Stereochemical Non-rigidity of a Metal Polyhedron; Fourier Transform Platinum-195 Nuclear Magnetic Resonance Spectra of $[Pt_n(Co)_{2n}]^{2-}$ ($n = 3, 6,$ or 9)

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Summary ^{195}Pt n.m.r. data are reported for $[Pt_n(CO)_{2n}]^{2-}$ ($n = 3$, 6, or 9) and, when $n = 9$, the spectra are consistent with rotation of the outer Pt_3-triangles with respect to the middle triangle about the principal 3-fold axis; inter-exchange of Pt_3-triangles occurs in mixtures of $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$ at 25 °C.

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TABLE. ^{195}Pt n.m.r. chemical shifts for $[Pt_n(CO)_{2n}]^{2-}$ (n = 3, 6, or 9) at 25 °C.

		δPt/p.p.m.[a]		
Cation	Solvent	$n = 3$	$n = 6$	$n = 9$
Li^+, Na^+, K^+	THF[b] + 10% C_6D_6	+32·5 (s)	−48·4(s)	
$[NBu_4]^+$	$(CD_3)_2CO$		−4·5(s)	69·7(q),[c] −513(q)[d]

[a] The standard frequency is taken as 21·4 MHz when the proton resonance of internal reference Me_4Si is at 100 MHz. Positive shifts are to high frequency. [b] THF = tetrahydrofuran. [c] Outer triangle. [d] Middle triangle (see Figure).

X-RAY structural investigations of $[Pt_n(CO)_{2n}]^{2-}$ (n = 6, 9, 12, or 15) have a repeated trigonal prismatic stacking of $Pt_3(\mu_1\text{-}CO)_3(\mu_2\text{-}CO)_3$ units along the pseudo three-fold axis,[1,2] whereas an antiprismatic structure is found for the analogous $[Ni_6(CO)_{12}]^{2-}$.[3] In order to obtain structural information on the platinum clusters in solution, we have investigated the Fourier transform ^{195}Pt n.m.r. spectra of $[Pt_n(CO)_{2n}]^{2-}$ (n = 3, 6, or 9).

The ^{195}Pt n.m.r. spectrum of $[Pt_6(CO)_{12}]^{2-}$ at 25 °C consists of a single line (Table) which, apart from shifting to lower frequency (3 Hz/°C) and slight broadening, is unchanged at −70 °C.‡ This could be attributed to the instantaneous structure[1] being retained in solution or to stereochemical non-rigidity as found for $[Pt_9(CO)_{18}]^{2-}$ (*vide infra*); present studies do not allow us to distinguish between these alternatives.

Addition of Na–K alloy to $[Pt_6(CO)_{12}]^{2-}$ produces an additional resonance (Table) to high frequency, which is assigned to $[Pt_3(CO)_6]^{2-}$,§ in keeping with previous suggestions based on i.r. evidence.[1]

In the case of $[Pt_9(CO)_{18}]^{2-}$ considerable difficulties were experienced initially in obtaining reproducible spectra, until it was realised that traces of $[Pt_{12}(CO)_{24}]^{2-}$ were sufficient to collapse the resonances at 25 °C to give a weak, very broad, signal. Removal of $[Pt_{12}(CO)_{24}]^{2-}$ either by addition of $[Pt_9(CO)_{12}]^{2-}$ or by stirring under a hydrogen atmosphere[4] then gave reproducible spectra due to $[Pt_9(CO)_{18}]^{2-}$. The spectra, which contain two symmetrical multiplets (Figure and Table), both at 25 °C and at −85 °C are consistent with rapid rotation of the outer Pt_3-triangles with respect to the middle Pt_3-triangle about the pseudo 3-fold axis.¶ This makes all the ^{195}Pt atoms in the outer triangles magnetically equivalent and, when there are 0, 1, 2, or 3 ^{195}Pt atoms in the middle triangle, results in a superimposed singlet, doublet, triplet, and quartet, respectively; similar reasoning predicts a symmetrical 13-line multiplet for the resonance due to the inner Pt_3-triangle. Consideration of all the possible isotopomers containing Pt (I = 0 or $\frac{1}{2}$) atoms and their statistical distributions 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 relatively, 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 agree well with the calculated relative intensities using the above ideas (Figure). The spacing within each of these multiplets is 137 Hz which allows the non-time-averaged value of ^{1}J(Pt–Pt) to be deduced (822 Hz). This is much lower than previously published values of ^{1}J(Pt–Pt),[5] although recent work[6] suggests that ^{1}J(Pt–Pt) covers a considerable range, and the low value observed in the present work is consistent with the large values of d(Pt–Pt) found between the Pt_3-triangles.[1]

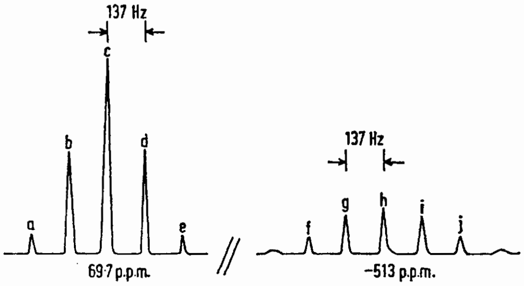

FIGURE. ^{195}Pt n.m.r. spectrum of $[NBu_4]_2[Pt_9(CO)_{18}]$ in $(CD_3)_2CO$ at 25 °C. (For explanation of calculated relative intensities and δ_{Pt}, see text and Table respectively). Intensities: calc. (found, in parentheses) a, 1·1 (1·1); b, 4·6 (4·6); c, 7·8 (7·8); d, 4·6 (4·5); e, 1·1 (1·1); f, 1·0 (1·0); g, 2·1 (2·2); h, 2·7 (2·7); i, 2·1 (2·2); j, 1·0 (1·1).

At 25 °C, only a very broad ^{195}Pt signal is observed for solutions of $[Pt_9(CO)_{18}]^{2-}$ containing traces of $[Pt_{12}(CO)_{24}]^{2-}$ whereas at −85 °C the same solutions give spectra similar to that shown in the Figure. The spectrum at 25 °C may be attributed to inter-exchange of Pt_3-triangles between the two clusters (Scheme). An increased lability in the series

$$[{}^*Pt_{12}(CO)_{24}]^{2-} + [Pt_9(CO)_{18}]^{2-} \rightleftharpoons [{}^*Pt_9(CO)_{18}]^{2-} + [Pt_9{}^*Pt_3(CO)_{24}]^{2-} \rightleftharpoons \textit{etc.}$$

SCHEME

(n = 6, 9, or 12) is expected owing to the presence of internal triangles which introduce steric destabilisation because an outward tilting of the carbonyl groups is not possible.[1] ^{195}Pt n.m.r. spectra due to $[Pt_{12}(CO)_{24}]^{2-}$ have not yet been observed (even at −85 °C) and their non-observance may be accounted for similarly.

Metal polyhedral rearrangements have previously been observed on addition of electrons {to $[Os_6(CO)_{18}]$[7]} or addition of a proton {to $[Fe_4(CO)_{13}]^{2-}$[8] *and* [9]$[HOs_6(CO)_{18}]^-$} but

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‡ As found previously (P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor, and I. R. H. Marshall, *J.C.S. Dalton*, 1976, 459, and references therein) non-systematic shifts of δ_{Pt} are observed on changing the solvent, although only one resonance due to $[Pt_6(CO)_{12}]^{2-}$ has been observed in all solvents studied.

§ $[Pt_3(CO)_6]^{2-}$ is very readily oxidised to $[Pt_6(CO)_{12}]^{2-}$ and has not been obtained free from $[Pt_6(CO)_{12}]^{2-}$.

¶ In the absence of dynamic effects, a different ^{195}Pt n.m.r. spectrum should result because of the statistical distribution of platinum isotopes (I = 0 or $\frac{1}{2}$) within the outer and middle platinum triangles.

$[Pt_9(CO)_{18}]^{2-}$ provides the first example of a cluster undergoing an internal metal polyhedral conformational change and this phenomenon is clearly related to the small difference in energies between the trigonal prismatic and trigonal antiprismatic structures. Consequently, we suggest that too much reliance on simple electron-counting procedures[10] for predicting the shapes of clusters should be avoided.

We thank the S.R.C. and C.N.R. for financial support, N.A.T.O. for a joint grant (to P.C. and B.T.H.) which enabled this co-operative research to be carried out, and Professor L. F. Dahl for communicating the structural data on $[Pt_{12}(CO)_{24}]^{2-}$ prior to publication.

(*Received*, *4th February* 1977; *Com.* 096.)

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