The *trans* Influence in Platinum Chemistry. A Platinum-195 Nuclear Magnetic Resonance Study of [^{15}N]Nitrito-, Chloro-, and Bromo-platinum-(II) and -(IV) Complexes

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Reactions of chloro–bromo-Pt^{II} and -Pt^{IV} complexes with sodium nitrite in aqueous solution have been studied by ^{195}Pt n.m.r. spectroscopy. Chemical shifts and $^1J(^{195}$Pt–^{15}N) coupling constants of all 21 possible Pt^{II} complexes, and 47 of the possible 56 Pt^{IV} complexes are reported. Regular incremental shift patterns were observed for Cl$^-$/Br$^-$ substitutions in each set of complexes, but only partially for NO$_2{}^-$ substitutions for Pt^{IV}, and not for Pt^{II}. NO$_2{}^-$/Cl$^-$ substitution shifts were in opposite directions for Pt^{II} (to low frequency) and Pt^{IV} (to high frequency), but in the same direction for NO$_2{}^-$/Br$^-$ substitutions. $^1J(^{195}$Pt–^{15}N) coupling constants were *linearly dependent* on the number of nitrite ligands for both Pt^{II} and Pt^{IV}. Both chemical shift and coupling constant changes upon ligand substitution are dominated by the nature of the *trans* ligand. *trans* Pairs of nitrite ligands destabilize complexes and account for the nine undetected Pt^{IV} complexes.

Platinum-195 n.m.r. studies have become routinely useful in studies of the chemistry of platinum in solution. This isotope ($I = \frac{1}{2}$) is 34% abundant and has a good sensitivity to detection. With modern Fourier transform spectrometers, signals from *ca.* 0.01 mol dm^{-3} solutions can be detected in a few hours. If there are coupled protons a nuclear Overhauser enhancement of signal intensity (maximum 3.3) can also be obtained. The total chemical shift range is very large [1–4] (>15 000 p.p.m.) and the behaviour is predictable on ligand (L) substitution, at least for halides.[5,6] One-bond ^{195}Pt–L coupling constants can also be of significant diagnostic value, as illustrated by $^1J(^{195}$Pt–^{15}N) values for n-dodecylamine and *o,o′*-dihydroxyazobenzene complexes,[7,8] anti-tumour drugs,[9] and aminoalkenyl complexes.[10,11]

We report here a ^{195}Pt n.m.r. study of reactions of Pt^{II} chloro- and bromo-complexes with ^{15}N-labelled sodium nitrite in aqueous solution. The incremental chemical shifts of the Pt^{IV} nitrites show a more regular dependence on the number of NO$_2{}^-$ nitrites present than do those of Pt^{II}, but in both Pt^{II} and Pt^{IV} complexes the one-bond coupling constants $^1J(^{195}$Pt–^{15}N) of the nitrites are found to be linearly dependent on the number of them present. Thus chemical shifts and coupling constants for all 21 possible Pt^{II}/NO$_2{}^-$/Br$^-$/Cl$^-$ species are reported. Of the 56 possible Pt^{IV} complexes, only nine were not observed and the data enable their shifts and coupling constants to be predicted. *trans* Pairs of NO$_2{}^-$ ligands strongly destabilize Pt^{IV} complexes and a strong dependence of shifts and coupling constants on the nature of the *trans* ligand is observed.

Experimental

The salts K$_2$[PtCl$_4$] and Na$_2$[PtCl$_6$] were kindly provided on loan by Johnson Matthey Ltd. Na^{15}NO$_2$ (>95% enriched) was purchased from Prochem Ltd.

Platinum-195 n.m.r. spectra were recorded on a JEOL FX60 spectrometer at 12.80 MHz using 10 mm tubes with an internal D$_2$O lock signal. The ambient probe temperature was 300 ± 1 K. A sweepwidth of 25 kHz (*ca.* 2 000 p.p.m.) was used routinely with 16K computer points (digital resolution 3 Hz, 0.25 p.p.m.), 70° pulse angle, and 1 s repetition interval. Since the instrument was not equipped with quadrature detection or a crystal filter, fold-back of peaks occurred from outside the spectral range selected, effectively giving a 4 000 p.p.m. or even 6 000 p.p.m. range. Folded-back peaks could usually be distinguished by their different phase, but where there was any doubt spectra were rerun with a change of offset of the carrier frequency. Our external shift reference was a 1 mol dm^{-3} solution of Na$_2$[PtCl$_6$] in D$_2$O. Low-frequency (high-field) shifts are given a negative sign. On this scale other commonly used references have the following chemical shifts: dichlorobis(4-n-pentylpyridine)platinum(II), −1 962 p.p.m. and *cis*-[PtCl$_2$(SMe)$_2$], −3 552 p.p.m. (21.4 MHz ≡ −4 535 p.p.m.).

Results

The [PtCl$_6$]$^{2-}$/NO$_2{}^-$/Br$^-$ *System.*—Platinum(IV) chloronitrito-complexes were obtained by addition of solid Na^{15}NO$_2$ to a 1 mol dm^{-3} solution of Na$_2$[PtCl$_6$] in D$_2$O. Typical spectra are shown in Figure 1(*a*) and (*b*). Ten different species are possible and all except [Pt(NO$_2$)$_6$]$^{2-}$ were observed. The latter is not obtained even in the presence of a large excess of nitrite. Previous workers have noted that it can be generated by further addition of concentrated nitric acid and bubbling oxides of nitrogen through the liquid.[12–14]

Of the nine remaining species, the only identification problem concerns the correct assignment of *cis*- and *trans*-[Pt(NO$_2$)$_2$Cl$_4$]$^{2-}$ which both appear as triplets. They were assigned by comparing their chemical shifts and coupling constants with other isomeric pairs which could be assigned unambiguously: *fac*-[Pt(NO$_2$)$_3$Cl$_3$]$^{2-}$ contains three equivalent NO$_2{}^-$ ligands and therefore appears as a quartet, whereas the resonance of the *mer* isomer is a doublet of triplets, and similarly *trans*-[Pt(NO$_2$)$_4$Cl$_2$]$^{2-}$ is a quintet whereas the *cis* isomer is a triplet of triplets. Chemical shifts and coupling constants are listed in Table 1 and are plotted in Figures 2 and 3 which illustrate the basis of assignment of the dinitrito-complexes.

At ambient temperature, these Pt^{IV} substitution reactions appeared to take weeks or even months to reach equilibrium; compare, for example, Figure 1(*a*) and (*b*). Figures 2 and 3 also illustrate that although species in which nitrite ligands are *trans* to each other may be kinetically favoured, they are *thermodynamically unstable* with respect to isomers in which NO$_2{}^-$ is *trans* to Cl$^-$. On a statistical basis the ratio of the *fac* : *mer* isomers of [Pt(NO$_2$)$_3$Cl$_3$]$^{2-}$ would be expected to be 2 : 3, and yet no *mer* isomer is observed at equilibrium. Similar observations were made for di- and tetra-nitrito-species, and the low stability of [Pt(NO$_2$)$_6$]$^{2-}$ also fits into this pattern.

By addition of Na^{15}NO$_2$ to solutions of [PtCl$_6$]$^{2-}$ con-

Table 1. Chemical shifts and coupling constants for the platinum(IV) complexes

	Complex *	δ/p.p.m.	*J*/Hz *trans* to		
			Cl^-	Br^-	NO_2^-
(1)	$[PtCl_6]^{2-}$	0			
(2)	$[PtCl_5Br]^{2-}$	−287			
(3)	*cis*-$[PtCl_4Br_2]^{2-}$	−584			
(4)	*trans*-$[PtCl_4Br_2]^{2-}$	−585			
(5)	*fac*-$[PtCl_3Br_3]^{2-}$	−893			
(6)	*mer*-$[PtCl_3Br_3]^{2-}$	−894			
(7)	*cis*-$[PtCl_2Br_4]^{2-}$	−1 214			
(8)	*trans*-$[PtCl_2Br_4]^{2-}$	−1 216			
(9)	$[PtClBr_5]^{2-}$	−1 548			
(10)	$[PtBr_6]^{2-}$	−1 894			
(11)	$[Pt(NO_2)Cl_5]^{2-}$	384	394		
(12)	*trans*-$[Pt(NO_2)Cl_4Br]^{2-}$	86	393		
(13)	*cis*-$[Pt(NO_2)Cl_4Br]^{2-}$	146		366	
(14)	*mer,trans*-$[Pt(NO_2)Cl_3Br_2]^{2-}$	−227	400		
(15)	*fac,cis*-$[Pt(NO_2)Cl_3Br_2]^{2-}$	−217	400		
(16)	*mer,cis*-$[Pt(NO_2)Cl_3Br_2]^{2-}$	−160		367	
(17)	*cis,mer*-$[Pt(NO_2)Cl_2Br_3]^{2-}$	−536	403		
(18)	*cis,fac*-$[Pt(NO_2)Cl_2Br_3]^{2-}$	−471		366	
(19)	*trans,mer*-$[Pt(NO_2)Cl_2Br_3]^{2-}$	−481		360	
(20)	*trans*-$[Pt(NO_2)ClBr_4]^{2-}$	−860	403		
(21)	*cis*-$[Pt(NO_2)ClBr_4]^{2-}$	−801		372	
(22)	$[Pt(NO_2)Br_5]^{2-}$	−1 135		372	
(23)	*trans*-$[Pt(NO_2)_2Cl_4]^{2-}$	500			336
(24)	*trans*-$[Pt(NO_2)_2Cl_3Br]^{2-}$	[210]			[339]
(25)	*trans*-$[Pt(NO_2)_2Cl_2Br_2]^{2-}$	[−86]			[339]
(26)	*trans*-$[Pt(NO_2)_2Cl_2Br_2]^{2-}$	[−95]			[339]
(27)	*trans*-$[Pt(NO_2)_2ClBr_3]^{2-}$	−397			342
(28)	*trans*-$[Pt(NO_2)_2Br_4]^{2-}$	−713			342
(29)	*cis*-$[Pt(NO_2)_2Cl_4]^{2-}$	862	424		
(30)	*cis*-$[Pt(NO_2)_2Cl_3Br]^{2-}$	563	427		
(31)	*cis*-$[Pt(NO_2)_2Cl_3Br]^{2-}$	614	430	399	
(32)	*cis*-$[Pt(NO_2)_2Cl_2Br_2]^{2-}$	248	430		
(33)	*cis*-$[Pt(NO_2)_2Cl_2Br_2]^{2-}$	310	427	391	
(34)	*cis*-$[Pt(NO_2)_2Cl_2Br_2]^{2-}$	360		394	
(35)	*cis*-$[Pt(NO_2)_2ClBr_3]^{2-}$	−11	433	397	
(36)	*cis*-$[Pt(NO_2)_2ClBr_3]^{2-}$	51		397	
(37)	*cis*-$[Pt(NO_2)_2Br_4]^{2-}$	−276		405	
(38)	*mer*-$[Pt(NO_2)_3Cl_3]^{2-}$	1 043	446		360
(39)	*mer*-$[Pt(NO_2)_3Cl_2Br]^{2-}$	[756]	[446]		[360]
(40)	*mer*-$[Pt(NO_2)_3Cl_2Br]^{2-}$	[804]		[415]	[360]
(41)	*mer*-$[Pt(NO_2)_3ClBr_2]^{2-}$	[456]	[446]		[363]
(42)	*mer*-$[Pt(NO_2)_3ClBr_2]^{2-}$	512		415	363
(43)	*mer*-$[Pt(NO_2)_3Br_3]^{2-}$	207		421	369
(44)	*fac*-$[Pt(NO_2)_3Cl_3]^{2-}$	1 375	460		
(45)	*fac*-$[Pt(NO_2)_3Cl_2Br]^{2-}$	1 133	466	427	
(46)	*fac*-$[Pt(NO_2)_3ClBr_2]^{2-}$	885	467	424	
(47)	*fac*-$[Pt(NO_2)_3Br_3]^{2-}$	631		430	
(48)	*trans*-$[Pt(NO_2)_4Cl_2]^{2-}$	1 280			376
(49)	*trans*-$[Pt(NO_2)_4ClBr]^{2-}$	[995]			[376]
(50)	*trans*-$[Pt(NO_2)_4Br_2]^{2-}$	[695]			[376]
(51)	*cis*-$[Pt(NO_2)_4Cl_2]^{2-}$	1 594	488		391
(52)	*cis*-$[Pt(NO_2)_4ClBr]^{2-}$	1 368	486	459	394
(53)	*cis*-$[Pt(NO_2)_4Br_2]^{2-}$	1 136		455	394
(54)	$[Pt(NO_2)_5Cl]^{2-}$	1 833	518		415
(55)	$[Pt(NO_2)_5Br]^{2-}$	1 629		482	415
(56)	$[Pt(NO_2)_6]^{2-}$	[2 080]			[439]

* For compounds (23)—(47) the terms *cis* and *trans*, *etc.*, refer to the geometrical arrangement of the nitrito-groups. For (12)—(21) these terms refer to the arrangement of the halides except in (12), (13), (20), and (21) where they refer to the arrangement of NO_2^- and the single halide. The listed couplings remove other ambiguities. In compound (25) the bromides are *cis*, in (26) they are *trans*. The values given in square brackets are those predicted for the nine unobserved species.

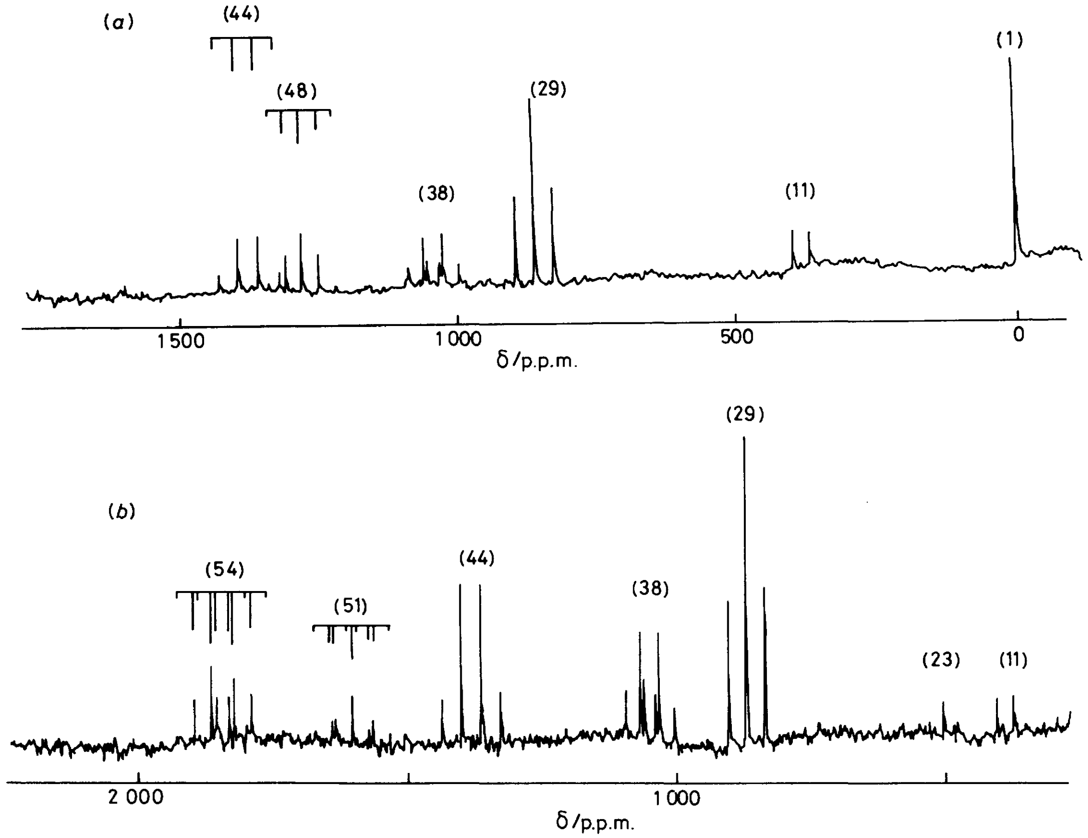

Figure 1. 195-Platinum n.m.r. spectra of a 1 mol dm^{-3} solution of $Na_2[PtCl_6]$ in D_2O containing 3 equivalents of $Na^{15}NO_2$ prepared by addition of 2 equivalents of $NaNO_2$ to a six-day old solution of $Na_2[PtCl_6]$–$NaNO_2$ (1 : 1). (*a*) Obtained within 24 h of this addition (*ca.* 200 K scans, 0.35 s interval); (*b*) obtained two days later (43 K scans, 0.35 s interval). Several examples of the instability of species containing *trans* pairs of NO_2^- ligands can be noted: the absence of resonances in (*a*) for *trans*-$[Pt(NO_2)_2Cl_4]^{2-}$ (23) despite the large peaks for the isomeric *cis* species, (29), and the replacement of resonances in (*a*) for *trans*-$[Pt(NO_2)_4Cl_2]^{2-}$ (48) by the isomeric *cis* species (51) in (*b*). After about two months, the only species present at high concentration were (29) and (44). Thus the *mer* isomer of the latter, (38), is also unstable with respect to (44)

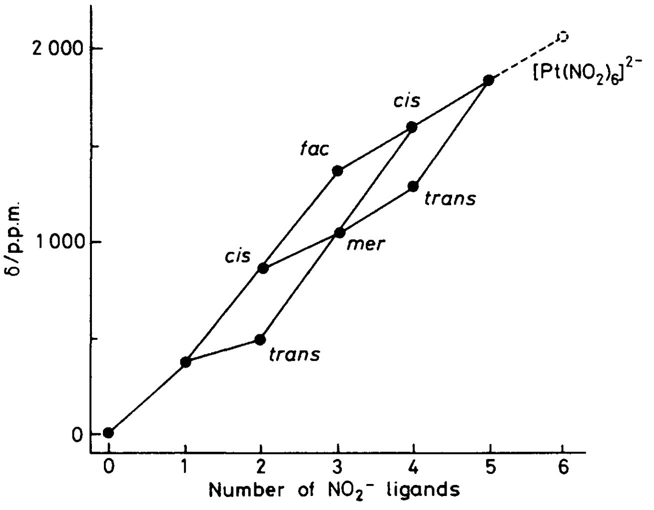

Figure 2. Platinum-195 n.m.r. chemical shifts of Pt^{IV} chloro–nitrite complexes as a function of the number of nitrite ligands. The connecting lines representing shift increments for substitutions *trans* to chloride are steeper than those for substitution *trans* to nitrite

taining NaBr, it was possible to extend the series to mixed Pt^{IV} chloro–bromo–nitrito complexes, see Figure 4. During this series of experiments it was found that the chemical shifts of the complexes were affected by the concentration of added nitrite, presumably due to the very high ionic strengths; Freeman *et al.*[15] have reported a similar effect for the shift for $Na_2[PtCl_4]$ in aqueous solution which differs by 24 p.p.m. for 2.3 and 0.13 mol dm^{-3} solutions. By appropriate correction, most shifts reported here could be related to $[PtCl_6]^{2-}$ at the lowest ionic strength used, since many species appeared in more than one solution at different nitrite concentrations. On addition of two equivalents of sodium nitrite the maximum overall correction required was *ca.* 4 p.p.m., but this is small compared to the separation of isomeric pairs. For the addition of four equivalents the correction is nearer 10 p.p.m. Unfortunately, complexes (12)—(16) appeared in only one spectrum and could not be corrected satisfactorily.

The resonances of the bromo-species were assigned using the values of chemical shifts caused by substitution of Cl^- by Br^- and NO_2^-, and values of $^1J(^{15}N-^{195}Pt)$ coupling constants with respect to geometry. The mononitrito-species (11)—(22) (Table 1) all give rise to doublets. The coupling constants fall into two distinct groups and are indicative of the ligand *trans* to nitrite: the coupling constant with nitrite *trans* to chloride is about 30 Hz greater than the coupling of nitrite *trans* to bromide. Complexes (14)—(16), isomers of $[Pt(NO_2)Cl_3Br_2]^{2-}$, and complexes (17)—(19), isomers of

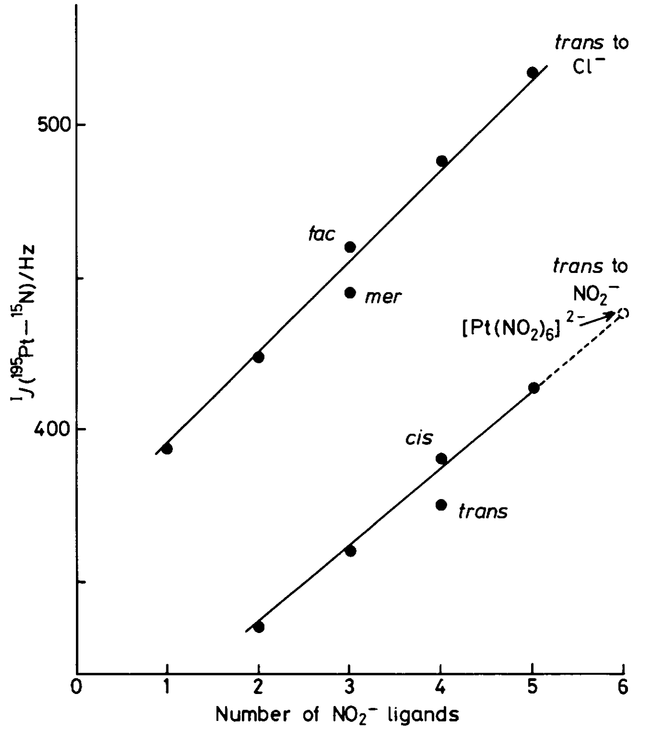

Figure 3. $^1J(^{15}N-^{195}Pt)$ values as a function of the number of nitrite ligands in mixed Pt^{IV} chloro–nitrite complexes. Where two complexes have equal numbers of nitrite ligands, the *cis* and *fac* isomers have the higher coupling constants by *ca.* 15 Hz

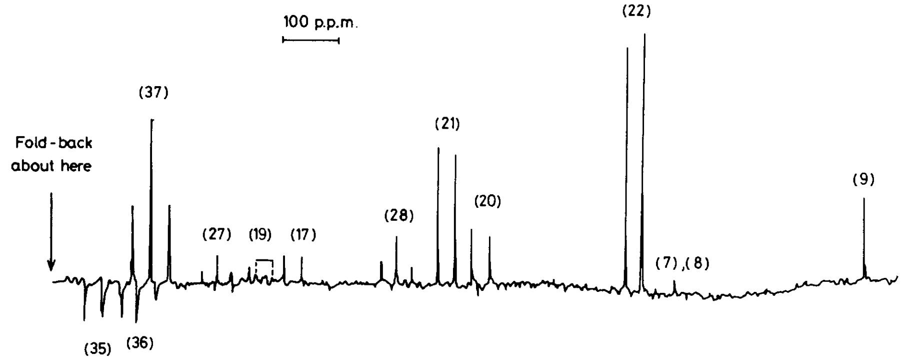

Figure 4. Platinum-195 n.m.r. spectrum of a 1 mol dm^{-3} solution of $Na_2[PtCl_6]$ in D_2O containing 4 equivalents of NaBr and 2 equivalents of $Na^{15}NO_2$. The inverted peaks are folded back from the low- frequency (left-hand) end of the spectrum

$[Pt(NO_2)Cl_2Br_3]^{2-}$, are illustrative. For the former case, one of the isomers (16) has bromide as the *trans* ligand whereas in the other two, (14) and (15), the ligand *trans* to nitrite is chloride. Thus (14) and (15), which have identical coupling constants of 400 Hz and differ by only 10 p.p.m. in chemical shifts, are about 62 p.p.m., away from (16) which has a coupling of 367 Hz. Complexes (14) and (15) can be assigned with the knowledge that the shift for substitution of chloride *trans* to bromide by nitrite is *ca.* 10 p.p.m. greater than the shift for substitution *trans* to chloride : complexes (29)—(37). Thus the assignment of the 12 possible Pt^{IV} complexes with one nitrite and various arrangements of chloride and bromide is complete, see Table 1.

The $[PtCl_4]^{2-}/NO_2^-/Br^-$ *System*.—Within one hour of the addition of one equivalent of $Na^{15}NO_2$ to a 0.4 mol dm^{-3} solution of $K_2[PtCl_4]$, two new species were visible in the spectrum. A doublet (J = 589 Hz) at −1 671 p.p.m. was presumed to be due to $[Pt(NO_2)Cl_3]^{2-}$ and a triplet (J = 679 Hz) for $[Pt(NO_2)_2Cl_2]^{2-}$ as the *cis* or *trans* isomer. With longer accumulation a third set of peaks for $[Pt(NO_2)_3Cl]^{2-}$ became visible at −1 949 p.p.m. (J = 535 and 757 Hz). Between 6 and 15 h after mixing, the approximate percentages of species (calculated from peak heights) were $PtCl_4^{2-}$, 24%; $[Pt(NO_2)Cl_3]^{2-}$, 40%; $[Pt(NO_2)_2Cl_2]^{2-}$, 29%; and $[Pt(NO_2)_3Cl]^{2-}$, 7%. Addition of a further equivalent of $Na^{15}NO_2$ causes all the $[PtCl_4]^{2-}$ to react, whilst with three equivalents only tri- and tetra-nitrite species are observed. A fourth equivalent does not lead to the complete conversion of trinitrite to tetranitrite. Chemical shifts and coupling constants are listed in Table 2.

The mixed chloro–bromo–nitrito-species were all observed in solutions containing 0.4 mol dm^{-3} $K_2[PtCl_4]$ to which had been added two equivalents of NaBr followed by 1.5 equivalents, and then a further equivalent of $Na^{15}NO_2$. The chemical shifts and coupling constants are listed in Table 2, and Figure 5 shows the linear relationship between the coupling constant and the number of nitrite ligands in the complex. From the latter, the previously unidentified triplet for $[Pt(NO_2)_2Cl_2]^{2-}$ was assigned to the *cis* isomer and a coupling constant of 478 Hz was predicted for the *trans* isomer. The chemical shift of the *trans* species can be located by extrapolation of the shifts of the two other species with the *trans* configuration. The value was −1 797 p.p.m., identical to that of the *cis* isomer. The triplet (J = 470 Hz) for the *trans* complex can be detected in spectra with high signal-to-noise ratios. Its intensity can be increased by the addition of acid, see Figure 6. Addition of 20 µl of concentrated H_2SO_4 to a 0.5 mol dm^{-3} solution of $K_2[PtCl_4]$ containing four equivalents of $NaNO_2$ leads to the formation of *trans*, but no *cis*, dinitrito-species.

Discussion

A striking feature arising from comparison of the chemical shift changes on substituting chloride for nitrite in Pt^{IV} and Pt^{II} complexes (Tables 1 and 2) is that they are in *opposite*

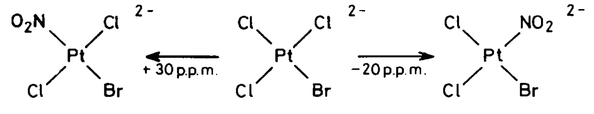

Table 2. Chemical shifts and coupling constants for the platinum(II) complexes

	Complex	δ/p.p.m.	J/Hz trans to Cl⁻	J/Hz trans to Br⁻	J/Hz trans to NO₂⁻
(57)	$[PtCl_4]^{2-}$	−1 631			
(58)	$[PtCl_3Br]^{2-}$	−1 858			
(59)	*trans*-$[PtCl_2Br_2]^{2-}$	−2 101			
(60)	*cis*-$[PtCl_2Br_2]^{2-}$	−2 111			
(61)	$[PtClBr_3]^{2-}$	−2 380			
(62)	$[PtBr_4]^{2-}$	−2 676			
(63)	$[Pt(NO_2)Cl_3]^{2-}$	−1 671	589		
(64)	*trans*-$[Pt(NO_2)Cl_2Br]^{2-}$	−1 828		570+*	
(65)	*cis*-$[Pt(NO_2)Cl_2Br]^{2-}$	−1 878	580		
(66)	*cis*-$[Pt(NO_2)ClBr_2]^{2-}$	−2 057		568	
(67)	*trans*-$[Pt(NO_2)ClBr_2]^{2-}$	−2 104	570		
(68)	$[Pt(NO_2)Br_3]^{2-}$	−2 303		562	
(69)	*trans*-$[Pt(NO_2)_2Cl_2]^{2-}$	−1 797			470
(70)	*trans*-$[Pt(NO_2)_2ClBr]^{2-}$	−1 994			459
(71)	*trans*-$[Pt(NO_2)_2Br_2]^{2-}$	−2 209			452
(72)	*cis*-$[Pt(NO_2)_2Cl_2]^{2-}$	−1 797	679		
(73)	*cis*-$[Pt(NO_2)_2ClBr]^{2-}$	−1 949	665	665	
(74)	*cis*-$[Pt(NO_2)_2Br_2]^{2-}$	−2 120		651	
(75)	$[Pt(NO_2)_3Cl]^{2-}$	−1 949	757		535
(76)	$[Pt(NO_2)_3Br]^{2-}$	−2 087	665	745	522
(77)	$[Pt(NO_2)_4]^{2-}$	−2 187			592

* One peak partially hidden.

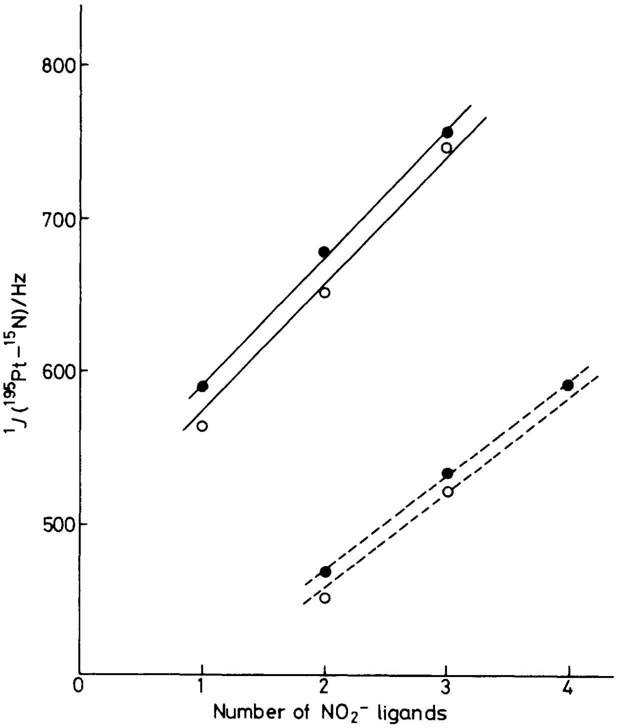

Figure 5. Coupling constants of the complexes $[Pt(NO_2)_{4-x}X_x]^{2-}$, X = Cl (●) or Br (○), plotted against the number of nitrite ligands: *trans* to halide (——), *trans* to NO_2^- (– – –)

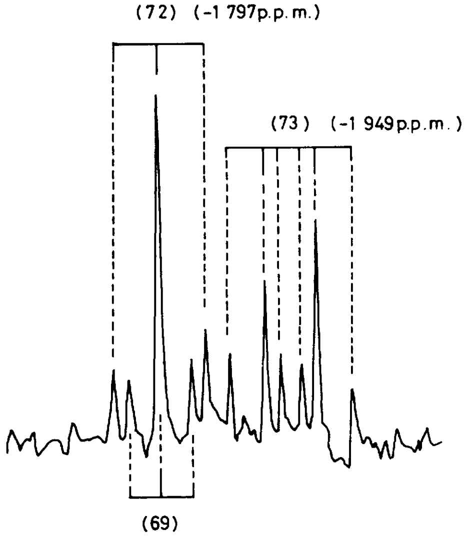

Figure 6. Platinum-195 n.m.r. spectrum of a $K_2[PtCl_4]$ solution (0.4 mol dm^{-3}) plus two equivalents of $Na^{15}NO_2$ to which 10 μl of concentrated H_2SO_4 has been added, showing the identical chemical shifts and differing coupling constants of *cis*- and *trans*-$[Pt(NO_2)_2Cl_2]^{2-}$, (72) and (69)

Table 3. Chemical shift changes for substitution of Cl^- by Br^- in Pt^{II} complexes

Parent complex	Substituted derivatives	−δ/p.p.m., for *trans* ligand [a] X [b]	−δ/p.p.m., for *trans* ligand [a] NO_2^-
$[PtCl_4]^{2-}$	(58)—(62)	203 + 23.5*n*	
$[Pt(NO_2)Cl_3]^{2-}$	(64)—(68)	187 + 19.5*n*	136 + 21*n*
$[Pt(NO_2)_2Cl_2]^{2-}$	(70), (71), (73), (74)	197 + 18*n*	133 + 19*n*
$[Pt(NO_2)Cl_3]^{2-}$	(76)		138

[a] *n* Is the number of bromides in the complex after substitution (substitution step number). [b] X = Cl^- or Br^-.

directions. For Pt^{II}, a low-frequency shift is usually observed whereas for Pt^{IV} shifts are to high frequency. An interesting exception is shown on p. 2366. In this case, substitution can lead to a shift in either direction depending on the isomer produced. Curiously, the Br^-/NO_2^- substitution shifts are in the same direction for both Pt^{II} and Pt^{IV}. The substitution shifts are much smaller for Pt^{II} than for Pt^{IV}. This created some difficulties with assignment expecially as the coupling constants differ only slightly for Cl^- and Br^- as *trans* ligands. In fact, *cis*-$[Pt(NO_2)_2ClBr]^{2-}$ shows only a single coupling constant instead of the two predicted.

The incremental shift principle is obeyed for chloride–bromide substitutions in nitrite complexes just as it is in the $[PtCl_4]^{2-}/Br^-$ system above. The relevant equations are given in Table 3. It can be seen that the shift change is some 50 p.p.m. bigger when the Cl^-/Br^- substitution is made *trans* to halide compared to *trans* to NO_2^-. There is little shift difference between Cl^- or Br^- as the *trans* ligand in the Pt^{II} complexes and hence one equation is given for both.

The platinum(IV) Cl^-/NO_2^- substitution shifts show incremental behaviour but only as far as the third or fourth NO_2^- substitution. The incremental shift for substitution *trans* to NO_2^- is much smaller than *trans* to Cl^-. For Pt^{II}, both Cl^-/NO_2^- and Br^-/NO_2^- substitution shifts show an approximate linear increase (opposite directions) if the tetranitrite and

Table 4. Chemical shift changes for substitution of Cl^- by Br^- in Pt^{IV} complexes

Substituted derivatives	Parent complex	$-\delta$/p.p.m. for *trans* ligand *		
		Br^-	Cl^-	NO_2^-
(2)—(10)	$[PtCl_6]^{2-}$		$275 + 11.7n$	$228 + 9.3n$
(12)—(22)	$[Pt(NO_2)Cl_xBr_{5-x}]^{2-}$	$306 + 7n$	$291 + 7n$	
(24)—(28)	*trans*-$[Pt(NO_2)_2Cl_xBr_{4-x}]^{2-}$	$300 + 5.5n$	$284 + 6n$	
(30)—(37)	*cis*-$[Pt(NO_2)_2Cl_xBr_{4-x}]^{2-}$	$309 + 6n$	$294 + 5n$	$243 + 5.5n$
(39)—(43)	*mer*-$[Pt(NO_2)_3Cl_xBr_{3-x}]^{2-}$	$295 + 5n$	$282 + 5n$	$234 + 5n$
(45)—(47)	*fac*-$[Pt(NO_2)_3Cl_xBr_{3-x}]^{2-}$			$242 + 6n$
(49), (50)	*trans*-$[Pt(NO_2)_4Cl_xBr_{2-x}]^{2-}$			
(52), (53)	*cis*-$[Pt(NO_2)_4Cl_xBr_{2-x}]^{2-}$			$226 + 6n$
(55)	$[Pt(NO_2)_5Cl]^{2-}$			204

* *n* Is the number of bromide ions in the complex after the substitution (substitution step number).

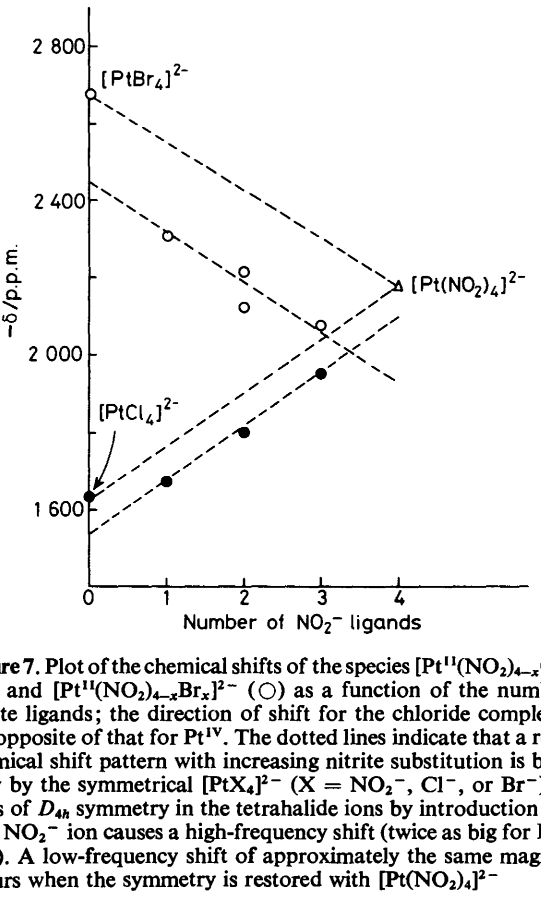

Figure 7. Plot of the chemical shifts of the species $[Pt^{II}(NO_2)_{4-x}Cl_x]^{2-}$ (●) and $[Pt^{II}(NO_2)_{4-x}Br_x]^{2-}$ (○) as a function of the number of nitrite ligands; the direction of shift for the chloride complexes is the opposite of that for Pt^{IV}. The dotted lines indicate that a regular chemical shift pattern with increasing nitrite substitution is broken only by the symmetrical $[PtX_4]^{2-}$ ($X = NO_2^-$, Cl^-, or Br^-) ions. Loss of D_{4h} symmetry in the tetrahalide ions by introduction of the first NO_2^- ion causes a high-frequency shift (twice as big for Br^- as Cl^-). A low-frequency shift of approximately the same magnitude occurs when the symmetry is restored with $[Pt(NO_2)_4]^{2-}$

tetrahalide complexes are not included, Figure 7. If all species are included, then the curved plots can be compared to similar ' sagging ' patterns observed for ^{29}Si shifts in the series SiX_nY_{4-n} and also found for ^{31}P chemical shifts in three-co-ordinated and four-co-ordinated phosphorus species. For ^{29}Si, the shielding change from SiX_4 is frequently in the opposite direction to the total SiX_4 to SiY_4 substitution shift (*e.g.* X = Br, Y = F).[16]

The incremental shifts for substitution of Cl^- by Br^- are again regular, as they are for Pt^{II}, and the equations are given in Table 4. As with Pt^{II}, the shift change for Cl^-/Br^- substitution *trans* to a halide is 50 p.p.m. or more greater than for substitution *trans* to NO_2^-.

The theoretical interpretation of ^{195}Pt n.m.r. shifts is far from clear. They are thought to be dominated by the paramagnetic shielding term (σ_p) as defined by Ramsey. For Pt^{II} complexes with D_{4h} symmetry, Goggin *et al.*[5] have shown, with some assumptions, that ^{195}Pt shifts should follow equation (1) where λ is the weighted mean of the reciprocal

$$\delta(\text{Pt}) = m\lambda + c \qquad (1)$$

transition energies. However, substitution of Cl^- by Br^- leads to an increase in λ and the equation therefore predicts the opposite shifts to that observed. We have not made detailed measurements of the electronic absorption spectra of the nitrites studied here, but $[PtCl_4]^{2-}$ is a red ion whereas $[Pt(NO_2)_4]^{2-}$ is colourless, and so in this case there would appear to be a positive correlation between chemical shift and wavelength.

The one-bond couplings of ^{195}Pt to ^{15}N in the Pt^{II} and Pt^{IV} series of chloro–bromo–nitrito-complexes are sensitive to the nature of the *trans* ligand and linearly dependent on the number of nitrite ligands present. In the Pt^{II} series they are also dependent on the number of bromide ligands. Chemical considerations suggest that the coupling constant should be smaller for a ligand which is *trans* to a ligand which has a large *trans* influence, since this tends to labilize the *trans* group through weakening of the bond. This is borne out by the equation in Table 5, from which the *trans* influence order is $Cl^- < Br^- \ll NO_2^-$. Similarly, *cis*-$[Pt(NH_3)_2Cl(dmso)]^+$ (dmso = dimethyl sulphoxide), as we have reported,[9] has a smaller $^1J(^{195}Pt-^{15}N)$ for NH_3 *trans* to dmso (232 Hz) than *trans* to Cl^- (335 Hz); dmso has a much higher *trans* influence than Cl^-.

Pople and Santry's treatment of Ramsey's equation for ^1J leads to the expression (2) for the Fermi contact term (see

$$^1J(\text{Pt, N}) \propto \{\gamma_{Pt}\gamma_N|\psi_{Pt,\,6s}(0)|^2|\psi_N(0)|^2\cdot\alpha_{Pt}^2\cdot\alpha_N^2\}/\Delta E \qquad (2)$$

ref. 8). Zero denotes the value of the wave function ψ at the nucleus, *i.e.* zero co-ordinates. There appears to be little correlation between the triplet excitation energy (ΔE) and ^1J. Coupling also depends upon the *s* character of the Pt orbitals used in bonding to the coupled atom. Thus, the linearity of the coupling constants of nitrite to platinum in Pt^{II} and Pt^{IV} series with the number of nitrite ligands may be explained by a similar increase in the *s* character of the bond between Pt and NO_2^-.

The ratios of Pt^{II} to Pt^{IV} coupling constants in complexes of the type *cis*-dichlorobis(n-dodecylamine)platinum(II) and *cis*-tetrachlorobis(n-dodecylamine)platinum(IV) have been discussed by Pregosin *et al.*,[7] and are close to 1.5. This has been explained on the basis of a change in hybridization from dsp^2 to d^2sp^3, so reducing the fractional *s* character of the bond from $\frac{1}{4}$ to $\frac{1}{6}$ giving a ratio of $(1/4)/(1/6) = 1.5$. A number of such comparisons can be made from our data on nitrite complexes.

Table 5. Equations for $^{195}Pt-^{15}N$ spin–spin coupling constants [a]

	Trans ligand	$^1J(^{195}Pt-^{15}N)$/ Hz
(*a*) Pt^{II}	Cl^-	$511 + 83n$
	Br^-	$494 + 83n$
	NO_2^- [b]	$348 + 62n$
	NO_2^- [c]	$336 + 62n$
(*b*) Pt^{IV}	Cl^-	$367 + 30n$
	Br^-	$342 + 28n$
	NO_2^- [b,c]	$289 + 25n$

[a] n Is the number of NO_2^- ligands in the complex. [b] In Cl^- complexes. [c] In Br^- complexes.

Table 6. Values of $^1J(^{195}Pt^{II}-^{15}N)/^1J(^{195}Pt^{IV}-^{15}N)$ for complexes of the type $[Pt(NO_2)_xCl_{4-x}]^{2-}$ and $[Pt(NO_2)_xCl_{6-x}]^{2-}$, and the corresponding bromides

	Ratio, *trans* to		
Complexes *	Cl^-	Br^-	NO_2^-
(63)/(11)	1.49		
(68)/(22)		1.51	
(69)/(23)			1.40
(71)/(28)			1.32
(72)/(29)	1.60		
(74)/(37)		1.61	
(75)/(38)	1.70		1.47
(76)/(43)		1.77	1.41
(77)/(48)			1.57

* See Tables 1 and 2.

These are listed in Table 6. It can be seen that they are indeed also clustered around 1.5 ± 0.2. The ratio tends to increase as the number of nitrite ligands increases, suggesting either that the types of orbitals used in the hybridization change, or that deviations from square-planar and octahedral symmetry become significant with large numbers of nitrite ligands.

Finally, a note of caution. We have not isolated and characterised any of the nitrite complexes described here and so there is no firm proof of their chemical identity apart from n.m.r. data. We considered the possibility that NO_2^- would favour the substitution of a *trans* Cl^- by water from the solvent. However, no coherent pattern of shifts and couplings arises with this assumption, and most solutions contain a high concentration of free halide ions.

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