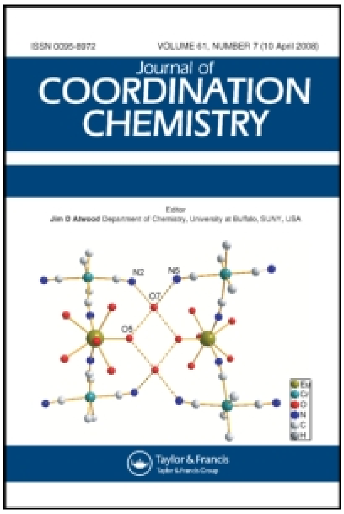

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A ^{195}Pt NMR study of the oxidation of $[PtCl_4]^{2-}$ with chlorate, bromate, and hydrogen peroxide in acidic aqueous solution

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^{195}Pt NMR has been used to investigate the distribution of Pt(IV) products after oxidation of $[PtCl_4]^{2-}$ with sodium chlorate ($NaClO_3$), sodium bromate ($NaBrO_3$), and H_2O_2 in acidic solutions and, for comparison, with H_2O_2 in water. The relative rates of oxidation of $[PtCl_4]^{2-}$ with $NaClO_3$ and H_2O_2 in $1\,mol\,L^{-1}$ $HClO_4$ at 50°C are comparable, while that with $NaBrO_3$ is significantly higher. Our ^{195}Pt NMR results confirm previous work on the oxidation of $[PtCl_4]^{2-}$ with H_2O_2 in water, which results in mainly *trans*-$[PtCl_4(OH)_2]^{2-}$ as product. By contrast oxidation of $[PtCl_4]^{2-}$ with $NaClO_3$ and $NaBrO_3$ in acidic solutions results in the distribution of several $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 2$–6) and $[PtCl_nBr_m(H_2O)_{6-n-m}]^{4-n-m}$ (n, $m = 2$–6) species; notably the distribution of product species is dominated by *cis*-$[PtCl_4(H_2O)_2]$ in solution. This species can be unambiguously identified by the ^{35}Cl/^{37}Cl-isotope-induced effects on the ^{195}Pt NMR resonance shape in solution. *trans*-$[PtCl_4(OH)_2]^{2-}$ was co-crystallized with 18-crown-6 to form *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$ and the single crystal X-ray structure is reported. Oxidation of $[PtCl_4]^{2-}$ with H_2O_2 in various acidic solutions gives qualitatively similar Pt(IV) species distributions as found for $NaClO_3$, and the implications of these results are discussed in the context of Pt(II)→Pt(IV) oxidation reactions by these oxidants in aqueous solutions.

Keywords: ^{195}Pt NMR; Oxidation of $[PtCl_4]^{2-}$ by $NaClO_3$, H_2O_2, and $NaBrO_3$; *cis*-$[PtCl_4(H_2O)_2]$; Molecular structure of *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$

1. Introduction

Large-scale separation of platinum from other platinum group metals (PGMs) is dependent, amongst other factors, on the efficient oxidation of Pt(II) to Pt(IV) in solution. The oxidation states of PGMs dissolved in HCl-rich process solutions are manipulated to allow for their separation with gel chromatography, solvent extraction (SX) or classical ion-exchange methods [1]. The liquid–liquid and ion-exchange extraction properties of $[PtCl_6]^{2-}$ are significantly more favorable compared with square-planar $[PtCl_4]^{2-}$ [2]. Oxidation of square-planar Pt(II) complexes to yield octahedral Pt(IV) oxidation products with H_2O_2 [3, 4], $S_2O_8^-$, MnO_4^- [5], Br_2, and Cl_2 [6, 7] have been reported previously. Of interest in this context is a study by Dunham *et al.* [4] who used ^{195}Pt NMR to examine in detail the oxidation of *inter alia*

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$K_2[Pt(ox)_2]\cdot 2H_2O$ (ox = oxalate anion) and $K_2[PtCl_4]$ with H_2O_2 in water to yield exclusively *trans*-dihydroxido-bis(oxalato)platinum(IV) and *trans*-dihydroxido-tetrachloridoplatinum(IV), respectively.

Oxidizing agents such as sodium chlorate ($NaClO_3$) and sodium bromate ($NaBrO_3$) have been used for the adjustment of oxidation states of various PGM chlorido complexes industrially, although few studies using these agents have appeared in the open literature [8, 9]. $NaClO_3$ has been used for oxidative stripping of Rh(III) from anion exchangers after extraction [10]. The use of $NaClO_3$ and $NaBrO_3$ as oxidants in the commercial refining of PGMs has been reported in the patent literature [11], although no detailed study of the oxidation of Pt(II) square-planar complexes with $NaClO_3$ and/or $NaBrO_3$ has been reported in the literature to our knowledge.

As part of our interest in the use of high-resolution ^{195}Pt NMR spectroscopy as a tool to examine the distribution and speciation of Pt(II/IV) complexes in chloride-rich aqueous solutions, we have shown the utility of ^{195}Pt "chemical-shift-trend" analysis as a means of rapid assignment of, for example, the entire series of $[PtCl_{6-n}(OH)_n]^{2-}$ (n = 0–6) and $[PtCl_{6-m-n}Br_m(OH)_n]^{2-}$ (m, n = 0–6) complexes in synthetic solutions intended to mimic process solutions [12, 13]. While this method provides for the rapid identification of such species in solution with considerable certainty, the sensitivity of the ^{195}Pt chemical shift to other factors such as concentration, solvent composition, temperature, and ionic strength (e.g., HCl concentration) makes an additional spectroscopic "fingerprint" for the unambiguous identification of Pt(IV) complex species desirable. Sadler *et al.* [14] demonstrated that small $^{35}Cl/^{37}Cl$-isotope-induced shifts at higher magnetic fields (9.4 T) are well-resolved for $[Pt^{35}Cl_n^{37}Cl_{6-n}]^{2-}$ (n = 0–6). We have recently shown that a detailed analysis of $^{35}Cl/^{37}Cl$ isotope shifts for the ^{195}Pt NMR signals of the isotopologues and isotopomers of $[PtCl_5(H_2O)]^-$ and *cis*-$[PtCl_4(H_2O)_2]$ leads to an unambiguous means for the assignment of ^{195}Pt resonances of such species [15]. This $^{35}Cl/^{37}Cl$-isotope-shift analysis has been extended to produce unique ^{195}Pt NMR spectroscopic "fingerprints" for unambiguous assignment of the complete series of $[PtCl_n(H_2O)_{6-n}]^{4-n}$ (n = 1–6) geometric and isotopic stereoisomer species [16]. The latter species can be synthesized by oxidation of $[PtCl_4]^{2-}$ and $[Pt(H_2O)_4]^{2-}$ in acidic solution using a variety of oxidants under well-defined conditions.

We here report a study of the oxidation of $[PtCl_4]^{2-}$ using ClO_3^- or BrO_3^- in acidic aqueous solution with reference to the identification and characterization of the oxidation products obtained by means of high-resolution ^{195}Pt NMR spectroscopy. We find that the distribution of product Pt(IV) complexes, particularly in acidic solutions is far from simple, and thus for comparison we have used the relatively well-studied oxidation of Pt(II) complexes by H_2O_2 [3, 4, 17, 18] as a benchmark, to elucidate this chemistry in acidic solutions.

2. Experimental

2.1. *Materials and method*

All solvents and chemicals were reagent grade as obtained from commercial sources and used without purification. *trans*-$[K_2PtCl_4(OH)_2]$ was prepared according to a literature method [17, 18]. UV-Vis absorption spectra were obtained with a single-beam diode array Agilent 8453E UV-Vis spectrophotometer; the temperature of the quartz cuvette was regulated to ±0.1°C *via* a water bath using a heater (Julabo LABORTECHNIK GMBH). ^{195}Pt NMR spectra were recorded on a Varian INOVA 600 MHz spectrometer operating at 128.8 MHz with a 5 mm broad-band probe. A 1 mm coaxial insert tube containing $[PtCl_6]^{2-}$ ($\delta\,^{195}Pt = 0.0$ ppm, 30°C) (500 mg cm^{-3} $H_2PtCl_6 \cdot 2H_2O$ in 30% (v/v) D_2O/1 mol L^{-1} HCl) served as external reference solution referred to as "ref" in the figures where relevant. As several ^{195}Pt spectra reported in this work were recorded at 20°C, being the optimum temperature for resolution of the ^{35}Cl/^{37}Cl-isotope-induced effects [15], it should be noted that in view of the sensitivity of $\delta\,^{195}$Pt to the temperature, the measured $\delta\,^{195}$Pt of the coaxial reference solution undergoes small changes in chemical shift to the extent of ~1 ppm °C^{-1}, so that at 20°C the coaxial "ref" peak appears at *ca* $-\,9 \pm 1$ ppm relative to that at 30°C [16, 19]. ^{195}Pt NMR spectra were typically recorded with spectral widths of 200–250 KHz with acquisition time of 1 s, using a 2.0 μs excitation pulse (corresponding to a ~20° pulse) at maximum practical power, to ensure approximately homogeneous and complete excitation of all the resonances over the large spectral width with no relaxation delay; the T_1 relaxation times of most of the platinum complexes were measured to be <150 ms in these solutions, which ensured essentially complete relaxation of all complex species in solution. At concentrations used in this study typical total acquisition times were *ca* 1 h.

2.2. *Oxidation of* $[PtCl_4]^{2-}$ *aqueous solutions*

The relative rates of oxidation of 1 mmol L^{-1} $[PtCl_4]^{2-}$ in 1 M $HClO_4$ after addition of 10 mol L^{-1} equivalents H_2O_2, $NaClO_3$, and $NaBrO_3$ were monitored at 50°C with UV-Vis spectroscopy in a 0.5 cm quartz cuvette by monitoring the absorbance increases at various wavelengths (261, 331, 391, and 476 nm) as a function of time. The UV-Vis spectra show a peak maximum at 261 nm at which the rate of change was examined. For ^{195}Pt NMR studies, oxidations were carried out by adding 5 mol L^{-1} equivalents H_2O_2, $NaClO_3$, and $NaBrO_3$, respectively, to stock the solutions of 0.2 mol L^{-1} K_2PtCl_4 prepared in distilled water, 1 mol L^{-1} $HClO_4$, a mixture of 0.5 mol L^{-1} $HClO_4$/1.5 mol L^{-1} $NaClO_4$, 2 mol L^{-1} $NaClO_4$, or 1 mol L^{-1} trifluoromethanesulfonic acid (TfOH) followed by stirring and heating for 10 min at 50°C. The ^{195}Pt NMR spectra of these solutions were acquired as soon as possible after cooling which typically took 10–15 min. Oxidation with H_2O_2 and $NaClO_3$ was essentially complete within at most 3000 s, while that with $NaBrO_3$ was complete in less than 100 s.

2.3. *Crystallization of* **trans**-$K_2[PtCl_4(OH)_2](18\text{-}cr\text{-}6)_2 \cdot 2H_2O$

A 0.2 mol L^{-1}solution of *trans*-$[PtCl_4(OH)_2]^{2-}$ was prepared by dissolving the appropriate amount of authentic *trans*-$K_2[PtCl_4(OH)_2]$ salt [17, 18] in water. To this solution was added 10 mol L^{-1} equivalents of 18-crown-6 ($C_{12}H_{24}O_6$) which was shaken until complete dissolution. Clear orange cube-shaped crystals formed in solution after 3 days on slow evaporation in a fume hood. The molecular structure of the platinum complex in these crystals was determined by single crystal X-ray diffraction analysis and the data and structure refinement parameters are shown in table 1.

Table 1. Crystal data and structure refinement for *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$.

Molecular formula	$C_{36}H_{74}K_2O_{14}Pt$
Molecular weight	1004.24
Molecular size (mm^3)	0.03 × 0.02 × 0.01
Molecular color	Orange
Crystal system	Monoclinic
Space group	$P2\bar{1}/c$
Unit cell dimensions (Å,°)	
a	10.1409(6)
b	10.0156(6)
c	18.9648(11)
β	98.0510(10)
V (Å^3)	1907.2(2)
D_{Calcd} ($g\,cm^{-3}$)	2.132
Z	4
F_{000}	1172
Absorption correction $T_{\max}/T_{\min}$	0.999/0.998
Goodness-of-fit on F^2	1.104
Absorption coefficient (mm^{-1})	8.16
Largest diff. peak and hole (e Å^{-3})	5.17/−0.84

2.4. *X-ray crystallography*

An orange single crystal with dimensions 0.33 mm × 0.25 mm × 0.18 mm was selected and mounted on a thin glass fibre. The data were collected on a Bruker-Nonius SMART Apex diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Intensity data were collected in the range $2.03° \leq \theta \leq 27.90°$ at 100(2) K. All data points collected were used in solving the structure by direct methods. All non-hydrogen atoms were determined with successive difference Fourier syntheses and refined by full-matrix least-squares of F^2. The structure was solved using SHELXS-97 [20] and refined using SHELXL-97 [21] with the aid of the interface program X-SEED [22]. All non-hydrogen atoms were modelled anisotropically at the 50% probability level, with the hydrogens placed in calculated geometric positions. Two water molecules were found within the crystal lattice, although both positions were severely disordered, no attempt to model these was carried out. An equal site occupancy for each of these water molecules at the two different sites resulted in the best refined model for the structure, resulting in a good R-factor of 0.0187. Experimental details, crystal data, and refinement parameters are listed in table 1 (Supplementary material).

3. Results and discussion

The relative rate of $[PtCl_4]^{2-}$ oxidation with $NaClO_3$, $NaBrO_3$ and, for comparison, H_2O_2 in $1\,mol\,L^{-1}$ $HClO_4$, as monitored by UV-Vis spectroscopy at absorbance maximum of 261 nm at 50°C, is shown in figure 1(a). Note that the relative rates of oxidation by ClO_3^- and H_2O_2 (figure 1a) are similar, while that with BrO_3^- is significantly higher (oxidation is complete within seconds) so that this reaction could not be studied without stopped-flow methods under these conditions (figure 1b). A kinetic study of the oxidation of $[PtCl_4]^{2-}$ with H_2O_2 in $1\,mol\,L^{-1}$ $HClO_4$ by Hindmarsh *et al.* [23], suggested that *trans*-$[PtCl_4(H_2O)_2]$ is the exclusive (kinetic)

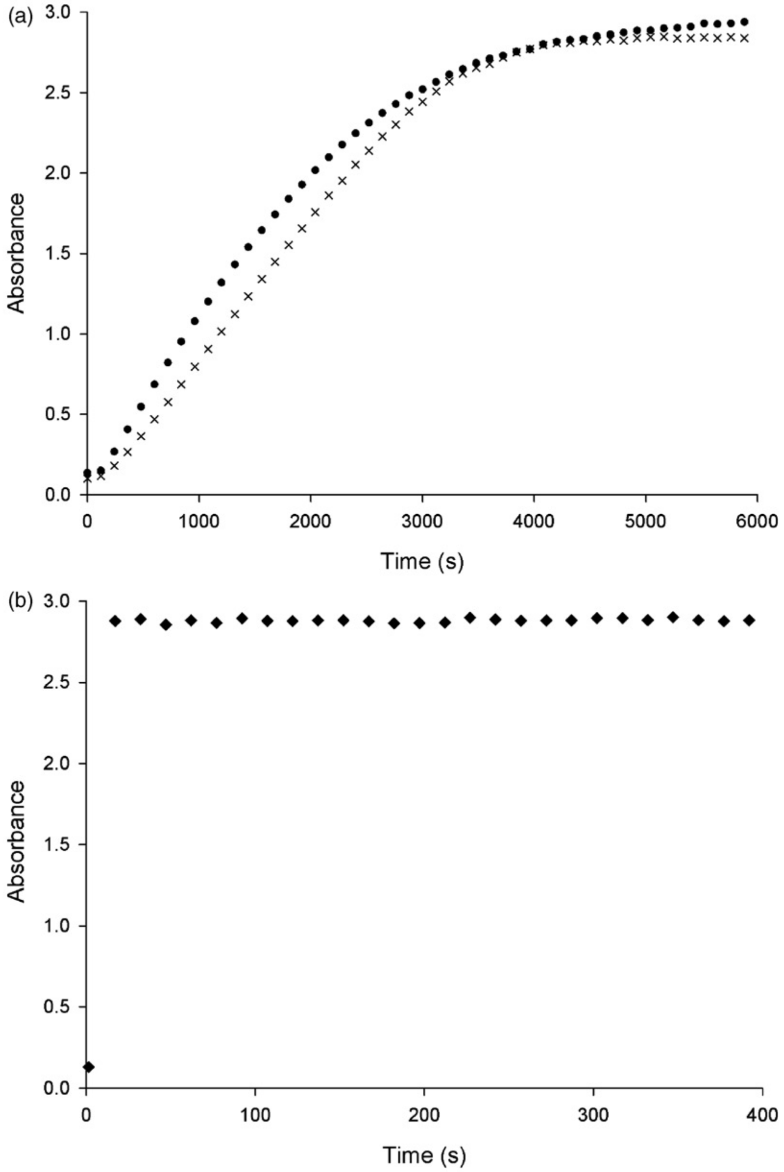

Figure 1(a). UV-Vis absorbance changes (monitored at 261 nm) with time obtained from oxidation of 1 mM [PtCl$_4$]$^{2-}$ (in 1 mol L^{-1} HClO$_4$) with 10 molar equivalents • H_2O_2, **X** $NaClO_3$ and (b) $NaBrO_3$ at 50°C, respectively.

oxidation product, according to a first order mechanism with respect to [PtCl$_4$]$^{2-}$ and H_2O_2. We applied this kinetic model to our UV-Vis data obtained in acidic solutions but could not satisfactorily fit a first order rate model as proposed by Hindmarsh *et al.* to our data. Given the relatively similar rate of oxidation of [PtCl$_4$]$^{2-}$ with ClO_3^- compared to that with H_2O_2, we could also not satisfactorily fit a similar rate model corresponding to a reaction leading to a single oxidation product with ClO_3^- in 1 mol L^{-1} HClO$_4$. Moreover, the UV-Vis spectra obtained under these conditions did not show any clear isosbestic points, and the observed spectra could not unambiguously be assigned to specific Pt(IV) complexes. This suggests the mechanism of oxidation and resultant species distribution in solution may be more complex than anticipated under our conditions and/or that ligand exchange processes take place in solution, possibly at comparable rates. As UV-Vis spectroscopy is not suited to provide detailed information about the nature and distribution of Pt(II/IV) complexes in these solutions, we examined the oxidation of relatively concentrated solutions of $[PtCl_4]^{2-}$ in acidic solutions by ClO_3^-, BrO_3^-, and H_2O_2 using ^{195}Pt NMR spectroscopy.

High-resolution ^{195}Pt NMR spectroscopy of the oxidation of $0.2\,mol\,L^{-1}$ K_2PtCl_4 by $NaClO_3$ and $NaBrO_3$ in $1\,mol\,L^{-1}$ $HClO_4$ after completion of the reaction shows that several Pt(IV) species exist in these solutions (figure 2a and b). The distribution of species following oxidation with $NaBrO_3$ is more complex than that obtained by $NaClO_3$ as might be anticipated; the former reaction results in several mixed chlorido/bromido/aqua-Pt(IV) species, in addition to some minor unassigned peaks as indicated (x_1 and x_2) in figure 2(b). The nomenclature code (e.g., 3^m12^c to designate the *mer*-trichloridobromido-*cis*-diaquaplatinum(IV)) for some of the species in figure 2(b) has been adopted from Preetz *et al.* [24] for convenience. All major Pt(IV) species in these solutions could be readily and unambiguously assigned by our method of chemical shift trend analysis [12, 13] with confirmation (*vide infra*) by $^{35}Cl/^{37}Cl$ isotope effects on the ^{195}Pt NMR resonance structure; the latter provides a unique "fingerprint" of a given $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 2$–6) complex [15, 16]. These results show clearly that the final distribution of oxidation products in acidic solutions under these conditions is much more complicated than anticipated, which may have profound implications on the understanding of the mechanism of oxidation by $NaClO_3$ and $NaBrO_3$.

In view of the distribution of several Pt(IV) oxidation products (figure 2) obtained by the oxidation of $0.2\,mol\,L^{-1}$ K_2PtCl_4 with $NaClO_3$ and $NaBrO_3$ in $1\,mol\,L^{-1}$ $HClO_4$, we re-examined the relatively well-studied oxidation of $0.2\,mol\,L^{-1}$ K_2PtCl_4 with H_2O_2 under various conditions, in particular acidic solutions for comparison. The oxidation of $[PtCl_4]^{2-}$ with H_2O_2 in water has been reported to result in the exclusive formation of *trans*-$[PtCl_4(OH)_2]^{2-}$ [4, 18]. Moreover, Dunham *et al.* established with ^{195}Pt NMR that the Pt(IV) *trans*-coordinated OH^- ligands are derived from both H_2O_2 and solvent H_2O in the resultant *trans*-$[PtCl_4(OH)_2]^{2-}$ species ($\delta\,^{195}Pt = 1247\,ppm$) using isotopically enriched $H_2^{18}O$ water [4]. Our equilibrated ^{195}Pt NMR spectrum recorded at 20°C resulting from the oxidation of $0.2\,mol\,L^{-1}$ K_2PtCl_4 with the $5\,mol\,L^{-1}$ equivalents of H_2O_2 in water confirmed that mainly *trans*-$[PtCl_4(OH)_2]^{2-}$ is formed at $\delta\,^{195}Pt = 1232 \pm 2\,ppm$ as shown in figure 3(a). The small difference in chemical shift for this complex may in part be ascribed to the lower temperature at which our ^{195}Pt NMR spectrum was recorded.†[2] In our ^{195}Pt NMR spectra, however, we also observe small amounts of *cis*-$[PtCl_4(OH)_2]^{2-}$ and $[PtCl_5(OH)]^{2-}$ as well as *mer*-$[PtCl_3(OH)_3]^{2-}$ (possibly formed as a result of the oxidation of $[PtCl_3(H_2O)]^{2-}$ due to $[PtCl_4]^{2-}$ aquation observed separately in $0.2\,mol\,L^{-1}$ K_2PtCl_4 solutions under our conditions) as shown in figure 3(a). These species are indeed the Pt(IV) chlorido-*hydroxido* complexes formed as a result of the reduction of H_2O_2, leading to an increase in solution pH to *ca* 7–8 (which consumes protons, according to $H_2O_2 + 2e^- + 2H^+ \longleftrightarrow 2H_2O$), is independently confirmed by high resolution ^{195}Pt NMR spectra of these species which are resolved into distinct $^{35}Cl/^{37}Cl$ isotopologues as shown for *trans*-$[PtCl_4(OH)_2]^{2-}$ (insert) in figure 3(b). The experimentally observed shape of this resonance shows a well-resolved set of $^{35}Cl/^{37}Cl$ isotope-induced $\delta\,^{195}$Pt

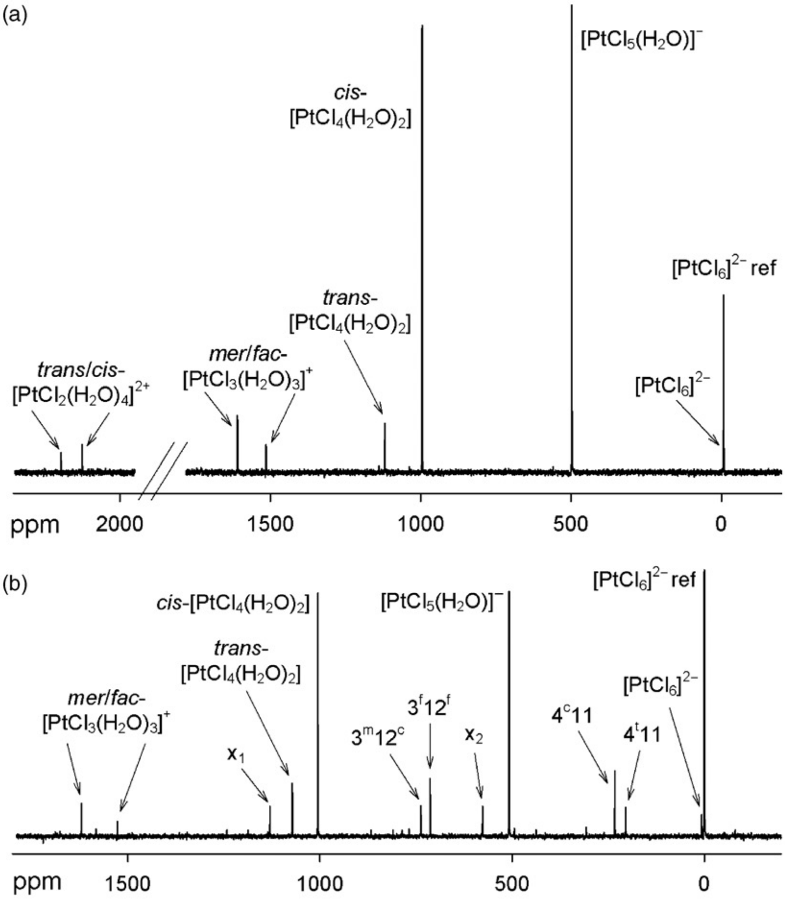

Figure 2. ^{195}Pt NMR spectrum of 0.2 mol L^{-1} K_2PtCl_4 in 1 mol L^{-1} $HClO_4$ oxidized at 50°C for 10 min with 5 mol L^{-1} equivalents (a) $NaClO_3$ and (b) $NaBrO_3$, respectively. Spectra were obtained immediately after cooling to 30°C (minor resonances x_1 and x_2 are unidentified).

shifts in the spectrum of the *hydroxido trans*-$[PtCl_4(OH)_2]^{2-}$ complex, showing an excellent least-squares fit with that of the statistically calculated isotopologue distribution (table 2) analogous to that for the corresponding *aqua cis*-$[PtCl_4(H_2O)_2]$ complex [15]. The ^{195}Pt NMR resonance shape of *trans*-$[PtCl_4(OH)_2]^{2-}$ closely resembles the resonance shape of the corresponding *trans*-$[PtCl_4(H_2O)_2]$ complex [16], with slight differences only in line-width and chemical-shift spacing (*vide infra*).

Although the identity of the major oxidation product *trans*-$[PtCl_4(OH)_2]^{2-}$ in figure 3(a) is adequately confirmed by the ^{195}Pt NMR spectroscopic data particularly due to its $^{35}Cl/^{37}Cl$ isotopologue "fingerprint," it was possible to co-crystallize *trans*-$[PtCl_4(OH)_2]^{2-}$ with 18-crown-6 forming *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$ directly from solutions used for the ^{195}Pt NMR experiments, from which the crystal and molecular structure was obtained by single crystal X-ray diffraction shown as an ORTEP diagram in figure 4. To our knowledge this is the first example of a *trans*-$[PtCl_4(OH)_2]^{2-}$ complex determined by X-ray diffraction. Octahedral *trans*-$[PtCl_4(OH)_2]^{2-}$ is sandwiched between two K^+ coordinated 18-crown-6 ether moieties.

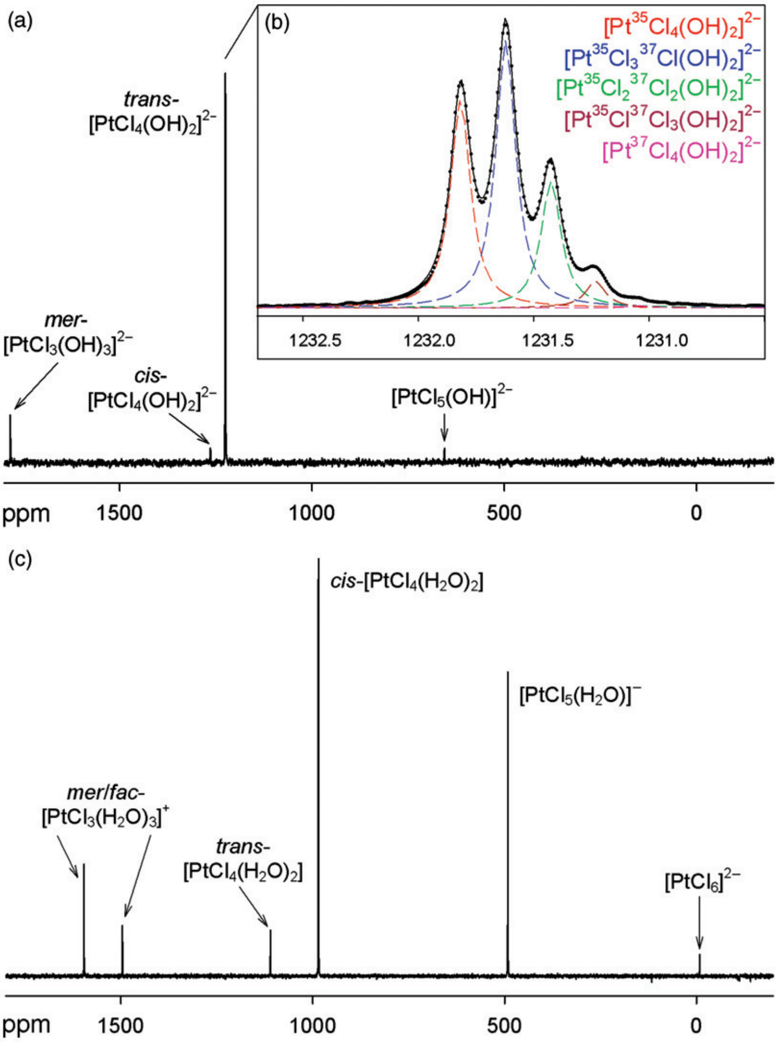

Figure 3. (a) ^{195}Pt NMR (recorded at 20°C) spectra of 0.2 mol L^{-1} $[PtCl_4]^{2-}$ oxidized in water with 10 mol L^{-1} equivalents H_2O_2 at 50°C for 10 min. (b) Expanded view of the experimental (●) ^{195}Pt spectrum of *trans*-$[PtCl_4(OH)_2]^{2-}$. The least-squares fit (solid line) between the experimental and the calculated ^{35}Cl/^{37}Cl isotopologue model (colored dashed lines) is shown. (c) ^{195}Pt NMR spectra of 0.2 mol L^{-1} $[PtCl_4]^{2-}$ oxidized in 1 mol L^{-1} $HClO_4$ with 10 mol L^{-1} equivalents H_2O_2 at 50°C for 10 min.

Two water molecules are found in highly disordered sites with similar occupancy in the crystal lattice on either side of a *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2$ unit. These were modelled anisotropically, excluding the calculated water hydrogen atoms, yielding a satisfactory goodness-of-fit for the model. Selected bond lengths and angles for *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2$ are given in table 3. Steinborn *et al.* [25, 26] previously reported the crystal and molecular structures of $[H_{13}O_6][PtCl_5(H_4O_2)] \cdot 2(18\text{-cr-}6)$ and *cis*-$[PtCl_4(H_2O)_2] \cdot (18\text{-cr-}6) \cdot 2H_2O$ showing the molecular structures of $[PtCl_5(H_2O)]^-$ and *cis*-$[PtCl_4(H_2O)_2]$ species obtained by co-crystallization with 18-crown-6.

Table 2. ^{195}Pt NMR experimental data, obtained from the least-squares fit of the spectrum figure 3(b), and the statistical calculated *trans*-$[PtCl_4(OH)_2]^{2-}$ isotopologue distribution arising from the natural $^{35}Cl/^{37}Cl$ isotope ratio.

	Percent isotopomers	
Pt(IV) isotopologue	Experimental	Statistical
$[Pt^{35}Cl_4(OH)_2]^{2-}$	33.0 (± 0.2)	32.96
$[Pt^{35}Cl_3^{37}Cl(OH)_2]^{2-}$	42.4 (± 0.1)	42.16
$[Pt^{35}Cl_2^{37}Cl_2(OH)_2]^{2-}$	20.1 (± 0.3)	20.22
$[Pt^{35}Cl^{37}Cl_3(OH)_2]^{2-}$	4.2 (± 0.1)	4.31
$[Pt^{37}Cl_4(OH)_2]^{2-}$	0.3 (± 0.1)	0.34

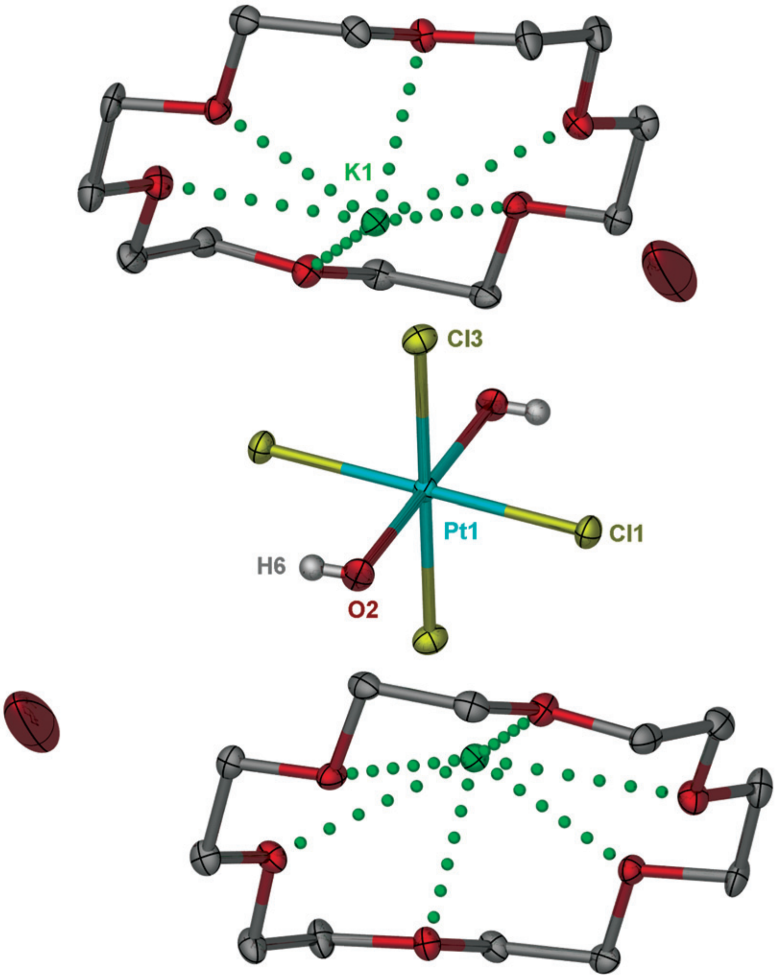

Figure 4. ORTEP diagram of the molecular structure of *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$ showing the atom numbering scheme; hydrogen atoms of the 18-crown-6 ethers are omitted for clarity. All non-hydrogen atoms were modelled anisotropically at the 50% probability level.

Table 3. Selected bond distances (Å) and angles (°) of *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$.

Bond distance (Å)	
Pt1–O2	2.022(4)
Pt1–O2^i	2.022(4)
Pt1–Cl1	2.3216(11)
Pt1–Cl1^i	2.3216(11)
Pt1–Cl3^i	2.3236(12)
Pt1–Cl3	2.3237(12)
Bond angles (°)	
O2–Pt1–O2^i	180.00(17)
O2–Pt1–Cl1	89.41(13)
O2^i–Pt1–Cl1	90.59(13)
O2–Pt1–Cl1^i	90.59(13)
O2^i–Pt1–Cl1^i	89.41(13)
Cl1–Pt1–Cl1^i	180.00(8)
O2–Pt1–Cl3^i	91.14(12)
O2^i–Pt1–Cl3^i	88.86(12)
Cl1–Pt1–Cl3^i	90.72(4)
Cl1^i–Pt1–Cl3^i	89.28(4)
O2–Pt1–Cl3	88.86(12)
O2^i–Pt1–Cl3	91.14(12)
Cl1–Pt1–Cl3	89.28(4)
Cl1^i–Pt1–Cl3	90.72(4)
Cl3^i–Pt1–Cl3	180.00(6)

Symmetry codes for symmetry linked atoms: x^i, y, z.

Figure 3(c) shows the corresponding ^{195}Pt NMR spectrum resulting from the oxidation of 0.2 mol L^{-1} K_2PtCl_4 by H_2O_2 carried out in 1 mol L^{-1} $HClO_4$ at 50°C, indicating that a distribution of several of the possible $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 2$–6) species is obtained. Apart from the expectation that any oxidation products are unlikely to be *hydroxido* Pt(IV) complexes in 1 mol L^{-1} $HClO_4$, the distribution of species in the ^{195}Pt NMR spectrum is interesting and somewhat surprising, in view of previous findings which indicate that only the *diaqua trans*-$[PtCl_4(H_2O)_2]$ species is formed [27]. Additionally only a relatively small amount of *trans*-$[PtCl_4(H_2O)_2]$ is present (figure 3c), the major species being *cis*-$[PtCl_4(H_2O)_2]$, together with smaller amounts of $[PtCl_5(H_2O)]^-$ and other species. Although the isotopologue distribution of the $\delta\,^{195}Pt$ resonance of the *hydroxido trans*-$[PtCl_4(OH)_2]^{2-}$ species (figure 3b) compared with the *aqua trans*-$[PtCl_4(H_2O)_2]$ complex [18] has a similar "isotopologue fingerprint" as expected, the average $^{35}Cl/^{37}Cl$ isotope shifts induced $\Delta\delta\,(^{195}Pt)$ between the various isotopologues as well as the peak widths at half-height ($\nu_{1/2}$) of the related *trans*-diaquatetrachloridoplatinum(IV) and *trans*-dihydroxido-tetrachlorido-platinum(IV) species differ significantly. The values of the isotopologue-induced $\Delta\delta\,(^{195}Pt)$ for *trans*-$[PtCl_4(OH)_2]^{2-}$ and *trans*-$[PtCl_4(H_2O)_2]$ are ~0.191 and 0.148 ppm, while the corresponding $\nu_{1/2}$ peak widths are ~16.7 and 23.2 Hz, respectively. In general our results indicate that the $^{35}Cl/^{37}Cl$-isotope-induced shifts of the isotopologues are better resolved for the *hydroxido* species compared with the corresponding *aqua* species. Such small detectable differences in the NMR parameters, are interesting in view of the greatly differing binding strengths between the OH^- ion and H_2O molecule as ligands to Pt(IV). It is tempting to ascribe the differing line-widths to differing dynamic effects (ligand exchange and/or H exchange) in solution, whereas the differing $\Delta\delta\,(^{195}Pt)$ values may arise from different binding enthalpies for the OH^- ion and H_2O molecule in these two complexes, although this is somewhat speculative in the absence of further study. The relatively large overall δ^{195}Pt chemical shift differences between *trans*-$[PtCl_4(OH)_2]^{2-}$ and *trans*-$[PtCl_4(H_2O)_2]$ species (~115 ppm, neglecting the ^{35}Cl/^{37}Cl isotope effects) is also diagnostic for differentiating between *trans*-$[PtCl_4(H_2O)_2]$ and its de-protonated (*hydroxido*) counterpart. Nevertheless such overall chemical shift differences are a good, albeit not sufficient, criterion for the unambiguous distinction between such closely related Pt(IV) complexes in solution. In this context, the ^{35}Cl/^{37}Cl isotope shifts observable in the δ^{195}Pt resonance structure of a given species are an invaluable aid to accurate assignments [15, 16].

To elucidate the differing species distributions obtained from the oxidation of $0.2\,\mathrm{mol\,L^{-1}}$ K_2PtCl_4 with H_2O_2 in the presence or absence of $HClO_4$ (figure 3a *vs.* c), and thus the oxidation by $NaClO_3$ and $NaBrO_3$ which were only examined in acidic solutions, several additional oxidation experiments under differing conditions were carried out. In view of the possibility that $HClO_4$ may act as oxidant of Pt(II) in such solutions, conceivably accounting for the observed species distributions as shown in figure 3, oxidation of $[PtCl_4]^{2-}$ by H_2O_2 was examined in $2\,\mathrm{mol\,L^{-1}}$ $NaClO_4$ (figure 5a), $1.5\,\mathrm{mol\,L^{-1}}$ $NaClO_4$, and $0.5\,\mathrm{mol\,L^{-1}}$ $HClO_4$ (figure 5b), as well as in $1\,\mathrm{mol\,L^{-1}}$ trifluoromethanesulfonic (triflic) acid (figure 5c). The triflic "super acid" ($pK_a \sim -15$) is thermally and chemically stable, and its conjugate base $CF_3SO_3^-$ (triflate) is weakly or non-coordinating, also resisting oxidation/reduction reactions [28]. We find that the distribution of Pt(IV) oxidation products does not change significantly during the acquisition of the ^{195}Pt NMR spectrum (*ca* 1 h), as the spectra of these solutions obtained after re-acquisition several hours later are similar.

There is no qualitative difference in the species distribution shown by ^{195}Pt NMR spectra between figure 5(a) and figure 3(a), the *hydroxido* species *trans*-$[PtCl_4(OH)_2]^{2-}$ and *mer*-$[PtCl_3(OH)_3]^{2-}$ being the main products in $2\,\mathrm{mol\,L^{-1}}$ $NaClO_4$ with the *trans*-$[PtCl_4(OH)_2]^{2-}$ anion present in highest concentration. However, oxidation carried out in an acidic solution of similar ionic strength ($1.5\,\mathrm{mol\,L^{-1}}$ $NaClO_4$ and $0.5\,\mathrm{mol\,L^{-1}}$ $HClO_4$) results in the formation of relatively high concentrations of $[PtCl_5(H_2O)]^-$, $[PtCl_6]^{2-}$, and *cis*-$[PtCl_4(H_2O)_2]$ (figure 5b, comparable to that obtained from the oxidation carried out in $1\,\mathrm{mol\,L^{-1}}$ $HClO_4$ (figure 3c). Interestingly, in figure 5(b) the concentration ratio of chloride-deficient species $[PtCl_n(H_2O)_{6-n}]^{4-n}$ (n = 2–3), compared with chloride-rich $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 5$–6) species is 1 : 99% by resonance integration, suggesting a re-distribution of the oxidation products to the presumably thermodynamically favored chloride-rich $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 5$–6) products. As the total Cl^- concentration must clearly be related to the initial $[PtCl_4]^{2-}$ concentration, the possibility of ClO_4^- reduction leading to an increase in Cl^- concentration was considered. Although the ClO_4^- anion is used as a supporting electrolyte in many kinetic and thermodynamic reaction studies, the ClO_4^- ion is known to be strongly oxidative in acidic media particularly at elevated temperatures and high concentration (thus possibly leading to increased Cl^- ion concentration in solution as by-products of ClO_4^- reduction) [29, 30]. To examine this possibility, oxidation of $[PtCl_4]^{2-}$ was carried out in triflic acid for comparison; figure 5(c) shows that the corresponding oxidation of $0.2\,\mathrm{mol\,L^{-1}}$ K_2PtCl_4 by H_2O_2 in $1\,\mathrm{mol\,L^{-1}}$ TfOH results in a qualitatively similar distribution of Pt(IV) species as seen in figure 3(c), the main difference being the presence of small quantities of *cis*/*trans*-$[PtCl_2(H_2O)_4]^{2+}$. The ratio of integrated peak areas in spectrum figure 5(c) of the $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 2$–3) species relative to the $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 5$–6) species is 55 : 45%, due to the

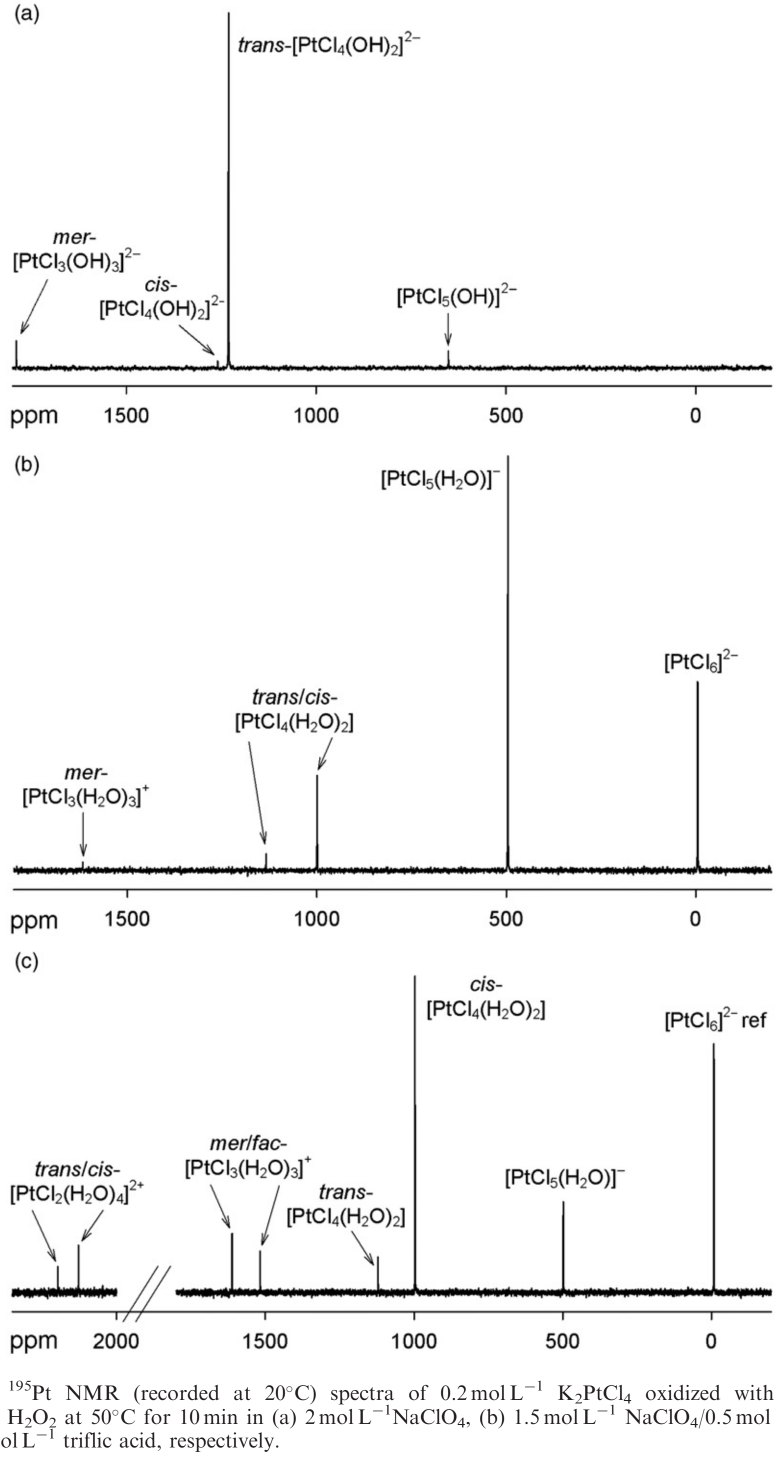

Figure 5. ^{195}Pt NMR (recorded at 20°C) spectra of 0.2 mol L^{-1} K_2PtCl_4 oxidized with 10 mol L^{-1} equivalents H_2O_2 at 50°C for 10 min in (a) 2 mol L^{-1}$NaClO_4$, (b) 1.5 mol L^{-1} $NaClO_4$/0.5 mol L^{-1} $HClO_4$, and (c) 1 mol L^{-1} triflic acid, respectively.

dominance of *cis*-$[PtCl_4(H_2O)_2]$ under these conditions. We thus conclude that $HClO_4$ is unlikely to participate in oxidation reactions in these solutions, and that the variable distribution of species from a quantitative point of view, is the result of relatively rapid ligand scrambling reactions during or after the oxidation reactions in the two different acid solutions. It is nevertheless clear that in acidic solutions, the distribution of oxidation products of $[PtCl_4]^{2-}$ by ClO_3^-, BrO_3^-, and H_2O_2 is *not* a single species as assumed by previous studies [8, 23], which is however largely the case for the oxidation of $[PtCl_4]^{2-}$ by H_2O_2 in water [4]. Unfortunately, the oxidation of $[PtCl_4]^{2-}$ with $NaClO_3$ or $NaBrO_3$ in water does not proceed to any significant extent because the oxidation reaction requires an acidic medium.

Previous work using an oxidative-addition quenching technique by Elding *et al.* [31] has shown the major oxidation products of $[PtCl_4]^{2-}$, *trans*-$[PtCl_2(H_2O)_2]$, and $[Pt(H_2O)_4]^{2+}$ with Cl_2 in 1 mol L^{-1} $HClO_4$ to be $[PtCl(H_2O)_5]^{3+}$, *mer*-$[PtCl_3(H_2O)_3]^+$, and $[PtCl_5(H_2O)]^-$, respectively. By contrast, in our solutions resulting from the oxidation of $[PtCl_4]^{2-}$ with ClO_3^-, BrO_3^-, and H_2O_2 (figures 2 and 5) in acidic solutions, the major product species obtained is *cis*-$[PtCl_4(H_2O)_2]$ not *trans*-$[PtCl_4(OH)_2]^{2-}$ species from oxidation of K_2PtCl_4 with H_2O_2 in water [4, 18, 31]. These observations suggest that oxidation of Pt(II) complexes in acidic solutions, and in particular the distribution of species resulting from such reactions, is significantly more complicated than may be assumed for such reactions in water. In acidic solutions the relatively higher rates of ligand exchange for any Pt(II) aqua-chlorido precursor complexes as well as the resultant Pt(IV) products need to be taken into account when studying the mechanisms of such oxidation reactions. The possibility of relatively rapid ligand scrambling and complex redistribution to the more thermodynamically stable forms in solution, complicate such mechanistic investigations significantly.

To illustrate qualitatively these effects, we prepared authentic *trans*-$K_2[PtCl_4(OH)_2]$ by oxidation of K_2PtCl_4 with 30% H_2O_2, followed by precipitating the complex as a pinkish salt with ethanol according to the literature method [17, 18]. The ^{195}Pt NMR spectrum of this salt dissolved in water shows only a single peak at $\delta\,^{195}Pt = 1241$ ppm (cf 1247 ppm [4]) corresponding to *trans*-$[PtCl_4(OH)_2]^{2-}$. The *trans*-$[PtCl_4(OH)_2]^{2-}$ complex is kinetically stable and persists for many hours at room temperature as the only species in solution, even after heating this solution at 50°C for 10 min. Addition of concentrated $HClO_4$ (70% w/w) directly to such an orange colored solution containing 0.1 mol L^{-1} *trans*-$[PtCl_4(OH)_2]^{2-}$ to obtain ~1.3 mol L^{-1} $HClO_4$, results in a white precipitate ($KClO_4$) removed from solution by filtration, while the color of the solution did not change perceptibly. The ^{195}Pt NMR spectrum of the latter solutions indicates that in addition to a peak due to the protonated *aqua trans*-$[PtCl_4(H_2O)_2]$ complex ($\delta\,^{195}Pt = 1117$ ppm, 82% integral area) an additional peak clearly assigned to *cis*-$[PtCl_4(H_2O)_2]$ ($\delta\,^{195}Pt = 993$ ppm, 18%) is present. Moreover, heating this solution for 10 min at 50°C shows a clear conversion of *trans*-$[PtCl_4(H_2O)_2]$ to *cis*-$[PtCl_4(H_2O)_2]$, which becomes the dominant complex, (48%) in addition to the formation of small quantities of $[PtCl_5(H_2O)]^-$ (5%) as a result of relatively fast ligand redistribution reactions of Pt(IV) species in acidic solution. This finding contrasts with the results of Elding *et al.* [27], who reported that the protonation of *trans*-$[PtCl_4(OH)_2]^{2-}$ results only in the formation of the *trans*-$[PtCl_4(H_2O)_2]$ species under comparable conditions. It is thus clear that the distribution of species in acidic solutions is significantly complicated by relatively rapid ligand exchange (chloride coordination and aquation reactions) of

Pt(IV) complexes under these conditions, something not observed in neutral to alkaline solutions in view of the kinetically inert nature of Pt(IV) *hydroxido* complexes.

A further level of complexity in understanding the plausible mechanisms of the oxidation reactions in acidic solutions arises from previous detailed mechanistic studies which indicate the possibility of Pt(II)–Pt(IV) associations *via* a bridging chloride ligand, resulting in accelerated ligand exchange rates in the Pt(IV) complexes [32, 33]. Hence, the presence of even catalytic concentrations of $[PtCl_4]^{2-}$ in solution undergoing oxidation reactions in acidic media to yield $[PtCl_{n-6}(H_2O)_n]$ ($n = 1-6$) complexes may result in significantly higher rates of ligand exchange reactions in Pt(II/IV) complexes by the postulated association processes between Pt(IV) and Pt(II) species [33], relevant to our solutions studied here.

To explore this possibility the ^{195}Pt NMR spectrum of a mixture containing $0.02\,mol\,L^{-1}$ $[PtCl_4]^{2-}$ and $0.2\,mol\,L^{-1}$ *trans*-$[PtCl_4(OH)_2]^{2-}$ in water, shown in figure 6(a), clearly illustrates only two peaks easily assigned to *trans*-$[PtCl_4(OH)_2]^{2-}$ and $[PtCl_4]^{2-}$ (in addition to a reference peak in the coaxial tube). No additional Pt(IV) complexes are observed in the solution if allowed to be aged overnight at room temperature or heated to 50°C for 10 min; the only other species observed in solution after heating is $[PtCl_3(OH)]^{2-}$, most likely due to some aquation/hydrolysis of $[PtCl_4]^{2-}$. Evidently in a fresh solution of the mixture, $[PtCl_4]^{2-}$ does not enhance ligand exchange of *trans*-$[PtCl_4(OH)_2]^{2-}$ at a pH $\sim 7-8$; presumably the two *trans* hydroxido ligands in *trans*-$[PtCl_4(OH)_2]^{2-}$ are poor "bridging" ligands resulting in little or no Pt(II)–Pt(IV) association of $[PtCl_4]^{2-}$ with *trans*-$[PtCl_4(OH)_2]^{2-}$ as envisaged by Mason [33]. The kinetic inertness of hydroxido ligands bound to Pt(IV) also contributes to the negligible ligand exchange in the time frame of our oxidation and NMR experiments in non-acidic solution. Essentially *trans*-$[PtCl_4(OH)_2]^{2-}$ under these conditions is quite unreactive.

By contrast, acidification of a sample of $0.02\,mol\,L^{-1}$ $[PtCl_4]^{2-}$ and $0.2\,mol\,L^{-1}$ *trans*-$[PtCl_4(OH)_2]^{2-}$ with a small amount of concentrated $HClO_4$ to result in *ca* $1.3\,mol\,L^{-1}$ $[H^+]$ results in an immediate color change from orange to bright yellow, and yields a ^{195}Pt NMR spectrum with the species distribution shown in figure 6(b). Clearly a rapid re-distribution of species takes place in acidic media, for both the Pt(IV) and Pt(II) complexes, resulting in a qualitative species distribution of Pt(IV) complexes very similar to that obtained in the 1800 to −200 ppm spectral window as observed in figures 3(c) and 5(c), obtained by oxidation of $[PtCl_4]^{2-}$ by H_2O_2 in $1\,mol\,L^{-1}$ $HClO_4$ and $1\,mol\,L^{-1}$ triflic acid, respectively. The relatively more rapid establishment of the distribution of species shown in figure 6(b) from *trans*-$[PtCl_4(OH)_2]^{2-}$ on acidification is only observed in the presence of $[PtCl_4]^{2-}$. Notably, the ^{195}Pt NMR spectrum in the −200 to −1800 ppm spectral widow shows the presence of several Pt(II) minor aqua-chlorido species $[PtCl_3(H_2O)]^-$ and *trans*/*cis*-$[PtCl_2(H_2O)_2]$, qualitatively consistent with the aquation of $[PtCl_4]^{2-}$ in $1\,mol\,L^{-1}$ $HClO_4$ reported by Gröning and Elding [27].

We conclude that the product distribution resulting from the oxidation of $[PtCl_4]^{2-}$ by H_2O_2 in acidic solution, may be due to the formation of *trans*-$[PtCl_4(H_2O)_2]$, which in turn undergoes relatively rapid ligand scrambling reactions, possibly in a manner suggested by Mason for Pt(II) catalyzed ligand scrambling *via* a Pt(II)–Pt(IV) association complex [33], prior to complete oxidation of Pt(II) complexes in solution. Evidently the *trans*-$[PtCl_4(H_2O)_2]$ complex also isomerizes to the thermodynamically more stable *cis* isomer, which becomes prominent in these solutions.

In this context the Pt(IV) aqua-chlorido species distribution resulting from the oxidation of $[PtCl_4]^{2-}$ by $NaClO_3$ and $NaBrO_3$ in acidic solutions can be understood

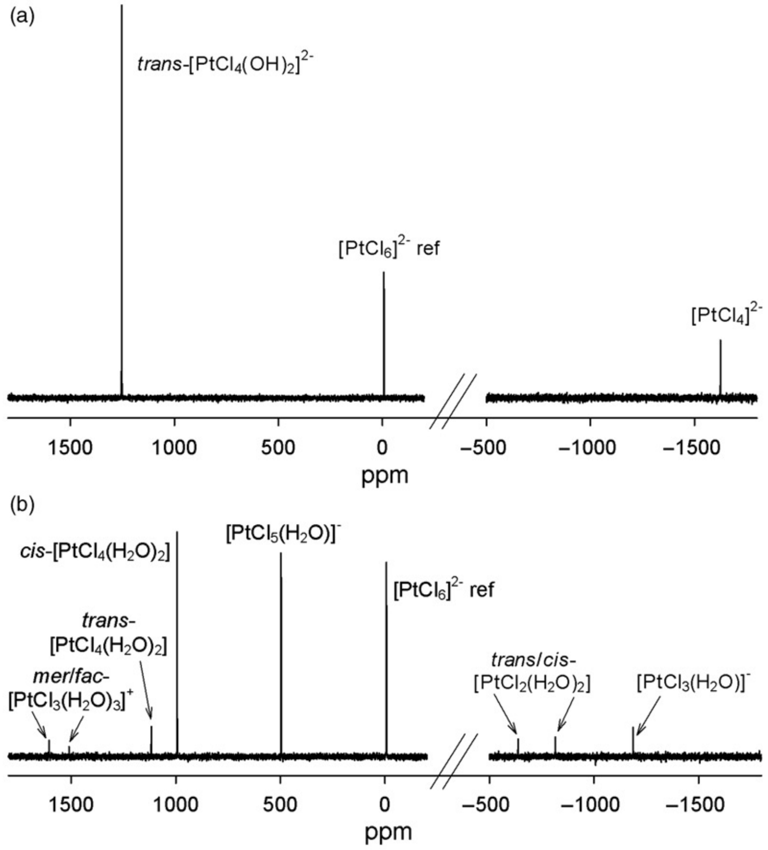

Figure 6. ^{195}Pt NMR spectra (recorded at 20°C) of (a) 0.2 mol L^{-1} *trans*-$[PtCl_4(OH)_2]^{2-}$ with 0.02 mol L^{-1} K_2PtCl_4 added in water after standing/heating (see text) (b) solution (a) made acidic with $HClO_4$ (final $[H^+] \approx 1.3$ M).

in part at least to proceed similarly, due to the rapid ligand redistribution reactions in acidic solutions of the more labile Pt(IV) complexes. We suggest that the Pt(IV) oxidation product initially formed is *trans*-$[PtCl_4(H_2O)_2]$, resembling the *trans*-$[PtCl_4(OH)_2]^{2-}$ complex arising from the oxidation with H_2O_2 in water. Moreover, from figure 2 it is clear that the oxidation product distribution obtained from H_2O_2 and $NaClO_3$ are qualitatively similar in acidic solutions.

4. Conclusions

The rate of oxidation of $[PtCl_4]^{2-}$ by $NaBrO_3$ is significantly higher than that with $NaClO_3$ which is comparable to that of H_2O_2. In acidic solutions, oxidation by $NaClO_3$ results in a distribution of $[PtCl_n(H_2O)_{6-n}]^{4-n}$ ($n = 2$–6) species while that with $NaBrO_3$ results in mixed chlorido/bromido/aqua-Pt(IV) species. The reason for the relative oxidation rate differences between $NaClO_3$ and $NaBrO_3$ is not clear, and work in an attempt to elucidate this is underway. ^{195}Pt NMR spectroscopy shows that *inter alia* the *cis*-[$PtCl_4(H_2O)_2$] species is finally predominant in acidic solutions, and not only the *trans*-[$PtCl_4(H_2O)_2$] as has been suggested in pervious studies. Our ^{195}Pt NMR spectra confirm that for oxidation of $[PtCl_4]^{2-}$ with H_2O_2 *in water*, the kinetically inert *trans*-$[PtCl_4(OH)_2]^{2-}$ species is the dominant product; however, in acidic solutions the corresponding protonated *aquated* Pt(IV) complexes undergo rapid ligand scrambling reactions to result in a very different distribution of species, which may be catalyzed by the presence of some residual $[PtCl_4]^{2-}$. Nevertheless, ^{195}Pt NMR spectroscopy is a powerful tool with which to elucidate this deceptively simple chemistry, allowing for easy distinguishing of, for example, *trans*-$[PtCl_4(OH)_2]^{2-}$ from its corresponding *aqua* counterpart *trans*-[$PtCl_4(H_2O)_2$] using ^{35}Cl/^{37}Cl-isotope-induced effects on the ^{195}Pt NMR resonance shape. The crystal structure of *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$ confirms the NMR assignment. From a mechanistic point of view, the elucidation of oxidation reactions using $NaClO_3$ and $NaBrO_3$ of PGMs in acidic solutions as encountered in the large scale separation and refining industry, must take into consideration the intricate kinetic and thermodynamic differences in the coordination chemistry of Pt(II/IV) hydroxido and aqua complexes in water as compared to the acidic solutions as shown here.

Supplementary material

CCDC 764253 contains supplementary crystallographic data for the *trans*-$K_2[PtCl_4(OH)_2](18\text{-cr-}6)_2 \cdot 2H_2O$ structure. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retreiving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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References

[1] F.L. Bernardis, R.A. Grant, D.C. Sherrington. *React. Funct. Polym.*, **65**, 205 (2005).
[2] J.D. Edwards, D.F. Colton, R.K. Lea, European Patent Application: EP0049567 A1, (Inco Ltd., Canada), p. 24 (1982).
[3] S.E. Livingstone, R.A. Plowman. *J. Proc. R. Soc. N. S. W.*, **84**, 107 (1951).
[4] S.O. Dunham, R.D. Larsen, E.H. Abbott. *Inorg. Chem.*, **32**, 2049 (1993).
[5] S.V. Zemskov, B.V. Ptitsyn, V.N. Lyubimov, V.F. Malakhov. *Russ. J. Inorg. Chem.*, **12**, 1223 (1967).
[6] M.M. Jones, K.A. Morgan. *J. Inorg. Nucl. Chem.*, **34**, 259 (1972).
[7] K.A. Morgan, M.M. Jones. *J. Inorg. Nucl. Chem.*, **34**, 275 (1972).
[8] B.V. Ptitsyn, S.V. Zemskov, A.V. Nikolaev. *Doklady Akad. Nauk SSSR*, **167**, 112 (1966).
[9] L. Treindl, T. Matsumura-Inoue, P. Ruoff. *J. Phys. Chem. A*, **106**, 5271 (2002).
[10] M.S. Alam, K. Inoue, K. Yoshizuka. *Hydrometallurgy*, **49**, 213 (1998).

[11] W.H. Pittie, G. Overbeek, K.F. Doig, Patent No. 1418060, ZA (Swarsab Mining, Exploration and Development Co. (Pty.) Ltd.) (1973).
[12] J. Kramer, K.R. Koch. *Inorg. Chem.*, **45**, 7843 (2006).
[13] J. Kramer, K.R. Koch. *Inorg. Chem.*, **46**, 7466 (2007).
[14] I.M. Ismail, S.J.S. Kerrison, P.J. Sadler. *J. Chem. Soc., Chem. Commun.*, 1175 (1980).
[15] W.J. Gerber, P. Murray, K.R. Koch. *Dalton Trans.*, 4113 (2008).
[16] P. Murray, K.R. Koch. (2010) (unpublished results).
[17] A.V. Babaeva. *Doklady Akad. Nauk SSSR, Seriya A*, **24**, 145 (1939).
[18] L.E. Cox, D.G. Peters. *Inorg. Chem.*, **9**, 1927 (1970).
[19] S.M. Cohen, T.H. Brown. *J. Chem. Phys.*, **61**, 2985 (1974).
[20] G.M. Sheldrick. *Acta Crystallogr., Sect. A*, 64, 112 (2008).
[21] L.J. Barbour. *J. Supramol. Chem.*, **1**, 189 (2001).
[22] J.L. Atwood, L.J. Barbour. *Cryst. Growth Des.*, **3**, 3 (2003).
[23] K. Hindmarsh, D.A. House, R. van Eldik. *Inorg. Chim. Acta*, **278**, 32 (1998).
[24] H.H. Drews, W. Preetz. *Z. Naturf. B*, **51**, 11 (1996).
[25] D. Steinborn, O. Gravenhorst, H. Hartung, U. Baumeister. *Inorg. Chem.*, **36**, 2195 (1997).
[26] C. Wagner, C. Bruhn, O. Gravenhorst, D. Steinborn. *Z. Kristallogr.*, **215**, 61 (2000).
[27] O. Gröning, L.I. Elding. *Inorg. Chem.*, **28**, 3366 (1989).
[28] G. Siegemund, W. Schwertfeger, A. Feiring, B. Smart, F. Behr, H. Vogel, B. McKusick. In *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, New York (2007), and references cited therein.
[29] G. Horanyi, I. Bakos. *J. Electroanal. Chem.*, **331**, 727 (1992).
[30] G. Lang, M. Ujvari, G. Horanyi. *Corros. Sci.*, **45**, 1 (2002).
[31] L.I. Elding, L. Gustafson. *Inorg. Chim. Acta*, **19**, 31 (1976).
[32] R.L. Rich, H. Taube. *J. Am. Chem. Soc.*, **76**, 2608 (1954).
[33] W.R. Mason. *Coord. Chem. Rev.*, **7**, 241 (1972).