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**STEREOCHEMICAL NON-RIGIDITY OF A METAL POLYHEDRON;
 CARBON-13 AND PLATINUM-195 FOURIER TRANSFORM NUCLEAR
 MAGNETIC RESONANCE SPECTRA OF $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ ($n = 3, 6, 9, 12$ or 15) ***

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Summary

Platinum-195 spectra are reported for $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ ($n = 3, 6, 9, 12$ and 15) and carbon-13 spectra are reported for $n = 6, 9$ and 12 over a range of temperatures. The spectra provide evidence for (a) intramolecular rotation of the Pt_3 -triangles about the principal three-fold axis, (b) inter-exchange of Pt_3 -triangles, (c) lack of terminal/edge carbonyl exchange within the $\text{Pt}_3(\text{CO})_3(\mu\text{-CO})_3$ group. Evidence is also presented for the formation of $[\text{Ni}_3\text{Pt}_3(\text{CO})_{12}]^{2-}$ on mixing $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$.

Introduction

Our interest in platinum carbonyl chemistry resulted from two of us (P.C. and B.T.H.) working in Professor Chatt's laboratory at the same time and the observation by Chatt and Booth [1] that "platinum dicarbonyl" dissolves in acetone in the presence of ammonia to give a dark green solution. Since then the preparation of the $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ ($n = 3, 6, 9, 12, 15, 18$) anions have been reported [2]. Their X-ray structures in the solid state show a repeated trigonal prismatic stacking of $\text{Pt}_3(\text{CO})_3(\mu\text{-CO})_3$ units along the pseudo three-fold axis [3,4] whereas an antiprismatic structure is found for the analogous $[\text{Ni}_6(\text{CO})_{12}]^{2-}$

* Dedicated to Prof. J. Chatt on the occasion of his 65th birthday.

[5]. Because of this difference we were particularly interested in obtaining structural information on the platinum clusters in solution and in this paper we report the ^{195}Pt and ^{13}C Fourier transform NMR spectra of $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ ($n = 3, 6, 9, 12, 15$); a preliminary account of some of this work has already appeared [6].

^{195}Pt NMR

^{195}Pt has $I = 1/2$ and occurs naturally with 33.8% abundance with the remaining platinum isotopes having $I = 0$. The direct observation of ^{195}Pt resonances using Fourier transform NMR presents little difficulty since the receptivity of ^{195}Pt is ca. 19 times greater than ^{13}C at natural abundance levels [7]. However, it should be mentioned that, because of the enormous frequency range covered by ^{195}Pt resonances coupled with the small range (6.25 kHz) which can be covered with our present instrumentation and the lack of data at the commencement of this work, initial difficulties were experienced in locating the signals.

In order to understand the ^{195}Pt NMR spectra of these clusters, it is necessary to enumerate all the isotopomers [8] containing platinum nuclei with $I = 0$ or $1/2$. This problem, which becomes formidable with the larger clusters because of the large number of unique isotopomers (see Table 1), has been solved using Polyá's fundamental theorem of pattern enumeration [9]. They have been deduced using D_{3h} symmetry for all the clusters: this, although not strictly correct, is a reasonable approximation as will become apparent later. In addition, the intensities of the resonances in the ^{195}Pt NMR spectrum depend on the normalised relative probabilities (NRP) of occurrence of the isotopomers

TABLE 1

NUMBER OF UNIQUE ISOTOPOMERS (not including enantiomeric isotopomers) OF $[\text{Pt}_z\text{Pt}_{n-z}(\text{CO})_{2n}]^{2-}$ WITH D_{3h} SYMMETRY

z	n				
	Pt ₆	Pt ₉	Pt ₁₂	Pt ₁₅	Pt ₁₈
00	1	1	1	1	1
1	1	2	2	3	3
2	3	6	10	15	21
3	3	12	24	51	83
4	3	16	54	138	297
5	1	16	76	285	768
6	1	12	96	467	1662
7		6	76	590	2766
8		2	54	590	3825
9		1	24	467	4200
10			10	285	3825
11			2	138	2766
12			1	51	1662
13				15	768
14				3	297
15				1	83
16					21
17					3
18					1

of $[\text{}^{195}\text{Pt}_z\text{Pt}_{n-z}(\text{CO})_{2n}]^{2-}$ ($z = 0, 1-n; n = 9, 12, 15$). These NRP's have been evaluated using the following equation (see also Table 5):

$$\text{NRP} = A(b/a)^{n-z}$$

NRP = the normalised relative probability of occurrence of an isotopomer containing z ^{195}Pt atoms in an n atom cluster. A = the degeneracy of occurrence of each unique isotopomer. $a = \% \text{}^{195}\text{Pt} = 33.8$. $b = \% \text{ of } (I = 0) \text{ Pt nuclei} = 66.2$.

For a given value of n , increasing values of z result in a decrease in the NRP of occurrence of each isotopomer. However, for ^{195}Pt NMR purposes, this decrease in NRP is partially offset by the increased ^{195}Pt content and, as a result, consideration of all the isotopomers is necessary.

The ^{195}Pt NMR spectra of both $[\text{Pt}_3(\text{CO})_6]^{2-}$ and $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ are, as expected, single lines. $[\text{Pt}_3(\text{CO})_6]^{2-}$ is very readily oxidised and has not yet been isolated in a pure form. However, addition of Na-K alloy to $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ at room temperature produces an additional very sharp resonance ($W_{1/2}$ ca. 3 Hz) to low frequency (Table 2), which is assigned to $[\text{Pt}_3(\text{CO})_6]^{2-}$, in keeping with previous infrared evidence [3]. Both resonances are still quite distinct at $+65^\circ\text{C}$ and, with increasing temperature, shift to low frequency by ca. 2 Hz/ $^\circ\text{C}$. The single line due to $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ can result from either the instantaneous structure being retained in solution or from stereochemical non-rigidity of the metal polyhedron as found for $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ (vide infra); present studies do not allow us to distinguish between these alternatives.

For $[\text{Pt}_9(\text{CO})_{18}]^{2-}$, the spectrum shows 2 symmetrical multiplets due to the inner and outer triangles, (Table 2) [6]. If the instantaneous structure was retained in solution and assuming that ${}^2J(\text{Pt}_o-\text{Pt}_i) \neq 0$ (Pt_o and Pt_i refer to ^{195}Pt nuclei on the outer and inner Pt_3 -triangles respectively) a more complex spectrum would be expected. The symmetry and relative intensities of the lines within the multiplets are consistent with rapid rotation, both at 25 and -85°C , of the outer Pt_3 -triangles with respect to the inner Pt_3 -triangle about the pseudo-3-fold axis. This makes all the ^{195}Pt nuclei in the outer triangles magnetically equivalent and, when there are 0, 1, 2 or 3 ^{195}Pt nuclei in the middle triangle, results in a superimposed singlet, doublet, triplet and quartet respectively; similar reasoning predicts a symmetrical 13-line multiplet for the inner Pt_3 -triangle resonance. Consideration of all the isotopomers and their relative probabilities of occurrence (Table 5) then gives calculated relative intensities of 0.1 : 1.1 : 4.6 : 7.8 : 4.6 : 1.1 : 0.1 for the predicted 7-line multiplet due to the outer Pt_3 -triangles and, using the same relativity, 0.3 : 1.0 : 2.1 : 2.7 : 2.1 : 1.0 : 0.3 for the central 7 lines due to the inner Pt_3 -triangle. For each of these multiplets, the central 5 lines are clearly observed and their relative intensities (outer 1.1 : 4.6 : 7.8 : 4.5 : 1.1; inner 1.0 : 2.2 : 2.7 : 2.2 : 1.1) agree well with the calculated relative intensities using the above ideas (see Fig. in ref. [6]).

Consideration of a non-fluxional metal skeleton with either a staggered or eclipsed arrangement of triangles and ${}^2J(\text{Pt}_o-\text{Pt}_i) = 0$ would give a maximum of 5 + 9 or 3 + 5 resonances due to Pt_o and Pt_i respectively. Although the observed number of resonances could be consistent with a static staggered arrangement of triangles in solution, this explanation is dismissed since not only is the assumption that ${}^2J(\text{Pt}_o-\text{Pt}_i) = 0$ unreasonable but also the calculated relative intensities of the resonances using these ideas are not consistent with those observed.

TABLE 2
 ^{195}Pt NMR CHEMICAL SHIFTS FOR $\text{M}_2[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ ($n = 3, 6, 9, 12, 15$)

M	n	Solvent	T(°C)	$\delta(\text{Pt})^{a,b}$ (ppm)	Relative intensities (calcd. (found)) of resonances within each multiplet ^f
Na/K	3	THF ^c /C ₆ D ₆ (10%)	25	-48.4	
Na/K	3	THF/C ₆ D ₆ (10%)	62	-50.4	
Na/K	6	THF/C ₆ D ₆ (10%)	25	+32.8	
Na/K	6	THF/C ₆ D ₆ (10%)	62	+28.7	
Na	6	MeOD	+25	-53.9	
NBu ₄	6	(CD ₃) ₂ CO	+25	-28.9	
NBu ₄	6	(CD ₃) ₂ CO	-70	-41.2	
NBu ₄	9	(CD ₃) ₂ CO	+25	+69.7 ^d (2)	0.1 : 1.1 : 4.6 : 7.8 : 4.6 : 1.1 : 0.1 (1.1 : 4.6 : 7.8 : 4.6 : 1.1)
				-512.7 ^e (1)	0.005 : 0.05 : 0.3 : 1.0 : 2.1 : 2.7 : 2.1 : 1.0 : 0.3 : 0.05 : 0.005 (1.0 : 2.2 : 2.7 : 2.2 : 1.1)
NBu ₄	12	THF/(CD ₃) ₂ CO (10%)	-90	+107 ^d (1)	0.07 : 1 : 3.7 : 6.1 : 3.7 : 1 : 0.07 (ca. 1 : 4 : 8 : 4 : 1)
				-545 ^e (1)	0.08 : 0.9 : 3.6 : 6.3 : 3.6 : 0.9 : 0.08
NBu ₄	15	THF/(CD ₃) ₂ CO (10%)	-99	ca. +122 ^d (2)	
				ca. -487 ^e (1)	
				ca. -558 ^e (2)	

^a The standard frequency is taken as 21.4 MHz when the proton resonance of internal reference Me₄Si is at 100 MHz. Positive shifts are to high frequency. ^b Figures in parentheses refer to the relative total intensities of each multiplet. ^c THF = tetrahydrofuran. ^d Resonance due to outer Pt₃-triangle. ^e Resonance due to inner Pt₃-triangle. ^f For calculation of relative intensities, see text.

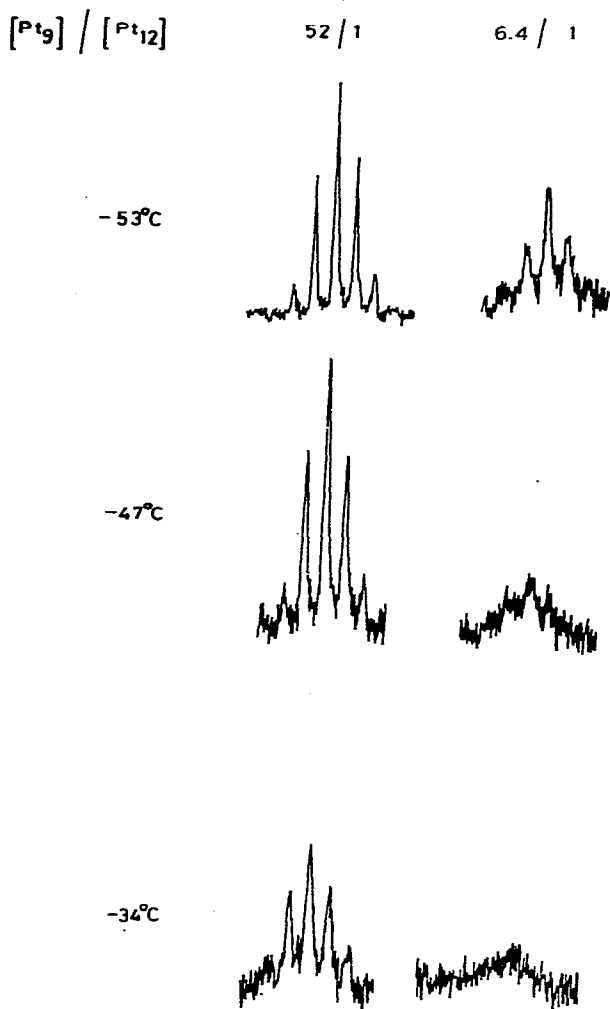


Fig. 1. Effect of varying the temperature and ratio of $[\text{Pt}_9]/[\text{Pt}_{12}]$ on the ^{195}Pt resonance of the outer Pt_3 -triangle in $[\text{Pt}_9(\text{CO})_{18}]^{2-}$.

The ^{195}Pt NMR spectra of solutions containing both $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ and $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ clearly show resonances due to both species with no significant broadening of their resonances even at $+62^\circ\text{C}$. On the other hand, at 25°C , traces of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ are sufficient to collapse completely the multiplets due to $[\text{Pt}_9(\text{CO})_{18}]^{2-}$. Fortunately, specific removal of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ can be accomplished either by addition of $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ or by stirring under a hydrogen atmosphere whereupon reproducible spectra due to $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ are obtained. However, in the absence of either of the above procedures it is difficult to be sure of the complete absence of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ in solutions of $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ since aerial oxidation of $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ instantly produces $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$. The effect of varying the temperature and ratio of $[\text{Pt}_9]: [\text{Pt}_{12}]$ is clearly shown in Fig. 1. We attribute these changes to inter-triangular exchange between the two

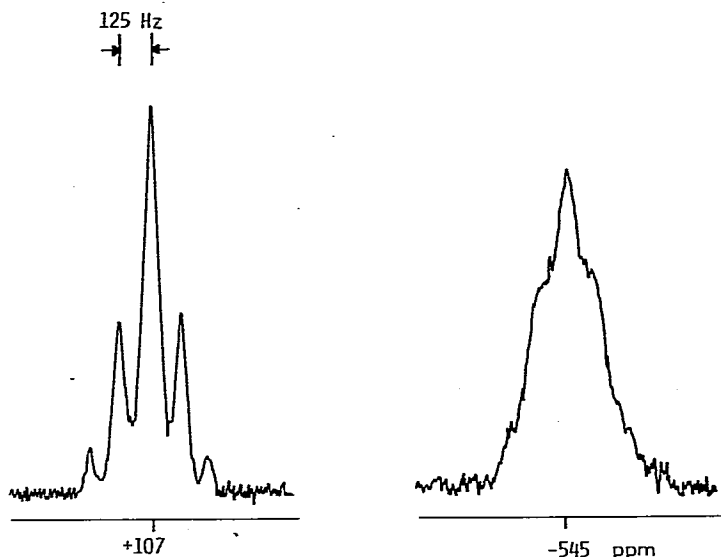


Fig. 2. ^{195}Pt NMR spectrum of $(\text{NBu}_4)_2[\text{Pt}_{12}(\text{CO})_{24}]$ in $\text{THF}/(\text{CD}_3)_2\text{CO}$ (10%) at -102°C .

clusters and an increase in temperature and/or an increase in $[\text{Pt}_{12}]$ content results in an increased rate of exchange. An increased lability with increasing values of n is expected owing to the presence of internal triangles, which introduce steric destabilisation because an outward tilting of the carbonyl groups is not possible [3]. It is significant that, up to $+60^\circ\text{C}$, inter-triangular exchange between different platinum clusters only occurs when both clusters contain inner Pt_3 -triangles.

Prevention of Pt_3 -triangle exchange is more difficult for $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ because of the possibility of self-exchange and because it is not possible to remove specifically either $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ or $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$, which could be present as trace impurities. As a result, well resolved spectra (Fig. 2) are only obtained at low temperatures and even at -102°C the resonance due to the inner triangles is not well resolved. The interpretation of this spectrum is similar to that of $[\text{Pt}_9(\text{CO})_{18}]^{2-}$. By assuming that there is: (a) rapid rotation of the triangles with respect to each other about the 3-fold axis and (b) only a significant "time-averaged one-bond coupling" between platinum nuclei on inner and outer triangles.

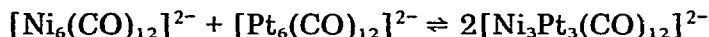
The resonance due to the outer triangle should appear as a septet with relative intensities 0.1 : 1 : 3.7 : 6.1 : 3.7 : 1 : 0.1 which are approximately the intensities found. The resonance due to the inner Pt_3 -triangles is less well resolved because the rate of rotation of the inner triangles with respect to each other is probably slower than with respect to the outer Pt_3 -triangle and hence the ^{195}Pt nuclei in the inner triangles do not totally become magnetically equivalent. Recording spectra at higher temperatures, in order to increase the rate of rotation, results in loss of resolution in both resonances because of the onset of inter- Pt_3 -triangular exchange.

The ^{195}Pt NMR spectrum of $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ at -100°C consists of one resonance due to the outer triangles and two resonances of intensity 2 : 1 due to the two types of inner triangles (Table 2). All these resonances are broad,

probably because of the increased ease with which this cluster can undergo inter-Pt₃-triangular exchange.

The spacings within the multiplets due to [Pt₉(CO)₁₈]²⁻ and [Pt₁₂(CO)₂₄]²⁻ are 137 and 125 Hz respectively; this allows approximate non-time averaged values for ¹J(Pt_o-Pt_i) to be deduced (822 and 750 Hz respectively). These low values of ¹J(Pt-Pt) are consistent with the large value of *d*(Pt-Pt) found between Pt₃-triangles, despite recent work which suggests otherwise [10].

On mixing equimolar solutions of [Pt₆(CO)₁₂]²⁻ and [Ni₆(CO)₁₂]²⁻ in per-deuterioacetone at 25°C, the ¹⁹⁵Pt NMR spectrum shows, in addition to the resonance due to [Pt₆(CO)₁₂]²⁻, an equally intense single resonance at +20.7 ppm which we assign to [Ni₃Pt₃(CO)₁₂]²⁻ resulting from random disproportionation of metal triangles:



Had a randomisation of metals, rather than triangles, occurred the resulting spectrum would have been more complicated.

¹³C NMR

The ¹³C NMR spectra of [Pt_{*n*}(CO)_{2*n*}]²⁻ (*n* = 6, 9, 12) show unambiguously that, over the temperature range studied (-100 to +60°C), there is no terminal/bridge carbonyl intra-exchange. This should be contrasted with [Ni₆(CO)₁₂]²⁻ which, at room temperature undergoes bridge/terminal exchange since the ¹³C NMR shows only one broad line at 196.52 ppm. Furthermore, when ¹⁹⁵Pt NMR suggested Pt₃-triangular inter-exchange was occurring, vide supra, ¹³C NMR spectra were in complete accord showing resonances due to only one type of Pt₃-(CO)₆ unit. In the absence of Pt₃-triangle exchange, carbonyls in similar situations on inner and outer triangles have similar chemical shifts and coupling constants but can be resolved (Table 3).

At low ¹³C-enrichments, the interpretation of the ¹³C NMR spectrum of [Pt₆(CO)₁₂]²⁻ (Fig. 3) follows from a consideration of the following isotopomers

TABLE 3
¹³C CHEMICAL SHIFT AND PLATINUM-CARBONYL COUPLING CONSTANT DATA FOR (NBu₄)₂[Pt_{*n*}(CO)_{2*n*}] (*n* = 6, 9, 12)

<i>n</i>	Solvent	<i>T</i> (°C)	Terminal CO			Bridging CO		
			δ(CO) (ppm) ^a	¹ J(PtC) ^b (Hz)	² J(PtC) ^b (Hz)	δ(CO) (ppm) ^a	¹ J(PtC) (Hz)	² J(PtC) (Hz)
6	(CD ₃) ₂ CO	-70	203.7	2203	192	216.4	783	0
9	(CD ₃) ₂ CO	-78	198.0(2)	2207	199	209.3	810.5	0
			197.5(1)	2160	230.5			
12	C ₄ D ₈ O	-105	197.5(2)	2223	192	209.85(2)	820	0
			196.2(2)	2162	162	209.6 (2)	834	0
12	C ₄ D ₈ O	+25	196.7	2218	212	210.1	769	0

^a Downfield from TMS. Figures in parentheses indicate relative intensities. ^b ¹J(PtC_{*t*}) and ²J(PtC_{*t*}) have the same sign.

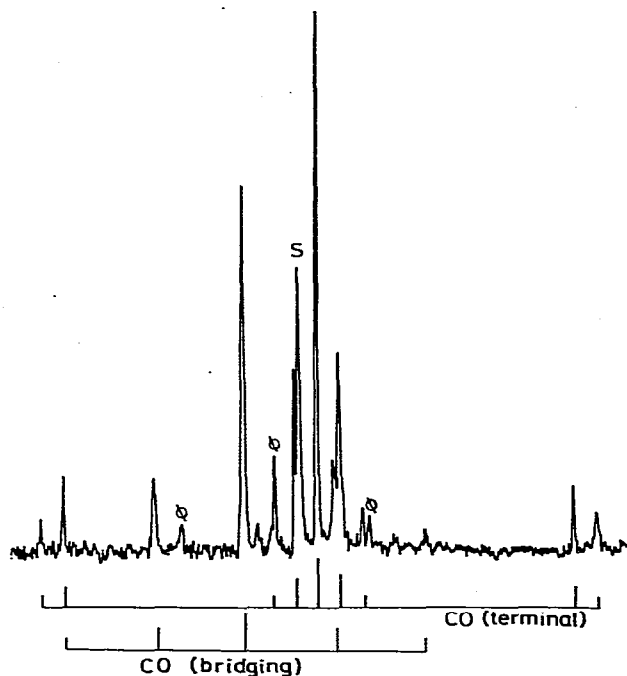


Fig. 3. ^{13}C NMR spectrum of $(\text{NBu}_4)_2[\text{Pt}_6(\text{CO})_{12}]$ in $\text{THF}/(\text{CD}_3)_2\text{CO}$ (10%) at -70°C . (ϕ = resonances due to $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ present as impurity; S = resonance due to carbonyl group in acetone).

together with their NRP's, (Fig. 4). Isotopomers F and L can be neglected because of their low NRP's and all the other isotopomers give simple first order spectra except E and J which give AA'X spectra. The results obtained using such an analysis are shown in Table 3. The values for $J(\text{Pt}-\text{CO})$ are similar to those of $J(\text{Pt}-\text{CNBu-t})$ obtained for the related cluster $\text{Pt}_3(\text{CNBu-t})_6$ [11], and similarly both $^1J(\text{Pt}-\text{CO}_t)$ and $^2J(\text{Pt}-\text{CO}_t)$ have the same sign with $^2J(\text{Pt}-\text{CO}_b) = 0$, (CO_t and CO_b are terminal and bridging CO's respectively). The spectra also clearly show that there is no 2-bond coupling between carbonyls and platinum nuclei in different triangles. However, compared with $[\text{Pt}_3(\text{CNBu-t})_6]$ which is claimed to have a low value of $^1J(\text{Pt}-\text{Pt})^*$, platinum coupling within a triangle in $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ ($n = 6, 9, 12$) is much bigger since the pairs of lines in the AA'X spectra due to isotopomers E and J (Fig. 4), which enable this value to be determined, are never seen; the lines within each pair separate and lose intensity as $^1J(\text{Pt}-\text{Pt})$ increases [12].

* This value was obtained from analysis of the AA'X component of the terminal isonitrile ^{13}C resonance; only one line of the pair, which enable $^1J(\text{Pt}-\text{Pt})$ to be determined, was observed with the other supposedly being hidden under a solvent resonance. However, the related pair of lines in the bridging region, resulting from the AA'X component due to the isotopomer analogous to J, were not observed; using the previously determined value of $^1J(\text{Pt}-\text{Pt})$, these should have had approximately the same intensity as the clearly observed outer lines of the triplet due to the isotopomer analogous to K (Fig. 4).

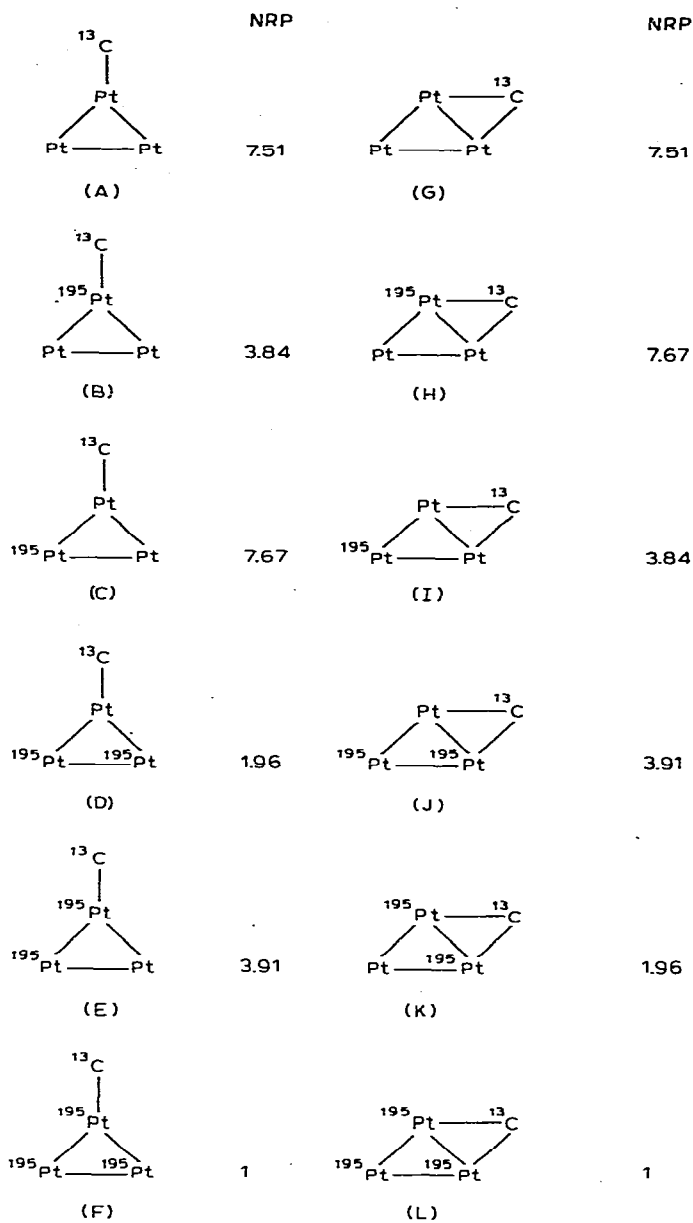


Fig. 4. Isotopomers of $[^{195}\text{Pt}_2\text{Pt}_{3-z}(\text{}^{13}\text{CO})(\text{}^{12}\text{CO})_5]$ ($z = 0, 1-3$). The 5 ^{12}CO 's have been omitted for clarity.

Discussion

Although metal polyhedral rearrangements in HNCC have previously been observed on addition of electrons [13] {to $[\text{Os}_6(\text{CO})_{18}]$ } or addition of a proton [14,15] {to $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ and $[\text{HOs}_6(\text{CO})_{18}]$ }, this present work provides the

first example of the HNCC undergoing an internal metal polyhedral conformational change. The metal polyhedral non-rigidity and inter-exchange of Pt₃-triangles in the [Pt_{*n*}(CO)_{2*n*}]²⁻ dianions is clearly related to the long inter-layer distances and to the consequent weakness of the inter-triangular bonds. This facilitates interconversion of prismatic/antiprismatic structures and clearly shows there to be little difference in energy between these two conformations. Although no significant variation in inter-layer Pt—Pt distance was found with increasing values of *n* for [Pt_{*n*}(CO)_{2*n*}]²⁻ in the solid state, steric repulsion is offset by an increased helical twisting with increasing values of *n*. As a result, an increased tendency towards Pt₃-triangular inter-exchange in [Pt_{*n*}(CO)_{2*n*}]²⁻ with increasing values of *n* could reasonably have been expected.

It should also be pointed out that although the carbonyl groups are coplanar with the Pt₃-triangle (fully in the case of inner triangles) no terminal/bridge exchange has been observed.

Metal polyhedral rearrangement has recently been found to occur in [Rh₉(CO)₂₁P]²⁻ [16]. In the solid state this anion has a capped square antiprismatic structure of metal atoms with the lone phosphorus atom encapsulated in the middle of the square antiprism. In solution, at 35°C, however, the ³¹P NMR is a symmetrical 10 line resonance due to coupling with 9 equivalent rhodium atoms. The equivalency of the rhodium atoms probably arises because of a ready interconversion of the capped square antiprism (C_{4*v*}) with the tricapped trigonal prism analogous to that postulated for the Sn₅²⁻ cluster [17].

As a result, metal polyhedral non-rigidity in carbonyl clusters may be more widespread than has hitherto been recognised. Recent work suggests that related rearrangements can also occur on the surface of bimetallic catalysts [18], and the unique "raft-like" crystallites observed on silica carriers may originate from similar rearrangements necessitated by interaction with the carrier [19].

Finally, although this work indicates the Pt₃ triangular arrangement to be quite robust, recently complete breakdown of [Pt₁₂(CO)₂₄]²⁻ has been observed on reaction with [Rh₁₂(CO)₃₀]²⁻ to give a quantitative yield of [PtRh₅(CO)₁₅]⁻ [20].

Experimental

¹³C and ¹⁹⁵Pt NMR spectra were obtained using a JEOL PS-100 spectrometer operating in the pulsed Fourier transform mode. Separate probes, tuned to 25 and 21 MHz for ¹³C and ¹⁹⁵Pt respectively, both capable of operation at 0 ± 100°C were employed, the desired radio-frequency signals being derived from a Schomandl ND100M frequency synthesiser. Probe temperatures were measured with a Comark 1605 Electronic thermometer using a Cr/Al thermocouple and are considered accurate to ±2°. Typically, 4K data points were used to define the FID signal and the data in Tables 2 and 3 are accurate to ±1 Hz for coupling constants and to ±0.1 ppm for chemical shifts.

In the case of ¹³C spectra, ca. 45° pulses (10 μs) and a repetition time of 1 s were routinely employed, using ca. 0.1 M solutions doped with Cr(acac)₃, at a level of 1 mg per 400 mg sample, and contained in 10 mm diameter tubes. At the level of ¹³C-enrichment used, 1000 to 3000 transients were usually sufficient to provide good quality spectra. In selected cases, control experiments on solu-

tions containing no added $\text{Cr}(\text{acac})_3$ using softer pulses and longer repetition times established that there were no significant differences in the spectra recorded with and without relaxation agent, apart from the anticipated T_1 differences.

^{195}Pt spectra were recorded using undoped, non-enriched samples of comparable concentrations to those used for the ^{13}C studies. In our experience [21] ^{195}Pt T_1 values are typically rather short, and full advantage was taken of this, ca. 50° pulses repeated every second being employed. Some difficulty was experienced initially in locating resonances, due to the limited spectral width currently available to us (6.25 kHz, ca. 300 ppm), but sensitivity was not a problem; good quality spectra were obtained for ca. 0.1–0.2 M solutions in 10 mm diameter tubes using as few as 1000 transients.

The preparation and manipulation of $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ was carried out in a nitrogen atmosphere essentially as described previously [3]. The ^{195}Pt NMR spectra were obtained on 0.1–0.2 M solutions using the cations and anions listed in Table 2. In the case of $n = 3$, an NMR tube containing Na/K alloy and a solution of $\text{Na}_2[\text{Pt}_6(\text{CO})_{12}]$ in THF/ C_6D_6 (10%) was sealed under nitrogen and the NMR spectrum obtained after manual manipulation of the Na/K alloy to the top of the tube.

^{13}C NMR spectra were obtained on the above solutions after direct enrichment (ca. 30–40%) with ^{13}CO .

$[\text{Pt}_3\text{Ni}_3(\text{CO})_{12}]^{2-}$ The room temperature ^{195}Pt NMR spectrum obtained immediately on mixing solutions of $(\text{NBU}_4)_2[\text{Pt}_6(\text{CO})_{12}]$ (0.621 g; 0.312 mol) and $(\text{NMe}_4)_2[\text{Ni}_6(\text{CO})_{12}]$ (0.265 g; 0.317 mol) in acetone- d_6 (1.5 ml) showed two equally intense singlet resonances (for a statistical exchange of Pt_3 - and Ni_3 -triangles 1 : 1 relative intensities are expected) at +20.7 and –4.8 ppm which are attributed to $[\text{Ni}_3\text{Pt}_3(\text{CO})_{12}]^{2-}$ and $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ respectively; this spectrum was unchanged after 30 h. Further addition of $(\text{NMe}_4)_2[\text{Ni}_6(\text{CO})_{12}]$ (0.16 g; 0.191 mol) to the above solution resulted in an increase in the relative intensity of the peak at +20.7 ppm to give a relative ratio close to 1 : 0.6.

Appendix

Delineation of Isotopomers of $[\text{Pt}_z\text{Pt}_{n-z}(\text{CO})_{2n}]^{2-}$ ($n = 6, 9, 12, 15, 18$; $z = 0, 1-n$)

The problem of finding the total number of unique isotopomers (not including enantiomeric isotopomers) for the stacked trigonal prismatic structures found for $[\text{Pt}_n(\text{CO})_{2n}]^{2-}$ has been solved using Polyá's fundamental theorem of pattern enumeration [9], which is fully explained and exemplified in combinatorial mathematics texts [22] *. In essence, it enables an inventory of the equivalence classes of the functions from D to R to be determined given two finite sets D and R and a permutation group G of D ; that is, an inventory of patterns generated by all mappings of D into R within the equivalence relationships introduced by the permutation group G of D can be made. The application of this theorem to the present problem is best presented by considering the Pt_9 cluster. D is the (numbered) set of atom sites, (Fig. 5), G is the point group

* Throughout this section, the terminology is the same as that used in Liu's text [22].

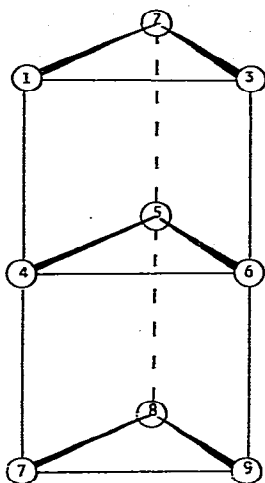


Fig. 5. Site numbering in the condensed trigonal prism of $[\text{Pt}_9(\text{CO})_{18}]^{2-}$.

of the set of atom sites, D_{3h} of order 12, and R is the set of two kinds of nuclei, $I = 1/2$ or 0. Let x and y be the weights (w) assigned to these types of nuclei, so that $R = \{x, y\}$ and $w(I = 1/2) = x$, $w(I = 0) = y$.

Table 4 sets out the data required for all the 12 permutations generated in the D_{3h} point group [23]. The first column gives the symmetry operation (π), the second gives the permuted order of site labels and the third and fourth give the number of cycles (b_i) and their lengths (i), respectively.

The cycle index, $P_G(x_1, \dots, x_K)$, is evaluated from the last two columns, with $K = 9$ and the order of the group $|G| = 12$, as

$$P_{D_{3h}} = \frac{1}{12} \{x_1^9 + 2x_3^3 + 3x_1x_2^4 + 4x_1^3x_2^3 + 2x_3x_6\}$$

where x_i are formal variables and i is the cycle length as above. Then with $R = \{x, y\}$, so that the store inventory is

$$\sum_{r \in R} w(r) = x + y,$$

the pattern inventory is directly:

$$\frac{1}{12} \{(x + y)^9 + 2(x^3 + y^3)^3 + 3(x + y)(x^2 + y^2)^4 + 4(x + y)^3(x^2 + y^2)^3 + 2(x^3 + y^3)(x^6 + y^6)\}.$$

With terms collected, this becomes:

$$x^9 + 2x^8y + 6x^7y^2 + 12x^6y^3 + 16x^5y^4 + 16x^4y^5 + 12x^3y^6 + 6x^2y^7 + 2xy^8 + y^9$$

Thus, there are six unique patterns or, in this chemical context, isotopomers containing seven ($x; I = 1/2$) and two ($y; I = 0$) nuclei; similarly there are six isotopomers containing seven ($y; I = 0$) and two ($x; I = 1/2$) nuclei. The number of unique isotopomers (not including enantiomeric isotopomers) of $[\text{}^{195}\text{Pt}_z\text{Pt}_{n-z}]$

TABLE 4

DATA PERTINENT TO THE CALCULATION OF THE CYCLE INDEX FOR Pt_9 WITH A D_{3h} POINT GROUP

π	Permuted order from {1,2,3,4,5,6,7,8,9}	b_i	i
E	{1,2,3,4,5,6,7,8,9}	9	1
C_3^1	{2,3,1,5,6,4,8,9,7}	3	3
C_3^2	{3,1,2,6,4,5,9,7,8}	3	3
C_2^1	{7,9,8,4,6,5,1,3,2}	1	1
		4	2
C_2^2	{9,8,7,6,5,4,3,2,1}	1	1
		4	2
C_2^3	{8,7,9,5,4,6,2,1,3}	1	1
		4	2
σ_h	{7,8,9,4,5,6,1,2,3}	3	1
		3	2
S_3^1	{8,9,7,5,6,4,2,3,1}	1	6
		1	3
S_3^2	{9,7,8,6,4,5,3,1,2}	1	6
		1	3
σ_v^1	{1,3,2,4,6,5,7,9,8}	3	1
		3	2
σ_v^2	{3,2,1,6,5,4,9,8,7}	3	1
		3	2
σ_v^3	{2,1,3,5,4,6,8,7,9}	3	1
		3	2

$(\text{CO})_{2n}]^{2-}$ ($n = 6, 9, 12, 15, 18; z = 0, 1 \dots n$) is shown in Table 1.

Although an analytical method of assigning the spatial distribution (point group) of each of the unique isotopomers tabulated in Table 5 has not yet been devised, a computationally efficient "search and file" method has been formulated and tested [24] utilising the properties of the matrix representations of the appropriate point group.

TABLE 5 (continued)

z	Sites in Pt ^a												Sites in Pt ^a												NRP ^b
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	
7	X	X			X	X			X	X	X	X	X	X			X	X			X	X	X	X	346
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	346
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	346
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	346
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	346
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	44
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	44
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	44
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177
	X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	88	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	
X	X		X	X	X			X	X	X	X	X	X			X	X			X	X	X	X	177	

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