 115.8° with the mean plane of Cl3, Cl5, Cl7 and Cl9 atoms, having Cl1 and Cl1' at a non-bonding distance (about 3.25 \AA). Table 2 lists the bond distances within the pentanuclear anion. As already noted by Shannon,[9] $\text{Pt}^{(\text{II})}$ in square planar coordination shows a radius, 0.60 \AA , slightly shorter than that of six-coordinated $\text{Pt}^{(\text{IV})}$, 0.62 \AA . In accordance with this, by looking on the Cambridge Crystallographic Data Base,[10] we found for the PtCl_4^{2-} anion a mean Pt–Cl distance of $2.307(7) \text{ \AA}$, while for PtCl_6^{2-} anion a mean Pt–Cl distance of $2.319(8) \text{ \AA}$. Pt3, showing a mean Pt–Cl distance of 2.299 \AA , is perfectly in keeping with $\text{Pt}^{(\text{II})}$ bond distances. By looking at Table S2 we see a significant difference among Pt–Cl distances within the octahedra around Pt1 and Pt2 depending on whether the chlorine are bridging or terminal, the former being markedly longer. For both Pt1 and Pt2, however, the average distances from chlorine, 2.323 and 2.320 \AA , respectively,

are perfectly consistent with the mean values recorded in the Cambridge database for the octahedra around $\text{Pt}^{\text{(IV)}}$. An interesting geometric detail follows from the smaller dimension of the side of $\text{Pt}^{\text{(II)}}$ coordination square with respect to the edge of coordination octahedron of $\text{Pt}^{\text{(IV)}}$. The two $\text{Pt}^{\text{(IV)}}$ atoms of the fragments $\text{Pt}_2\text{Cl}_{10}$, that share the vertices Cl3 and Cl7 with the smaller central $\text{Pt}^{\text{(II)}}$ (Fig. 1), show the equatorial planes Cl1, Cl2, Cl6, Cl4 and Cl1, Cl2, Cl10, Cl8 with a dihedral angle of 170.9° in order to minimize the repulsions between Cl3 and Cl7 and between Cl5 and Cl9, at variance with the centrosymmetric arrangement observed in the anion $[\text{Pt}_2\text{Cl}_{10}]^{2-}$ [5] (dihedral angle 180°). The $\text{Pt}^{\text{(II)}}\text{-Cl}$ and $\text{Pt}^{\text{(IV)}}\text{-Cl}$ bond distances are in good agreement with those reported for the mixed-valence anion $[\text{Pt}_3\text{Cl}_{12}]^{2-}$ [6].

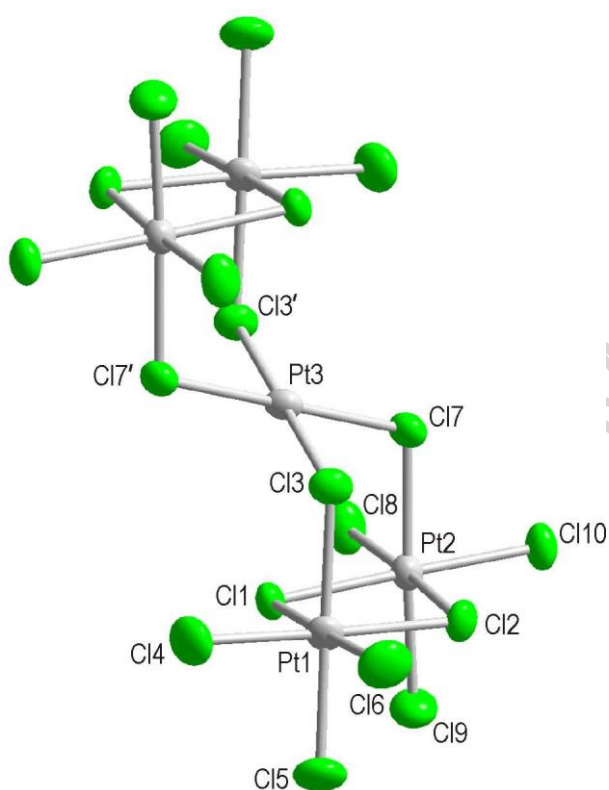


Figure 1. View of the molecular structure of anion $\text{Pt}_5\text{Cl}_{20}^{2-}$. ' = $-x, -y, -z$.

Figure 2 shows a sketch of the crystal packing in a unit cell viewed along the shortest axis. Each cation is surrounded by four anions and each anion by eight cations.

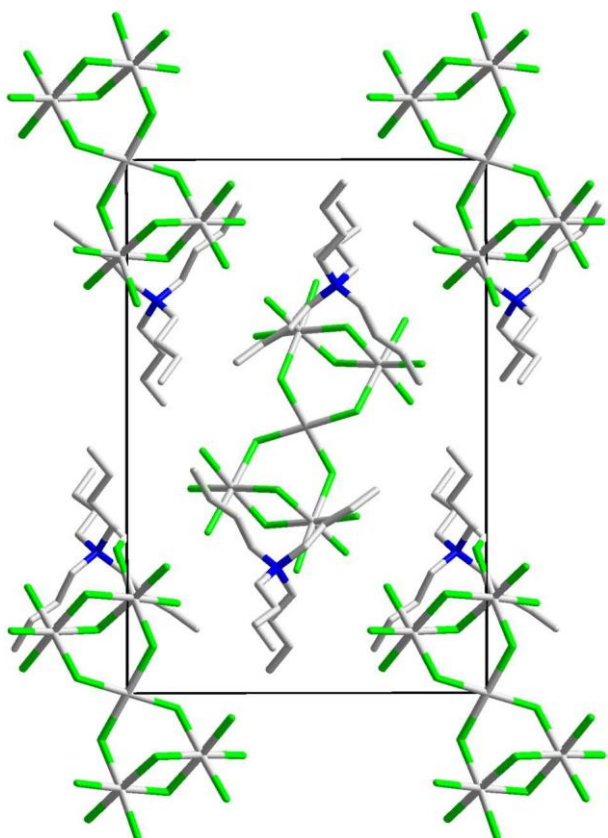


Figure 2. View along a of the crystal packing of $[t\text{Bu}_4\text{N}]_2\text{Pt}_5\text{Cl}_{20}$.

It is worth to mention that mixed valence $\text{Pt}^{\text{II}}\text{-Pt}^{\text{IV}}$ compounds usually occur as alternating Pt^{II} and Pt^{IV} chains where Pt^{II} and Pt^{IV} are connected by a quasi linear halide bridge, as for instance in $\{[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{X}_2](\text{ClO}_4)_4\}$ ($\text{X} = \text{Cl}, \text{Br}$) [11], or as a mixture of separate Pt^{II} and Pt^{IV} units as found in PtCl_3 that consists of hexanuclear $\text{Pt}_6\text{Cl}_{12}$ molecules embedded into $[\text{PtCl}_4]$ chains, formed by a zig-zag sequence of edge-sharing PtCl_6 octahedra [12].

Moreover, in the trinuclear salt $[\text{CPh}_3]_2[\text{Pt}_3\text{Cl}_{12}]$ [6] two side $[\text{PtCl}_6]$ octahedra share each an edge with the central square-planar Pt^{II} to make a structure with three linearly arranged platinum atoms. The authors suggest that the anion could result from the initial formation of a similar linear, chloride-bridged $[\text{Pt}_3\text{Cl}_{14}]^{2-}$ anion, containing Pt^{IV} only, followed by the loss of two axial chlorine atoms from the central metal centre. The bromo analogue anion, $[\text{Pt}_3\text{Br}_{12}]^{2-}$ [13], reported in the salt $[\text{TBA}]_2[\text{Pt}_3\text{Br}_{12}]$ was obtained by reaction of $[\text{TBA}]_2[\text{PtBr}_6]$ with $[\text{TBA}]_2[\text{PtBr}_4]$. Finally, it is worth to mention also the dinuclear anion $[\text{Pt}_2\text{I}_8]^{2-}$ [14] and the trinuclear neutral $[\text{Pt}_3\text{I}_8(\text{NH}_2)_2]$, [15] obtained by partial oxidation with I_2 of $[\text{Pt}_2\text{I}_6]^{2-}$ salts and $[\text{Pt}_2\text{I}_4(\text{NH}_2)_2]$, respectively.

In conclusion, starting from platinum^(IV) derivatives, we have prepared two salts by two different routes, containing a new mixed valence platinum^(II/IV) anionic chlorido-complex, [Pt₅Cl₂₀]²⁻. The crystal and molecular structure of [TBA][Pt₅Cl₂₀] has been determined and displays the pentanuclear anion as formed by two [Pt₂Cl₁₀]²⁻ dinuclear fragments, each behaving as a chelating ligand for the central square-planar platinum^(II) *via* two axial chlorides. Although the presence of disorder does not allow to present the X-ray diffraction results obtained with [PPN][Pt₅Cl₂₀], we can clearly observe that the same anion is present. Multiple synthetic access is consistent with a definite structural stability and a well defined composition that could be exploited for synthetic purposes as for reactivity studies. In view of the interest towards the use of platinum^(IV) derivatives as prodrugs in the field of the anticancer therapies, studies concerning the process responsible of the partial metal reduction of these salts are in progress in our labs.

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Appendix A

Supplementary data CCDC 1843419 contains the supplementary crystallographic data for [TBA]₂[Pt₅Cl₂₀]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Additional supplementary data contains details of synthesis, summary of X-ray data, structure solution and refinement description, crystal data and structure refinement parameters (Table S1), selected geometric parameters (Table S2). Supplementary data to this article can be found online at doi: <https://doi.org/10.xxxx/j.inoche.xxxx.xxx2.xxx>.

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