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A ^{195}Pt N.M.R. Study of the Solvolysis Products of $[PtCl_6]^{2-}$

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There are ten possible species of formula $[PtCl_n(OH)_{6-n}]^{2-}$. Of these, salts of $[PtCl_6]^{2-}$ [1], *trans*-$[PtCl_4(OH)_2]^{2-}$ [2], and $[Pt(OH)_6]^{2-}$ [3] have been isolated and structurally characterised and salts of $[PtCl(OH)_5]^{2-}$ and $[PtCl_2(OH)_4]^{2-}$ [4] have been reported. Solvolysis studies of $[PtCl_6]^{2-}$ have been interpreted in terms of initial formation of $[PtCl_5(OH)]^{2-}$ [5]. The range of ^{195}Pt n.m.r. shifts, and the regularity of changes caused by ligand substitution [6], suggested that ^{195}Pt n.m.r. would be an excellent tool for identifying the complexes formed by solvolysis of $[PtCl_6]^{2-}$.

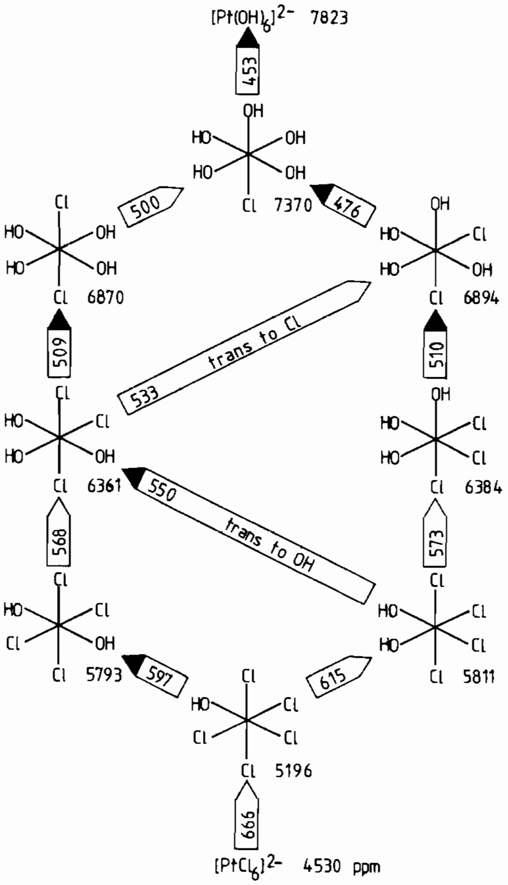
Figure 1 shows the spectra of two reaction mixtures together with those of $Na_2[PtCl_6]$ and $Na_2[Pt(OH)_6]$. Assignments are based on the following criteria (when n is the number of Cl ligands):

(a) the six large steps (*ca.* 500 p.p.m.) between resonances correspond to changes in n; the three smaller differences are between pairs of isomers.

(b) substitution of OH for Cl *trans* to Cl causes a different increase in δ(Pt) to that *trans* to OH.

(c) changes caused by each type of substitution depend on n in a regular and continous way.

(d) either substitution *trans* to OH causes the greater change in δ(Pt) for every value of n, or it causes the smaller change for every value of n.



Scheme 1. Assignment of ^{195}Pt chemical shifts for hydrolysis products of $[PtCl_6]^{2-}$ in alkaline aqueous solution (pH 10–12).

Scheme 1 gives the assignments which conform with these criteria. In it the two types of change are distinguished. They are distributed in an asymmetric

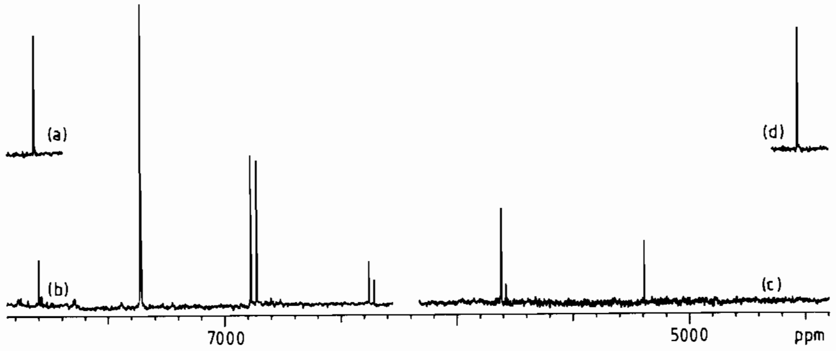


Fig. 1. 19.3 MHz ^{195}Pt n.m.r. spectra of (a) $Na_2[Pt(OH)_6]$, (b) result of adding a further equivalent of $Na_2[PtCl_6]$ to a solution, Na_2PtCl_6 + 5 NaOH, that had been aged for 7 days at *ca.* 15 °C, (c) solution produced by boiling $Ag_2[PtCl_6]$ in water and adjusting to *ca.* pH 10, and (d) $Na_2[PtCl_6]$. [$\delta(^{195}Pt)$ to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz].

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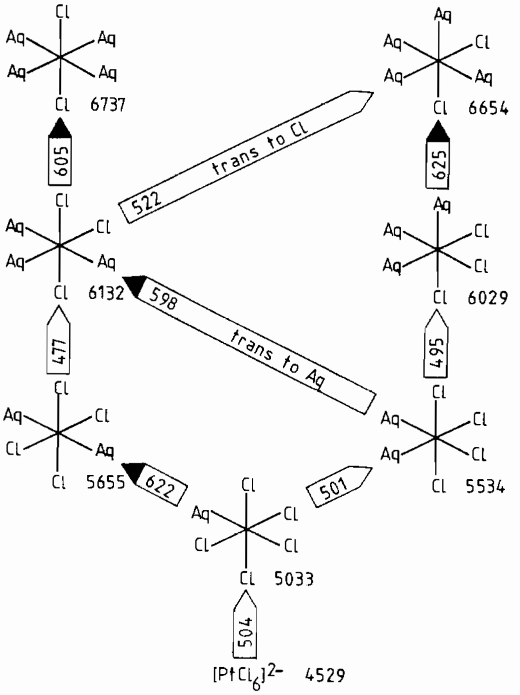
way across the series, *e.g.* between the isomers with n = 4 and n = 3 there are two examples of hydrolysis *trans* to Cl but only one *trans* to OH. The increases in δ(Pt) for the transformations *cis* → *fac* and *trans* → *mer* are expected to be approximately the same. The assignment of *trans*-$[PtCl_4(OH)_2]^{2-}$ is confirmed with a pure sample of *trans*-$K_2[PtCl_4(OH)_2]$ [2]. Thus substitutions *trans* to Cl cause larger increases in δ(Pt) in this system than those *trans* to OH. Changes accompanying each type of substitution decrease uniformly as n is reduced (by *ca.* 8% between successive steps).

The alternative assignment, which requires substitutions *trans* to Cl to give the smaller changes, fails on criterion (c). As it interchanges the δ(Pt) values of the isomers it assigns *trans*-$[PtCl_4(OH)_2]^{2-}$ incorrectly. All the measurements discussed above were of solutions at pH 10–12.



Scheme 2. Assignment of ^{195}Pt chemical shifts for hydrolysis products of $[PtCl_6]^{2-}$ in acid aqueous solution (pH 1–3).

Although the ^{195}Pt chemical shift of $[PtCl_6]^{2-}$ does not depend on pH those of the other species are reduced on acidification. (Complexes with n = 0 or 1 are insoluble in acidic solution). The values and assignments for species observed at pH 1–3 are shown in Scheme 2, where Aq is used to indicate that OH ligands have acquired some unspecified degree of additional protonation. The assignments are based on the best possible agreement with the criteria outlined above and now require that the larger changes (by *ca.* 110 p.p.m.) are caused by replacing Cl *trans* to the O-donor. Whilst there is not perfect conformity with criterion (c), the alternative assignment gives a much more erratic result. In any case there may be a lack of complete comparability between the δ(Pt) values in Scheme 2 since the degree of ionisation of all these 'acids' is not necessarily the same at a particular pH. Evidently the degree of protonation of the oxygen ligands has a profound effect on the complexes through the Pt–O bond.

Scheme 2 requires that the order of ^{195}Pt shifts of *cis* and *trans* isomers has reversed between alkaline and acidic solutions and we have confirmed that this is so in the case with n = 4 by observing the changes in δ(Pt) with small decrements in pH between the extremes.

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