

## NMR Spectra of Platinum(III) Complexes with Sulfato- and Phosphato-bridges

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## Abstract

$^{195}\text{Pt}$  NMR data are reported for Pt(III) dimeric anions  $\text{Pt}_2(\text{Z})_4\text{XY}^{n-}$ , where  $\text{Z} = \text{SO}_4$  or  $\text{PO}_4\text{H}$ , and X, Y are anionic or neutral ligands.  $^{13}\text{CN}^-$ ,  $^{15}\text{NO}_2^-$ , and  $^{15}\text{NH}_3$  were included among these, and couplings between  $^{195}\text{Pt}$  and  $^{13}\text{C}$  or  $^{15}\text{N}$  allowed unambiguous assignments to be made in the  $^{195}\text{Pt}$  spectra of their compounds. Substitution of one water molecule in  $\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2^{2-}$  frequently causes large shifts of the Pt atom not directly involved in the substitution.

Where X and Y are different,  $^1J(\text{Pt}-\text{Pt})$  has been measured directly from the  $^{195}\text{Pt}$  spectrum, and this coupling constant has also been obtained for  $\text{Pt}_2(\text{Z})_2(^{13}\text{CN})_2^{4-}$  by analysis of the spectrum. For corresponding compounds,  $^1J(\text{Pt}-\text{Pt})$  is always larger in magnitude for  $\text{Z} = \text{PO}_4\text{H}$  than for  $\text{Z} = \text{SO}_4$ , although  $\nu(\text{Pt}-\text{Pt})$  from Raman spectra and Pt–Pt bond lengths do not indicate a stronger Pt–Pt bond.

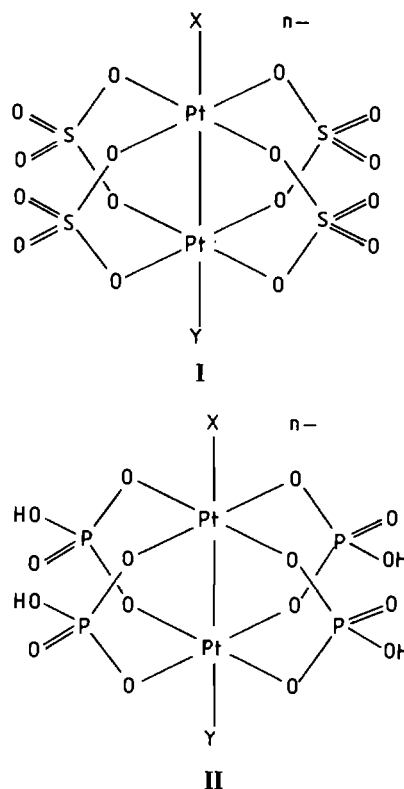
In a series  $\text{Pt}_2(\text{Z})_4\text{XY}^{n-}$  where X is kept constant (e.g.,  $\text{X} = \text{H}_2\text{O}$ ,  $\text{CN}^-$ ),  $J(\text{Pt}-\text{Pt})$  decreases with increasing *trans* influence of Y. For  $\text{Pt}_2(\text{SO}_4)_4(^{13}\text{CN})\text{Y}^{n-}$ ,  $^1J(\text{Pt}-\text{C})$  and  $^2J(\text{Pt}-\text{Pt}-\text{C})$ , both decrease as the *trans* influence of Y increases, and  $\delta_{\text{C}}$  becomes more positive.

These and other observations are interpreted in terms of rehybridization of both Pt-atoms when one of them is substituted.

## Introduction

The platinum(III) dimeric anions,  $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$  [1] and  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$  [2] are stable and diamagnetic. X-ray crystallography has shown that they have the 'lantern' structures (I) [3, 4] and (II) [4, 5] respectively (with  $\text{X} = \text{Y} = \text{H}_2\text{O}$ ,  $n = 2$ ). They may be regarded as possessing a Pt–Pt single bond [4, 5]. The axial water ligands are readily displaced by a range of neutral and anionic ligands to give the series of compounds  $\text{Pt}_2(\text{Z})_4\text{X}_2^{n-}$  ( $\text{Z} = \text{SO}_4$ ,  $\text{PO}_4\text{H}$ ) [2–4, 6, 7].

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In this paper, we discuss the  $^{195}\text{Pt}$  NMR spectra ( $^{195}\text{Pt}$ ,  $I = 1/2$ , 33.6% abundance) of the dimers, and the effects of axial ligand substitution on these spectra. A preliminary account of some of this work has been published [8].

## Experimental

 $K_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$ 

The following procedure was modified slightly from that used by Muraveiskaya *et al.* [1].

1 g  $\text{K}_2[\text{Pt}(\text{NO}_2)_4]$  [9] was added to 10 ml 50% sulfuric acid solution at 100–120 °C. The solution was stirred at this temperature while the colour changed from blue, through green, to brown, when a yellow precipitate formed and evolution of nitrogen

oxides ceased. Heating was continued for 30 min after initial formation of this precipitate (in our hands, further prolonged heating caused the precipitate to turn brown). The yellow solid was filtered off, and the filtrate was reheated to obtain a second crop. The solid was washed with a small volume of ice-cold water, followed by ethanol and ether, and air-dried. Yield was 0.72 g (75%).

The solid was analysed by ignition with  $\text{H}_2\text{SO}_4$ , to give  $(\text{Pt} + \text{K}_2\text{SO}_4)$ . Calcd. for  $\text{H}_4\text{O}_{18}\text{S}_4\text{K}_2\text{Pt}_2$  63.5%. Found, 62.7%.

#### $\text{K}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$

Muraveiskaya et al. [2] prepared  $(\text{NH}_4)_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  by reaction of *cis*- $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$  with  $\text{H}_3\text{PO}_4$ . The following procedure, starting from readily-prepared  $\text{K}_2[\text{Pt}(\text{NO}_2)_4]$ , gives the potassium salt in comparable yield.

1 g  $\text{K}_2[\text{Pt}(\text{NO}_2)_4]$  was added to 10 ml 84% orthophosphoric acid at 100 °C and the solution was stirred at this temperature while the colour changed from blue, through green, to dark red, and evolution of gaseous products ceased (3–4 h). The solution was cooled to room temperature and filtered. 0.5 g  $(\text{NH}_4)_2\text{HPO}_4$  was added followed by 20 ml water to precipitate the product. After the mixture had stood overnight, the yellow-orange solid was filtered off, washed with a small volume of cold water, then ethanol and ether, and air-dried. A second crop was obtained on concentration of the filtrate at 100 °C under 20 mm Hg pressure. Combined yield was 0.54 g (56%).

The sample was analysed by ignition with  $\text{H}_2\text{SO}_4$  to give  $(\text{Pt} + \text{K}_2\text{SO}_4)$ . Calcd. for  $\text{H}_8\text{O}_{18}\text{P}_4\text{K}_2\text{Pt}_2$ , 63.5%. Found 63.7%.

#### Preparation of Lithium Salts of Dimeric Anions

A column of BDH Amberlite IR-120 (H) cation exchange resin was converted to the lithium form by passing 1 M LiCl solution down the column, then washing with water until the washings were chloride-free. A saturated aqueous solution of the potassium salt was then passed down the column, with washing until the eluant was colourless. The solvent was removed at 100 °C under a pressure of 20 mm Hg, as quickly as possible to minimize decomposition (especially for the sulfate), to yield the product as a light brown solid, in near-quantitative yield ( $\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  or  $\text{Li}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ).

*Anal.* Calcd. for the sulfate,  $\text{H}_{10}\text{O}_{21}\text{S}_4\text{Li}_2\text{Pt}_2$ : H, 1.2; S, 14.6. Found: H, 1.0; S, 14.3. Calcd. for the phosphate,  $\text{H}_{10}\text{O}_{19}\text{P}_4\text{Li}_2\text{Pt}_2$ : H, 1.2; P, 14.7. Found: H, 1.2; P, 14.3.

#### $\text{K}_4[\text{Pt}_2(\text{SO}_4)_4(\text{CN})_2] \cdot 2\text{H}_2\text{O}$

0.25 g  $\text{K}_4[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  (0.28 mmol) was dissolved in 25 ml water, and 0.048 g KCN (0.74

mmol) was added, with stirring, to give a pale yellow solution. 25 ml ethanol was added, and the pale yellow precipitate filtered off, washed with ethanol and ether, and air-dried. Yield was 0.21 g (73%). *Anal.* Calcd. for  $\text{C}_2\text{H}_4\text{K}_4\text{N}_2\text{O}_{18}\text{Pt}_2\text{S}_4$ : C, 2.4; H, 0.4; N, 2.8. Found: C, 2.5; H, 0.5; N, 2.7.

#### $\text{K}_4[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{CN})_2] \cdot \text{H}_2\text{O}$

0.25 g  $\text{K}_4[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  (0.28 mmol) was suspended in 20 ml water. 0.045 g KCN (0.70 mmol) was added, with vigorous stirring. The mixture was heated at 40°, to give a pale yellow solution, which was filtered. 15 ml ethanol was added, and the pale yellow precipitate filtered off, washed with ethanol, then ether, and air-dried. Yield was 0.20 g (69%). *Anal.* Calcd. for  $\text{C}_2\text{H}_6\text{K}_4\text{N}_2\text{O}_{17}\text{P}_4\text{Pt}_2$ : C, 2.4; H, 0.6; N, 2.8. Found: C, 2.3; H, 1.2; N, 3.1.

#### $\text{K}_4[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{SCN})_2] \cdot 2\text{H}_2\text{O}$

A procedure similar to that described above for the cyanide but using 0.083 g KSCN (0.85 mmol) gave the product as a pale orange solid, 0.18 g (59%). *Anal.* Calcd. for  $\text{C}_2\text{H}_8\text{K}_4\text{N}_2\text{O}_{18}\text{P}_4\text{Pt}_2\text{S}_2$ : C, 2.2; H, 0.7; N, 2.6. Found: C, 2.2; H, 0.7; N, 3.0.

#### Preparation of NMR Samples

In most cases, an approximately 0.1 M solution of  $\text{Li}_2[\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2]$  ( $\text{Z} = \text{SO}_4, \text{PO}_4\text{H}$ ) was prepared by dissolving 0.165 g solid compound in 2 ml water. Appropriate quantities of a suitable ligand were then added, either as weighed solids, or as a 5 M solution. Lithium salts were used whenever possible, with sodium salts used if the lithium salt was unavailable.

Isotopically enriched compounds,  $\text{Na}^{13}\text{CN}$  (99%  $^{13}\text{C}$ ) (Stohler),  $(^{15}\text{NH}_4)_2\text{SO}_4$  (99.5%  $^{15}\text{N}$ ) (Stohler), and  $\text{Na}^{15}\text{NO}_2$  (99.5%  $^{15}\text{N}$ ) (KOR Isotopes) were used as supplied.

The ammine complexes,  $\text{Pt}_2(\text{Z})_4(\text{NH}_3)_2^{2-}$  and  $\text{Pt}_2(\text{Z})_4(\text{NH}_3)(\text{H}_2\text{O})^{2-}$  were obtained as follows.

The appropriate quantity of  $(\text{NH}_4)_2\text{SO}_4$  (either  $^{15}\text{N}$  or  $^{14}\text{N}$ ) was added to a solution of  $\text{Li}_2[\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2]$ . A yellow precipitate of  $(\text{NH}_4)_2[\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2]$  formed. 1 M LiOH was added dropwise until the precipitate just dissolved (pH 8.3 for  $\text{Z} = \text{SO}_4$ , 5.5 for  $\text{Z} = \text{PO}_4\text{H}$ ). Addition of dilute  $\text{HClO}_4$  to reduce pH to the range 2–5 did not cause re-precipitation of the ammonium salt, and NMR spectra of the solution (independent of pH over this range) showed that ammonia was coordinated.

#### Reaction of $\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$ with $\text{PMePh}_2$

0.1648 g  $\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  was dissolved in 20 ml water. 0.2 ml  $\text{PMePh}_2$  was added, with stirring under nitrogen, and rinsed into the solution from the syringe with 0.2 ml ethanol. An orange precipitate formed immediately. The solid was filtered off.

Dichloromethane was used to dissolve a soluble component of the solid, using a Soxhlet apparatus. Addition of ether to the dichloromethane solution gave a white solid, which was filtered off. The  $^1\text{H}$ -decoupled  $^{31}\text{P}$  NMR spectrum of this solid showed a singlet at  $-8.90$  ppm, with satellites due to coupling with  $^{195}\text{Pt}$ ,  $^1J(\text{Pt}-\text{P})$  3889.2 Hz. The large Pt-P coupling indicates that the phosphine is *trans* to a ligand of low *trans* influence [11]. The  $^1\text{H}$ -decoupled  $^{195}\text{Pt}$  NMR spectrum showed a triplet, with the same coupling, at  $-4287.8$  ppm, in the region typical of bis(tertiary phosphine)platinum(II) compounds [12]. The IR spectrum showed bands assignable to bidentate coordinated sulfate at 1283, 1144, 882, and  $665\text{ cm}^{-1}$ , very similar to those reported for  $\text{Pt}(\text{SO}_4)(\text{PPh}_3)_2$  [13, 14]. This solid was therefore assigned as  $\text{Pt}(\text{SO}_4)(\text{PMePh}_2)_2$ .

Recrystallization from hot water of the residue remaining after dichloromethane extraction gave a white solid, whose IR spectrum showed, in addition to bands assigned to the phosphine substituents, a strong band at  $995\text{ cm}^{-1}$  assigned to  $\nu(\text{P}=\text{O})$ . This compound was therefore identified as  $\text{Ph}_2\text{MeP}=\text{O}$ .

#### Instrumentation and Techniques

C, H and N analyses were performed by J. Kent of this Department, S and P analyses by the Australian Microanalytical Service, Melbourne.

NMR spectra were obtained using a JEOL FX-100 spectrometer, with a 10 mm multinuclear tunable probe, on double precision mode, using 8K or 16K data points as described previously [10]. Except for  $^{13}\text{C}$  spectra, for which internal locking on solvent deuterium was used, spectra were run using external lock ( $^7\text{Li}$ ). In all cases, shifts to lower shielding have been taken as positive. 21.4 MHz  $^{195}\text{Pt}$  spectra were referenced to aqueous  $\text{Na}_2\text{PtCl}_6$  (0.5 g/ml) as a separate sample. Baseline distortion in some spectra was corrected using a pulse sequence developed by Canet *et al.* [15]. 40.32 MHz  $^{31}\text{P}$  spectra are referenced relative to 85%  $\text{H}_3\text{PO}_4$  in a coaxial capillary. 10.04 MHz  $^{15}\text{N}$  NMR spectra are referenced relative to the  $^{15}\text{NH}_4^+$  signal of a 5 M solution of  $^{15}\text{NH}_4^{15}\text{NO}_3$  in 2 M  $\text{HNO}_3$ . 25.05 MHz  $^{13}\text{C}$  NMR spectra are referenced to external tetramethylsilane, taking  $\delta_{\text{C}}$  for internal dioxane as 67.73 ppm.  $^{13}\text{C}$  and  $^{15}\text{N}$  spectra were  $^1\text{H}$ -decoupled.

Because linewidths were smaller in  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{31}\text{P}$  NMR spectra than in  $^{195}\text{Pt}$  spectra, coupling constants between  $^{195}\text{Pt}$  and these nuclei were, where possible, measured from these spectra rather than the  $^{195}\text{Pt}$  spectrum.

NMR parameters were obtained from second-order spectra using an iterative program which gave the best least-squares fit between experimental and theoretical spectra. Raman spectra were run using a Cary 82 spectrometer with 514.5 nm radiation from a Coherent Radiation CR4 argon ion laser. Slight de-

composition of the sample at this wavelength necessitated the use of a spinning cell and reduced incident power (100 mW at the sample). 0.01 M solutions were prepared, and filtered through  $0.2\text{ }\mu\text{m}$  millipore filters prior to irradiation. A slit width of  $7\text{ cm}^{-1}$  was used to compensate for the low power, and difference spectra were run over the region 300 to  $100\text{ cm}^{-1}$  to remove the effect of low-frequency scattering of water.

#### Results

NMR parameters for sulfato-bridged complexes, (I), are given in Table I, and for phosphato-bridged complexes, (II), in Table II. Raman frequencies are listed in Table III.

Many of the complexes  $\text{Pt}_2(\text{Z})_4\text{X}_2^{n-}$  have previously been isolated as salts [2-4, 6, 7]. These preparations have been repeated, with generally similar results. A few new compounds have also been prepared. Details of these are given in the Experimental. No attempt has been made to isolate compounds with mixed axial ligands.

For NMR and Raman studies, the more soluble lithium salts of the dimers were used, rather than the potassium salts initially isolated.

#### NMR spectra of Aqua and Hydroxo Compounds

$\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  readily dissolved in water to give a pale orange solution, whose 21.4 MHz  $^{195}\text{Pt}$  NMR spectrum showed a sharp singlet (width at half height 8 Hz) at  $+1755.9$  ppm. Solutions were significantly acidic (pH 2.5) indicating that there was some deprotonation of coordinated water, but addition of dilute  $\text{HClO}_4$  did not change  $\delta_{\text{Pt}}$  significantly. This shift is close to the average of those for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ,  $+31$  ppm, [16] and  $\text{Pt}(\text{OH})_6^{2-}$ ,  $+3294$  ppm [17].

Addition of LiOH solution to increase pH to 12.5 caused the solution to become dark brown, and shifted the  $^{195}\text{Pt}$  peak to  $+2049.3$  ppm. This peak, also sharp (width 8 Hz), was assigned to  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})_2^{4-}$ .

At intermediate pH,  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})(\text{H}_2\text{O})^{3-}$  would be in equilibrium with  $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$  and  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})_2^{4-}$ . At pH 10.2, the peak occurred at 2041.7 ppm, and was much broader (width 80 Hz), presumably due to incomplete averaging of the  $^{195}\text{Pt}$  environments on the time scale of the NMR measurement. At pH 9, no signal could be observed, presumably because the peak was very broad.

The  $^{195}\text{Pt}$  NMR spectrum of a solution of  $\text{Li}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  showed a quintet at  $+1795.7$  ppm, due to coupling of  $^{195}\text{Pt}$  with four equivalent  $^{31}\text{P}$  nuclei. The  $^{31}\text{P}$  NMR spectrum showed, at  $+21.3$  ppm, the expected 1:8:18:8:1 multiplet, from the probability-weighted sum of spectra from iso-

TABLE I. NMR Data for Sulfato-Bridged Complexes,  $\text{Pt}_2(\text{SO}_4)_4\text{XY}^{n-}$ .<sup>a</sup>

X	Y	$\delta_{\text{Pt}(X)}$	$\delta_{\text{Pt}(Y)}$	$^1J_{\text{Pt}-\text{Pt}}$	$\delta_{\text{C}}$ or $\delta_{\text{N}}^{\text{b}}$	$^1J_{\text{Pt}-\text{C}}^{\text{b}}$ or $^1J_{\text{Pt}-\text{N}}$	$^2J_{\text{Pt}-\text{Pt}-\text{C}}^{\text{b}}$ or $^2J_{\text{Pt}-\text{Pt}-\text{N}}$	$^3J_{\text{C}-\text{Pt}-\text{Pt}-\text{C}}^{\text{b}}$ or $^3J_{\text{N}-\text{Pt}-\text{Pt}-\text{N}}$
H <sub>2</sub> O	H <sub>2</sub> O	1755.9	—	—	—	—	—	—
OH <sup>-</sup>	OH <sup>-</sup>	2049.3	—	—	—	—	—	—
Cl <sup>-</sup>	H <sub>2</sub> O	1638.4	1808.5	3464	—	—	—	—
Cl <sup>-</sup>	OH <sup>-</sup>	1529.1	2261.8	2473	—	—	—	—
Cl <sup>-</sup>	Cl <sup>-</sup>	1720.0	—	—	—	—	—	—
Br <sup>-</sup>	H <sub>2</sub> O	1439.5	1866.2	3472	—	—	—	—
Br <sup>-</sup>	Br <sup>-</sup>	1592.1	—	—	—	—	—	—
Cl <sup>-</sup>	Br <sup>-</sup>	1783.9	1534.9	3081	—	—	—	—
SCN <sup>-</sup>	H <sub>2</sub> O	1216.0	1891.6	3064	—	—	—	—
SCN <sup>-</sup>	SCN <sup>-</sup>	1433.4	—	—	—	—	—	—
NO <sub>2</sub> <sup>-</sup>	H <sub>2</sub> O	1944.1	1479.5	2727	<sup>c</sup>	293.0	170.9	—
NO <sub>2</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	1665.3	—	<sup>d</sup>	<sup>c</sup>	241.7	95.2	~0
dmsO	H <sub>2</sub> O	1723.7 <sup>e</sup>	1804.4 <sup>e</sup>	~3965	—	—	—	—
dmsO	dmsO	1767.7	—	—	—	—	—	—
NH <sub>3</sub>	H <sub>2</sub> O	1717.5	1575.7	2539	-36.2	203.6	95.7	—
NH <sub>3</sub>	NH <sub>3</sub>	1643.3	—	<sup>d</sup>	-27.6	164.9	64.6	4.6
CN <sup>-</sup>	H <sub>2</sub> O	1763.8	1299.3	1665	73.2	1093.8	279.3	—
CN <sup>-</sup>	OH <sup>-</sup>	1731.7	1908.8	1128	117.6	976.6	166.0	—
CN <sup>-</sup>	Cl <sup>-</sup>	1769.3	1398.5	1518.6	86.5	1069.3	216.8	—
CN <sup>-</sup>	Br <sup>-</sup>	1794.2	1294.3	1572.3	87.6	1076.2	196.3	—
CN <sup>-</sup>	SCN <sup>-</sup>	1838.6	1142.0	1443.4	101.7	1063.5	169.9	—
CN <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	1731.7	1454.5	1269.5	C 93.6 N <sup>c</sup>	C 1033.2 N 210.0	168.9 53.7	—
CN <sup>-</sup>	CN <sup>-</sup>	1601.9	—	703.7	112.2	957.9	59.0	58.6
CN <sup>-</sup>	NH <sub>3</sub>	1742.5	1460.9	1074.2	C 97.8 N -23.32	C 1005.2 N 145.5	155.3 36.6	—

<sup>a</sup>Chemical shifts in ppm, lower shielding positive. Coupling constants in Hz. For reference compounds see experimental section.

<sup>b</sup>For compounds containing <sup>13</sup>C-cyanide or <sup>15</sup>N-ammine or nitrite. <sup>c</sup><sup>15</sup>N signal not detected. <sup>d</sup> $^1J_{\text{Pt}-\text{Pt}}$  could not be determined. <sup>e</sup>These assignments could be reversed.

TABLE II. NMR Data for Phosphato-Bridged Complexes,  $\text{Pt}_2(\text{PO}_4\text{H})_4\text{XY}^{n-}$ .<sup>a</sup>

X	Y	$\delta_{\text{Pt}(X)}$	$\delta_{\text{Pt}(Y)}$	$^1J_{\text{Pt}-\text{Pt}}$	$\delta_{\text{C}}$ or $\delta_{\text{N}}^{\text{b}}$	$^1J_{\text{Pt}-\text{C}}^{\text{b}}$ or $^1J_{\text{Pt}-\text{N}}$	$^2J_{\text{Pt}-\text{Pt}-\text{C}}^{\text{b}}$ $\delta_{\text{P}}$ or $^2J_{\text{Pt}-\text{Pt}-\text{N}}$	$^2J_{\text{Pt}(X)-\text{O}-\text{P}}$	$^2J_{\text{Pt}(Y)-\text{O}-\text{P}}$	Other couplings
H <sub>2</sub> O	H <sub>2</sub> O	1795.7	—	—	—	—	—	21.3	71.8	—
Cl <sup>-</sup>	H <sub>2</sub> O	1713.1	1886.2	5342	—	—	—	23.4	46.4	92.8
Cl <sup>-</sup>	Cl <sup>-</sup>	1822.1	—	—	—	—	—	26.3	73.2	—
Br <sup>-</sup>	H <sub>2</sub> O	1549.8	1972.6	5349	—	—	—	24.3	41.2	95.2
Br <sup>-</sup>	Br <sup>-</sup>	1743.9	—	—	—	—	—	28.7	63.5	—
SCN <sup>-</sup>	H <sub>2</sub> O	1256.9	2017.3	4368	—	—	—	23.6	36.6	112.3
SCN <sup>-</sup>	SCN <sup>-</sup>	1543.1	—	—	—	—	—	27.8	68.4	—
NO <sub>2</sub> <sup>-</sup>	H <sub>2</sub> O	1987.3	1496.5	3951	<sup>c</sup>	214.9	166.2	21.2	26.8	120.2
NO <sub>2</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	1708.8	—	<sup>d</sup>	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	—
CN <sup>-</sup>	H <sub>2</sub> O	1835.5	1427.3	2422	69.2	1053.7	382.3	24.0	<20	148.9
CN <sup>-</sup>	CN <sup>-</sup>	1759.5	—	1175	113.1	849.6	94.8	34.4	73.2	—
dmsO	H <sub>2</sub> O	1787.3 <sup>e</sup>	1817.2 <sup>e</sup>	<sup>d</sup>	—	—	—	21.9	78.1	80.6
dmsO	dmsO	1809.0	—	—	—	—	—	22.5	80.6	—
NH <sub>3</sub>	H <sub>2</sub> O	1727.3	1569.2	3872	-37.6	164.9	146.5	22.6	38.0	111.3
NH <sub>3</sub>	NH <sub>3</sub>	1652.9	—	<sup>d</sup>	-25.9	112.2 <sup>f</sup>	106.5 <sup>f</sup>	26.1	68.4	—

<sup>a</sup>Chemical shifts in ppm, lower shielding positive. Coupling constants in Hz. For reference compounds, see Experimental. <sup>b</sup>For

compounds containing <sup>13</sup>C-cyanide or <sup>15</sup>N-ammine or nitrite. <sup>c</sup><sup>15</sup>N signal not detected. <sup>d</sup>Could not be determined.

<sup>e, f</sup>These assignments could be reversed.

TABLE III. Raman Data.

Compound <sup>a</sup>	$\nu(\text{Pt-Pt})$ $\text{cm}^{-1}$	Other bands $\text{cm}^{-1}$
$\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$	297	
$\text{Pt}_2(\text{SO}_4)_4(\text{OH})(\text{H}_2\text{O})^{3-}$	236	
$\text{Pt}_2(\text{SO}_4)_4\text{Cl}(\text{H}_2\text{O})^{3-}$	224	$\nu(\text{Pt-Cl})$ 320
$\text{Pt}_2(\text{SO}_4)_4(\text{NO}_2)(\text{H}_2\text{O})^{3-}$	228	
$\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{H}_2\text{O})^{3-}$	224	
$\text{Pt}_2(\text{SO}_4)_4(\text{NH}_3)(\text{H}_2\text{O})^{2-}$	232	
$\text{Pt}_2(\text{SO}_4)_4\text{Cl}_2^{4-}$	211	$\nu(\text{Pt-Cl})$ 340
$\text{Pt}_2(\text{SO}_4)_4\text{Br}_2^{4-}$	210, 193	mix with $\nu(\text{Pt-Br})?$
$\text{Pt}_2(\text{SO}_4)_4(\text{CN})_2^{4-}$	215	
$\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$	291	
$\text{Pt}_2(\text{PO}_4\text{H})_4(\text{OH})(\text{H}_2\text{O})^{3-}$	229	
$\text{Pt}_2(\text{PO}_4\text{H})_4(\text{CN})(\text{H}_2\text{O})^{3-}$	217	
$\text{Pt}_2(\text{PO}_4\text{H})_4(\text{CN})_2^{4-}$	211	$\nu(\text{C-N})$ 2149
$\text{Pt}_2(\text{PO}_4\text{H})_4(\text{NH}_3)_2^{2-}$	226	$\nu(\text{Pt-N})$ 421

<sup>a</sup>All as lithium salts in H<sub>2</sub>O.

topomers with zero, one, and two <sup>195</sup>Pt nuclei in the dimeric unit.

At high pH, insoluble Li<sub>4</sub>[Pt<sub>2</sub>(PO<sub>4</sub>H)<sub>4</sub>(OH)<sub>2</sub>] precipitated, leaving insufficient compound in solution for NMR spectra to be obtained.

#### NMR Spectra of Cyanide Complexes

The <sup>195</sup>Pt NMR spectrum of the pale yellow solution obtained by addition of Na<sup>12</sup>CN to an aqueous solution of Li<sub>2</sub>[Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)] is shown in Fig. 1(a) (CN<sup>-</sup>:Pt ratio approx. 3:2). A singlet at 1601.9 ppm increased in intensity as more cyanide was added, and so was assigned to Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>4-</sup>. The remaining peaks, assigned to Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(CN)(H<sub>2</sub>O)<sup>3-</sup>, were two singlets, corresponding to the isotopomers (H<sub>2</sub>O)<sup>195</sup>Pt(SO<sub>4</sub>)<sub>4</sub>-Pt(CN) and (H<sub>2</sub>O)Pt(SO<sub>4</sub>)<sub>4</sub><sup>195</sup>Pt(CN), superimposed on an AB pattern from the isotopomer (H<sub>2</sub>O)<sup>195</sup>Pt(SO<sub>4</sub>)<sub>4</sub><sup>195</sup>Pt(CN). <sup>1</sup>J(Pt-Pt) was measured directly from peak separations in the AB spectrum.

When Na<sup>13</sup>CN was used rather than Na<sup>12</sup>CN, the resultant <sup>195</sup>Pt spectrum is shown in Fig. 1(b) and the <sup>13</sup>C spectrum in Fig. 2. The <sup>195</sup>Pt spectrum of Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(<sup>13</sup>CN)<sub>2</sub><sup>4-</sup> is the probability-weighted sum of those for the isotopomer with one <sup>195</sup>Pt nucleus (A part of AXX' spectrum) and the isotopomer with two <sup>195</sup>Pt nuclei (A part of AA'XX' spectrum, one half of intensity of AXX' spectrum). The <sup>13</sup>C spectrum for this species consists of a central singlet (mainly from the isotopomer with no <sup>195</sup>Pt nuclei, A<sub>2</sub>) flanked by peaks from isotopomers with one (X part of AXX' spectrum) and two (X part of AA'XX' spectrum) <sup>195</sup>Pt nuclei. These spectra were analysed and simulated, using an iterative program, to give the coupling constants listed in Table I, including <sup>1</sup>J(Pt-Pt).

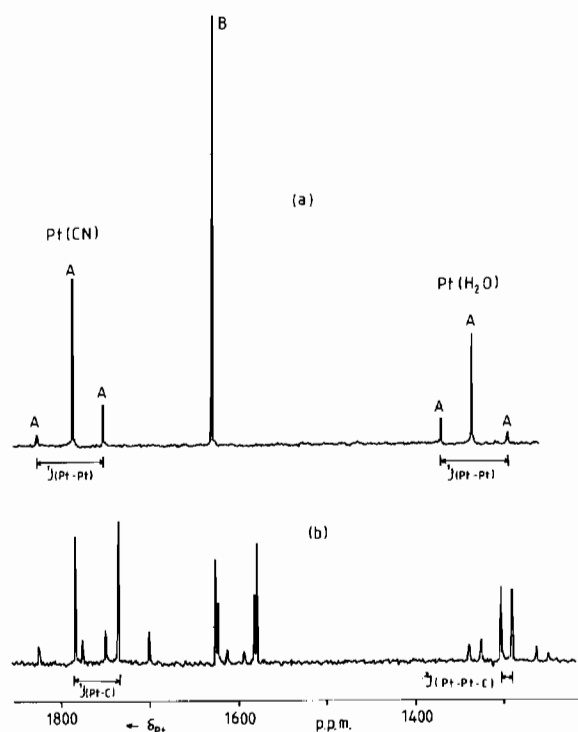


Fig. 1. 21.4 MHz <sup>195</sup>Pt NMR spectra of solutions obtained by addition to Li<sub>2</sub>[Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)] solution of: (a) Na-<sup>12</sup>CN solution. Peaks marked A are due to Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(CN)(H<sub>2</sub>O)<sup>3-</sup>, and that marked B to Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>4-</sup>. (b) Na<sup>13</sup>CN solution.

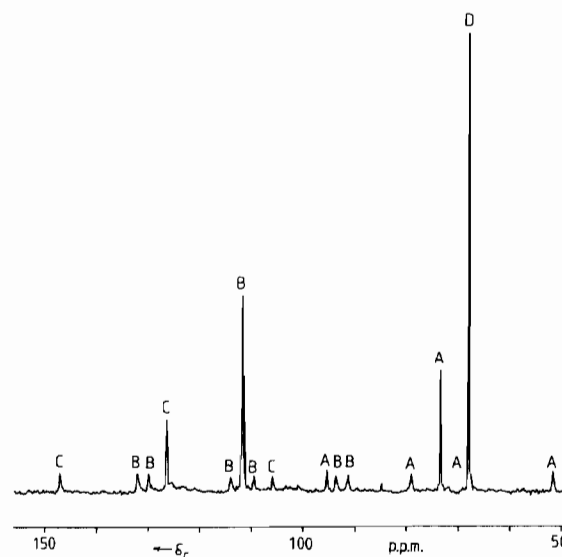


Fig. 2. 25 MHz <sup>13</sup>C NMR spectrum of solution obtained by adding Na<sup>13</sup>CN to Li<sub>2</sub>[Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)] solution: (A) peaks due to Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(<sup>13</sup>CN)(H<sub>2</sub>O)<sup>3-</sup>; (B) peaks due to Pt<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(<sup>13</sup>CN)<sub>2</sub><sup>4-</sup>; (C) Peaks due to Pt(<sup>13</sup>CN)<sub>4</sub><sup>2-</sup>; (D) dioxane reference.

The two  $^{195}\text{Pt}-^{13}\text{C}$  coupling constants for  $\text{Pt}_2(\text{SO}_4)_4(^{13}\text{CN})_2^{4-}$  are very different, 957.9 Hz and 59.0 Hz. The larger coupling may be compared with  $^1J(\text{Pt}-\text{C})$  in  $\text{Pt}(\text{CN})_4^{2-}$ , 1028.3 Hz, and  $\text{Pt}(\text{CN})_6^{2-}$ , 808 Hz [18], and must clearly be assigned to  $^1J(^{195}\text{Pt}-^{13}\text{C})$ , with the smaller coupling assigned as  $^2J(^{195}\text{Pt}-\text{Pt}-^{13}\text{C})$ . The analysis of the spectra also shows that these two coupling constants have the same sign.

All of the peaks in the  $^{195}\text{Pt}$  spectrum due to  $\text{Pt}_2(\text{SO}_4)_4(^{13}\text{CN})(\text{H}_2\text{O})^{3-}$  were split into doublets (Fig. 1(b)), and the Pt-C coupling constants were measured directly from the spectrum. The  $^{13}\text{C}$  peaks due to this species showed a singlet (isotopomer with no  $^{195}\text{Pt}$ ) superimposed on two doublets (one from each isotopomer with one  $^{195}\text{Pt}$  nucleus) and a very weak doublet of doublets (isotopomer with two  $^{195}\text{Pt}$  nuclei) (not observable in Fig. 2). The two Pt-C coupling constants are again quite different (1093.8, 279.3 Hz), and again the only reasonable assignment is that  $|^1J(\text{Pt}-\text{C})| > |^2J(\text{Pt}-\text{Pt}-\text{C})|$ . Since it is the less shielded platinum nucleus ( $\delta_{\text{Pt}}$  1763.8 ppm) which has the larger coupling to  $^{13}\text{C}$ , this must therefore be assigned as the platinum atom bound directly to cyanide, while the more shielded ( $\delta_{\text{Pt}}$  1299.3 ppm) corresponds to platinum bound to water. This is remarkable, since it implies that replacement of one water molecule in  $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$  ( $\delta_{\text{Pt}}$  1755.9 ppm) with cyanide causes a shift for the Pt atom actually substituted of only +7.9 ppm, while the remote platinum atom, which can be affected only through the Pt-Pt bond, shifts -456.6 ppm.

If water coordinated to platinum(II) or -(IV) in a mononuclear complex is replaced by a more strongly bonding ligand with a 'first-row' donor atom, such as cyanide, the platinum resonance shifts to higher shielding [12, 19-21]. This is usually interpreted in terms of the effect of stronger metal-ligand bonding on the paramagnetic contribution to nuclear shielding,  $\sigma^{\text{P}}$ , through (i) increased average singlet-triplet excitation energy. (ii) increased average distance of d-electrons from the nucleus. (iii) restriction of free circulation of d-electrons about the nucleus, by formation of localized covalent bonds.

In  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{H}_2\text{O})^{3-}$ , the large deshielding of the Pt-atom which remains bound to water can only be explained if, as the axial ligands are changed, variations in the Pt-Pt bond make a large contribution to changes in  $\delta_{\text{Pt}}$ . The change in the metal-metal bond should also make a significant contribution for the Pt-atom actually involved in the substitution, presumably superimposed on the local effects of (i)-(iii) above, with an 'accidental' near-cancellation of contributions of opposite sign.

In addition to peaks due to the Pt(III) complexes, the  $^{13}\text{C}$  spectrum showed a singlet with satellites ( $\delta_{\text{C}}$  125.9 ppm,  $J(\text{Pt}-\text{C})$  1028.3 Hz) assigned to

$\text{Pt}(\text{CN})_4^{2-}$  [18], indicating that the solution slowly decomposed.

The  $^{195}\text{Pt}$  NMR spectrum of the solution obtained by addition of  $\text{Na}^{12}\text{CN}$  to  $\text{Li}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  showed, at 1759.5 ppm, a quintet for  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{CN})_2^{4-}$ , due to coupling of the  $^{195}\text{Pt}$  nuclei with four equivalent  $^{31}\text{P}$  nuclei.  $^2J(\text{Pt}-\text{O}-\text{P})$ , 73.2 Hz, was very similar to the value for  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ , 71.8 Hz. The  $^{31}\text{P}$  NMR spectrum for this complex showed the expected 1:8:18:8:1 multiplet.

The  $^{195}\text{Pt}$  spectrum of  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{12}\text{CN})(\text{H}_2\text{O})^{3-}$  would be expected to be similar to that of  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{H}_2\text{O})^{3-}$ , but with each peak split into a quintet by phosphorus coupling. The more shielded resonance (Pt bound to  $\text{H}_2\text{O}$ , 1427.3 ppm) did show a large Pt-O-P coupling (148.9 Hz) but the less shielded resonance (Pt bound to  $\text{CN}^-$ , 1835.5 ppm) did not show any resolved coupling ( $<20\text{Hz}$ ). The  $^{31}\text{P}$  signal for this complex showed only a singlet with one set of satellites.

The  $^{195}\text{Pt}$  spectrum of the solution obtained using  $\text{Na}^{13}\text{CN}$  was complicated by the presence of the additional nuclei with  $I = 1/2$ , but it was possible to analyse the spectra to give the coupling constants listed in Table II. Again, the less shielded Pt atom had the larger Pt-C coupling.

The  $^{13}\text{C}$  spectrum was analogous to that of the sulfato-bridged analogue, except that the peaks were all significantly broadened by unresolved P-O-Pt-C coupling ( $\leq 5$  Hz).

A solution containing  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{OH})^{4-}$  (using  $^{12}\text{C}$  or  $^{13}\text{C}$ ) was prepared by addition of 5 M LiOH solution to a solution containing  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{H}_2\text{O})^{3-}$ , prepared as described above, to increase pH to 13. There was little tendency for hydroxide to displace coordinated cyanide. With  $^{12}\text{C}$ -cyanide, the  $^{195}\text{Pt}$  spectrum showed the expected two singlets superimposed on an AB pattern, and with  $^{13}\text{C}$ -cyanide each peak was split into a doublet. Accurate Pt-C coupling constants were obtained from the  $^{13}\text{C}$  spectrum. Again, the larger Pt-C coupling was assigned as  $^1J(\text{Pt}-\text{C})$ . With the deprotonation, the shift for Pt bound to cyanide scarcely changed (1763.8 to 1731.7 ppm) but there was a remarkable shift for platinum bound to oxygen (1299.3 to 1908.8 ppm).

Solutions containing  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})\text{X}^{n-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{SCN}, \text{NO}_2$ ) were obtained by adding excess of a lithium or sodium salt of  $\text{X}^-$  to a solution of  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{H}_2\text{O})^{3-}$ . For  $\text{X} = \text{NH}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  was added to a solution of  $\text{Li}_3[\text{Pt}_2(\text{SO}_4)_4(\text{CN})(\text{H}_2\text{O})]$  (no ammonium salt precipitated), and LiOH solution was added to increase pH to 9.4. The solution was allowed to stand five minutes, then pH was reduced to 6.6.

For the nitrite and ammine complexes, to avoid unnecessary complication,  $^{195}\text{Pt}$  spectra were run on

complexes with  $^{12}\text{C}$ -cyanide and  $^{15}\text{N}$ -ligand, to give Pt–N couplings, and with  $^{13}\text{C}$ -cyanide and  $^{14}\text{N}$ -ligand, to give Pt–C couplings.

For all of the above complexes, the less shielded platinum nucleus had the larger coupling to  $^{13}\text{C}$ , and was therefore assigned as that bound to cyanide. In each of the complexes with  $^{15}\text{N}$  bound to the other Pt-atom, this allowed the larger of the two Pt–N couplings to be assigned as  $^1J(^{195}\text{Pt}-^{15}\text{N})$ . When  $^{14}\text{N}$  was bound to platinum, the  $^{195}\text{Pt}$  signal was moderately broadened, owing to partial decoupling from  $^{14}\text{N}$ .

If  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})_2^{4-}$  is included in the series,  $\delta_{\text{Pt}}$  for platinum bound to cyanide lies within the relatively narrow range 1601–1839 ppm for all of the compounds  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})\text{X}^{n-}$  that were studied.

#### Other Compounds $\text{Pt}_2(\text{Z})_4\text{XY}^{n-}$

Addition of  $\text{Na}^{15}\text{NO}_2$  to a solution of  $\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  gave  $^{195}\text{Pt}$  NMR patterns of the same general type as those obtained using  $^{13}\text{C}$ -cyanide. The complex multiplet due to  $\text{Pt}_2(\text{SO}_4)_4(^{15}\text{NO}_2)_2^{4-}$  was analysed to give the Pt–N coupling constants listed in Table I, with the assumption that  $|^1J(^{195}\text{Pt}-^{15}\text{N})| > |^2J(^{195}\text{Pt}-\text{Pt}-^{15}\text{N})|$ , as in  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})(^{15}\text{NO}_2)^{4-}$ .  $^1J(\text{Pt}-\text{Pt})$  could not be calculated from the spectra, the only deduction possible being that it is very much larger in magnitude than the Pt–N coupling constants. The two Pt–N coupling constants have the same sign.

For  $\text{Pt}_2(\text{SO}_4)_4(^{15}\text{NO}_2)(\text{H}_2\text{O})^{3-}$ , if it is again assumed that  $|^1J(\text{Pt}-\text{N})| > |^2J(\text{Pt}-\text{Pt}-\text{N})|$ , the less shielded Pt atom is that bound to nitrite.

Attempts to obtain  $^{15}\text{N}$  spectra for these solutions were unsuccessful. There is no nuclear Overhauser effect to enhance sensitivity, and relaxation times for  $^{15}\text{N}$  in such environments tend to be long [22].

The  $^{195}\text{Pt}$  spectra of these solutions showed, in addition to peaks due to the Pt(III) complexes, a quintet at  $-2166.6$  ppm. ( $^1J(\text{Pt}-\text{N})$  590.8 Hz), assigned to  $\text{Pt}(^{15}\text{NO}_2)_4^{2-}$  [23], and, with higher intensity, a doublet of triplets at  $-1798.1$  ppm. The doublet splitting was 820.3 ppm, and the triplet splitting 571.3 Hz. This multiplet is clearly due to a species  $\text{Pt}(^{15}\text{NO}_2)_3\text{X}^{n-}$ , and the NMR parameters are intermediate between those reported for  $\text{Pt}(^{15}\text{NO}_2)_3(\text{H}_2\text{O})^-$  and  $\text{Pt}(^{15}\text{NO}_2)_3(\text{OH})^{2-}$  [23]. The multiplet was therefore assigned as an averaged signal from a rapidly interconverting mixture of these anions.

The  $^{195}\text{Pt}$  spectrum of  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{15}\text{NO}_2)(\text{H}_2\text{O})^{3-}$  was complicated by Pt–O–P coupling to both Pt atoms, although the couplings are very different (26.8 Hz for Pt bound to nitrite, 120.2 Hz for Pt bound to  $\text{H}_2\text{O}$ ). However, the Pt–N coupling constants could be measured.  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{15}\text{NO}_2)_2^{4-}$ , however, gave too complex an envelope to be satis-

factorily analysed. The  $^{31}\text{P}$  spectrum of a solution containing both these species showed a single broad resonance at 21.2 ppm. The  $^{31}\text{P}$  peaks for the two species apparently coincide there, and unresolved  $^{15}\text{N}-\text{Pt}-\text{O}-^{31}\text{P}$  coupling probably contributes to the line broadening.

The  $^{195}\text{Pt}$  NMR spectra of the  $^{15}\text{N}$ -ammine complexes were qualitatively similar to those for  $^{15}\text{N}$ -nitrite. Again, the assumption for  $\text{Pt}_2(\text{SO}_4)_4(^{15}\text{NH}_3)(\text{H}_2\text{O})^{2-}$  that  $|^1J(^{195}\text{Pt}-^{15}\text{N})| > |^2J(^{195}\text{Pt}-\text{Pt}-^{15}\text{N})|$  allowed the less shielded Pt atom to be assigned as that bound to  $^{15}\text{NH}_3$ . Because of the relatively small chemical shift difference between the non-equivalent Pt-atoms of  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{15}\text{NH}_3)(\text{H}_2\text{O})^{2-}$ , the inner multiplets of the 'AB multiplets' were much more intense than the outer lines, which were not observed. For  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{14}\text{NH}_3)(\text{H}_2\text{O})^{2-}$ , although peaks were broadened, the spectrum was simpler, and  $^1J(\text{Pt}-\text{Pt})$  could be determined after long accumulation.  $^1\text{H}$ -decoupled  $^{15}\text{N}$  NMR spectra were obtained for all the ammine complexes. Small  $^{31}\text{P}-\text{O}-\text{Pt}-^{15}\text{N}$  coupling ( $\sim 3$  Hz) was observed. The spectra of the bis(ammine) complexes were analysed, but  $^1J(\text{Pt}-\text{Pt})$  could not be determined ( $|^1J(\text{Pt}-\text{Pt})| \gg |J(\text{Pt}-\text{N})|$ ). There is a much smaller difference between  $^1J(\text{Pt}-\text{N})$  and  $^2J(\text{Pt}-\text{Pt}-\text{N})$  for the phosphato-bridged compounds relative to the sulfates, and for  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{15}\text{NH}_3)_2^{2-}$ , the two coupling constants are nearly equal.

As with cyanide, the lower shielding of platinum bound to N relative to platinum bound to  $\text{H}_2\text{O}$  in the nitro and ammine complexes is the reverse of what would be expected for mononuclear complexes.

The  $^{195}\text{Pt}$  spectrum of each of the solutions obtained by addition of LiCl, LiBr, or NaSCN to a solution of  $\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  showed a singlet due to  $\text{Pt}_2(\text{SO}_4)_4\text{X}_2^{4-}$ , and two singlets superimposed on an AB quartet for  $\text{Pt}_2(\text{SO}_4)_4\text{X}(\text{H}_2\text{O})^{3-}$ . As there is no major broadening of any peaks when  $\text{X} = \text{SCN}$ , this ligand is S-bound.

All of these ligands, replacing  $\text{H}_2\text{O}$  in a mononuclear complex of platinum(II) or -(IV), would cause significant shielding of the Pt nucleus [12, 19–21]. McFarlane *et al.* [21, 24] have proposed a 'heavy atom effect', and have suggested that, in addition to the effect on the Pt d-electrons through covalent bonding, the platinum nucleus experiences diamagnetic and paramagnetic shielding from the electrons of the bound heavy atom. Unlike the effects of covalent bonding of the axial ligands, this 'heavy atom' component would be unlikely to be transmitted through the Pt–Pt bond.

We therefore assign the more shielded Pt nucleus for each of these compounds  $\text{Pt}_2(\text{SO}_4)_4\text{X}(\text{H}_2\text{O})^{3-}$  to platinum bound to  $\text{X}^-$ . With this assignment, the shielding of the Pt nucleus bound to X increases in the order  $\text{Cl} < \text{Br} < \text{SCN}$ , which is the same

order as observed for the cyanide complexes,  $\text{Pt}_2(\text{SO}_4)_4(\text{CN})\text{X}^{4-}$ , for which assignment is more certain.

An analogous assignment has been used for the phosphato-bridged compounds. With this assignment, variations in  ${}^2J(\text{Pt}-\text{O}-\text{P})$  appear to be most consistent, and effects transmitted through the Pt-Pt bond remain consistently greater relative to effects on the Pt-atom being substituted for the phosphato-bridged series than for the sulfates (see Discussion section below).

Attempts to obtain solutions containing  $\text{Pt}_2(\text{SO}_4)_4\text{X}(\text{OH})^{4-}$  with  $\text{X} = \text{Cl}, \text{Br}, {}^{15}\text{NO}_2$  were less successful than for  $\text{X} = \text{CN}$  (see above). At pH 11 these ligands were displaced completely by hydroxide, and the  ${}^{195}\text{Pt}$  spectrum showed only the peak due to  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})_2^{4-}$ . Solutions containing bromide also rapidly decomposed at high pH. With an excess of LiCl present, at pH 9.2, peaks due to  $\text{Pt}_2(\text{SO}_4)_4\text{Cl}(\text{OH})^{4-}$  (perhaps partly protonated) were observed, together with a very broad resonance from  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})(\text{H}_2\text{O})^{3-}$ . If platinum bound to hydroxide is assigned to the peak observed to low shielding (2261.8 ppm) (as with other hydroxo compounds), then  $\delta_{\text{Pt}}$  for platinum bound to chloride (1529.1 ppm) is in the vicinity of that for other chloro compounds. When pH was increased to 11.9, these peaks disappeared, and were just observable after a 30-fold excess of LiCl had been added.

Addition of a stoichiometric amount of NaI to a solution of  $\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2^{2-}$  caused rapid generation of a purple-red solution, from which a black solid precipitated. The  ${}^{195}\text{Pt}$  spectrum of the supernatant solution showed in the Pt(III) region only peaks due to  $\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2^{2-}$ . Shaking the solid with chloroform imparted a violet colour to the chloroform solvent, but not all the precipitate dissolved. These results are interpreted as showing that iodide reduces the Pt(III) complexes to Pt metal, with concomitant oxidation to iodine.

Addition of  $\text{PMePh}_2$  to  $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$  gave  $\text{Pt}(\text{SO}_4)(\text{PMePh}_2)_2$  and  $\text{Ph}_2\text{MeP}=\text{O}$  (see Experimental). A similar experiment using  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$  gave  $\text{Ph}_2\text{MeP}=\text{O}$ , and a mixture of Pt(II) products.

Addition of a large excess of dimethylsulfoxide (dmsO) to solutions of  $\text{Li}_2[\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2]$  caused new peaks to appear assigned to  $\text{Pt}_2(\text{Z})_4(\text{dmsO})(\text{H}_2\text{O})^{2-}$  and  $\text{Pt}_2(\text{Z})_4(\text{dmsO})_2^{2-}$ . In solid  $\text{K}_2[\text{Pt}_2(\text{SO}_4)_4(\text{dmsO})_2] \cdot 4\text{H}_2\text{O}$ , dmsO is O-bound [6], and O-bonding is also likely in solution. Platinum chemical shifts are only slightly changed from those for the diaqua complexes, and there is no basis for assigning the individual peaks for  $\text{Pt}_2(\text{Z})_4(\text{dmsO})(\text{H}_2\text{O})^{2-}$ . The outer lines of the AB quartet for the isotopomer with two  ${}^{195}\text{Pt}$  atoms are consequently very weak, and  $J_{\text{Pt}-\text{Pt}}$  could not be determined with confidence for this compound.

### Raman Spectra

The Raman spectrum of a solution of  $\text{Li}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$  showed a strong polarized band at  $297\text{ cm}^{-1}$ , which was unaffected by change of solvent from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$ . This band was assigned to  $\nu(\text{Pt}-\text{Pt})$  in  $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$ . A much weaker polarized band was observed at  $236\text{ cm}^{-1}$ , which increased in intensity at the expense of the higher frequency band when pH was raised to 10. This peak was assigned to  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})(\text{H}_2\text{O})^{3-}$ . Attempts to obtain spectra of  $\text{Pt}_2(\text{SO}_4)_4(\text{OH})_2^{4-}$ , at higher pH, were unsuccessful, because of the dark brown colour of the solution, and the slow formation of a dark brown colloidal suspension by slow decomposition of the sample.

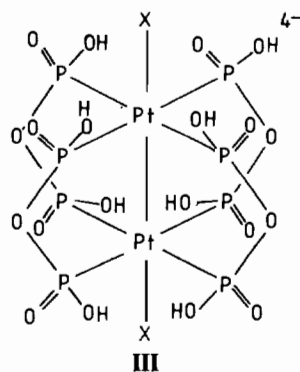
Solutions of  $\text{Li}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$  gave a strong band at  $291\text{ cm}^{-1}$ , and a weak band at  $229\text{ cm}^{-1}$ , assigned to  $\nu(\text{Pt}-\text{Pt})$  in  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$  and  $\text{Pt}_2(\text{PO}_4\text{H})(\text{OH})(\text{H}_2\text{O})^{3-}$  respectively.

Solutions of other complexes were prepared as for NMR spectra. In most cases,  $\nu(\text{Pt}-\text{Pt})$  could be assigned without difficulty. For the bromo complex  $\text{Pt}_2(\text{SO}_4)_4\text{Br}_2^{4-}$  assignment was uncertain as  $\nu(\text{Pt}-\text{Br})$  and  $\nu(\text{Pt}-\text{Pt})$  are both expected in the vicinity of  $200\text{ cm}^{-1}$ , and the bands observed at 210 and  $193\text{ cm}^{-1}$  probably arise from vibrational modes which are coupled.

### Discussion

#### $J(\text{Pt}-\text{Pt})$ and the Metal-Metal Bond

In our complexes,  $\nu(\text{Pt}-\text{Pt})$  from the Raman spectra has higher frequency than for the series of complexes  $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$  (III) ( $\text{pop}^{2-} = \{\text{P}(\text{O})(\text{OH})_2\text{O}^{2-}\}$ ), for which the observed range was  $110-158\text{ cm}^{-1}$  [25]. The lower frequency would



be expected, since the Pt-Pt bond length in  $\text{K}_4[\text{Pt}_2(\text{pop})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,  $2.695(1)\text{ \AA}$  [26] is longer than in  $[\text{Et}_4\text{N}]_2[\text{Pt}_2(\text{PO}_4\text{H}_2)_2(\text{PO}_4\text{H})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ ,  $2.529(1)\text{ \AA}$  [4].

The Pt-Pt bond length in  $\text{Na}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$ ,  $2.486(2)\text{ \AA}$ , is slightly longer than for  $\text{K}_2$ -



$[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$ , 2.461(1) Å [4]. With the slightly higher frequency for  $\nu(\text{Pt}-\text{Pt})$  for  $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2^{2-}$ , 297  $\text{cm}^{-1}$ , compared with  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ , 291  $\text{cm}^{-1}$ , this would indicate that the Pt-Pt bonds in the two compounds are very similar, with that in the sulfato complex perhaps slightly stronger.  $\nu(\text{Pt}-\text{Pt})$  frequencies for other species (e.g.  $\text{Pt}_2(\text{Z})_4(\text{CN})(\text{H}_2\text{O})^{3-}$ , Table III) show similar small increases for  $\text{Z} = \text{SO}_4$  relative to  $\text{Z} = \text{PO}_4\text{H}$ .

It is therefore surprising that, for any pair of compounds  $\text{Pt}_2(\text{Z})_4\text{XY}^{n-}$  for which  $^1J(\text{Pt}-\text{Pt})$  has been measured, the coupling is much larger for  $\text{Z} = \text{PO}_4\text{H}$  than for  $\text{Z} = \text{SO}_4$ . Figure 3 shows a plot of  $J(\text{Pt}(\text{PO}_4\text{H})_4\text{Pt})$  against  $J(\text{Pt}(\text{SO}_4)_4\text{Pt})$  for corresponding complexes. The relationship is linear (correlation coefficient 0.995). The equation for the line of best (least squares) fit is:

$$J(\text{phosphate}) = \{1.49 \pm 0.13\}J(\text{sulfate}) + \{17 \pm 357\}$$

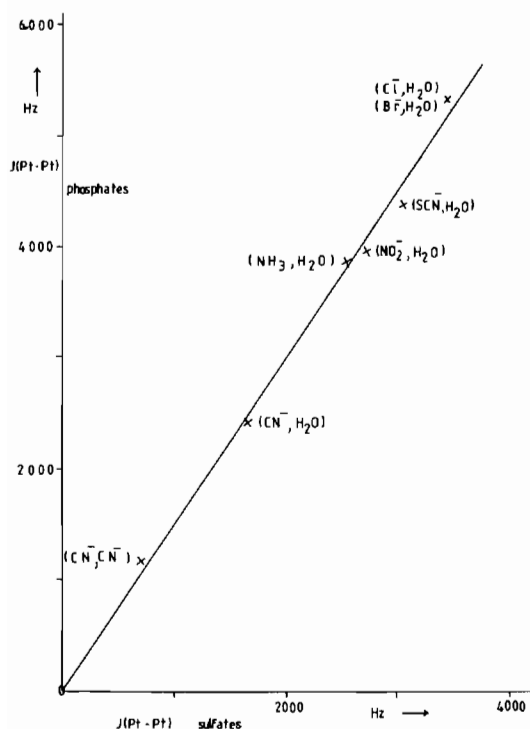


Fig. 3. Plot of  $^1J(\text{Pt}-\text{Pt})$  for  $\text{Pt}_2(\text{PO}_4\text{H})_4\text{XY}^{n-}$  against  $^1J(\text{Pt}-\text{Pt})$  for corresponding complexes  $\text{Pt}_2(\text{SO}_4)_4\text{XY}^{n-}$ .

The line passes through the origin, so that the increased coupling constant for the phosphato complexes does reflect a greater sensitivity of this coupling to variations in the Pt-Pt bond caused by changes in the axial ligands.

The lack of correlation between  $^1J(\text{Pt}-\text{Pt})$  and other indicators of Pt-Pt bond strength over a wide range of complexes has previously been noted [12], but it is surprising that such a large difference should occur for complexes which are so similar structurally and chemically. The coupling must

be very sensitive to electronic changes in the metal-metal bond (including Pt 6s contribution from each Pt atom—see below) which do not greatly affect the other properties of the bond. As will be noted below, transmission of the effects of axial ligands through the Pt-Pt bond is always greater in the phosphate series.

Within a series  $\text{XPt}(\text{Z})_4\text{PtY}^{n-}$ , changing the ligand Y while holding X constant produces changes in  $J(\text{Pt}-\text{Pt})$  which depend on the NMR *trans* influence of Y, as measured by such widely-studied coupling constants as  $^1J(\text{Pt}-\text{H})$  or  $^1J(\text{Pt}-\text{P})$  [27]. For example, Fig. 4 shows a plot of  $^1J(\text{Pt}-\text{Pt})$  for the series  $(\text{H}_2\text{O})\text{Pt}(\text{SO}_4)_4\text{PtY}^{n-}$  against  $^1J(\text{Pt}-\text{H})$  for the corresponding complexes *trans*-Pt(H)Y(PMe-Ph<sub>2</sub>)<sub>2</sub> or Pt(H)Y(PEt<sub>3</sub>)<sub>2</sub> (values from ref. 27). A dependence close to linear is observed, although the line does not pass through the origin.

Variations in  $^1J(\text{Pt}-\text{H})$  in such a series are normally interpreted in terms of variations in the Fermi Contact contribution to the coupling constant, using the simplified equation for coupling between nuclei A and B:

$$|J_{AB}| \propto \gamma_A \gamma_B S_{ms}(\text{O})_A S_{ms}(\text{O})_B \alpha_A^2 \alpha_B^2 (\Delta E)^{-1} \quad (1)$$

where  $\gamma_i$  is the magnetogyric ratio for nucleus i.  $S_{ms}(\text{O})_i$  is the density at the nucleus i of the valence s-orbital, ms.  $\alpha_i^2$  is the s-character of the hybrid orbital used by nucleus i in its bond with the other nucleus.  $\Delta E$  is an average singlet-triplet excitation energy. Increasing the *trans* influence of Y increases the Pt 6s contribution to the Pt-Y bond at the expense of the contribution to the Pt-H bond *trans* to Y,  $\alpha_{\text{Pt}}^2$ , causing a decrease in the coupling constant. In the Pt(III) complexes, a similar rehybridization of Pt(Y) must occur, to give the observed dependence of  $J(\text{Pt}-\text{Pt})$  on the *trans* influence of Y.

An analogous variation is observed for series with X a ligand other than H<sub>2</sub>O—the extensive series with X = CN<sup>-</sup>, and more limited series with, for example, X = Cl<sup>-</sup>, NH<sub>3</sub>. A good straight line passing through the origin is obtained if  $J(\text{Pt}-\text{Pt})$  for  $\text{NCPt}(\text{SO}_4)_4\text{PtY}^{n-}$  is plotted against  $J(\text{Pt}-\text{Pt})$  for corresponding complexes  $\text{H}_2\text{OPt}(\text{SO}_4)_4\text{PtY}^{n-}$  (slope 0.48).

Because of coupling and mass effects,  $\nu(\text{Pt}-\text{Pt})$  from Raman spectra cannot be related directly to the Pt-Pt bond strength, but there is an obvious trend for the stretching frequency to decrease with increasing *trans* influence of the axial ligands.

The Pt-Pt bond length in  $[\text{Et}_4\text{N}]_2[\text{Pt}_2(\text{PO}_4\text{H}_2)_2(\text{PO}_4\text{H})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ ; 2.529(1) Å, is significantly longer than in  $\text{Na}_2[\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2]$ , 2.486(2) Å [4], which probably is due to the higher *trans* influence of chloride relative to water.

#### Other Correlations Involving Coupling Constants

For the series  $\{(\text{MeO})_3\text{P}\}\text{Rh}(\mu\text{-O}_2\text{CMe})_4\text{RhL}$ , Boyar and Robinson [28] found that  $\delta_{\text{P}}$  increased

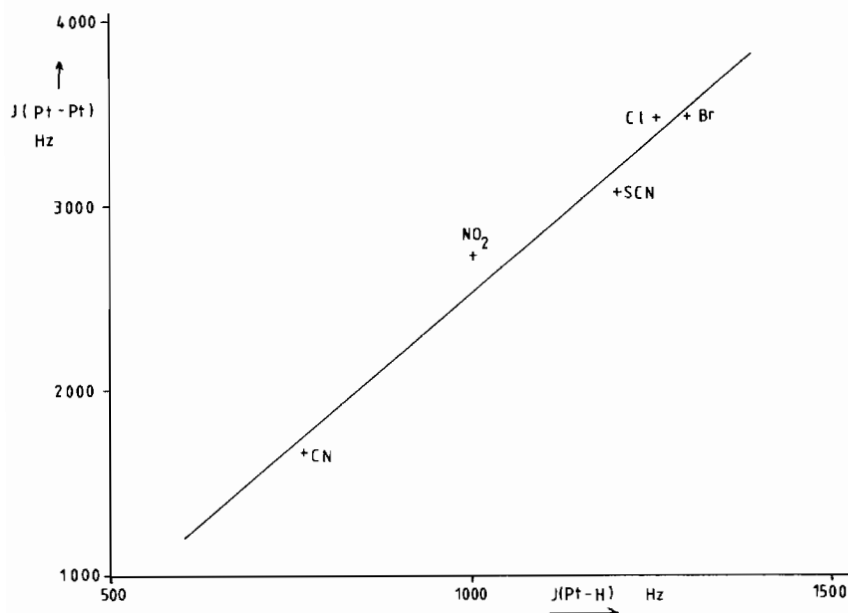


Fig. 4. Plot of  $^1J(\text{Pt-Pt})$  for  $\text{Pt}_2(\text{SO}_4)_4(\text{Y})(\text{H}_2\text{O})^{3-}$  against  $^1J(\text{Pt-H})$  for corresponding complexes *trans*-Pt(H)(Y)(PMePh<sub>2</sub>) or Pt(H)(Y)(PEt<sub>3</sub>)<sub>2</sub>.

and  $^2J(^{103}\text{Rh-Rh-}^{31}\text{P})$  decreased as the *trans* influence of L decreased, and that these two parameters were related linearly. They also noted that 'there is some evidence of a linear correlation between  $^1J(^{103}\text{Rh-}^{31}\text{P})$  and  $^2J(^{103}\text{Rh-Rh-}^{31}\text{P})$ ', although the range of values for the direct coupling was small.

For our series,  $\text{N}^{13}\text{C}(\text{Pt}(\text{SO}_4)_4\text{PtY}^{n-})$ , both  $^1J(\text{Pt-C})$  and  $^2J(\text{Pt-Pt-C})$  decrease in magnitude as the *trans* influence of X decreases, and each varies linearly with  $^1J(\text{Pt-Pt})$  (Fig. 5). It is remarkable that the magnitude of the slope of the line for  $^1J(\text{Pt-C})$ , relatively remote from the substitution site, (0.15 ± 0.035) is only slightly less than for  $^2J(\text{Pt-Pt-C})$ , which involves the Pt-atom directly substituted. (0.18 ± 0.06).

If the variation in  $^1J(\text{Pt-C})$  is interpreted in the usual way as due mainly to changes in  $\alpha^2_{\text{Pt}}$  in eqn. (1), one may postulate that increasing the *trans* influence of Y has the following effect. The Pt-atom directly substituted contributes a greater proportion of its 6s-orbital to its bond with Y, at the expense of its contribution to the Pt-Pt bond. The remote Pt-atom partly compensates for this by rehybridizing to increase its 6s contribution to the Pt-Pt bond, at the expense of the Pt-C bond, causing a decrease in  $^1J(\text{Pt-C})$ .

$\delta_{\text{C}}$  and  $^1J(\text{Pt-C})$  in these Pt(III) cyanide complexes are in a similar range to cyanide complexes of Pt(II) and -(IV) [18], so that the Pt-CN bond is presumably similar to the bond in these simple monomeric compounds. There is a general trend for  $\delta_{\text{C}}$  to increase as the *trans* influence of Y increases. Pesek and Mason [18] interpret a shift in this direc-

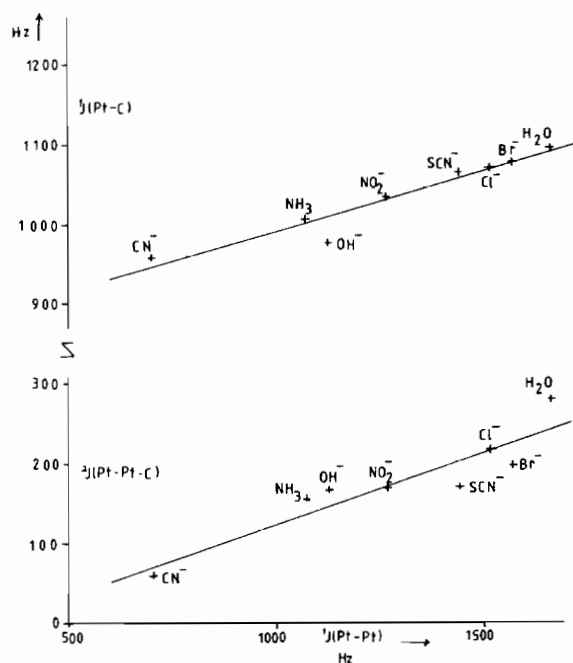


Fig. 5. Plot of  $^1J(\text{Pt-C})$  and  $^2J(\text{Pt-Pt-C})$  against  $^1J(\text{Pt-Pt})$  for the series  $\text{Pt}_2(\text{SO}_4)_4(^{13}\text{CN})(\text{Y})^{n-}$ .

tion (toward free cyanide) as indicating a weakening of the metal-cyanide bond, consistent with the concept of the transmission of the *trans* influence of Y through the Pt-Pt bond.

By analogy with the plot of Boyar and Robinson [28],  $\delta_{\text{C}}$  was plotted against  $^2J(\text{Pt-Pt-C})$ . If the point for Y = OH<sup>-</sup> is ignored, there is a reasonable linear relationship between these parameters (Fig. 6).

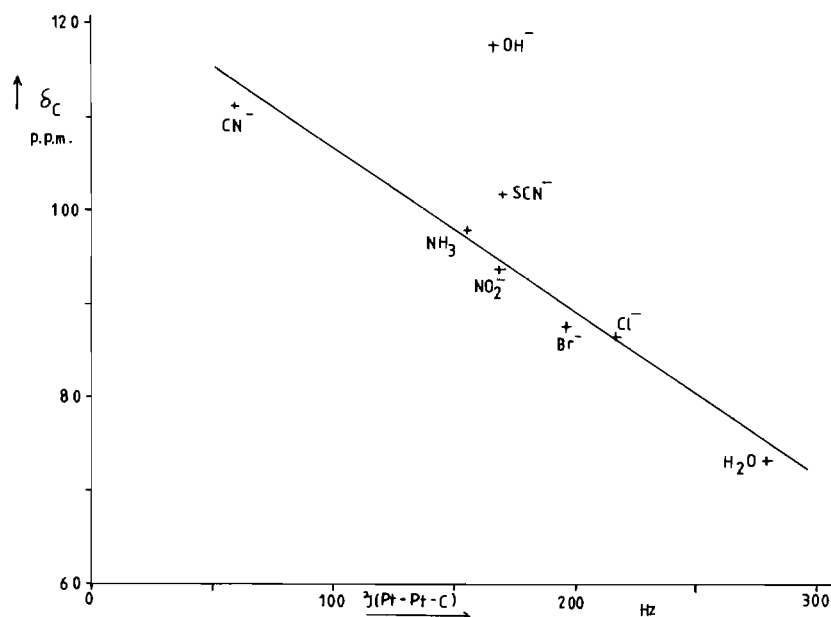


Fig. 6. Plot of  $\delta_C$  against  ${}^2J(\text{Pt-Pt-C})$  for the series  $\text{Pt}_2(\text{SO}_4)_4(^{13}\text{CN})(\text{Y})^{\text{n-}}$ . In calculating the line of best fit, the point for  $\text{Y} = \text{OH}^-$  was disregarded.

Comparing the coupling constants for  $(\text{N}^{13}\text{C})\text{-Pt}(\text{Z})_4\text{Pt}(\text{H}_2\text{O})_3^{3-}$  for  $\text{Z} = \text{PO}_4\text{H}$  and  $\text{Z} = \text{SO}_4$ , one notes that  ${}^1J(\text{Pt-C})$  is smaller (1054 Hz) and  ${}^2J(\text{Pt-Pt-C})$  is larger (382 Hz) for  $\text{Z} = \text{PO}_4\text{H}$  than when  $\text{Z} = \text{SO}_4$  (1094, 279 Hz respectively). A similar observation can be made for the compounds  $\text{Pt}_2(\text{Z})_4(^{13}\text{CN})_2^{4-}$ . The coupling transmitted through the Pt-Pt bond is larger for the phosphate compound than for the sulfate, while the direct one-bond coupling is smaller.

The typical  ${}^{15}\text{N}$  chemical shift range for ammine complexes of platinum(II) is  $-32$  to  $-90$  ppm, and for platinum(IV)  $-20$  to  $-55$  ppm, with the  ${}^{15}\text{N}$  nucleus tending to become less shielded as the Pt-N bond is weakened *trans* to ligands of higher *trans* influence [29-32]. For our platinum(III) compounds, the range is  $-23$  to  $-38$  ppm, overlapping the lower end of these scales. As well, the  ${}^{195}\text{Pt}\text{-}{}^{15}\text{N}$  coupling constants, 106-205 Hz, in the Pt(III) complexes are lower than for Pt(II) (237-408 Hz) or Pt(IV) (199-305 Hz). These data appear to indicate that the Pt-NH<sub>3</sub> bond is relatively weak in the Pt(III) complexes (*cf.* the apparently normal bonding of cyanide mentioned above).

For the limited series of compounds  $(\text{H}_3^{15}\text{N})\text{-Pt}(\text{Z})_4\text{PtY}^{\text{n-}}$  that were available, it is clear that trends paralleled those for  ${}^{13}\text{C}$  in the cyano complexes.  $\delta_N$  tends to move to lower shielding, and  ${}^1J(^{195}\text{Pt}\text{-}{}^{15}\text{N})$  and  ${}^2J(^{195}\text{Pt}\text{-Pt}\text{-}{}^{15}\text{N})$  both decrease in magnitude as the *trans* influence of Y increases. Again, for  $\text{Z} = \text{PO}_4\text{H}$ ,  ${}^2J(\text{Pt-Pt-N})$  is larger and  ${}^1J(\text{Pt-N})$  is smaller than in the corresponding compound with  $\text{Z} = \text{SO}_4$ .

${}^{15}\text{N}$  chemical shifts are not available for the nitro complexes. The Pt-N coupling constants are again low (210-293 Hz) compared with observed ranges for Pt(II) (470-757 Hz) and Pt(IV) (336-518 Hz) nitro complexes [23, 33].  ${}^1J(\text{Pt-N})$  in  $\text{Pt}_2(\text{PO}_4\text{H})_4(^{15}\text{NO}_2)(\text{H}_2\text{O})_3^{3-}$  is less than  ${}^1J(\text{Pt-N})$  in  $\text{Pt}_2(\text{SO}_4)_4(^{15}\text{NO}_2)(\text{H}_2\text{O})_3^{3-}$ , in accordance with the usual rule, but the Pt-Pt-N couplings are exceptional in that they are very similar for the two complexes. In the series  $(\text{O}_2^{15}\text{N})\text{Pt}(\text{SO}_4)_4\text{PtY}^{\text{n-}}$ , both  ${}^1J(\text{Pt-N})$  and  ${}^2J(\text{Pt-Pt-N})$  decrease in magnitude as Y changes from  $\text{H}_2\text{O}$  to  $\text{NO}_2^-$  to  $\text{CN}^-$ , as expected.

In phosphato complexes of platinum(II), such as  $\text{Pt}(\text{NH}_3)_2(\text{OPO}_3\text{H}_2)(\text{H}_2\text{O})^+$ ,  ${}^2J(\text{Pt-O-P})$  is relatively small, 0-30 Hz [10]. The coupling in  $\text{Pt}(\text{PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ , 71.8 Hz, is therefore surprisingly large. For all the compounds  $\text{Pt}_2(\text{PO}_4\text{H})_4\text{X}_2^{\text{n-}}$ , in which both axial ligands are the same,  ${}^2J(\text{Pt-O-P})$  lies in the range 63.5-80.6 Hz, and the variation within this range shows no obvious dependence on the properties of X—for example, the values for  $\text{X} = \text{H}_2\text{O}$  and  $\text{X} = \text{CN}^-$  are nearly identical.

For compounds  $\text{Pt}_2(\text{PO}_4\text{H})_4(\text{H}_2\text{O})\text{Y}^{\text{n-}}$ , where the axial ligands are different, the two different Pt-O-P coupling constants are usually quite different, but their average remains nearly constant, 68-80 Hz. The coupling to the Pt atom bound to water is always the larger of the two (giving additional grounds for confidence in our assignments for these compounds). Steric interactions cannot make a major contribution to this difference between the two Pt-O-P couplings, as the largest difference is observed when  $\text{Y} = \text{CN}^-$ , one of the

TABLE IV. Pt Chemical Shifts Relative to  $\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2^{2-}$  (ppm).

X	$\text{Pt}_2(\text{Z})_4\text{X}(\text{H}_2\text{O})^{n-}$		$\text{Pt}_2(\text{Z})_4\text{X}_2^{n-}$	
	Direct effect on Pt(X) x	Remote effect on Pt(H <sub>2</sub> O) y	x + y	Experimental shift
Z = SO <sub>4</sub>				
Cl <sup>-</sup>	-117.5	+52.6	-64.9	-35.9
Br <sup>-</sup>	-316.4	+110.3	-206.1	-163.8
SCN <sup>-</sup>	-539.9	+135.7	-404.2	-322.5
NO <sub>2</sub> <sup>-</sup>	+188.2	-276.4	-88.2	-90.6
NH <sub>3</sub>	-38.4	-180.2	-218.6	-112.6
CN <sup>-</sup>	+7.9	-456.6	-448.7	-154.0
Z = PO <sub>4</sub> H				
Cl <sup>-</sup>	-82.6	+90.5	+7.9	+26.4
Br <sup>-</sup>	-245.9	+176.9	-69.0	-51.8
SCN <sup>-</sup>	-538.8	+221.6	-317.2	-252.6
NO <sub>2</sub> <sup>-</sup>	+191.6	-299.2	-107.6	-86.9
NH <sub>3</sub>	-68.4	-226.5	-294.9	-142.8
CN <sup>-</sup>	+39.8	-368.4	-325.6	-36.2

least bulky ligands. The difference does depend mainly on the electronic properties of Y, tending to increase as the *trans* influence of Y increases. Indeed, a good linear correlation is obtained between the difference between the Pt–O–P couplings and  $^1J(\text{Pt}–\text{Pt})$  for this series of compounds.

The difference between the couplings to phosphorus probably arises from an asymmetry in the electron distribution within the Pt–Pt bond when the two axial ligands are different. It is possible that this induces a geometrical distortion in the Pt–O–P–O–Pt bridges.

Overall, in the series  $\text{Pt}_2(\text{PO}_4\text{H})_4\text{XY}^{n-}$ , there is a tendency for  $\delta_{\text{P}}$  to move toward lower shielding as X and Y become more strongly bonding (e.g. least shielded for X = Y = CN<sup>-</sup>).

#### <sup>195</sup>Pt Chemical Shifts

Table IV lists the shifts of the Pt atoms of  $\text{Pt}_2(\text{Z})_4\text{X}(\text{H}_2\text{O})^{n-}$  relative to  $\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2^{2-}$ . The shift of the Pt atom bound to X is labelled the 'direct effect' of replacing bound water by X<sup>-</sup>, 'x', and the shift of the Pt atom that remains bound to water, 'y', is labelled the 'remote effect'. For all ligands except X = NH<sub>3</sub>, x and y have opposite sign. It is interesting to note that direct and remote effects also have opposite sign when halides are substituted in the Pt(I) anions,  $\text{Pt}_2\text{X}_4(\text{CO})_2^{2-}$  [34].

The sensitivity of  $\delta_{\text{Pt}}$  for the 'remote' Pt-atom to substitution on the other Pt atom has already been noted. The rehybridization of the remote Pt-atom suggested above in our discussion of coupling constant correlations may be a contributing factor to these shifts.

For a given ligand X, x and y have the same signs for Z = SO<sub>4</sub> and Z = PO<sub>4</sub>H. However, the magnitude of y is usually greater for the phosphate-bridged complexes than for the sulfates (exception: X = CN<sup>-</sup>), in keeping with the usual trend for effects transmitted via the Pt–Pt bond.

In our preliminary communication [8] we noted that, when X = Cl<sup>-</sup>, Br<sup>-</sup>, a reasonable approximation to the shift of  $\text{Pt}_2(\text{Z})_4\text{X}_2^{4-}$  could be obtained by assuming that the effects of substituting the two water molecules of  $\text{Pt}_2(\text{Z})_4(\text{H}_2\text{O})_2^{2-}$  were additive—that is, the shift relative to the diaqua complex was x + y. From Table IV, it is evident that this assumption is not applicable for all of the wider range of ligands studied here. The observed shift is usually more positive (toward lower shielding) than predicted on this simple basis (except for  $\text{Pt}_2(\text{SO}_4)_4(\text{NO}_2)_2^{4-}$ ), and for X = NH<sub>3</sub> or CN<sup>-</sup>, the deviations from the 'predicted' values are large.

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