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Structure and Hydrolysis of Heterovalent Polynuclear Oxonitrocomplexes of $Pt^{II,IV}$ in Aqueous Solutions by ^{195}Pt and ^{15}N NMR Spectroscopy

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^{195}Pt and ^{15}N NMR chemical shifts and constants of scalar spin–spin coupling, ^{195}Pt–^{15}N and $^{195}Pt^{II}$–$^{195}Pt^{IV}$, for the heterovalent platinum tetra- and hepta-meric oxonitrocomplexes $[(NO_2)_3Pt^{IV}(\mu\text{-}O)_3Pt^{II}{}_3(NO_2)_6]^{5-}$ and $[(NO_2)_6Pt^{II}{}_3(\mu\text{-}O)_3Pt^{IV}(\mu\text{-}O)_3Pt^{II}{}_3(NO_2)_6]^{8-}$, and for products of hydrolysis of these complexes have been obtained by ^{195}Pt and ^{15}N NMR spectroscopic studies on freshly prepared aqueous solutions and also on two month old solutions.

In order to identify the structure of the polynuclear heterovalent oxonitro-complexes of $Pt^{II,IV}$, in aqueous solutions, and to characterize the hydrolysis of these complexes, we obtained and analysed the ^{195}Pt and ^{15}N NMR spectra of aqueous solutions of $K_5[(NO_2)_3Pt^{IV}(\mu\text{-}O)_3Pt^{II}{}_3(NO_2)_6]\cdot 3H_2O$ **1** and $K_8[(NO_2)_6Pt^{II}{}_3(\mu\text{-}O)_3Pt^{IV}(\mu\text{-}O)_3Pt^{II}{}_3(NO_2)_6]\cdot 7H_2O$ **2**. Both compounds, enriched with ^{15}N (95%), were synthesized by thermal denitration of $K_2[Pt(NO_2)_4]$.[1,2] The solid state molecular structures of **1** and **2** have been obtained previously (Fig. 1) by X-ray techniques.[2,3]

^{195}Pt, ^{15}N NMR spectra were obtained using Bruker/Spectrospin AC-250, AMX-400, AMX-500 and AMX-600 spectrometers. Measurements were performed at room temperature. The ^{195}Pt, ^{15}N spin systems were excited with an ordinary one-pulse program with 20–30° pulses of 6–10 μs duration at 2–4 s intervals. The spectra were accumulations of 10000–

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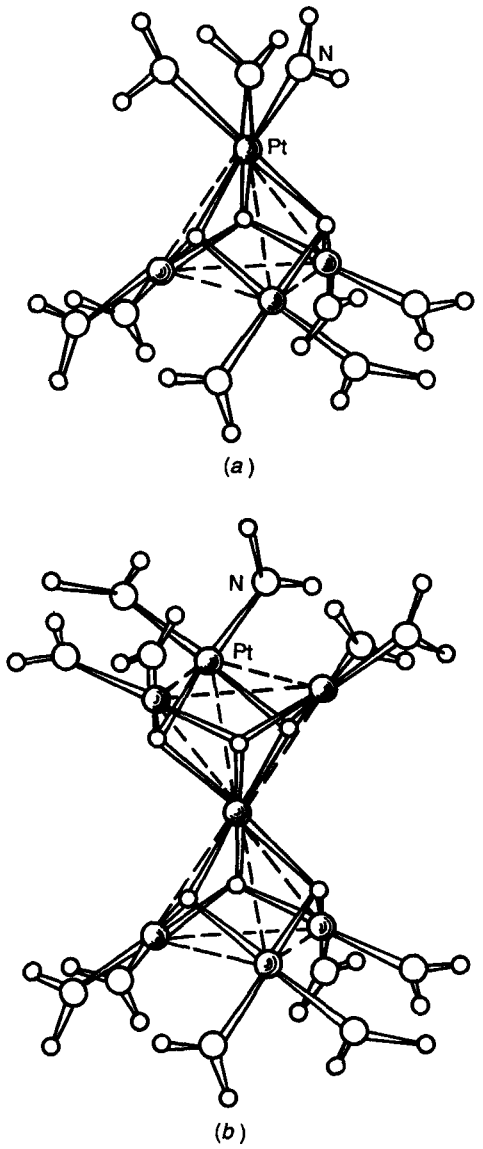

Fig. 1 Structure of tetrameric (*a*) and heptameric (*b*) oxonitrocomplexes of $Pt^{II,IV}$; (*a*) $[(NO_2)_3Pt^{IV}(\mu\text{-}O)_3Pt^{II}_3(NO_2)_6]^{5-}$ and (*b*) $[(NO_2)_6Pt^{II}_3(\mu\text{-}O)_3Pt^{IV}(\mu\text{-}O)_3Pt^{II}_3(NO_2)_6]^{8-}$.

60 000 free induction decay signals. The concentration of the aqueous solutions was 0.05 mol dm^{-3}. NMR spectra were obtained for both freshly prepared solutions (Figs. 2 and 3) and for solutions two months after their preparation. In the latter case the spectra demonstrated signals of the original complexes and also products of their hydrolysis.

In accordance with the structure of the complexes in the solid state (Fig. 1) the multiplets in the ^{195}Pt NMR spectra from divalent platinum (Fig. 2) comprise a triplet and an overlapping triplet of doublets for both complexes. The triplet is due to spin–spin coupling, $^{195}Pt^{II}$–$(^{15}NO_2)_2$, with associated $J(Pt^{II}\text{-}N)$ constant, and the doublets are due to scalar spin–spin coupling, $^{195}Pt^{II}$–$^{195}Pt^{IV}$, with associated $J(Pt^{II}\text{–}Pt^{IV})$ constant. $^{195}Pt^{IV}$ NMR signals were not detected. The difficulty in obtaining signals from $^{195}Pt^{IV}$ may be due to the more complex multiplicity of spin–spin interaction of Pt^{IV} with three nuclei of divalent platinum and three nuclei of ^{15}N, in the case of the tetrameric complex, or with six Pt^{II} nuclei in the case of the heptameric complex. Moreover, the signal from $^{195}Pt^{IV}$ must have three or six times less integrated intensity for the tetra- and hepta-meric complexes, respectively, when compared with the signals from $^{195}Pt^{II}$. The ^{15}N NMR spectrum of **1** [Fig. 3(*a*)] consists of two triplets, and gives direct evidence for the presence of Pt^{II} and

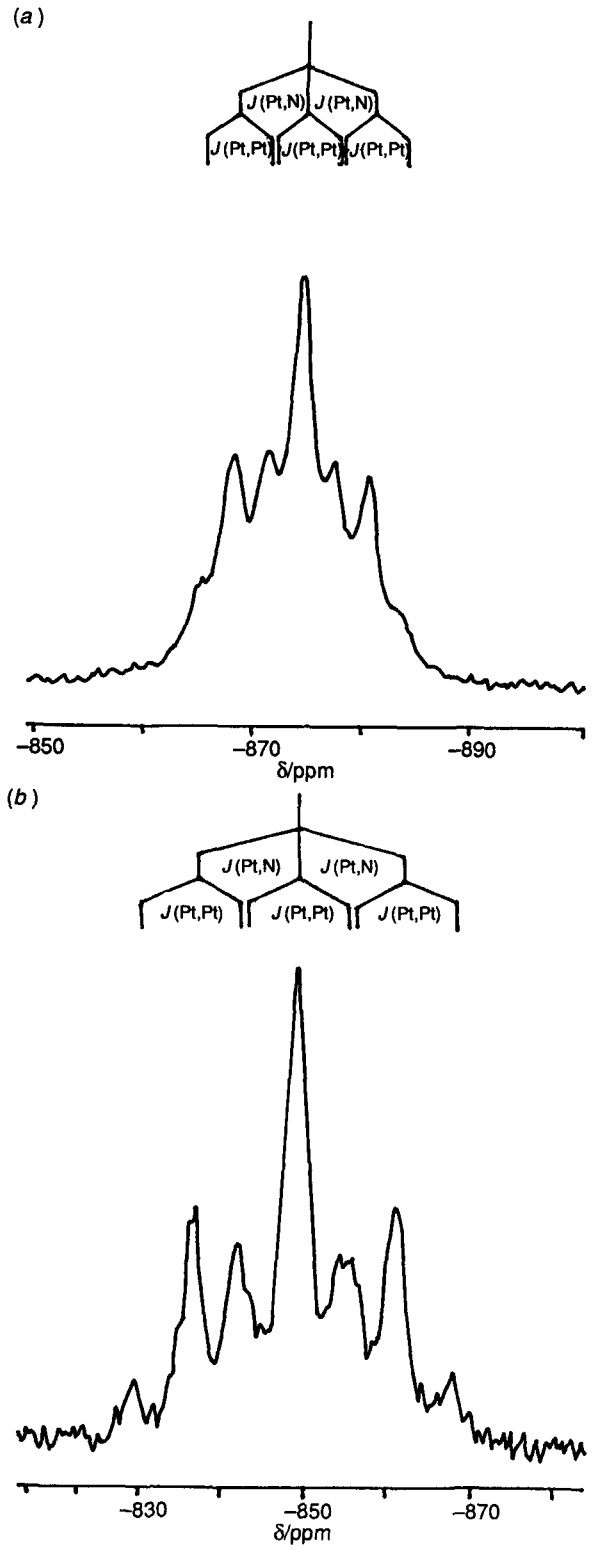

Fig. 2 ^{195}Pt NMR spectra of freshly prepared aqueous solutions of tetrameric (*a*) and heptameric (*b*) oxonitrocomplexes of $Pt^{II,IV}$, obtained at NMR frequencies 107.41 and 53.73 MHz, respectively; 50 000 accumulations.

Pt^{IV} centres in the solution of the heterovalent complex. The corresponding spectrum of **2** [Fig. 3(*b*)] consists of one triplet, because the Pt^{IV} atoms are not bonded to the nitro-groups in this compound. The ^{15}N signal showing a Pt^{IV}–^{15}N spin–spin interaction [Fig. 3(*a*)] has lower chemical shift, less than half the integral intensity and essentially a smaller line width than the ^{15}N signals exhibiting a Pt^{II}–^{15}N interaction [Fig. 3(*a*, *b*)]. Each ^{15}N triplet arises from a singlet of the ^{15}N nuclei bonding with non-magnetic platinum isotopes, combined with a doublet

Table 1 Chemical shifts for ^{195}Pt and ^{15}N NMR and spin–spin coupling constants, ^{195}Pt–^{15}N, $^{195}Pt^{II}$–$^{195}Pt^{IV}$, for tetra- and hepta-meric oxonitrocomplexes of $Pt^{II,IV}$ and complexes of Pt^{II} produced by their hydrolysis, obtained from the ^{195}Pt and ^{15}N NMR spectra; all chemical shifts relative to the signals from $[PtCl_6]^{2-}$ and NO_3^- in aqueous solutions

Complexes	Spin–spin coupling constants ^{195}Pt–^{15}N and $^{195}Pt^{II}$–$^{195}Pt^{IV}$/Hz			Chemical shifts δ/ppm	
	Pt^{II}–Pt^{IV}	Pt^{II}–N	Pt^{IV}–N	$^{195}Pt^{II}$	^{15}N
$[Pt_7O_6(NO_2)_{12}]^{8-}$	774(10)[b]	630(30)[a] 651(10)[b]	–	– 848	50.2
$[Pt_4O_3(NO_2)_9]^{5-}$	634(10)[b]	665(20)[a] 673(10)[b]	457(6)[a]	– 874	45.4 30.4
$[Pt(NO_2)_4]^{2-}$		– 590[d]		– 2167	
$[Pt(NO_2)_3(H_2O)]$		630[c] 584[d]		– 1795	
cis-$[Pt(NO_2)_2(H_2O)_2]$		628[c] –		– 1379	
$[Pt_3(\mu\text{-}OH)_3(NO_2)_6]^{3-}$		715[c] –		– 1331	
$[Pt_2(\mu\text{-}OH)_2(NO_2)_4]^{2-}$		725[c] –		– 1076	

[a] Data obtained from ^{15}N NMR spectra. [b] Data obtained from the ^{195}Pt NMR spectra. [c] Data for axis (O—Pt—N). [d] Data for axis (N—Pt—N).

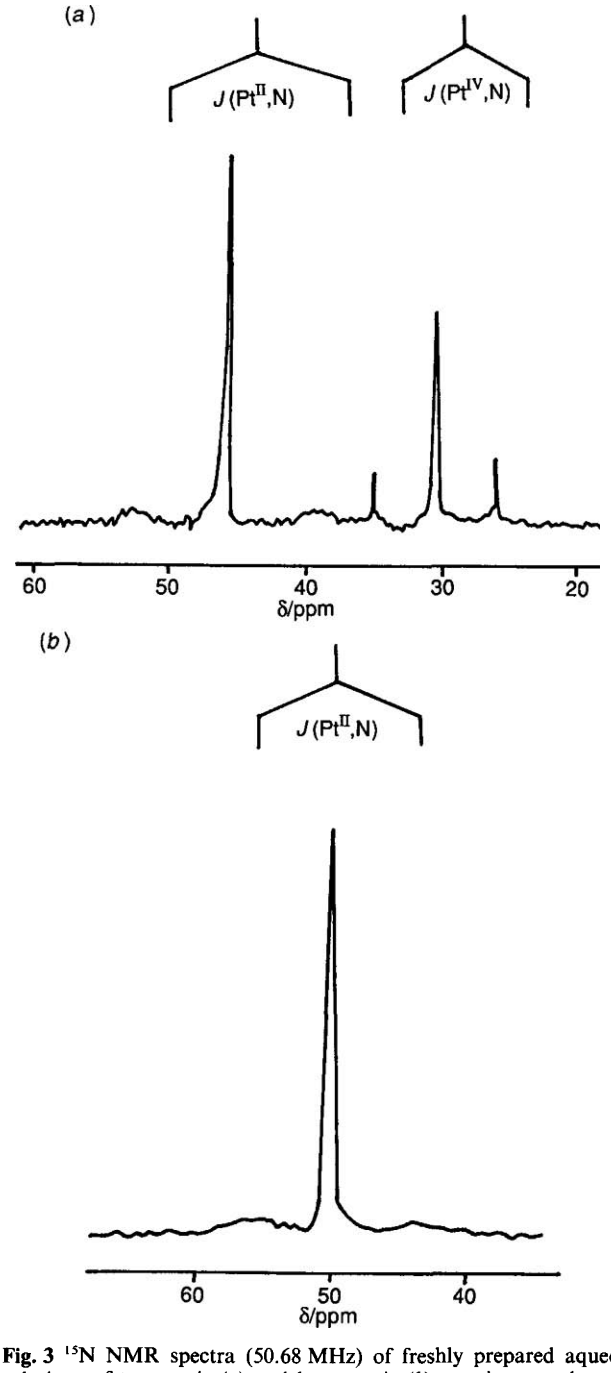

Fig. 3 ^{15}N NMR spectra (50.68 MHz) of freshly prepared aqueous solutions of tetrameric (*a*) and heptameric (*b*) oxonitrocomplexes of $Pt^{II,IV}$; 10 000 accumulations, pulse interval is 4 s.

resulting from scalar spin–spin coupling, ^{195}Pt–^{15}N. Table 1 gives the spectral parameters from ^{195}Pt and ^{15}N NMR for the tetra- and hepta-meric oxonitrocomplexes in aqueous solutions. The measured values of the coupling constants, $J(Pt^{II}$–$Pt^{IV})$, (774 and 634 Hz for the hepta- and tetra-meric complexes, respectively) correlate with the mean Pt^{II}—Pt^{IV} distances of 3.035 and 3.057 Å, respectively.[2,3] There is no information in the literature on the values of coupling constants $^nJ(Pt^{II}$–$Pt^{IV})$ for any heterovalent platinum complexes. However, taking into account the data available on spin–spin coupling constants: 50–8000 Hz for $J(Pt^{II}$–$Pt^{II})$[4] and 700–5000 Hz for $J(Pt^{III}$–$Pt^{III})$,[5] we assume that $^{195}Pt^{II}$–$^{195}Pt^{IV}$ scalar spin–spin coupling in the tetra- and hepta-meric complexes occurs through two bonds with a ^2J constant.

In the ^{195}Pt NMR spectra of aged aqueous solutions of compounds **1** and **2** additional signals can be assigned to the following complex forms, in accordance with refs. 6 and 7. For solutions of **1**: $[Pt(NO_2)_4]^{2-}$ (δ – 2167 ppm), $[Pt(NO_2)_3(H_2O)]^-$ (– 1795), $[Pt_3(\mu\text{-}OH)_3(NO_2)_6]^{3-}$ (– 1331), $[Pt_2(\mu\text{-}OH)_2(NO_2)_4]^{2-}$ (– 1076); and for solutions of **2**: $[Pt(NO_2)_3(H_2O)]^-$, $[Pt_3(\mu\text{-}OH)_3(NO_2)_6]^{3-}$, $[Pt_2(\mu\text{-}OH)_2(NO_2)_4]^{2-}$ and *cis*-$[Pt(NO_2)_2(H_2O)_2]$ (– 1379). The difference observed between the hydrolysis products of the tetrameric and heptameric complexes is due to the formation in the former case of the relatively stable aquated form of the tetrameric complex to which we have assigned the formula $[(NO_2)_2(H_2O)Pt^{IV}(\mu\text{-}OH)_3Pt^{II}{}_3(NO_2)_6]^{2-}$. This hydrolysis releases the active nitrating agent, NO_2^-, and, consistent with this, the equilibrium of the reaction [eqn. (1)] is shifted to the right for the solution of the tetrameric complex.

$$[Pt(NO_2)_2(H_2O)_2] \overset{NO_2^-}{\rightleftarrows} [Pt(NO_2)_3(H_2O)]^- \overset{NO_2^-}{\rightleftarrows} [Pt(NO_2)_4]^{2-} \quad (1)$$

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