constants k_d ($=1/\tau_c$) ≥ 3000 s^{-1} in dimethyl sulfoxide at 300 K, and $k_d \geq 265$ s^{-1} in propylene carbonate at 280 K were calculated from the fast exchange limiting equation.[35] In dimethylformamide, a broad resonance was observed at 220 K, which partially resolved into two broad coalescing resonances ($[Na.C22C_5]^+$ upfield) in the range 240–280 K (this broadening probably arises from a combination of viscosity and exchange broadening dominating at lower and higher temperatures, respectively) and at higher temperatures coalesced to a single resonance consistent with exchange entering the fast exchange limit. While the resolution of this coalescence was insufficient for the quantitative derivation of exchange rate constants through a line-shape analysis, $k_d \approx 500$ s^{-1} (270 K) was calculated from the equation for coalescence.[35] In contrast, two well-resolved ^{23}Na resonances were observed for solvated Na$^+$ and $[Na.C22C_5]^+$ (485 Hz upfield at 360 K) in pyridine. At the highest temperature studied, 360 K, no significant broadening of the resonances was observed, consistent with exchange between the solvated Na$^+$ and $[Na.C22C_5]^+$ environments being in the very slow exchange limit from which $k_d \leq 500$ s^{-1} was calculated.[35]

For $[Na.C221]^+$, k_d(298.2 K) = 0.75, 0.25, and 0.0196 s^{-1} are reported in dimethyl sulfoxide, dimethylformamide,[36] and methanol,[37] from which it is apparent that $[Na.C22C_5]^+$ is substantially more labile in these solvents. Similarly both $[Na.C21C_5]^+$ and $[Li.C21C_5]^+$ are more labile than their C211 analogues.[12,15]

Conclusion

The replacement of an oxygen by a methylene moiety results in a structural change from *inclusive* $[Na.C221]^+$ to *exclusive* $[Na.C22C_5]^+$ in the solid state. This produces a substantial decrease and increase in the stability and lability, respectively, of $[Na.C22C_5]^+$ in solution by comparison to $[Na.C221]^+$. The decreased stability and increased lability of $[Na.C22C_5]^+$ arises from both the decrease in electrostatic attraction of $C22C_5$ for Na$^+$ resulting from the replacement of an oxygen donor atom by a methylene moiety, and from the change from an *inclusive* structure for $[Na.C221]^+$ to an *exclusive* structure for $[Na.C22C_5]^+$. In a membrane transport system, this should result in a greater proportion of $C22C_5$ being available for back-diffusion across a membrane, which together with the greater lability of $[Na.C22C_5]^+$, accounts for greater efficiency of $C22C_5$ as a Na$^+$ carrier by comparison to C221.[4] These observations are consistent with the efficiency of a given cryptand in transporting different alkali-metal ions across membranes tending to increase in the sequence in which the thermodynamic stabilities and labilities of the cryptates decrease and increase, respectively.[4]

Acknowledgment. The support of this research by the Australian Research Council and the award of a Commonwealth Postgraduate Award to P.C. are gratefully acknowledged. David Beard is thanked for making available his programs for generating computer graphics.

Supplementary Material Available: Listings of atomic coordinates and anisotropic thermal parameters (Table S(1)), hydrogen atom parameters (Table S(2)), and sample potentiometric titration data (Tables S(4) and S(5)) (5 pages); a listing of structure factors (Table S(3)) (10 pages). Ordering information is given on any current masthead page.

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(35) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd. ed.; Academic Press: San Diego, CA, 1988. In the fast exchange limit k_d may be calculated through

$$\pi W_{1/2\,obs} = X_c \pi W_{1/2\,c} + X_s \pi W_{1/2\,s} + X_c^2 X_s^2 4\pi^2 (\nu_c - \nu_s)^2 (\tau_c + \tau_s) \quad (3)$$

where $W_{1/2\,obs}$ (310 and 160 Hz for the dimethyl sulfoxide and propylene carbonate solutions, respectively) is the observed width at half-amplitude of the singlet resonance arising from the environmental averaging of the resonances of $[Na.C22C_5]^+$ and $Na^+_{solvated}$, $W_{1/2\,c}$ and $W_{1/2\,s}$ are the widths of these respective species in the absence of exchange, X_c and X_s are their mole fractions, and τ_c ($=1/k_d$) and τ_s are their mean lifetimes. In the cases of dimethyl sulfoxide and propylene carbonate, $W_{1/2\,c}$ and $W_{1/2\,s}$ = 265 and 60 Hz and 760 and 92 Hz, respectively, determined from solutions of $[Na.C22C_5]^+$ and $Na^+_{solvated}$ alone at the same temperatures and total Na$^+$ concentration as that of the exchanging solutions and with the corresponding $\nu_c - \nu_s = 530$ Hz. At the coalescence temperature an approximate k_d may be obtained through

$$1/k_d = 2^{1/2}/\pi(\nu_c - \nu_s) \quad (4)$$

when X_c and X_s are equal, and where ν_c and ν_s are the frequencies of $[Na.C22C_5]^+$ and $Na^+_{solvated}$ in the absence of exchange. In the case of the dimethylformamide solution, $\nu_c - \nu_s = 241$ Hz was determined from solutions of $[Na.C22C_5]^+$ and $Na^+_{solvated}$ alone at the same temperature and total Na$^+$ concentration as that of the exchanging solution. In the very slow exchange limit an upper limit for k_d may be obtained through

$$k_d = \pi 1.5 W_{1/2\,c} - \pi W_{1/2\,c} \quad (5)$$

where $1.5W_{1/2\,c}$ is the width that would be observed if the exchange rate was sufficient to increase $W_{1/2\,c}$ (175 Hz) by a factor of 0.5.

(36) Cox, B. G.; Garcia-Rosa, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054–1059.

(37) Cox, B. G.; Schneider, I.; Schneider, H. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 470–474.

Contribution from the Department of Chemistry,
The University of Queensland, Brisbane, Australia 4072

Reactions of Nitroplatinum Complexes. 1. ^{15}N and ^{195}Pt NMR Spectra of Platinum(II) Nitrite Complexes[1]

Trevor G. Appleton,* Kevin J. Barnham, John R. Hall, and Michael T. Mathieson

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^{15}N and ^{195}Pt NMR spectra have been used to characterize the products of reaction of $Pt(^{15}NO_2)_4^{2-}$ with sulfamic acid, $Pt(^{15}NO_2)_3(H_2O)^-$ and *cis*-$Pt(^{15}NO_2)_2(H_2O)_2$, and the hydroxo complexes $Pt(^{15}NO_2)_3(OH)^{2-}$ and *cis*-$Pt(NO_2)_2(OH)_2^{2-}$ derived from them by deprotonation. At intermediate pH values, the dinitro complexes rapidly form the hydroxo-bridged compounds $[\{Pt(^{15}NO_2)_2(\mu\text{-}OH)\}_n]^{n-}$ (n = 2, 3). The acid dissociation constant for $Pt(^{15}NO_2)_3(H_2O)^-$ (pK_a 5.32) was determined from the variation with pH of δ_N for nitro ligands cis to water/hydroxide. ^{15}N and ^{195}Pt NMR parameters were obtained for the series $Pt(^{15}NO_2)_3Z^{m-}$. The changes in these parameters as Z was changed correlated with those in the series $Pt(^{15}NH_3)_3Z^{n+}$. δ_N and J(Pt–N) values are much more sensitive to change in the ligand Z for the nitro ligand trans to Z than for that cis to Z.

Introduction

When ammine or amine ligands bound to platinum are highly enriched in ^{15}N ($I = {}^1/_2$), ^{15}N and ^{195}Pt NMR spectra can be very useful in elucidating the solution chemistry of these complexes.[2-10] We have previously studied[11] the effect of the ligand Z on ^{15}N and ^{195}Pt NMR parameters in the series $Pt(^{15}NH_3)_3Z^{n+}$.[12]

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(1) Presented in part at the XXVII International Conference on Coordination Chemistry, July 2–7, 1989, Broadbeach, Australia; Abstract M27.

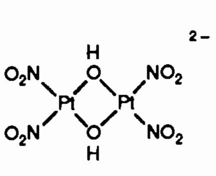
(2) Pregosin, P. S.; Omura, H.; Venanzi, L. M. *J. Am. Chem. Soc.* **1973**, *95*, 2047.

(3) Al-Najjar, I. M.; Green, M.; Kerrison, S. J. S.; Sadler, P. J. *J. Chem. Res., Synop.* **1979**, 206.

(4) Alei, M.; Vergamini, P. J.; Wageman, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 5415.

0020-1669/91/1330-2751$02.50/0

We were drawn to the study of platinum(II) nitrite complexes because of the variety of products that can be formed from the reaction of $Pt(NO_2)_4^{2-}$ with acids. Reaction of $K_2[Pt(NO_2)_4]$ with sulfuric acid yields the platinum(III) complex $K_2[Pt_2(\mu\text{-}SO_4)_4(H_2O)_2]$,[13] and that with phosphoric acid, the phosphate analogue, $K_2[Pt_2(\mu\text{-}PO_4H)_4(H_2O)_2]$.[14] Nitrosylplatinum(IV) complexes have also been isolated.[15] Abbott et al.[16] reported that reaction of $K_2[Pt(NO_2)_4]$ with dilute sulfuric acid, followed by neutralization, gave two crystalline products, $K_2[Pt_2(NO_2)_4(\mu\text{-}OH)_2]\cdot 1.5H_2O$, containing the anion **3**, and $K_3[\{Pt^{II}{}_3(NO_2)_6(\mu_3\text{-}O)_3\}\{Pt^{IV}(NO_2)_3\}]$, which may be regarded as a trinitroplatinum(IV) moiety coordinated by the triply deprotonated form of $[Pt_3(\mu\text{-}OH)_3(NO_2)_6]^{3-}$ (**4**).[16] The structure of the mixed-valence complex has been independently reported by Koz'min et al.[17] We have recently been studying the reactions of $K_2[Pt(NO_2)_4]$ with other acids (results from which will be published in subsequent papers in this series). ^{195}Pt and ^{15}N NMR spectra are potentially useful in the study of these reactions, but this requires some understanding of the parameters affecting NMR spectra of platinum nitrite complexes.



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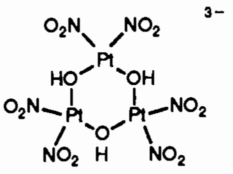

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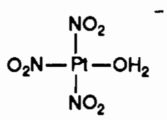
Wood and Balch[18] reported ^{195}Pt NMR spectra of some platinum(II) complexes obtained by reaction of $Pt(^{15}NO_2)_4^{2-}$ with sulfamic acid, and Kerrison and Sadler[19] described the ^{195}Pt spectra of the series of complexes $Pt^{II}(^{15}NO_2)_{4-n}X_n^{2-}$ and $Pt^{IV}(^{15}NO_2)_{6-n}X_n^{2-}$ (X = Cl, Br). In neither case was there any attempt to obtain ^{15}N spectra. Indeed, there have been very few reports of ^{15}N NMR spectra of coordinated nitrite. Bell et al.[20] reported the ^{15}N spectra of some complexes *trans*-$[RhCl(^{15}NO)(^{15}NO_2)(PR_3)_2]$. We recently reported the ^{15}N spectrum of coordinated nitrite in $Rh(^{15}NH_3)_5(^{15}NO_2)^{2+}$.[21]

In this work, we set out to study the chemistry of the mixed nitro–aqua complexes $Pt(NO_2)_3(H_2O)^-$ (**1**) and *cis*-$Pt(NO_2)_2(H_2O)_2$ (**2**) by ^{15}N and ^{195}Pt NMR spectroscopy and then to determine the effect of Z on NMR parameters in the series of complexes $Pt(^{15}NO_2)_3Z^{m-}$ (**5**). As in the series $Pt(^{15}NH_3)_3Z^{n+}$, this allows the effect of Z to be determined for nitrogen trans to Z (N_t) and cis to Z (N_c) in the one complex and also allows direct comparisons between the two series. Where possible, we also obtained spectra for the complexes *cis*-$Pt(^{15}NO_2)_2Z_2^{q-}$, to ascertain whether NMR parameters were as predicted from cis and trans influence parameters derived from the trinitro complexes.



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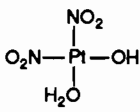

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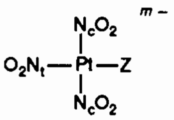

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The starting materials for these studies, $Pt(^{15}NO_2)_3(H_2O)^-$ (**1**) and *cis*-$Pt(^{15}NO_2)_2(H_2O)_2$ (**2**), may be conveniently obtained in solution by reaction of $K_2[Pt(^{15}NO_2)_4]$ with sulfamic acid. The general reaction for coordinated nitrite is shown in eq 1.[22] Wood and Balch[18] used these reactions to prepare in solution complexes formulated as **1** and **2** with ^{15}N in the nitrite ligands, although, as we describe below, their ^{195}Pt NMR spectra do not correspond to these species. Privalov et al.[23] have also reported ^{195}Pt spectra of *cis*-$Pt(^{14}NO_2)_2(H_2O)_2$ and some derivatives, but some of their assignments also differ from ours.

$$M{-}NO_2^- + {}^+NH_3SO_3^- \rightarrow M{-}OH_2 + HSO_4^- + N_2 \quad (1)$$

We have also obtained the ^{15}N NMR spectrum of *trans*-$Pt(^{15}NO_2)_4Cl_2^{2-}$, as a typical nitroplatinum(IV) complex.

Experimental Section

Starting Materials. $Na(^{15}NO_2)$ and $(^{15}NH_4)_2SO_4$ (>98% ^{15}N) (Cambridge Isotopes) were supplied by Novachem (Melbourne, Australia). The labeled sodium nitrite was converted to the potassium salt by elution through a column containing cation-exchange resin (Amberlite IR 120(H), commercial grade) that had been converted to the potassium form by passing through 1 M KCl solution, followed by rinsing with distilled water. The $K(^{15}NO_2)$ was used to prepare $K_2[Pt(^{15}NO_2)_4]\cdot 2H_2O$ by using the method described in the literature[24] for $K_2[Pt(^{14}NO_2)_4]\cdot 2H_2O$. Sulfamic acid used was from a freshly opened bottle supplied by Ajax Chemicals (Sydney, Australia). Once opened, the bottle was stored in a desiccator over *silica gel*. IR spectra showed no detectable sulfate or hydrogen sulfate (by comparison of spectra with those of $KHSO_4$ and K_2SO_4).

Preparation of Solutions Containing $Pt(^{15}NO_2)_3(H_2O)^-$ (1) and *cis*-$Pt(^{15}NO_2)_2(H_2O)_2$ (2). $K_2[Pt(^{15}NO_2)_4]\cdot 2H_2O$ (0.10 g, 0.20 mmol) was dissolved in 3 mL of water. Solid sulfamic acid (0.02 g, 0.21 mmol) was slowly added, and the solution was then allowed to stand overnight at room temperature. The ^{195}Pt NMR spectrum of the resultant solution showed peaks due to **1** (approximately 82% of total intensity), with weaker peaks due to residual $Pt(^{15}NO_2)_4^{2-}$ (approximately 10%) and **2** (approximately 8%). When the sulfamic acid used was pure, peaks due to sulfato complexes were not detected.

If a solution containing predominantly **2** was desired, 2 mol equiv of sulfamic acid was added to $K_2[Pt(^{15}NO_2)_4]$, and the solution was allowed to stand for 3 days. The ^{195}Pt NMR spectrum also usually showed weak peaks from **1**.

The remaining nitrite ligands in **2** do not readily react with sulfamic acid. Addition of excess sulfamic acid to a solution of **2** caused formation of *cis*-$Pt(^{15}NO_2)_2(NH_2SO_3)_2^{2-}$, which was characterized by NMR spectroscopy.

Preparations of Solutions Containing $Pt(^{15}NO_2)_3Z^{m-}$ (5) and *cis*-$Pt(^{15}NO_2)_2Z_2^{q-}$. Solutions containing the hydroxo complexes $Pt(^{15}NO_2)_3(OH)^{2-}$ and *cis*-$Pt(^{15}NO_2)_2(OH)_2^{2-}$ were obtained by rapid addition of 1 M KOH solution to solutions of the aqua complexes **1** and **2**, respectively, to increase the pH of the solutions to 9–12. Addition of a salt NaX (X = Cl, Br, SCN, CH_3CO_2) to a solution containing both **1** and **2** gave a solution containing $Pt(^{15}NO_2)_3X^{2-}$ and *cis*-$Pt(^{15}NO_2)_2X_2^{2-}$, with peaks from *cis*-$Pt(^{15}NO_2)_2X(H_2O)^-$ observed in a few instances. With acetate, an excess of the salt was required; with the other salts, 1 mol equiv was used. With excess Na_2SO_4, sulfato complexes were observed. Considerable effort was expended in attempting to obtain pure solids containing $[Pt(NO_2)_3(SO_4)]^{3-}$. Concentration of any of these solutions caused formation of gums, usually with a reddish color, probably from traces of

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(5) Boreham, C. J.; Broomhead, J. A.; Fairlie, D. P. *Aust. J. Chem.* **1981**, *34*, 659.

(6) Nee, M.; Roberts, J. D. *Biochemistry* **1982**, *21*, 4920.

(7) Ismail, I. M.; Sadler, P. J. In *Platinum, Gold, and Other Metal Chemotherapeutic Agents*; Lippard, S. J., Ed.; American Chemical Society: Washington, DC, 1983; p 171.

(8) Appleton, T. G.; Berry, R. D.; Davis, C. A.; Hall, J. R.; Kimlin, H. A. *Inorg. Chem.* **1984**, *23*, 3514.

(9) Hollis, L. S.; Stern, E. W.; Amundsen, A. R.; Miller, A. V.; Doran, S. L. *J. Am. Chem. Soc.* **1987**, *109*, 3596.

(10) Appleton, T. G.; Hall, J. R.; Ralph, S. F.; Thompson, C. S. M. *Inorg. Chem.* **1989**, *28*, 1989.

(11) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 4685.

(12) As in ref 11, we will, throughout this paper, use the symbol X to denote an anionic ligand, L a neutral ligand, and Z a ligand that may be either neutral or anionic.

(13) Muraveiskaya, G. S.; Orlova, V. S.; Evstaf'eva, O. N. *Zh. Neorg. Khim.* **1974**, *19*, 1030.

(14) Appleton, T. G.; Hall, J. R.; Neale, D. W. *Inorg. Chim. Acta* **1985**, *104*, 19.

(15) Peterson, E. S.; Larsen, R. D.; Abbott, E. H. *Inorg. Chem.* **1988**, *27*, 3514.

(16) Min, D.; Larsen, R. D.; Emerson, K.; Abbott, E. H. *Inorg. Chem.* **1990**, *29*, 73.

(17) Koz'min, P. A.; Lapkin, V. V.; Shubachkin, L. K. *Dokl. Akad. Nauk SSSR* **1986**, *286*, 125.

(18) Wood, F. E.; Balch, A. L. *Inorg. Chim. Acta* **1983**, *76*, L63.

(19) Kerrison, S. J. S.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2363.

(20) Bell, L. K.; Mason, J.; Mingos, D. M. P.; Tew, D. G. *Inorg. Chem.* **1983**, *22*, 3497.

(21) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1988**, *27*, 4435.

(22) Kukushkin, Yu N.; Stefanova, O. V. *Zh. Neorg. Khim.* **1977**, 22, 3375.

(23) Privalov, V. I.; Lapkin, V. V.; Shubochkina, E. F.; Tasasov, V. P. *Koord. Khim.* **1988**, *14*, 390.

(24) Kuebler, J. R.; Bailar, J. C. *J. Am. Chem. Soc.* **1952**, *14*, 3535.

substances with platinum in mixed-oxidation states. Nitrate salts of La^{3+}, $[Co(en)_3]^{3+}$, $[P(C_6H_5)_4]^+$, and Cs^+ were used in attempts to obtain more sparingly soluble salts with these large cations, but we did not succeed in isolating pure compounds. The nitro compounds crystallized by Abbott et al.[16] were obtained from solutions at higher pH, where oligomeric hydroxo complexes predominate.

Addition of 1 mol equiv of KI to a solution of **1** caused reduction of the complex to platinum metal, with formation of I_2. Addition of KI to a solution of $K_2[Pt(^{15}NO_2)_4]$ gave $Pt(^{15}NO_2)_3I^{2-}$ and, subsequently, *trans*-$Pt(^{15}NO_2)_2I_2^{2-}$. Similar reactions with $Pt(^{15}NO_2)_4^{2-}$ occurred more slowly with bromide and chloride.

Attempts to prepare solutions of $Pt(^{15}NO_2)_3(CN)^{2-}$ by careful addition of KCN solution to a solution of **1** produced only $Pt(^{15}NO_2)_3(OH)^{2-}$. Addition of KCN solution to $Pt(^{15}NO_2)_4^{2-}$ gave a solution with a complex ^{15}N NMR spectrum, with no peaks that could be clearly assigned to $Pt(^{15}NO_2)_3(CN)^{2-}$.

A solution of $Pt(^{15}NO_2)_3(tu)^-$ was obtained by reaction of **1** with 1 mol equiv of thiourea (tu). A solution of $Pt(^{15}NO_2)_3(^{15}NH_3)^-$ was formed by addition of 0.5 mol equiv of $(^{15}NH_4)_2SO_4$ to a solution of **1**, followed by addition of 1 M NaOH solution to increase the pH to 9.

Addition of 4 mol equiv of sulfamic acid quickly to a solution of **1** gave a solution of $Pt(^{15}NO_2)_3(NH_2SO_3)^{2-}$. Reaction of $K_2[Pt(^{15}NO_2)_4]$ with a large excess (5 mol equiv) of sulfamic acid gave a solution of *cis*-$Pt(^{15}NO_2)_2(NH_2SO_3)_2^{2-}$.

Dimethyl sulfoxide did not react significantly with **1** or **2** in aqueous solution, even with prolonged heating.

Preparation of *trans*-$K_2[Pt(^{15}NO_2)_4Cl_2]$. Chlorine gas was bubbled through an aqueous solution of $K_2[Pt(^{15}NO_2)_4]$ for 2 min. The solution was then evaporated to dryness, to give the product as a pale yellow solid. Anal. Calcd for $Cl_2K_2{}^{15}N_4O_8Pt$: N, 10.6; Cl, 13.4. Found: N, 10.5; Cl, 13.1.

NMR Spectra. The 21.4-MHz ^{195}Pt and 10.1-MHz ^{15}N NMR spectra were obtained with the use of a JEOL FX-100 FT-NMR instrument with external ^7Li lock and a broad-band tunable 10-mm probe. The probe temperature was 28 °C. The 40.4-MHz ^{15}N NMR spectra were obtained with the use of a JEOL GX-400 spectrometer, run without lock, at probe temperature 25 °C. All spectra were run in ^1H_2O, with total concentration of platinum complexes approximately 0.1 M. Chemical shifts are positive to lower shielding.

For the ^{195}Pt NMR spectra, the spectrum width was 30000 Hz. Approximately 10000 scans were used 0.5 s apart. The pulse sequence described by Canet et al.[25] was used to eliminate "baseline roll". A separate sample of Na_2PtCl_6 solution (0.5 g in 2 mL of H_2O) was used as the reference.

For 40.4-MHz ^{15}N NMR spectra, the spectrum width was 40000 Hz. A total of 1000 scans were used, each with 22° tilt of the magnetization vector, and there was 5-s total delay between pulses. For platinum(II) samples, the "satellite" peaks from coupling with ^{195}Pt were broad, owing to chemical shift anisotropy-induced relaxation of the ^{195}Pt nuclei at high magnetic fields.[26] For 10.1-MHz spectra, the spectrum width was 10000 Hz, and 10000 scans (22° tilt of magnetization vector) 3 s apart were used. The satellite peaks were sharp (Pt–N coupling constants were therefore measured where possible from these spectra), but the lower sensitivity increased the time to obtain a spectrum on a given solution by a factor of approximately 5. The reference was a solution of 5 M $(^{15}NH_4)_2SO_4$ in 1 M H_2SO_4 in a coaxial capillary.

These conditions gave good ^{15}N NMR spectra from coordinated nitrite without the application of any proton-decoupling irradiation. The $^{15}NH_4^+$ reference signal was then a quintet. For species such as $Pt(^{15}NO_2)_3(^{15}NH_3)^-$, it was desirable to obtain simultaneously the spectrum of the nitrite ligands and a ^1H-decoupled spectrum for the ammine ligand. Application of simple broad-band noise-decoupling radiation caused the nitrite signals not to be observed, presumably due to negative nuclear Overhauser enhancement cancelling the signal.[27] Use of a gated-decoupling mode, which applies the decoupling radiation only during signal acquisition, allowed the nitrite ^{15}N signals to be observed. Some nuclear Overhauser enhancment remained for ^{15}N nuclei directly bound to protons, as the reference $^{15}NH_4^+$ and coordinated $^{15}NH_3$ signals remained inverted.

pH Measurements. All pH measurements were made with the use of an Ionode combination glass/reference electrode and a TPS digital pH meter calibrated against standard phthalate (pH 4.01) and phosphate (pH 6.86) buffers at 25 °C. The pH of the solution was adjusted and measured before each NMR run and measured again immediately after the spectrum was run. The average value was then calculated. Maximum pH variation during a run was 0.02.

Table I. NMR Parameters for Complexes $Pt(^{15}NO_2)_3Z^{m-}$[a]

Z	δ_{Pt}[b]	δ_N $(J(Pt–N))$[c] trans to Z	δ_N $(J(Pt–N))$[c] cis to Z
H_2O	−1797	382 (821)	408 (572)
OH^-	−1792	405 (623)	415 (579)
$CH_3CO_2^-$	−1801	397 (733)	411 (583)
OSO_3^{2-}	−1930	400 (755)	415 (535)
Cl^-	−1934	400 (754)	414 (533)
Br^-	−2063	403 (745)	414 (522)
I^-	−2391	414 (699)	415 (506)
NO_2^-	−2166	410 (591)	410 (591)
NH_3	−2231	421 (637)	406 (559)
$NH_2SO_3^-$	−2243[d]	410 (684)	406 (562)
SCN^-	−2317	421 (638)	412 (524)
tu	−2509	431 (587)	412 (524)

[a] All nitro and ammine ligands contain ^{15}N. Spectra were run in H_2O. [b] Relative to Na_2PtCl_6. [c] Shifts relative to NH_4^+. Coupling constants are in Hz. [d] ^{195}Pt peaks broad.

Measurement of acid dissociation behavior by the NMR method has the advantage that the presence of a variety of other species in solution does not interfere with the measurement, as long as the peaks due to the species of interest can be distinguished. A disadvantage is that the relatively low sensitivity of the technique requires relatively concentrated solutions, with consequent high ionic strength. The solutions used were 0.05 M in platinum complex and also, unavoidably, contained K_2SO_4. With NaOH added to deprotonate half of the original $[Pt(NO_2)_3(H_2O)]^-$ (corresponding to the steepest part of the curve in Figure 1), the ionic strength is 0.25 M. No attempt was made to correct meter readings for effects such as liquid junction potentials.

Results

NMR Spectra. NMR data for complexes $Pt(^{15}NO_2)_3Z^{m-}$ are given in Table I, and those for other complexes in Table II.

A solution of $K_2[Pt(^{15}NO_2)_4]\cdot 2H_2O$ in H_2O gave a ^{195}Pt NMR spectrum showing a 1:4:6:4:1 quintet at −2166 ppm, with $^1J(^{195}Pt–^{15}N) = 591$ Hz, in good agreement with results previously reported by others.[18,19] The ^{15}N spectrum showed a singlet with satellites at 410 ppm from reference $^{15}NH_4^+$.

The complexes $Pt(^{15}NO_2)_3Z^{m-}$ (**5**) all gave the expected doublet of triplets in the ^{195}Pt NMR spectrum and two singlets with satellites (broad at 40.4 MHz, sharp at 10.1 MHz) in the ^{15}N NMR spectrum, except for $Pt(^{15}NO_2)_3(^{15}NH_3)^-$, which gave a doublet of doublets of triplets in the platinum spectrum. In the $^{15}N\{^1H\}$ spectrum the ammine complex showed a doublet from the ammine nitrogen and a doublet from the nitrite nitrogen trans to it ($J(^{15}N–Pt–^{15}N) = 6.7$ Hz). The mutually trans nitrite ligands showed no coupling to ammine nitrogen.

The different ^{15}N peaks in the trinitro complexes were easily assigned, on the basis that the more intense peak corresponded to the mutually trans nitro ligands.

The dinitro complexes $Pt(^{15}NO_2)_2Z_2{}^{q-}$ (either cis or trans) gave the expected 1:2:1 triplet in the ^{195}Pt NMR and a singlet with satellites in the ^{15}N NMR spectrum. Once again, the exception was the $^{15}NH_3$ complex *cis*-$Pt(^{15}NO_2)_2(^{15}NH_3)_2$, which gave a triplet of triplets in the ^{195}Pt NMR spectrum and doublet with satellites for each of the ammine and nitrite ^{15}N resonances (trans $^{15}N–Pt–^{15}N$ coupling constant 7.3 Hz). Each of the few complexes of the type *cis*-$Pt(^{15}NO_2)_2Z(H_2O)^{p-}$ that were examined gave a doublet of doublets in the ^{195}Pt spectrum and two singlets with satellites in the ^{15}N spectrum.

Solutions of $Pt(^{15}NO_2)_3(H_2O)^-$ (1) and *cis*-$Pt(NO_2)_2(H_2O)_2$ (2). When a solution of $K_2[Pt(^{15}NO_2)_4]$ was allowed to react with 1 mol equiv of sulfamic acid, the resultant solution gave a doublet of triplets in its ^{195}Pt spectrum at −1797 ppm, with the doublet coupling 821 Hz and the triplet coupling 572 Hz. The splitting pattern corresponds to a complex with three $^{15}NO_2^-$ groups bound to the metal, and from the ^{195}Pt chemical shift, the fourth ligand must be an oxygen donor.[11] With all of the added sulfamic acid consumed, the only potential O-donor ligands in the solution are H_2O and SO_4^{2-}. When Na_2SO_4 was added, a new doublet of

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(25) Canet, D.; Brondeau, J.; Marchal, J. P.; Robin-Lherbier, B. *Org. Magn. Reson.* **1982**, *20*, 51.

(26) Lallemand, J.-Y.; Soulie, J.; Chottard, J.-C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

(27) Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 31.

Table II. NMR Parameters for Other Nitro Complexes

		δ_N[c]		J(Pt–N)[d]		
complex[a]	δ_{Pt}[b]	obsd	calcd[e]	obsd	calcd[e]	ligand trans to nitro
cis-$Pt(NO_2)_2(H_2O)_2$	−1365	375	380	790	802	H_2O
cis-$Pt(NO_2)_2(OH)_2^{2-}$	−1375	413	410	624	611	OH^-
cis-$Pt(NO_2)_2(OSO_3)(H_2O)$[f]	−1524			726	736	OSO_3^{2-}
				747	765	H_2O
cis-$Pt(NO_2)_2(CH_3CO_2)_2^{2-}$	−1394	397	398	719	725	$CH_3CO_2^-$
cis-$Pt(NO_2)_2(CH_3CO_2)(H_2O)^-$	1349	386	395	711	714	$CH_3CO_2^-$
		378	383	801	813	H_2O
cis-$Pt(NO_2)_2Cl_2^{2-}$	−1783	405	404	679	696	Cl^-
trans-$Pt(NO_2)_2Cl_2^{2-}$	−1784	414	418	466	475	NO_2^-
trans-$Pt(NO_2)_2Br_2^{2-}$	−2192	414	418	455	453	NO_2^-
cis-$Pt(NO_2)_2Br(H_2O)^-$[f]	−1636			708	726	Br^-
				730	752	H_2O
trans-$Pt(NO_2)_2I_2^{2-}$	−3144	413	420	437	421	NO_2^-
cis-$Pt(NO_2)_2(NH_3)_2$	−2214	411	417	608	605	NH_3
cis-$Pt(NO_2)_2(NH_2SO_3)_2^{2-}$	*g*	399	406	677	655	$NH_2SO_3^-$
trans-$Pt(NO_2)_2(SCN)_2^{2-}$	−2472	412	414	469	457	NO_2^-
trans-$Pt(NO_2)_4Cl_2^{2-}$	+1280[h]	375		392		NO_2^-

[a] All nitro and ammine ligands contain ^{15}N. Spectra were run in H_2O. [b] Relative to Na_2PtCl_6. [c] Relative to NH_4^+. [d] In Hz. [e] Calculated figures based on trans and cis influence parameters from spectra in the trinitro series—see text. [f] ^{195}Pt spectrum only run. [g] ^{195}Pt spectrum not run. [h] From ref 19.

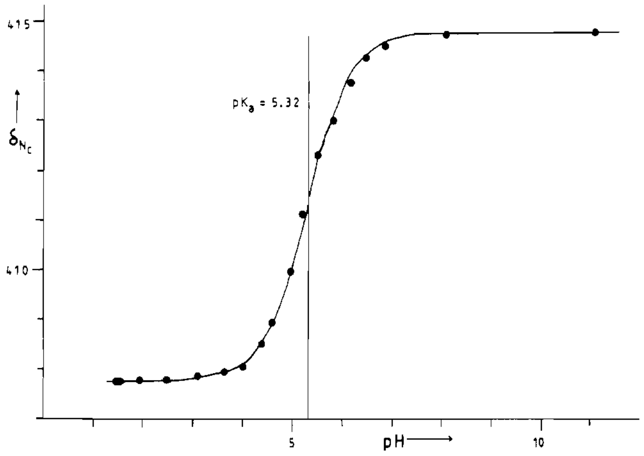

Figure 1. Variation in δ_N for the mutually trans nitro ligands in $Pt(^{15}NO_2)_3(H_2O)^-$ (**1**) with pH. The curve shown is that calculated from eq 2 with pK_a = 5.32.

triplets appeared, whose intensity increased as more sulfate was added (δ_{Pt} −1930, triplet splitting 535 Hz, doublet splitting 755 Hz). This signal, at −1930 ppm, was therefore assigned to the sulfato complex $[Pt(^{15}NO_2)_3(OSO_3)]^{3-}$, and the original signal at −1797 ppm to the aqua complex $[Pt(^{15}NO_2)_3(H_2O)]^-$ (**1**). Wood and Balch[18] reported that the solution they obtained from reaction of $Pt(^{15}NO_2)_4^{2-}$ with sulfamic acid gave a doublet of triplets at −1928 ppm, with triplet splitting 531 Hz and doublet splitting 754 Hz. They assigned these peaks to the aqua complex, **1**, but from our results, they correspond instead to the sulfato complex. To obtain a solution with the sulfato species predominating required, in our experience, a large excess of sulfate, the most likely source of which, if present unintentionally, would be as an impurity in the sulfamic acid used. When we tried the reaction with an "old" bottle of sulfamic acid that had stood for some years in a screw-cap bottle on the laboratory shelf (and that showed IR bands characteristic of sulfate), we obtained variable proportions of the aqua and sulfato complexes.

Each of these complexes showed in its ^{15}N NMR spectrum two singlets with satellites in the intensity ratio 2:1 (Table I).

When 2 mol equiv of sulfamic acid was added to a solution of $K_2[Pt(^{15}NO_2)_4]$, and the solution was allowed to stand, the major signal in the ^{195}Pt spectrum was a 1:2:1 triplet, with Pt–N coupling 790 Hz, at −1365 ppm, which we assigned to *cis*-$Pt(^{15}NO_2)_2(H_2O)_2$ (**2**). Wood and Balch[18] assigned to this species a triplet at −1777 ppm, with J(Pt–N) = 679 Hz, and claimed that, on heating, this triplet decayed with the rise of a new triplet at −1780 ppm, J(Pt–N) = 470 Hz, which they assigned to the trans isomer. When we added excess Na_2SO_4 to our solution, we observed a doublet of doublets in the ^{195}Pt NMR spectrum, at −1524 ppm (Pt–N couplings 747, 726 Hz), which we assigned to *cis*-$Pt(^{15}NO_2)_2(OSO_3)(H_2O)^{2-}$. With a large excess of sulfate, we did not observe any additional peaks that could be assigned to a bis(sulfato) complex. When we allowed our solutions of **2** to stand, or heated them at 60 °C, we observed no new peaks. The trans isomer therefore does not appear to form under these conditions. The triplets observed by Wood and Balch at −1777 and −1780 ppm cannot, therefore, be explained as being due to sulfato complexes. If the peaks were not "folded" from another region of the spectrum, it is possible that they were observing the doublet of triplets due to **1**, which we observed at −1797 ppm, although it would then be difficult to explain the reported coupling constants and changes on heating. Privalov et al.[23] have repoted δ_{Pt} for *cis*-$Pt(^{14}NO_2)_2(H_2O)_2$ as −1370, in good agreement with our value.

The ^{15}N NMR spectrum of a solution of **2** showed, as expected, a singlet with satellites (Table II).

$Pt(^{15}NO_2)_3(OH)^{2-}$ and the Acid Dissociation of 1. Rapid addition of 1 M NaOH solution to a solution of **1** (at pH 1.5), to increase the pH to 11, gave a doublet of triplets in the ^{195}Pt spectrum, corresponding to $Pt(^{15}NO_2)_3(OH)^{2-}$. As with ammine systems,[5,8,11] the replacement of H_2O by OH^- has little effect on δ_{Pt} but causes a large reduction in the trans Pt–N coupling constant (Table I). A similar spectrum was obtained when alkali was added to a solution of $[Pt(^{15}NO_2)_3(OSO_3)]^{3-}$. Hydroxide therefore displaces sulfate. Not surprisingly, then, our values agree with those reported by Wood and Balch[18] for $[Pt(^{15}NO_2)_3(OH)]^{2-}$. The ^{15}N NMR spectrum showed two singlets with satellites (intensity ratio 2:1).

At intermediate pH values, the spectrum showed two signals, at shifts correponding to the concentration-weighted averages of the shifts from aqua and hydroxo complexes. There was, in our spectra, considerable broadening of the peaks between pH 5 and 6, especially for the peak trans to water/hydroxide, for which the chemical shift difference between protonated and deprotonated complexes is 23 ppm. The broadening is much less for the peak from the cis nitro groups (shift difference 7 ppm), and the shifts for this peak were used in subsequent calculations. The protonation/deprotonation reaction would be expected to be too fast to contribute much to this broadening. Buffers were not used to control pH, because of the likelihood that they will react with platinum–aqua complexes,[8] so there was usually a small variation in pH during a run in this pH range (up to 0.02). Since the shift is very sensitive to pH in this region, this can also contribute to the broadening observed.

Figure 1 shows a plot of δ_N against pH for the mutually trans nitrite ligands. The pK_a of the complex was calculated by using a form of the Henderson–Hasselbach equation[28]

$$pK_a = pH + \log [(\delta - \delta_B)/(\delta_A - \delta)] \qquad (2)$$

where δ is the observed chemical shift and δ_A and δ_B are the shifts for the protonated and deprotonated compounds, respectively. The best least-squares fit of the experimental data to eq 2 over the pH range 4.6–5.9 gave a value for pK_a for **1** of 5.32 ± 0.01 (25 °C). As pointed out in the experimental section, the ionic strength of the solution was 0.25 M. This limits the accuracy of the value obtained, but it is difficult to envisage other experimental methods that allow pK_a measurements on such systems which have any validity. Kukushkin and Stefanova[29] reported a value of approximately 7 from potentiometric titration of a solution of $Pt(NO_2)_3(H_2O)^-$ they obtained by the sulfamic acid reaction, but from our experience, it is unlikely that their solution contained this complex only.

Deprotonation of 2 and Generation of Hydroxo-Bridged Oligomers. Addition of 1 M NaOH solution to a solution of **2**, to increase the pH to 10.5, gave a triplet at −1375 ppm, assigned to *cis*-$Pt(^{15}NO_2)_2(OH)_2^{2-}$. This represented only a small change in δ_{Pt} from **2**, but δ_N changed from 375 to 413, and J(Pt–N) decreased from 790 to 624 Hz.

We attempted to observe the shifts in the ^{15}N signal at intermediate values of pH, as NaOH solution was added slowly to a solution of **2**, but once the pH had increased to approximately 2.9, two new ^{15}N peaks (at 389 and 391 ppm) dominated the spectrum. These corresponded to triplets in the ^{195}Pt spectrum, each with J(Pt–N) 716.5 Hz, at −1072 and −1324 ppm (it was not possible to correlate a particular ^{15}N peak with each ^{195}Pt signal). In the analogous diammineplatinum(II) system, oligomers $[\{Pt(NH_3)_2(\mu\text{-}OH)\}_n]^{n+}$ (n = 2, 3) rapidly form once one of the water ligands of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ is deprotonated.[5,8,30-33] While the Pt shift in the trimer is "normal", the Pt nucleus in the dimer is much deshielded from that in *cis*-$Pt(NH_3)_2(OH)_2$, due to incorporation of platinum in a four-membered $Pt(\mu\text{-}OH)_2Pt$ ring.[5] By analogy, we have assigned the triplet to low shielding in the ^{195}Pt spectrum of the nitro complexes (−1072 ppm) to $[\{Pt(^{15}NO_2)_2(\mu\text{-}OH)\}_2]^{2-}$ (**3**). As mentioned above, the crystal structure of the potassium salt of this anion has been determined.[16] We have assigned the triplet at −1324 ppm to the trimer $[\{Pt(^{15}NO_2)_2(\mu\text{-}OH)\}_3]^{3-}$ (**4**). Such a trimer is presumably a precursor to the oxo-bridged mixed-valence complex $[Pt^{II}_3(NO_2)_6(\mu_3\text{-}O)_3Pt^{IV}(NO_2)_3]^{5-}$, whose crystal structure has also been determined.[16,17] Addition of dilute HNO_3 to decrease the pH below 2 caused **3** and **4** to convert to the diaqua complex **2**, and addition of NaOH solution to increase the pH to 8.5 caused a decrease in the intensities of peaks due to **3** and **4** and the growth of peaks due to the monomeric dihydroxo complex, $Pt(^{15}NO_2)_2(OH)_2^{2-}$. There were also some additional very weak peaks present, including a broad triplet at −966 ppm (J(Pt–N) = ~655 Hz). With additional base added to increase the pH to 10.5, all peaks except those due to $Pt(^{15}NO_2)_2(OH)_2^{2-}$ effectively disappeared. In their ^{195}Pt study of the $^{14}NO_2^-$ system, Privalov et al.[23] assigned a signal at −1075 ppm to **3**, consistent with our assignment, but a signal at −1335 ppm (that we would assign to **4**) they assigned to $Pt(NO_2)_2(OH)(H_2O)^-$. Proton-exchange reactions are unlikely to be slow enough to allow this to be observed as a separate species. They claimed that a peak due to $Pt(NO_2)_2(OH)_2^{2-}$ was not observed at all at high pH, which certainly did not correspond with our experience, but claimed that a peak at −963 ppm (very weak in our spectra) was the only one present at pH > 9.5. They assigned this peak to "$[Pt_3(NO_2)_6O_2]^{4-}$", with little justification.

The rapid formation of **3** and **4** at intermediate pH prevented us from obtaining any plots of δ_N against pH as alkali was added to a solution of **2**, but since the hydroxo-bridged species began to form rapidly once the pH had increased to 2.9, it is likely that pK_{a1} for **2** is approximately 3. Kukushkin and Stefanova[29] claimed to obtain values of approximately 10^{-7} and 10^{-11} for K_{a_1} and K_{a_2} for **2** from potentiometric titration, but from our observations, any analysis of titration curves that does not take into account the oligomerization of partially deprotonated complexes will not produce realistic acid dissociation constants.

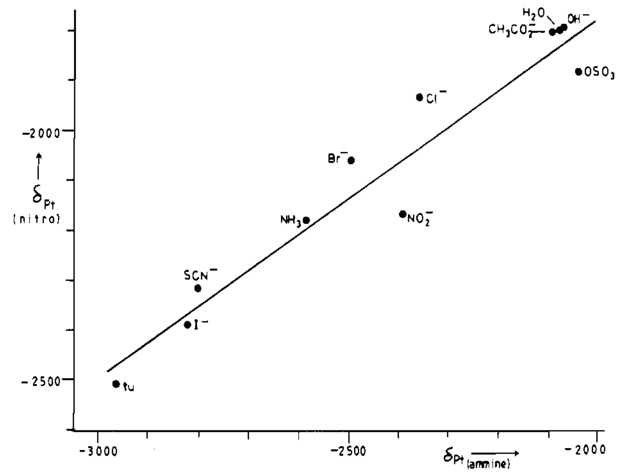

Figure 2. Plot of δ_{Pt} in the series $Pt(^{15}NO_2)_3Z^{m-}$ against δ_{Pt} for corresponding complexes in the series $Pt(^{15}NH_3)_3Z^{n+}$. The line of best fit is δ_{Pt}(trinitro) = $0.767\delta_{Pt}$(triammine) − 237. Data for the triammine complexes here, and in Figure 3, are from ref 11, except for Z = $CH_3CO_2^-$, from ref 44.

Discussion

^{195}Pt NMR Chemical Shifts. For the ligands Z that were studied, δ_{Pt} for $Pt(^{15}NO_2)_3Z^{m-}$ varies from −1792 (Z = OH^-) to −2509 ppm (Z = tu), a range of 812 ppm. This may be compared with the range of 900 ppm for the same ligands in the series $Pt(^{15}NH_3)_3Z^{n-}$.[11] The sensitivity of δ_{Pt} toward changes in Z is thus almost as great in the trinitro series as in the triammine series. The shifts for the trinitro complexes are plotted against those for corresponding triammine complexes in Figure 2. Changes in δ_{Pt} are usually interpreted in terms of the effect of the ligands on the paramagnetic contribution, σ_p, to shielding of the metal nucleus.[11,21,31-33] A ligand that causes radial expansion of the Pt 5d-orbitals, that increases singlet–triplet electronic excitation energy, or that tends to localize the 5d orbitals into metal–ligand covalent bonds will tend to decrease the magnitude of this paramagnetic term, causing a shift to higher shielding of the metal nucleus. The good linear correlation (correlation coefficient r = 0.96) for shifts in the two series indicates that the ligands Z are affecting the Pt 5d orbitals in similar ways in the two series.

^{15}N Chemical Shifts. There is a large coordination shift for nitrite nitrogen from nitrite ion (588.1 ppm in aqueous $Na^{15}NO_2$) to $Pt(^{15}NO_2)_4^{2-}$ (410 ppm) and *trans*-$Pt(^{15}NO_2)_4Cl_2^{2-}$ (375 ppm). The coordination shift is much larger in magnitude than the ammonia in ammine complexes (approxmately 70 ppm).[11] The nitro nitrogen nucleus is more shielded in the platinum(IV) complex than in the platinum(II) complex. This contrasts with ammine complexes, where the nitrogen nucleus is less shielded in platinum(IV) complexes compared with platinum(II).[11]

There is an inverse correlation (r = −0.87) between δ_N for the nitro ligand trans to Z(N_t) in $Pt(^{15}NO_2)_3Z^{m-}$ (**5**) and δ_{Pt} in the same series as Z is changed. Similar inverse correlations between δ_N trans to Z and δ_{Pt} have been previously observed for the series $Pt(^{15}NH_3)_3Z^{n+}$ [11] and for amine[3,34] and Schiff base[35] N atoms in other series. We pointed out[11] that this behavior paralleled that of δ_H in platinum(II) hydrides *trans*-$Pt(H)ZL_2$ and suggested that the changes in δ_N in these series could be explained on the same basis as the changes in δ_H in the hydride complexes,[36] where the

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(28) Edward, J. T.; Leane, J. B.; Wang, I. C. *Can. J. Chem.* **1962**, *40*, 1521.
(29) Kukushkin, Yu N.; Stefanova, O. V. *Koord. Khim.* **1979**, *5*, 1379.
(30) (a) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *J. Am. Chem. Soc.* **1977**, *99*, 777. (b) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1978**, *17*, 2971.
(31) Dean, R. R.; Green, J. C. *J. Chem. Soc. A* **1968**, 3047.
(32) McFarlane, W. J. *J. Chem. Soc., Dalton Trans.* **1974**, 324.
(33) Kennedy, J. D.; McFarlane, W.; Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1976**, 874.
(34) Motschi, H.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1979**, *62*, 667.
(35) Motschi, H.; Pregosin, P. S. *Inorg. Chim. Acta* **1980**, *40*, 141.
(36) Buckingham, A. D.; Stephens, P. J. *J. Chem. Soc.* **1964**, 2747.

electronic circulation responsible for the paramagnetic contribution to δ_{Pt} produces a diamagnetic effect at the nucleus trans to Z. Since then, Bramley et al.[37] have noted an analogous inverse correlation between δ_N trans to Z and δ_{Co} in the series $Co(NH_3)_5Z_n^+$. The relationship established in the present series of nitro complexes illustrates that these considerations apply to a wide range of types of complexes.

From the discussion above, it is not surprising that there is some correlation between δ_N trans to Z in the trinitro series and δ_N trans to Z in corresponding complexes in the triammine series, albeit not as good as the correlations previously discussed ($r = 0.82$).

From Table I, it is clear that δ_{N_t} (trans to Z) in the series $Pt(^{15}NO_2)_3Z^{m-}$ (**5**) is much more sensitive to changes in Z($\Delta\delta$ 49 ppm) than δ_{N_c} (cis to Z) ($\Delta\delta$ 9 ppm). Indeed, there is a much smaller cis influence relative to trans influence in this series than in the triammine series $Pt(^{15}NH_3)_3Z^{n+}$ ($\Delta\delta_{N_t}$ 42.8 ppm; $\Delta\delta_{N_c}$ 16.3 ppm[11]). The small changes in δ_{N_c} in the series **5** do not correlate well with any other NMR parameter.

By comparison of δ_{N_t} and δ_{N_c} for a complex $Pt(^{15}NO_2)_3Z^{m-}$, it is possible to calculate a trans and a cis influence on δ_N for each ligand Z, relative to NO_2^-, in a way similar to that for calculations of influences relative to NH_3 in the triammine series.[11] That is, the trans influence of a ligand Z on δ_N is

$$T(\delta)_Z = \delta_{N_t}(Pt(NO_2)_3Z^{m-}) - \delta_N(Pt(NO_2)_4^{2-}) \quad (3)$$

and the cis influence is

$$C(\delta)_Z = \delta_{N_c}(Pt(NO_2)_3Z^{m-}) - \delta_N(Pt(NO_2)_4^{2-}) \quad (4)$$

These values have not been included in Table I, but we have used them to calculate predicted values for δ_N for all of the platinum(II) complexes listed in Table II, which are given in that table along with observed shifts. There is excellent agreement between the calculated and observed shifts, with the greatest discrepancy being 7 ppm (for *trans*-$Pt(^{15}NO_2)_2I_2$). The ^{15}N chemical shifts in platinum(II) nitro complexes can therefore be used with confidence to indicate the nature of the ligand trans to nitrite.

$^{195}Pt-^{15}N$ Coupling Constants. $^{195}Pt-^{15}N$ coupling constants,[11,34,35] like other one-bond couplings between a transition-metal nucleus and a ligand nucleus (e.g., ^1H, ^{13}C, ^{31}P)[31,38-41] have usually been interpreted in terms of the Fermi contact contribution to the coupling being dominant—that is, the coupling is transmitted between the nuclei through s electrons, which have a finite probability of being at the nucleus and which also participate in covalent bonding. The magnitudes of $^{195}Pt-^{15}N$ coupling constants for nitro ligands in the series **5** are much greater than Pt–N coupling constants for ammine ligands in corresponding complexes in the series $Pt(^{15}NH_3)_3Z^{n+}$. It is tempting to ascribe this, at least in part, to the greater contribution of the N 2s orbital to the $Pt-NO_2$ bond ("sp^2") compared with the $Pt-NH_3$ bond ("sp^3").

In the series **5**, $J(Pt-N_t)$ (trans to Z) is much more sensitive to changes in Z ($\Delta J = 234$ Hz) than $J(Pt-N_c)$ (cis to Z) ($\Delta J = 85$ Hz). As with other series in which a coupling constant between ^{195}Pt and a ligand nucleus varies in response to the changes in a trans ligand,[11,34,35,39-41] the changes in $J(Pt-N_t)$ are caused primarily by changes in the Pt 6s contribution to the $Pt-N_t$ bond as Z is changed. There is a good linear correlation ($r = 0.95$) with $J(Pt-N_t)$ for corresponding complexes in the triammine series (Figure 3). There is also a general trend for $J(Pt-N_t)$ to decrease in magnitude as δ_{N_t} increases, but as in the triammine series, the correlation is not good. $J(Pt-N_c)$ (cis to Z) does not correlate well with any other NMR parameter. Once again, the trans and cis influences of Z on $J(Pt-N)$ may be calculated from the trinitro series by equations analogous to (3) and (4) and values calculated for the other platinum(II) complexes. These calculated values are included, along with the experimental ones, in Table II. Agreement is generally good, with the greatest discrepancy being 22 Hz (for *cis*-$Pt(^{15}NO_2)_2(NH_2SO_3)_2^{2-}$). The Pt–N coupling constants may then be used in a way similar to those for ammine complexes to indicate the ligand trans to a particular nitro ligand.

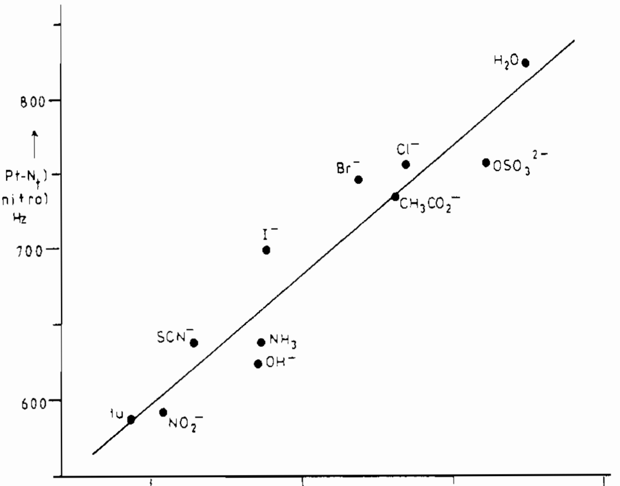

Figure 3. Plot of $J(Pt-N_t)$ (trans to Z) in the series $Pt(^{15}NO_2)_3Z^{m-}$ against $J(Pt-N_t)$ for corresponding complexes in the series $Pt(^{15}NH_3)_3Z^{n+}$. The line of best fit is $J(Pt-N_t)(trinitro) = 1.70J(Pt-N_t)(triammine) + 172$.

Table III. Acid Dissociation Constants for Platinum(II) Aqua Complexes[a]

complex	pK_{a_1}	pK_{a_2}	ref
$Pt(NO_2)_3(H_2O)^-$	5.32		this work
$Pt(NH_3)_3(H_2O)^{2+}$	6.37		10
$Pt(dien)(H_2O)^{2+}$	5.87		43
cis-$Pt(NH_3)_2(H_2O)_2^{2+}$[b]	5.93	7.87	10
trans-$Pt(NH_3)_2(H_2O)_2^{2+}$	4.24	7.29	42
cis-$Pt(NH_3)_2Cl(H_2O)^+$	6.85		10

[a] At 25 °C, unless otherwise stated. [b] At 5 °C.

The ratio of $J(Pt-N)$ in *trans*-$Pt(^{15}NO_2)_4Cl_2^{2-}$ (392 Hz) to $J(Pt-N)$ in $Pt(^{15}NO_2)_4^{2-}$ (591 Hz) is 0.66, very close to the "theoretical" value of 0.67 expected if the change in the contribution of the Pt 6s orbital is the most important variable that changes on oxidation.[38]

Acid Dissociation Constants for Mixed Aqua–Nitro Complexes. The acid dissociation constants for a number of platinum(II) aqua complexes are listed in Table III. $Pt(NO_2)_3(H_2O)^-$ is significantly more acidic than $Pt(NH_3)_3(H_2O)^{2+}$ or $Pt(dien)(H_2O)^{2+}$, despite the expectation that coordinated water in a 2+ cation would be more acidic than in an anionic complex. As is evident from comparison of the values for *cis*– and *trans*–$Pt(NH_3)_2(H_2O)_2^{2+}$, the nature of the other ligands present and their geometrical relationship to the aqua ligand in the complex are at least as important in determining the acid dissociation constant as the formal charge on the complex. The acid dissociation constants are consistent with a greater effective positive charge residing on the protons of the coordinated water in the nitro complexes. This suggests a smaller net transfer of negative charge from nitro to platinum than from ammine to platinum, even though all the NMR parameters indicate strong covalent nitro–platinum bonding. This, in turn, is consistent with significant π bonding from filled metal d orbitals to the vacant π^* orbitals of the nitro ligand.

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(37) Bramley, R.; Brorsen, M.; Sargeson, A. M.; Schaffer, C. E. *Inorg. Chem.* **1987**, *26*, 314.
(38) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.
(39) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
(40) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1973**, *95*, 8574.
(41) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.
(42) Appleton, T. G.; Bailey, A. J.; Barnham, K. J.; Hall, J. R. To be submitted for publication.
(43) Erickson, L. E.; Erickson, H. L.; Meyer, T. Y. *Inorg. Chem.* **1987**, *26*, 997.
(44) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Aust. J. Chem.* **1986**, *39*, 1347.