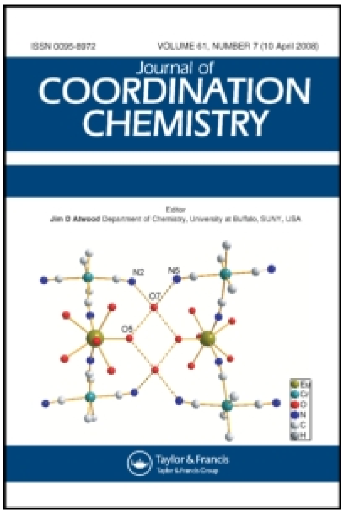

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Coordination Chemistry of Higher Oxidation States. Part 36. Periodato Complexes of Palladium(IV) and Platinum(IV). Crystal Structure of $K_4Na_2[Pt(OH)_2(HIO_6)_2]\cdot 10H_2O$

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COORDINATION CHEMISTRY OF HIGHER OXIDATION STATES. PART 36.[1] PERIODATO COMPLEXES OF PALLADIUM(IV) AND PLATINUM(IV). CRYSTAL STRUCTURE OF $K_4Na_2[Pt(OH)_2(HIO_6)_2].10H_2O$

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Periodate complexes of Pd(IV) and Pt(IV) have been prepared from $[MCl_6]^{2-}$ (M = Pd or Pt) and IO_4^- in aqueous alkaline solution. They are formulated as $M'_6[M(OH)_2(HIO_6)_2].nH_2O$ (M′ = Na or K) on the basis of analysis, vibrational spectroscopy, and an X-ray structure determination of the platinum complex. The title compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 7.588(2)$, $b = 8.110(2)$, $c = 9.864(2)$ Å, $\alpha = 82.00(2)$, $\beta = 83.79(2)$, $\gamma = 81.76(2)°$ with $Z = 1$. Based on 2283 observed reflections ($F > 3\sigma(F)$), the structure refined to $R = 0.034$. Two bidentate $[HIO_6]^{4-}$ anions coordinate to a central Pt atom which is also coordinated by two *trans* OH groups. The charge balance is maintained by sodium and potassium cations which are extensively hydrated. ^{195}Pt and ^{127}I NMR data are reported, and the variation in the former with pH interpreted in terms of differing degrees of protonation of the anions. EXAFS data are reported for the platinum complex in solution at pH = 2.

Keywords: Palladium, platinum, periodate complex, X-ray structure

INTRODUCTION

Periodate, $[H_nIO_6]^{(5-n)-}$ and tellurate, $[H_nTeO_6]^{(6-n)-}$ anions can function as strongly coordinating ligands towards metal centres, often in unusually high oxidation states. A variety of such complexes have been reported,[2] but only a few have been characterised in detail or their structures established. Among the recently characterised examples with periodate ligands are the Cu(III), Ag(III) and Au(III) species $[M(HIO_6)_2]^{5-}$ (M = Cu, Ag, or Au) which contain the square planar M(III) centre chelated by two bidentate periodates,[3–5] whilst in $[MO_2(HIO_6)_2]^{6-}$ (M = Ru or Os) there are *trans* $M^{VI}O_2$ moieties, with pseudo-octahedral coordination completed by chelating periodates.[6,7] Platinum(IV) and palladium(IV) complexes, which on the basis of analytical data were formulated $K_{6-n}H_n[Pt(IO_6)_2].xH_2O$ (n = 0, 3) and $K_6[Pd(IO_6)_2].KOH.xH_2O$, have been described,[8] and it was proposed that terdentate periodate groups (*fac* coordinated) were present. We report here a spectroscopic and structural reinvestigation of these complexes.

EXPERIMENTAL

Multinuclear NMR spectra were recorded on a Bruker AM360 spectrometer in 10 mm O/D tubes with the lock provided by a small quantity of D_2O added to the

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solutions. Iodine-127 (72.5 MHz) and platinum-195 (77.6 MHz) were referen respectively to external 1.0 mol dm^{-3} aqueous KI (subsequently corrected to infi dilution using published data)[9] and aqueous K_2PtCl_6.

Analytical data were obtained from energy dispersive X-ray fluorescence s troscopy and thermogravimetric analysis. The former (utilising a standard E system attached to a Cambridge Stereoscan 150 electron microscope) yielded Na Pd/Pt:I atom ratios, whilst the latter (employing a Stanton-Redcroft TG760) gave estimate of the degree of hydration of the complexes.

EXAFS data were obtained at the Pt L_{III} edge from concentrated aque solutions in PTFE cells fitted with Mylar windows. The data were recorded transmission mode on beam-line 7 at the Daresbury Synchrotron Radiation Sou using a silicon (111) order-sorting monochromator. Background subtraction carried out using the program PAXAS[10] and curve fitting employed the si scattering curved wave theory incorporated in EXCURVE90.[11]

Preparation of $M_6[Pd(OH)_2(HIO_6)_2].nH_2O$ (M = Na, K)

$PdCl_2$ (0.20 g, 1.13 mmol) was dissolved in hot water (20 cm^3) containing conc. (5 drops) and then cooled to room temperature. Chlorine gas was bubbled thro this solution until no further colour change was observed. After purging nitrogen, MIO_4 (M = Na, K; 2.3 mmol) was added together with MOH (to 4 mol dm^{-3} in hydroxide) and the mixture then boiled until a clear orange solut was obtained. This was filtered, the filtrate reduced in volume on a hot-plate u crystallisation began and cooled to room temperature. On standing overnight orange-yellow powder was obtained, which was collected, washed with cold wa ethanol, and diethyl ether and finally dried in a stream of air. Yield: 85%. Anal atom ratios (EDX) Na:Pd:I 5.77:0.99:2.00, %H_2O = 20.5; K:Pd:I 5.60:1.03:2 %H_2O = 22.1.

Preparation of $K_6[Pt(OH)_2(HIO_6)_2].10H_2O$

K_2PtCl_6 (0.22 g, 0.46 mmol) in water (15 cm^3) was added dropwise to aqueous K (0.27 g in 1 cm^3). KIO_4 (0.22 g, 0.94 mmol) and KOH (1.25 g) were added and mixture boiled for 3–4 hrs to give a pale yellow solution. This was concentrate approximately half the starting volume and cooled to −18°C for 16 hrs resultin the precipitation of a pale yellow solid. This was collected, washed with a s quantity of ice-cold water, ethanol and finally diethyl ether and air dried. Yield: 7 Analysis: atom ratios (EDX) K:Pt:I 5.67:0.97:2.00; %H_2O = 16.2 (calc. 16.5).

Preparation of $K_4Na_2[Pt(OH)_2(HIO_6)_2].10H_2O$

H_2PtCl_6 (2.25 g) in water (25 cm^3) was added to aqueous KOH solution (2.5 10 cm^3), KIO_4 (2.15 g) and KOH (12.5 g) were added and the mixture heated un clear solution resulted. This was transferred to a Carius tube, sealed and heate 140°C for 6–8 hrs. The solution was recovered and after standing in a closed flas room temperature for 5 days precipitation of a crystalline solid was complete. was filtered and air dried. Yield: 60%. Analysis: atom ratios (EDX) Na:K:Pt:I 1 3.92:0.99:2.0; %H_2O = 17.4 (calc. 17.0).

X-Ray Structure Determination

Pale yellow, air-stable crystals of the platinum complex were isolated from the reaction mixture and mounted in glass capillaries. The crystal system and approximate cell dimensions were established by photographic X-ray methods and the density measured by flotation ($CCl_4/CHBr_3$). Using an Enraf-Nonius CAD4 diffractometer fitted with graphite monochromator and MoK_α radiation, data were measured at room temperature with a crystal of size 0.15 × 0.22 × 0.35 mm. Accurate cell dimensions were obtained from 25 centred reflections, and 2328 diffracted intensities were recorded in $\theta/2\theta$ mode using the same crystal. No decay was noted in the check reflection, and in addition to the usual Lorentz and polarisation corrections, an empirical ψ-scan absorption correction based on 3 reflections was applied to the data. After data reduction, there remained 2319 unique reflections of which 2288 with $F > 3\sigma(F)$ were used in the analysis. The heavy atom positions were obtained by inspection of the Patterson synthesis and repeated structure factor and electron-density syntheses located the remaining non-H atoms. Bond lengths and peak height data supported one cation in the asymmetric unit being a sodium. A difference electron-density synthesis towards the end of the refinement gave good indications for the 12 hydrogen atoms [0.96–0.54 e $Å^{-3}$, chemically sensible d(O–H) distances and H–O–H angles for H_2O, and the peaks as the top band of features in the difference electron-density map]. Hydrogen atoms were introduced into the model with a common refined temperature factor, and five reflections thought to be subject to extinction were removed. Full-matrix least-squares refinement converged to $R = 0.034$ {188 parameters, 2283 reflections, anisotropic (Pt, I, K, Na, O) and isotropic (H) atoms, $w = 1/[\sigma^2(F) + 0.001F^2]$, max. shift/error (non-H) = 0.2}. The residual electron-density was in the range 1.02 to -4.31 e$Å^{-3}$ with the negative region at the Pt site. Tables I and II give the crystallographic details and the final

TABLE I
Crystallographic data for $K_4Na_2[Pt(OH)_2(HIO_6)_2].10H_2O$.

molecular formula	$H_{24}I_2K_4Na_2O_{24}Pt$
fw	1059.5
a, Å	7.588(2)
b, Å	8.110(2)
c, Å	9.864(2)
α, deg	82.00(2)
β, deg	83.79(2)
γ, deg	81.76(2)
V, $Å^3$	592.5(3)
Space group	$P\bar{1}$ (No. 2), triclinic
λ, Å	0.71069 (MoK_α)
Z	1
$F(000)$	498
ρ obsvd, g cm^{-3}	2.84(2)
ρ calcd, g cm^{-3}	2.968
μ, cm^{-1}	93.7
2θ range, deg	2.0–52.0
R^a	0.034
R_w^b	0.050

[a] $R = \Sigma \| Fo| - |Fc\| / \Sigma |Fo|$. [b] $R_w = [\Sigma w \| Fo| - |Fc\|^2 / \Sigma w |Fo|^2]^{\frac{1}{2}}$.

atomic coordinates, respectively. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX-76[12] (O, H) and ref. 13 (Pt, I, K, Na). All calculations were performed using the programs SHELX-76,[12] ORTEP-II,[14] and PLUTO[15] on an IBM 3090 computer.

TABLE II
Atomic coordinates and isotropic temperature factors ($Å^2 \times 10^3$).

Atom	x/a	y/b	z/c	U
Pt	0.0000	0.0000	0.0000	9.9(2)*
I	0.17112(4)	0.14406(3)	−0.27697(3)	12.0(2)*
K(1)	0.2176(2)	0.5456(2)	0.5118(2)	36.3(10)*
K(2)	0.2255(2)	0.0479(2)	0.3666(1)	29.5(9)*
Na	0.4006(3)	0.4254(3)	0.1629(2)	26.8(13)*
O(1)	0.0079(6)	−0.2281(6)	−0.0594(5)	22.9(28)*
O(2)	−0.0621(5)	0.1052(5)	−0.1850(4)	17.1(22)*
O(3)	0.2393(5)	0.0255(5)	−0.1017(4)	17.9(23)*
O(4)	0.4035(6)	0.1311(6)	−0.3469(4)	23.5(27)*
O(5)	0.1747(6)	−0.0873(6)	−0.3334(5)	20.0(27)*
O(6)	0.0703(5)	0.2291(5)	−0.4331(4)	22.5(24)*
O(7)	0.1636(5)	0.3447(4)	−0.2095(4)	23.8(24)*
O(8)	0.4090(7)	0.1467(6)	0.1124(5)	29.9(29)*
O(9)	0.0988(6)	0.3984(6)	0.2525(4)	28.3(27)*
O(10)	0.3127(5)	0.5428(6)	−0.0678(5)	28.2(27)*
O(11)	0.5025(6)	0.2868(5)	0.4017(5)	30.2(28)*
O(12)	0.3634(6)	0.6792(6)	0.2595(5)	31.8(30)*
H(1)	−0.0477(109)	−0.2700(98)	−0.0083(82)	23(5)
H(2)	0.1276(109)	−0.1321(101)	−0.2848(87)	23(5)
H(3)	0.5110(91)	0.1078(79)	0.1049(63)	23(5)
H(4)	0.3473(86)	0.1713(76)	0.0443(70)	23(5)
H(5)	0.0599(80)	0.3272(83)	0.2008(66)	23(5)
H(6)	0.0103(92)	0.4853(88)	0.2371(63)	23(5)
H(7)	0.2764(84)	0.4866(86)	−0.1178(66)	23(5)
H(8)	0.1725(87)	0.6423(81)	−0.0714(62)	23(5)
H(9)	0.4827(84)	0.2510(77)	0.4741(70)	23(5)
H(10)	0.6583(83)	0.2129(73)	0.3774(62)	23(5)
H(11)	0.2620(82)	0.7504(72)	0.2147(62)	23(5)
H(12)	0.4743(86)	0.6815(77)	0.2308(66)	23(5)

* Equivalent isotropic temperature factor from anisotropic atom. $U_{eq} = 1/3$ [trace of orthogonalized U]. Hydrogen atoms were given a common refined temperature factor.

RESULTS AND DISCUSSION

The title complexes were obtained by boiling together aqueous alkaline solutions of $M'IO_4$ (M' = K or Na) and $[MCl_6]^{2-}$ (M = Pd or Pt). Several variations on the method were tried including conducting the reactions in Carius tubes at *ca* 140°C, and using pre-formed $[M(OH)_6]^{2-}$ in place of $[MCl_6]^{2-}$. The analytical data from the various preparations always had Pd(Pt) : I ratios of 1 : 2, but the alkali metal content and the water were rather variable, as is often found with this type of complex.[3,6,7,16] In particular, the products from the Carius tube reactions, although made from potassium periodate and hydroxide, also contained sodium originating from attack on the glass. Despite the variation in cations the spectroscopic evidence supports the presence of the same complex anion in each preparation. The palladium complex is an orange powder, the platinum pale-yellow. Repeated attempts to obtain crystals of the palladium complex were unsuccessful, however the Carius tube synthesis of the platinum complex gave some small yellow crystals which were used for the X-ray study. Obtaining crystals from this type of material often seems to require a mixture of cations (*c.f.* ref. 6, $K_5Na[RuO_2(HIO_6)_2].8H_2O$), and in the present case the sodium-free samples of the platinum salt failed to produce crystals suitable for an X-ray study.

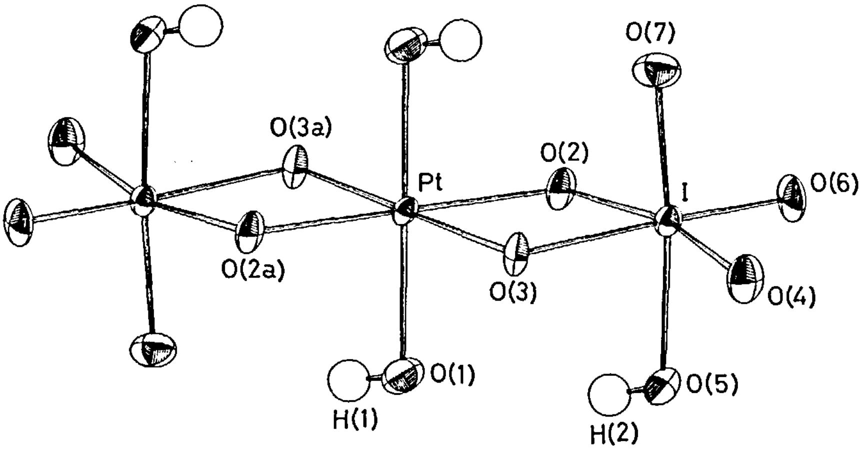

FIGURE 1 The $[Pt(OH)_2(HIO_6)_2]^{6-}$ anion showing the geometry and the atom labelling scheme. The thermal ellipsoids are drawn at the 50% probability level. [Symmetry operation: $a = -x, -y, -z$]

Crystal Structure of $K_4Na_2[Pt(OH)_2(HIO_6)_2].10H_2O$

The structure consists of discrete $[Pt(OH)_2(HIO_6)_2]^{6-}$ anions (see Figure 1) together with potassium and sodium ions and a hydrogen bonded network of water molecules (see Figure 2). Selected bond lengths and angles are given in Table III. The anion is centrosymmetric and the formula is consistent with the expected Pt(IV) oxidation state. The I–O distances show short terminal I–O bonds (1.82 Å av), one long I–O(H) bond (2.025(4) Å) and I–O bridge bonds (1.943 Å av). In the present example there was persuasive evidence that at least the majority of the hydrogen atoms had been correctly located, but as expected the d(O–H) and H–O–H angles for water molecules were poorly determined (Table III). The location of the H atom and the associated I–O distances accord well with the data for the $[H_2I_2O_{10}]^{4-}$ anion,[17] which consists of two edge-sharing octahedra. In cases where the H atoms were not located, *e.g.* $[RuO_2(HIO_6)_2]^{6-}$ the I–O distances have been used to identify the I–O(H) bond.[6] However in $KNa_4[Cu(HIO_6)_2].12H_2O$, the H atom of one of the periodate groups was tentatively said[5] to be associated with a short I–O distance and this result must be regarded with suspicion. The presence of Na and K in the crystals, which is supported by EDX measurements, is by no means unusual; rather it is the norm. In the present case the sodium presumably comes from the glass of the reaction vessel.

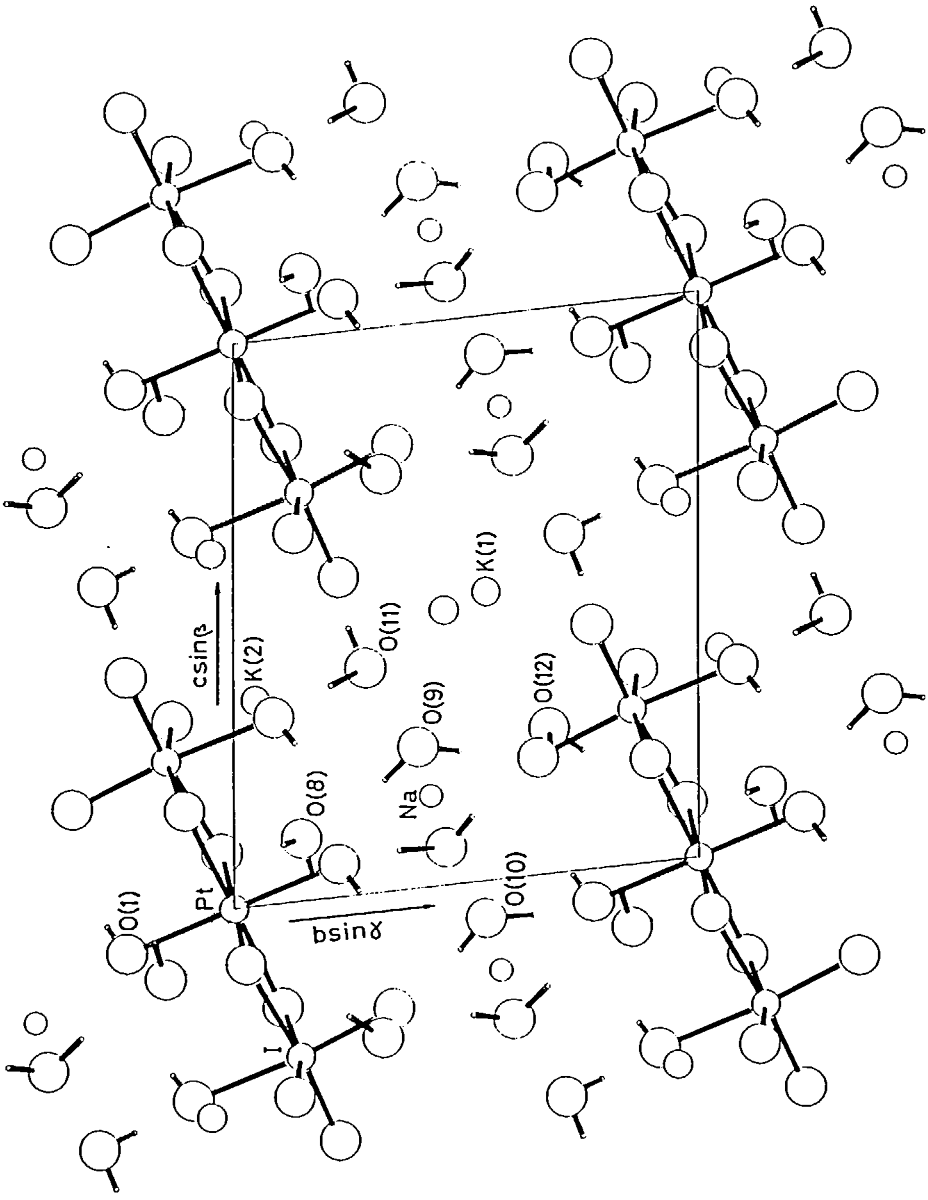

FIGURE 2 Unit cell packing diagram of $K_4Na_2[Pt(OH)_2(HIO_6)_2].10H_2O$ viewed from the positive *x*-direction showing the atom labelling scheme.

TABLE III
Selected bond lengths (Å) and angles (deg) for $K_4Na_2[Pt(OH)_2(HIO_6)_2].10H_2O$.

Pt-O(1)	2.008(4)	I-O(2)	1.946(3)
Pt-O(2)	1.980(4)	I-O(3)	1.941(4)
Pt-O(3)	2.001(4)	I-O(4)	1.817(4)
Pt....I	3.049(1)	I-O(5)	2.025(4)
H(1)-O(1)	0.70(8)	I-O(6)	1.800(4)
H(2)-O(5)	0.66(8)	I-O(7)	1.833(3)
O(1)-Pt-O(2)	89.8(2)	O(1)-Pt-O(2*a*)	90.2(2)
O(1)-Pt-O(3)	90.6(2)	O(1)-Pt-O(3*a*)	89.4(2)
O(2)-Pt-O(3)	77.1(1)	O(2)-Pt-O(3*a*)	102.9(2)
O(2)-I-O(3)	79.4(2)	O(3)-I-O(7)	89.8(2)
O(2)-I-O(4)	167.0(2)	O(4)-I-O(5)	86.3(2)
O(2)-I-O(5)	84.0(2)	O(4)-I-O(6)	98.0(2)
O(2)-I-O(6)	90.4(2)	O(4)-I-O(7)	96.1(2)
O(2)-I-O(7)	92.8(2)	O(5)-I-O(6)	87.8(2)
O(3)-I-O(4)	91.2(2)	O(5)-I-O(7)	174.7(2)
O(3)-I-O(5)	85.5(2)	O(6)-I-O(7)	96.5(2)
O(3)-I-O(6)	168.3(2)		
H(1)-O(1)-Pt	104(6)	H(2)-O(5)-I	108(7)
Na...O	min. 2.309(5)	max. 2.610(5)	mean 2.42(10)
K...O	min. 2.694(4)	max. 3.231(5)	
O-H	min. 0.66(8)	max. 1.24(5)	mean 0.9(2)
H-O-H	min. 91(5)	max. 124(5)	mean 107(13)

Symmetry operation: $a = -x, -y, -z$

The sodium ion is surrounded by an approximate octahedron of oxygen atoms whereas the potassium ions have a higher coordination number (8 for K(1) and 9 for K(2)) which form irregular polyhedra. The O(2)-Pt-O(3) and O(2)-I-O(3) angles involving the bridge bonds are less than 90°, presumably indicating some repulsion between the non-bonded Pt and I atoms; a similar effect was observed in the ruthenium compound above.[6] X-ray powder diffraction studies on comparable platinum and palladium compounds (the K_6 salts) established that the samples examined were not isomorphous.

Spectroscopic Data

The IR and Raman spectra of the corresponding palladium and platinum salts were very similar, differing only in the relative intensities of some of the minor bands, and suggest that the complexes contain anions of similar structures. Electronic spectra are rather uninformative, both ions showing long tails from the UV into the visible, and in the case of $[Pd(OH)_2(HIO_6)_2]^{6-}$ a shoulder at *ca* 34 000 cm^{-1}, all of which are likely to be charge transfer in origin. The presence of orthoperiodate ligands was indicated[5] by very broad ($W_{1/2}$ *ca* 25 kHZ) resonances at *ca* +3000 ppm in the ^{127}I NMR spectra, but due to the line-width, the spectra are uninformative as to the number of species present. The ^{195}Pt NMR spectra obtained by dissolving various samples of $M_6[Pt(OH)_2(HIO_6)_2]$ in water were effectively identical, consisting of the main resonance at +2620 ppm, a weaker feature at +2400 ppm, and very small signals at +2655 and +2730 ppm. The spectra did not change with time, but were sensitive to pH, in particular adding acid (HNO_3 or H_5IO_6) to the solution resulted in a decrease in the intensity of the resonance at +2620 ppm, and a growth of the lower frequency signal. At pH = 2, only the resonance at +2400 ppm was present.

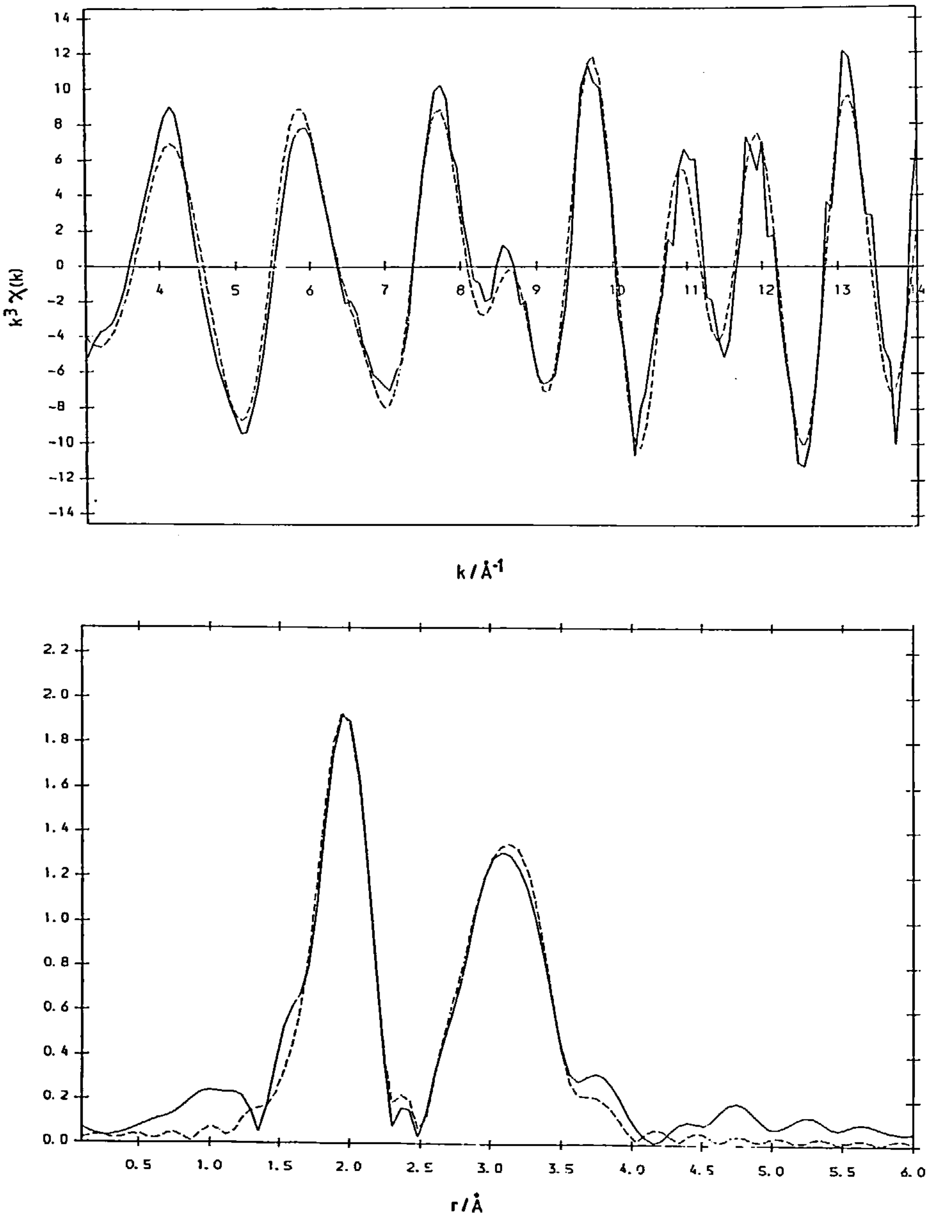

FIGURE 3 Background subtracted Pt L_{III}-edge EXAFS and its Fourier transform obtained from $[Pt(OH)_2(HIO_6)_2]^{6-}$ in solution at pH = 2. —— experimental, --- calculated.

However, concentration of this solution resulted in precipitation of the original solid complex. Conversely, at high pH, the +2400 ppm resonance is absent. For comparison $[Pt(OH)_6]^{2-}$ has a chemical shift of +3292 ppm. The presence of several pH dependent resonances in the solution of the platinum complex is most likely due to variations in the degree of protonation of the anion. Studies of the systems $[PtCl_{6-n}(OH)_n]^{2-}$ by Carr *et al.*[18] showed that stepwise protonation of the hydroxo groups caused low frequency shifts in the ^{195}Pt resonances of *ca* 150–300 ppm, which are of similar magnitude to the differences in the present system. Although we were unable to isolate the complex with the +2400 ppm resonance, by suitable adjustment of the pH it could be obtained as the only platinum species in solution, and this solution was studied by the EXAFS technique.

Platinum L_{III} edge EXAFS (extended X-ray absorption fine structure) data were obtained from a solution, the integrity of which was checked both before and after data collection by ^{195}Pt NMR. The background subtracted EXAFS and its Fourier transform with the best fit calculated model are shown in Figure 3. Attempts were made to fit three plausible model structures to the data: 1) the structure obtained for the anion by X-ray diffraction, 2) a complex of type $[Pt(HIO_6)_3]^{8-}$ with three bidentate periodate ligands and 3) a complex $[Pt(IO_6)_2]^{6-}$ with facially bound periodate ligands. The distances obtained from this data were d(Pt–O) = 1.99(1) Å and d(Pt...I) = 3.04(1) Å, in good agreement with the distances obtained from the crystal structure, and exclude a facially bound structure which would have a markedly shorter Pt...I distance. Refinement of models with two and three periodate ligands gave rise to *R* factors of *ca* 20% and 26% respectively (on un-Fourier filtered data) and other refined parameters also supported the model with two periodate ligands. We are thus able to conclude that the resonance which occurs at +2400 ppm in the ^{195}Pt NMR spectrum arises not from a new structural form, but rather from a more subtle modification of the established structure such as the protonation postulated above.

Other Anions

Platinum-195 NMR spectroscopy was also used to monitor any reaction in aqueous solution between $[Pt(OH)_6]^{2-}$ and other p-block oxo-anions, including ClO_4^-, BrO_4^-, BrO_3^-, IO_3^-, SeO_4^{2-}, and TeO_6^{6-}. The tellurate complexes will be described elsewhere,[19] but of the other ions only iodate showed any evidence for complex formation. Solid $K_2[Pt(IO_3)_6]$ was obtained by the literature route,[20] and in solution exhibited a ^{195}Pt resonance at +1975 ppm.

SUMMARY

The complexes previously reported as $[M(IO_6)_2]^{6-}$ (M = Pt and Pd), and thought to contain facially bound terdentate IO_6^{5-} groups, have been shown to be $[M(OH)_2(HIO_6)_2]^{6-}$ and contain two bidentate $IO_5(OH)^{4-}$ ligands, as found in the Ru(VI), Cu(III) and Ag(III) complexes.

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of anisotropic thermal parameters, full bondlength and angle data, and observed and calculated structure factors (16 pages) are available from M.W.

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