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^{195}Pt Chemical Shifts and Pt–Pt Coupling Constants for Sulfato- and Phosphato-Bridged Platinum(III) Dimeric Anions

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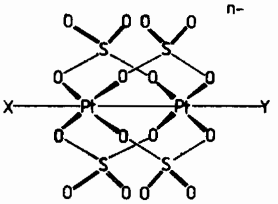
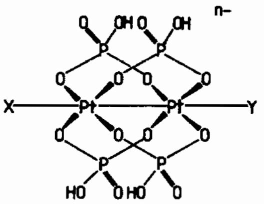
Although $K_2[Pt_2(SO_4)_4(H_2O)_2]$ (I) was one of the first platinum(III) compounds to be prepared [1], and this compound [2], $K_2[Pt_2(SO_4)_4(Me_2SO)_2]\cdot 4H_2O$ [3], and $Na_2[Pt_2(PO_4H)_4(H_2O)_2]$ (II) [4] have all been characterised crystallographically, no NMR data are available for these compounds. The only platinum(III) complexes for which NMR spectra have been reported are $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$ (III) and analogues [5]. The Pt–P–O–P–Pt bridges in these compounds are very different from those in (I) and (II), and no Pt–Pt coupling constants were reported.





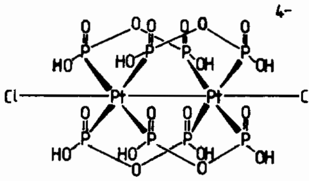
(I) X=Y=H_2O, n=2 (II)

(IV) X=Y=Cl, n=4 (V)

(VI) X=Y=Br, n=4 (VII)

(VIII) X=H_2O, Y=Cl, n=3 (IX)

(X) X=H_2O, Y=Br, n=3 (XI)



(III)

The potassium salts of (I) and (II) were prepared by reaction of $K_2Pt(NO_2)_4$ with H_2SO_4 [1] and H_3PO_4 respectively (this preparation for (II) was more convenient than that previously described, using *cis*-$Pt(NH_3)_2(NO_2)_2$ [6]). They were then converted into the more soluble sodium salts using a cation exchange resin.

The ^{195}Pt NMR spectrum of a solution of $Na_2[Pt_2(SO_4)_4(H_2O)_2]$ (I) in water showed a sharp singlet at +1752.9 p.p.m. from aqueous Na_2PtCl_6 (with the usual convention that shifts to lower shielding are positive). This is remarkably close to the average of shifts for platinum(II) and platinum(IV) complexes with the metal coordinated by O-donor ligands (*e.g.*, $Pt(H_2O)_4^{2+}$ +31 p.p.m. [7], $Pt(OH)_6^{2-}$ +3277 p.p.m. [8]). Nuclear shielding is very much less than for (III) (δ_{Pt} −4236 p.p.m. [5]). It is well established for platinum(II) and -(IV) [9, 10] that the tendency of a coordinated ligand to shift the platinum nucleus to higher shielding increases in the order, O-donors < Cl^- < Br^- < P-donors.

The ^{195}Pt spectrum of the phosphato-bridged dimer, (II), is a quintet, due to coupling with four equivalent ^{31}P nuclei, at 1795.2 p.p.m. The ^{31}P spectrum shows the predicted 1:8:18:8:1 multiplet – the sum of spectra from dimers with 0, 1, and 2 ^{195}Pt nuclei (abundance 33.6%).

If excess NaCl is added to a solution of (I), and the solution is allowed to stand, the ^{195}Pt spectrum shows a singlet at 1720 p.p.m., assigned to $Pt_2(SO_4)_4Cl_2^{4-}$ (IV) (the sparingly soluble potassium salts of all the anions (IV)–(VII) have been isolated [2, 6]). With a smaller proportion of NaCl added, peaks in addition to those from (I) and (IV) are observed (Fig. 1), which are assigned to $Pt_2(SO_4)_4Cl(H_2O)^{3-}$ (VIII) – a singlet from each isotopomer with one ^{195}Pt nucleus, and an AB pattern from the isotopomer with two ^{195}Pt nuclei. If the resonance at higher shielding is assigned to the Pt atom bound to chloride, shifts are as listed in Table I. It is noteworthy that the Pt nucleus bound to chloride is more shielded in the mixed complex, (VIII), than in the dichloro complex, (IV), and that the Pt nucleus bound to water is less shielded in (VIII) than in the diaqua complex, (I). This may be explained if the shifts are determined mainly by two additive effects – the direct effect of replacing water by halide on the Pt atom observed, x, and the 'remote' effect of replacement on the adjacent Pt atom, y. From the spectrum of (VIII), x = −114.5 p.p.m., and y = +55.6 p.p.m. The predicted shift for (IV) from (I) would then be predicted to be −58.9 p.p.m. The observed shift is −32.9 p.p.m. – that is, the experimental shift is slightly more positive than would be predicted on this very simple basis. The same conclusion may be reached for the other halide complexes discussed below.

For the analogous bromo complexes, x = −313.4 p.p.m., y = +113.3 p.p.m., giving a predicted shift for the dibromo complex −200.1 p.p.m., compared with the observed shift, −140.8 p.p.m. for (X).

Similar behaviour occurs when halide ion is added to a solution of $Na_2[Pt_2(PO_4H)_4(H_2O)_2]$ (II) (Fig. 2). All platinum resonances now appear as quintets.

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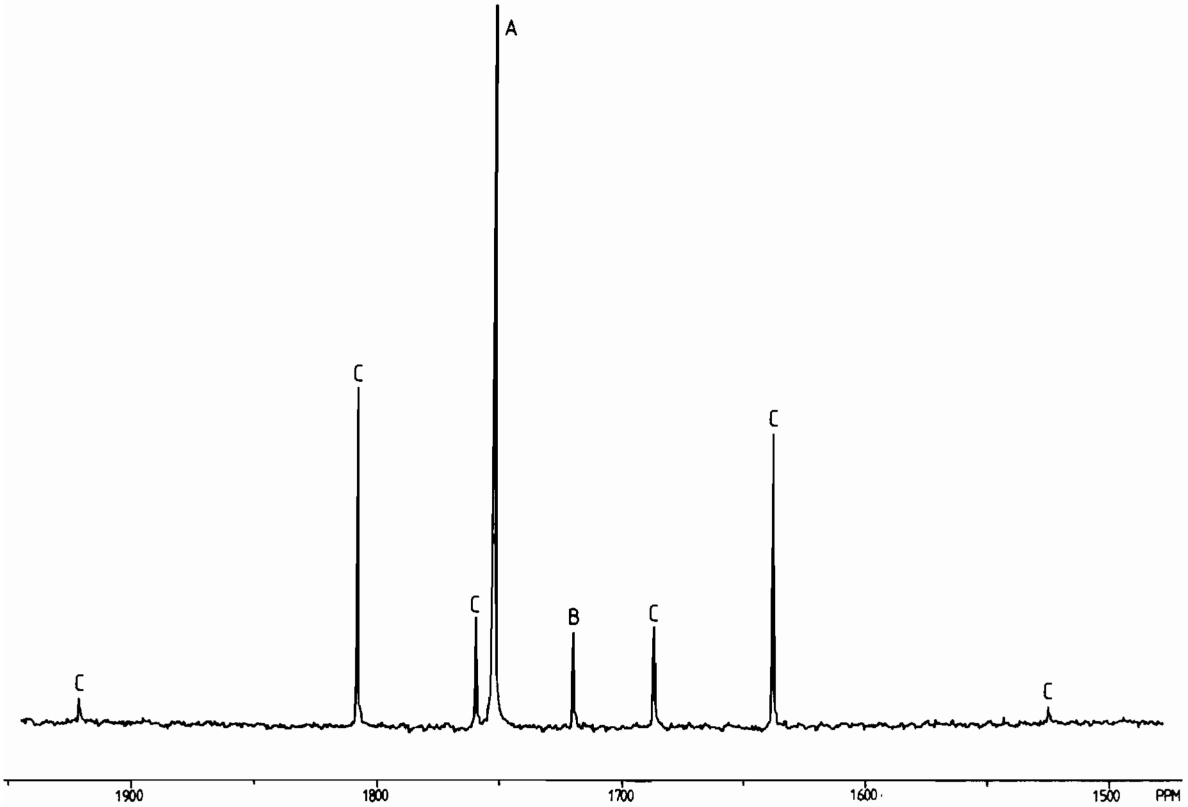

Fig. 1. 21.4 MHz ^{195}Pt NMR spectrum of an aqueous solution of $Na_2[Pt_2(SO_4)_4(H_2O)_2]$ (0.10 *M*) to which NaCl has been added (initially 0.005 *M*). A, $Pt_2(SO_4)_4(H_2O)_2^{2-}$ (I); B, $Pt_2(SO_4)_4Cl_2^{4-}$ (IV); C, $Pt_2(SO_4)_4Cl(H_2O)^{3-}$ (VIII) (20,000 scans, 70° tilt, 0.30 sec between plulses).

TABLE I. NMR Data.

Compound	δ_{Pt}[a]	Bound Ligand	^2J(Pt–O–P) Hz	δ_P[b]	^1J(Pt–Pt) Hz
$Pt_2(SO_4)_4(H_2O)_2^{2-}$(I)	1752.9	H_2O	–	–	–
$Pt_2(PO_4H)_4(H_2O)_2^{2-}$(II)	1795.7	H_2O	71.8	21.3	–
$Pt_2(SO_4)_4Cl_2^{4-}$(IV)	1720.0	Cl^-	–	–	–
$Pt_2(PO_4H)_4Cl_2^{4-}$(V)	1822.1	Cl^-	73.2	26.3	–
$Pt_2(SO_4)_4Br_2^{4-}$(VI)	1592.1	Br^-	–	–	–
$Pt_2(PO_4H)_4Br_2^{4-}$(VII)	1743.9	Br^-	63.5	28.7	–
$Pt_2(SO_4)_4Cl(H_2O)^{3-}$(VIII)	1808.5	H_2O	–	–	3464
	1638.4	Cl^-	–	–	
$Pt_2(PO_4H)_4Cl(H_2O)^{3-}$(IX)	1889.9	H_2O	92.8	23.4	5342
	1713.1	Cl^-	46.4		
$Pt_2(SO_4)_4Br(H_2O)^{3-}$(X)	1866.2	H_2O	–	–	3472
	1439.5	Br^-			
$Pt_2(PO_4H)_4Br(H_2O)^{3-}$(XI)	1972.6	H_2O	95.2	24.3	5349
	1549.8	Br^-	41.2		

[a] P.p.m. to lower shielding from aqueous Na_2PtCl_6. [b] P.p.m. to lower shielding from external 85% H_3PO_4.

From the sepctrum of the mixed chloroaqua complex, (IX), x = –82.1 p.p.m., and y = +94.7 p.p.m. As usual, the shift for the dichloro complex, (V), is more positive (+26.9 p.p.m.) than that predicted (+12.6 p.p.m.), but the prediction that the shift would be more positive than for the diaqua complex (II) was correct. From the spectrum of the bromoaqua complex, (XI), x = –245.9 p.p.m., y = +176.9 p.p.m., and the predicted shift for the dibromo complex, (VII), is –69.0 p.p.m. (*cf.* experimental shift, –51.8 p.p.m.)

Some consistent trends are evident from these data. In the phosphate-bridged compounds, the direct

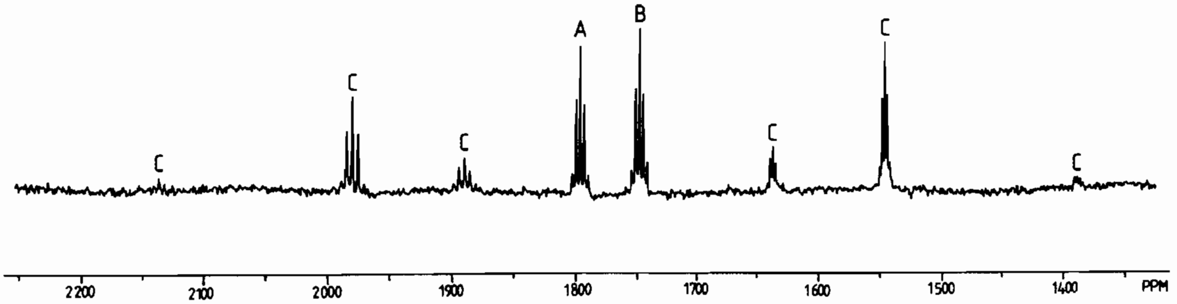

Fig. 2. 21.4 MHz ^{195}Pt NMR spectrum of an aqueous solution of $Na_2[Pt_2(PO_4H)_4(H_2O)_2]$ (0.06 *M*) to which NaBr has been added (initially 0.084 *M*). A, $Pt_2(PO_4H)_4(H_2O)_2^{2-}$(II); B, $Pt_2(PO_4H)_4Br_2^{4-}$(VII); C, $Pt_2(PO_4H)_4Br(H_2O)^{3-}$(XI) (170,000 scans, 70° tilt, 0.30 sec between pulses).

effect, x, is smaller in magnitude than in the corresponding sulfate-bridged compounds, and the remote effect, y, is larger—*i.e.*, an electronic effect mediated by the metal–metal bond is relatively more important.

Pt–Pt coupling constants given in the Table may be measured directly from the AB portions of the spectra of the haloaqua complexes. Within the one bridging system, the effect of substituting bromide for chloride is very small. Most remarkable is the much larger value in the phosphato complexes compared with the sulfato complexes. The Pt–Pt distance in $Na_2[Pt_2(PO_4H)_4(H_2O)_2]$ (II) (2.486(2) Å) [4] is slightly *longer* than in $K_2[Pt_2(SO_4)_4(H_2O)_2]$ (I) (2.466 Å) [2] and $Na_2[Pt_2(SO_4)_4(Me_2SO)_2]\cdot 4H_2O$ (2.471(1) Å) [3], and there is no reason to expect major variations in bond lengths in the mixed haloaqua complexes. Pregosin [9] has commented on the lack of correlation between the Pt–Pt distance and J(Pt–Pt) when compounds of very different structural types are being considered, but we had expected some similarity in the couplings in our very closely related compounds. J(Pt–Pt) must be extremely sensitive to variations in electronic structure which have little effect on the molecular structure.

The Pt–O–P coupling constants in the phosphate complexes also show unexpected variations. The values in the Table may be obtained from quintet separations in the ^{195}Pt spectra, or, with greater accuracy, from the ^{31}P spectra. Like the symmetrical species (II), both (V) and (VII) give the expected 1:8:18:8:1 multiplet. To a first approximation, the ^{31}P spectrum of each of the unsymmetrical complexes, (IX) and (XI) shows a singlet with two sets of 'satellites' (the doublet of doublets from the isotopomer with two ^{195}Pt nuclei is much less intense). The Pt–O–P couplings in the symmetric compounds (II), (V), and (VII), are quite similar (68.5 ± 5 Hz), but in each of the unsymmetrical compounds, (IX) and (XI), the two couplings are very different (one is approximately twice the other). However, the average of the two couplings falls in the same narrow range as for the symmetric compounds. The most likely explanation for this variation is that the Pt–O–P coupling is very sensitive to small distortions in the structure of the tetrakis(phosphato) bridge in the unsymmetrical complexes. Such sensitivity to the geometry of the Pt–O–P linkage would help to explain the variation in the few Pt–O–P coupling constants measured to date (*e.g.*, 26.8 Hz in *cis*-$Pt(NH_3)_2(OPO_3H_2)(H_2O)^+$, but <8 Hz in $\{Pt(NH_3)_2\}_2(\mu\text{-}OH)(\mu\text{-}PO_4H)^+$ [11]).

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