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Contribution from the Department of Chemistry,
University of Queensland, Brisbane, Australia 4067

^{15}N and ^{195}Pt NMR Spectra of Platinum Ammine Complexes: Trans- and Cis-Influence Series Based on ^{195}Pt–^{15}N Coupling Constants and ^{15}N Chemical Shifts

Trevor G. Appleton, John R. Hall,* and Stephen F. Ralph

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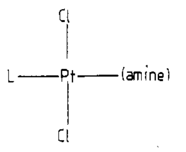
^{195}Pt and ^{15}N NMR spectra have been obtained for the series of platinum(II) complexes $Pt(^{15}NH_3)_3Z^{n+}$, *cis*-$Pt(^{15}NH_3)_2Z_2^{m+}$, and *cis*-$Pt(^{15}NH_3)_2YZ^{m+}$ (Z, Y are neutral or anionic ligands) and for the platinum(IV) complexes derived from them by peroxide oxidation, *mer*-$Pt(^{15}NH_3)_3Z(OH)_2^{n+}$ and $Pt(^{15}NH_3)_2Z_2(OH)_2^{m+}$. From the spectra of the triammineplatinum(II) complexes, the effects on δ_N and ^1J(Pt–N) trans and cis to Z, and on δ_{Pt}, of replacing one of the ammine ligands of $Pt(^{15}NH_3)_4^{2+}$ by Z were measured. With the assumption that the effects of replacing two ammine ligands are additive, the NMR parameters for diammineplatinum(II) complexes were calculated. Agreement with experimental values was good overall. NMR data for the platinum(IV) complexes were treated similarly, again with good agreement between calculated and experimental values for the diammine complexes. The influence of different ligands Z on the NMR parameters for the two different oxidation states, while generally similar, did show some consistent differences in detail. The influences of the halide ions on δ_{Pt}, and on δ_N and J(Pt–N) trans to Z, were greater for platinum(IV) relative to platinum(II). For the series $Pt(^{15}NH_3)_3Z^{n+}$, results are consistent with previous generalizations, that changes in δ_{Pt} mainly depend on the influence of Z on Pt 5d orbitals (through involvement in the Pt–Z σ-bond and through splitting of the d-orbital energy levels) and that changes in J(Pt–N) trans to Z depend mainly on variations in the Pt 6s contribution to the Pt–N bond. δ_N trans to Z shows an inverse linear correlation with δ_{Pt}. Cis influences on δ_N and J(Pt–N) are smaller than trans influences but are still significant.

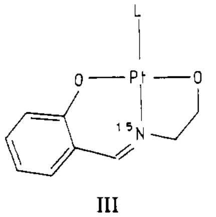
Introduction

The first report of ^{15}N NMR spectra in platinum amine complexes, with ^{15}N-enriched dodecylamines,[1] showed that $^1J(^{195}Pt–^{15}N)$ depends on the nature of the ligand trans to ^{15}N (^{15}N, $I = {}^1/_2$; ^{195}Pt, $I = {}^1/_2$, 33.6% abundance). These results, and comparisons of coupling constants in platinum(II) and platinum(IV) compounds, led to the conclusion that ^1J(Pt–N) is dominated by the Fermi contact contribution and that variations in this coupling constant are due primarily to variations in the contribution of the Pt 6s orbital to the Pt–N bond.

Since then, several other series of complexes have been examined in more detail, I,[2] II,[3] III,[4] with results consistent with J(Pt–N) variations being dominated by variations in platinum hybridization. It was also noted[3,4] that δ_N is sensitive to the ligand trans to N and that changes in δ_N correlate linearly with variations in δ_{Pt}.

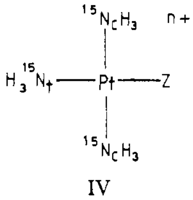


I, amine = $^{15}NH(CH_3)_2$
II, amine = $^{15}NH_2(CH_2)_5CH_3$

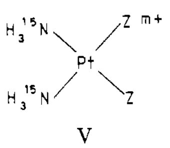


III

In part because of the biological activity of some ammine-platinum(II) complexes, ^{195}Pt and ^{15}N NMR methods have recently been extensively used to study reactions of ammine complexes of platinum(II) in solution and to characterize compounds, with use of complexes of ^{15}N-enriched ammonia.[5-16] Most of the authors in this area have commented on the dependence of the ^{15}N NMR parameters on the trans ligand and used this dependence in making assignments of the species present in solution. There has, however, been no systematic study of the NMR trans influence in ammine–platinum compounds and, in particular, no study that has allowed simultaneous measurement of the cis influence. In this work, we report ^{15}N and ^{195}Pt NMR data for a series of triammineplatinum(II) compounds, $Pt(^{15}NH_3)_3Z^{n+}$ (IV),[17] to determine the influence of Z on δ_{Pt} and on δ_N and ^1J(Pt–N) for N_t trans to Z and N_c cis to Z. Spectra were also measured for the series *cis*-$Pt(^{15}NH_3)_2Z_2^{m+}$ (V), for which ^{15}N NMR parameters are affected by both trans and cis influences of Z, to test the extent to which these influences are additive.



IV



V

Although Cleve's salt, $[Pt(NH_3)_3Cl]_2[PtCl_4]$, was reported in 1872,[18] and King[19] systematically studied the salts of triammineplatinum(II) complexes in 1948, more recent reports on the chemistry of these compounds have been sparse. ^{15}N or ^{195}Pt

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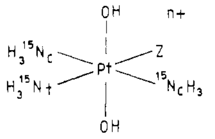
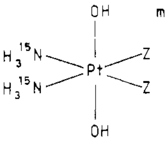
NMR data have previously been reported for only a few triammineplatinum(II) compounds.[5,10,12]

Peroxide oxidation of a platinum(II) complex usually gives initially a product in which two OH groups have added across the plane of the platinum(II) compound.[16,20] Peroxide oxidations of IV and V would be expected to yield the platinum(IV) series VI and VII, respectively, to allow comparison of NMR parameters with those of the platinum(II) compounds.



VI



VII

NMR data have been previously reported for only a few compounds of type VII[12,16] and for no compounds of type VI.

Experimental Section

Starting Materials. $^{15}NH_4Cl$, $(^{15}NH_4)_2SO_4$, and $Na^{15}NO_2$ ($^{15}N \geq 99\%$) were supplied by Novachem Ltd., Melbourne, Australia. $Ag^{15}NO_2$ was prepared from $Na^{15}NO_2$ by Ketelaar's method.[21] Aqueous solutions of $^{15}NH_4ClO_4$ were prepared by reaction of $^{15}NH_4Cl$ in solution with an equimolar amount of $AgClO_4$, followed by removal of precipitated AgCl by filtration. *cis*-$Pt(^{15}NH_3)_2Cl_2$, *cis*-$Pt(^{15}NH_3)_2(ONO_2)_2$, and solutions of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ and *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2]SO_4$ were prepared as previously described,[7,13] with use of the appropriate silver salt.

Preparation of "Stock Solutions" of $[Pt(^{15}NH_3)_3(H_2O)](ClO_4)_2$. In a typical preparation, 0.6 mmol of $^{15}NH_4ClO_4$ in 1 mL of water was added to 2 mL of 0.3 M *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ (0.6 mmol). NaOH solution (1 M) was added to increase the pH to 9.5–10.5. Careful pH control is important, since at pH ≤ 9 the oligomers $[Pt(NH_3)_2(\mu\text{-}OH)]_n^{n+}$ ($n = 2, 3$) tend to form rapidly,[7] and at pH ≥ 10.5, ammonia does not readily displace hydroxide from *cis*-$Pt(NH_3)_2(OH)_2$. The solution was heated at 70 °C for 15 min. NMR spectra (see Results) showed the presence of $Pt(^{15}NH_3)_3(OH)^+$, $Pt(^{15}NH_3)_4^{2+}$, and a small proportion of *cis*-$Pt(^{15}NH_3)_2(OH)_2$. $HClO_4$ (1 M) solution was added to reduce the pH below 3, to give a solution containing approximately 50% of the platinum present as $[Pt(^{15}NH_3)_3(H_2O)](ClO_4)_2$, with the remainder as $[Pt(^{15}NH_3)_4](ClO_4)_2$ and *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$.

Perchlorate was chosen as the counteranion for these solutions since, unlike nitrate or sulfate, it does not displace water from aquaplatinum(II) complexes in aqueous solution.[13]

Preparation of $[Pt(NH_3)_3Cl]Cl$. The following procedure was developed with ammine-^{14}N and then used for ammine-^{15}N compounds.

cis-$Pt(NH_3)_2(ONO_2)_2$ (0.30 g, 0.84 mmol) was dissolved with warming in 2 mL of water, and 0.0567 g of $(NH_4)_2SO_4$ (0.84 mmol of NH_4^+) was added. NaOH solution (1 M) was added to increase the pH to 9.5–10.5, and the solution was heated at 70 °C for 15 min. HCl solution (1 M) was added to reduce the pH to 1. The mixture was allowed to cool to room temperature and then allowed to stand for several hours in a refrigerator. The yellow precipitate of *cis*-$Pt(NH_3)_2Cl_2$ was filtered off and washed with 2 mL of cold water.

The filtrate and washings from several such preparations were combined. A small excess of aqueous K_2PtCl_4 solution was added, to precipitate a mixture of Cleve's salt, $[Pt(NH_3)_3Cl]_2[PtCl_4]$ (pink), and Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$. The solids were separated as described by Chugaev,[22] by dissolving the more soluble Cleve's salt in hot water, filtering the solution, and allowing $[Pt(NH_3)_3Cl]_2[PtCl_4]$ to reprecipitate with cooling. This compound was then converted to $[Pt(NH_3)_3Cl]Cl$ as described by King,[19] by reaction with $[Pt(NH_3)_4]Cl_2$, which precipitates the tetrachloroplatinate ion as $[Pt(NH_3)_4][PtCl_4]$. If $[Pt(^{15}NH_3)_3Cl]Cl$ is being prepared, $[Pt(^{14}NH_3)_4]Cl_2$ may be used at this stage. The overall yield of $[Pt(NH_3)_3Cl]Cl$, based on *cis*-$Pt(NH_3)_2(ONO_2)_2$, was 30%. Properties of the solid were as described by King.[19]

Other Triammineplatinum(II) Compounds. The following procedures were carried out with both ammine-^{14}N and -^{15}N complexes. Solutions containing $Pt(NH_3)_3(H_2O)^{2+}$ were prepared by reaction of $[Pt(NH_3)_3Cl]Cl$ with 2 mol equiv of $AgClO_4$ or $AgNO_3$ in aqueous solution. $[Pt(NH_3)_3Cl]NO_3$, $[Pt(NH_3)_3(ONO_2)]NO_3$, $[Pt(NH_3)_3(OSO_3)]$, and $[Pt(NH_3)_3(NO_2)]NO_3$ were prepared from $[Pt(NH_3)_3Cl]Cl$, by King's methods.[19]

Solutions containing $[Pt(NH_3)_3X]NO_3$ (X = Br, I, SCN) were prepared by mixing 0.04 g of $[Pt(NH_3)_3(ONO_2)]NO_3$ with 1 mol equiv of NaX in 2 mL of water. If excess NaX was present, *trans*-$Pt(NH_3)_2X_2$ formed. $[Pt(NH_3)_3(tu)](NO_3)_2$ was obtained in solution similarly, except that solid thiourea (tu) was added. Dimethyl sulfoxide (Me_2SO) reacted only slowly with $[Pt(NH_3)_3(H_2O)](NO_3)_2$ at 25 °C, but solutions of $[Pt(NH_3)_3(Me_2SO)](NO_3)_2$ were readily obtained by heating a solution containing equimolar amounts of the aqua complex and Me_2SO at 80 °C for several minutes.

Diammineplatinum(II) Complexes. Each of the compounds *cis*-$Pt(^{15}NH_3)_2X_2$ (X = Br, I, SCN, $^{15}NO_2$) was prepared by addition of 2 mol equiv of NaX to a solution of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$, followed by filtration of the sparingly soluble product. These compounds were insufficiently soluble at 25 °C to allow satisfactory ^{15}N and ^{195}Pt spectra to be obtained under equilibrium solubility conditions.

When a suspension of 0.4 mmol of *cis*-$Pt(^{15}NH_3)_2X_2$ (X = Cl, Br, I) in 5 mL of water was heated with 1 mol of equiv of $AgNO_3$ at 60 °C for 10 min, the mixture cooled, and AgX filtered off, the NMR spectra showed peaks due to *cis*-$Pt(^{15}NH_3)_2X_2$, *cis*-$Pt(^{15}NH_3)_2X(H_2O)^+$, and *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$ in varying proportions. This allowed spectra to be obtained not only for *cis*-$Pt(^{15}NH_3)_2X(H_2O)^+$, but for *cis*-$Pt(^{15}NH_3)_2X_2$ as well. Although the latter complexes did eventually precipitate from these solutions with standing, this deposition was slow, allowing sufficient time for spectra to be obtained. When thiocyanate was added to a solution of *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$, sufficient *cis*-$Pt(^{15}NH_3)_2(SCN)_2$ remained in solution long enough to allow ^{15}N, but not ^{195}Pt, spectra to be obtained. Even with use of equimolar amounts of the reactants, no detectable *cis*-$Pt(^{15}NH_3)_2(SCN)(H_2O)^+$ was formed. Addition of 1 mol equiv of $Na^{15}NO_2$ to a solution of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$ gave a solution containing unreacted *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$ (40%), *cis*-$Pt(^{15}NH_3)_2(^{15}NO_2)_2$ (40%) (which precipitated slowly enough to allow the ^{15}N ammine spectrum and a poor-quality ^{195}Pt spectrum to be obtained), and *cis*-$Pt(^{15}NH_3)_2(^{15}NO_2)(H_2O)^+$ (20%). A better ^{195}Pt spectrum of *cis*-$Pt(^{15}NH_3)_2(^{15}NO_2)_2$ was obtained at 90 °C, where the complex was much more soluble. There was no significant change in NMR parameters between 25 and 90 °C.

When 2 mol equiv of Me_2SO was added to a solution of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$, *cis*-$Pt(^{15}NH_3)_2(Me_2SO\text{-}S)(H_2O)^{2+}$ was formed, but no peaks assignable to *cis*-$Pt(^{15}NH_3)_2(Me_2SO)_2^{2+}$ were observed. After several days' standing, the solution showed peaks due to a number of other species, including $Pt(^{15}NH_3)_3(Me_2SO)^{2+}$, but *cis*-$Pt(^{15}NH_3)_2(MeSO)_2^{2+}$ was still not detected. By contrast, when 2 mol equiv of thiourea was added to a solution of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$, *cis*-$Pt(^{15}NH_3)_2(tu)_2^{2+}$ formed rapidly. When a solution was allowed to stand, a dark brown precipitate slowly formed, and NMR spectra showed that the amount of *cis*-$Pt(^{15}NH_3)_2(tu)_2^{2+}$ diminished and ammonia was being liberated.

Formation of Platinum(IV) Complexes in Solution. Solutions of *mer*-$Pt(^{15}NH_3)_3Z(OH)_2^{n+}$ (VI) were prepared by addition of 0.5 mL of 30% hydrogen peroxide solution to 2 mL of a solution containing $Pt(^{15}NH_3)_3Z^{n+}$ (IV). After the solution was allowed to stand at 25 °C for 15 min, the solution was heated at 70 °C for a further 10 min. If $Pt(^{15}NH_3)_4^{2+}$ and *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$ were also present in the starting solution, they were converted by this procedure to *trans*-$Pt(^{15}NH_3)_4(OH)_2^{2+}$ and *cis*-$Pt(^{15}NH_3)_2(H_2O)_2(OH)_2^{2+}$, respectively.

Solutions of $Pt(^{15}NH_3)_2X_2(OH)_2$ (VIII) were prepared in a similar way, except that the peroxide solution was added to a suspension of *cis*-$Pt(^{15}NH_3)_2X_2$ in 2 mL of water when X = Cl, Br, I, $^{15}NO_2$. For X = SCN, a lower temperature (40 °C) was used for the heating stage, as there was a tendency for *cis*-$Pt(NH_3)_2(SCN)_2$ to isomerize to the trans isomer at higher temperature.

Instrumentation and Techniques. ^{15}N (10.1 MHz) and ^{195}Pt (21.4 MHz) NMR spectra were obtained as previously described.[13] ^{15}N shifts were measured relative to the $^{15}NH_4^+$ signal from 5 M $^{15}NH_4{}^{15}NO_3$ in 2 M HNO_3 contained in a coaxial capillary (estimated error in δ_N ±0.2). ^{195}Pt NMR spectra were referenced to the ^{195}Pt signal of a separate aqueous solution of Na_2PtCl_6 (estimated error in δ_{Pt} ±5). All shifts are positive to lower shielding. The Pt–N coupling constants reported herein are the values obtained from the ^{15}N spectra, as the narrower line widths of ^{15}N signals permit greater accuracy in measurements (estimated error in J(Pt–N) ±1 Hz). High-temperature NMR spectra were measured with a JEOL NM PVT unit.

Results

Preparation of Compounds. The starting material for preparation of triammineplatinum(II) compounds, $[Pt(NH_3)_3Cl]Cl$, is not easily obtained in high yield. Reactions of *cis*- or *trans*-$Pt(NH_3)_2Cl_2$ with 1 mol equiv of ammonia or, under forcing conditions, of $Pt(NH_3)_4^{2+}$ with 1 mol equiv of chloride always give mixtures of $Pt(NH_3)_2Cl_2$, $[Pt(NH_3)_3Cl]Cl$, and $[Pt(N-$

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Table I. NMR Parameters of $Pt(^{15}NH_3)_3Z^{n+}$ (IV) in H_2O

			δ_N		influence on δ_N[a]		^1J(Pt–N), Hz		influence on J(Pt–N)[b]	
Z	δ_{Pt}	$\Delta(\delta_{Pt})$[d]	trans to Z	cis to Z	$T(\delta)_Z$, ppm	$C(\delta)_Z$, ppm	trans to Z	cis to Z	$T(J)_Z$, Hz	$C(J)_Z$, Hz
$^{15}NH_3$	−2580	0	−66.9	−66.9	0	0	287	287	0	0
H_2O (pH 1)	−2070	+510	−88.6	−63.8	−21.7	+3.1	376	299	+89	+12
OH^- (pH 10.3)	−2062	+518	−80.4	−64.3	−13.5	+2.6	286	294	−1	+7
OSO_3^{2-}	−2035	+545	−89.4	−62.3	−22.5	+4.6	362	303	+75	+16
Cl^-	−2353	+227	−69.8	−66.0	−2.9	+0.9	331	281	+44	−6
Br^-	−2492	+88	−63.2	−68.4	+3.7	−1.5	319	276	+32	−11
I^-	−2819	−239	−50.3	−72.2	+16.6	−5.3	289	269	+2	−18
$^{15}NO_2^-$[c]	−2390	+190	−70.9	−52.1	−4.0	+14.8	254	319	−33	+32
Me_2SO-*S*	−3213	−633	−44.5	−54.4	+22.4	+12.5	243	303	−44	+16
tu	−2962	−382	−46.6	−65.1	+20.3	+1.8	243	277	−44	−10
$-SCN^-$	−2798	−218	−50.8	−65.0	+16.1	+1.9	264	282	−23	−5

[a] From eq 2 and 3. [b] From eq 7 and 8. [c] $^1J(Pt-N)_{NO_2^-}$ = 574 Hz, $^2J(N-Pt-N)_{trans}$ = 6.9 Hz. [d] Shift relative to $Pt(^{15}NH_3)_4^{2+}$.

Table II. NMR Data for Diammineplatinum(II) Complexes *cis*-$Pt(^{15}NH_3)_2Z_2^{m+}$ and *cis*-$Pt(^{15}NH_3)_2YZ^{m+}$

			δ_N		^1J(Pt–N), Hz	
Z	Y (if Y ≠ Z)	δ_{Pt} obsd (calcd)[a]	trans to Z obsd (calcd)[a]	trans to Y obsd (calcd)[a]	trans to Z obsd (calcd)[a]	trans to Y obsd (calcd)[a]
H_2O[b]		−1593 (−1560)	−84.9 (−85.5)		390 (388)	
OH^-[b]		−1572 (−1544)	−76.9 (−77.8)		296 (293)	
OSO_3^{2-}[c]	H_2O	−1550 (−1525)	−86.3 (−86.8)	−84.0 (−85.1)	378 (374)	396 (392)
Cl^-		−2100 (−2126)	−67.6 (−68.9)		326 (325)	
Cl^-	H_2O	−1841 (−1843)	−65.8 (−66.7)	−88.9 (−87.7)	343 (343)	369 (370)
Cl^-	OH^-	−1826 (−1835)	−66.5 (−67.2)	−78.5 (−79.5)	347 (338)	288 (280)
Br^-		−2459 (−2404)	−62.6 (−64.7)		310 (308)	
Br^-	H_2O	−1934 (−1982)	−59.0 (−60.1)	−91.5 (−90.1)	332 (331)	362 (365)
Br^-	OH^-	−1915 (−1974)	−59.8 (−60.6)	−82.0 (−81.9)	337 (326)	282 (275)
I^-		−3198 (−3058)	−57.0 (−55.6)		311 (271)	
I^-	H_2O	−2224 (−2309)	−45.8 (−47.2)	−95.3 (−95.9)	300 (301)	350 (358)
$^{15}NO_2^-$[d]		−2214 (−2200)	−61.5 (−56.1)		278 (286)	
$^{15}NO_2^-$[e]	H_2O	−1981 (−1880)	−66.6 (−67.8)	−72.3 (−73.8)	269 (266)	415 (408)
SCN^-		(−3016)	−46.3 (−48.9)		267 (259)	
Me_2SO	H_2O	−2813 (−2703)	−41.8 (−41.4)	−68.0 (−76.1)	250 (255)	387 (392)
tu		−3400 (−3344)	−43.8 (−44.8)		237 (233)	

[a] For calculation, see text. [b] From ref 7. [c] From ref 13. [d] $^1J(Pt-N)_{NO_2^-}$ = 613 Hz, $^2J(N-Pt-N)_{trans}$ = 6.8 Hz. [e] $^1J(Pt-N)_{NO_2^-}$ = 571 Hz, $^2J(N-Pt-N)_{trans}$ = 7.3 Hz.

$H_3)_4]Cl_2$. Chugaev[22] attempted to improve the yield of $Pt(NH_3)_3Cl^+$ by generating the ammonia required to react with *cis*-$Pt(NH_3)_2Cl_2$ slowly in situ by hydrolysis of potassium cyanate. This remains the most widely used preparative method, although yields are near 50% only. Other reported methods for preparing triammineplatinum(II) compounds give relatively low yields.[23,24]

Chugaev's method is less suitable for the preparation of $[Pt(^{15}NH_3)_3Cl]Cl$, as it would require the use of $K(^{15}NCO)$, which is much more expensive on a mole basis than ^{15}N-substituted ammonium salts. By careful control of reaction conditions (see Experimental Section) it has been possible to obtain solutions containing approximately 50% $Pt(^{15}NH_3)_3(H_2O)^{2+}$, together with *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$ and $Pt(^{15}NH_3)_4^{2+}$, from *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ and $(^{15}NH_4)ClO_4$. In some cases, to obtain a solution of $Pt(^{15}NH_3)_3Z^{n+}$ to run NMR spectra, it sufficed to add excess ligand Z to such a mixture, as peaks due to *cis*-$Pt(^{15}NH_3)_2Z_2^{m+}$ and $Pt(^{15}NH_3)_4^{2+}$ seldom interfered. However, it was important to avoid the presence of excess ligand Z when this ligand has a relatively high trans effect (Z = I^-, NO_2^-, S-donors), to avoid reaction of $Pt(^{15}NH_3)_3Z^{n+}$ with excess Z to give *trans*-$Pt(^{15}NH_3)_2Z_2^{m+}$. When a solution was to be oxidized with peroxide, it was also desirable to avoid the presence of excess ligand Z, to prevent displacement of hydroxide in *mer*-$Pt(^{15}NH_3)_3Z(OH)_2^{n+}$ (VI) by Z. It was therefore necessary to prepare pure $[Pt(^{15}NH_3)_3(ONO_2)]NO_3$.

Reaction of excess chloride with a mixture of $Pt(^{15}NH_3)_3(H_2O)^{2+}$, *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$, and $Pt(^{15}NH_3)_4^{2+}$ gave $Pt(^{15}NH_3)_3Cl^+$ and $Pt(^{15}NH_3)_4^{2+}$ in solution, with most of the *cis*-$Pt(^{15}NH_3)_2Cl_2$ also formed precipitating out. The two soluble ions were then separated via their tetrachloroplatinate salts, as described by Chugaev[22] and King,[19] to give pure $[Pt(^{15}NH_3)_3Cl]Cl$, from which $[Pt(^{15}NH_3)_3(ONO_2)](NO_3)$ was obtained by reaction with $AgNO_3$.[19]

As indicated above, more careful control of reaction conditions was required when Z was a ligand with relatively high trans effect, to avoid displacement of one of the ammine ligands. We were unsuccessful in attempting to prepare $Pt(NH_3)_3(CN)^+$. For example, even when small amounts of NaCN were added to a solution of $Pt(^{15}NH_3)_3(H_2O)^{2+}$, a complex mixture of species was formed in solution. Once $Pt(NH_3)_3(CN)^+$ forms, the high trans effect of cyanide must so labilize the trans ammine that its displacement becomes competitive with displacement of coordinated water from $Pt(NH_3)_3(H_2O)^{2+}$. Attempts to prepare $[Pt(NH_3)_3(CN)]NO_3$ by reaction of $[Pt(NH_3)_3Cl]NO_3$ with silver cyanide were also unsuccessful.

The NMR spectra are consistent with peroxide oxidation giving a simple addition of two hydroxo ligands across the plane of the platinum(II) complex (see below). The precise protonation state of these complexes is unknown but, except in very acidic solution, probably correspond to the dihydroxo formulations VI or VII. When Z = H_2O, there will obviously be equilibria between isomers protonated at different sites. These aqua complexes have not been included in any of the NMR correlations discussed below.

NMR Spectra. NMR data for triammine- and *cis*-diammineplatinum(II) complexes are presented in Tables I and II, respectively.

The ^1H-decoupled ^{15}N NMR spectrum of a typical triammineplatinum(II) complex, $Pt(^{15}NH_3)_3Z^{n+}$ (IV), in H_2O consisted of two singlets, each with "satellites" from coupling to ^{195}Pt (Figure 1a). As the two signals usually gave the statistically predicted intensity ratio 2:1, there can be only minor differences

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Table III. NMR Parameters for *mer*-Triammineplatinum(IV) Complexes, $Pt(^{15}NH_3)_3Z(OH)_2^+$ (VI)

Z	δ_{Pt}	$\Delta(\delta_{Pt})^d$	δ_N trans to Z	δ_N cis to Z	influence on δ_N[a] $T(\delta)_Z$, ppm	influence on δ_N[a] $C(\delta)_Z$, ppm	^1J(Pt–N), Hz trans to Z	^1J(Pt–N), Hz cis to Z	influence on J(Pt–N)[a] $T(J)_Z$, Hz	influence on J(Pt–N)[a] $C(J)_Z$, Hz
$^{15}NH_3$	+583	0	−42.7	−42.7	0	0	261	261	0	0
"H_2O"	+1157	*b*	−54.6	−38.8	*b*	*b*	303	262	*b*	*b*
OH^-	+1116	+533	−51.0	−40.4	−8.3	+2.3	255	268	−6	+7
Cl^-	+659	+76	−38.2	−41.9	+4.5	+0.8	273	256	+12	−5
Br^-	+475	−118	−30.6	−44.6	+12.1	−1.9	247	254	−14	−7
I^-	+74	−509	−21.1	−50.2	+21.6	−7.5	193	255	−68	−6
$^{15}NO_2^{-\,c}$	+908	+325	−51.2	−32.1	−8.5	+10.6	228	282	−33	+21
$-SCN^-$	+130	−453	−24.5	−43.2	+18.2	−0.5	215	260	−46	−1
tu	+190	−393	−23.4	−44.7	+19.3	−2.0	196	257	−65	−4

[a] See text. [b] Not calculated, owing to uncertainty on protonation state. [c] $^1J(Pt-N)_{NO_2^-}$ = 409 Hz, $^2J(N-Pt-N)_{trans}$ = 9.8 Hz. [d] Shift relative to *trans*-$Pt(^{15}NH_3)_4(OH)_2^{2+}$.

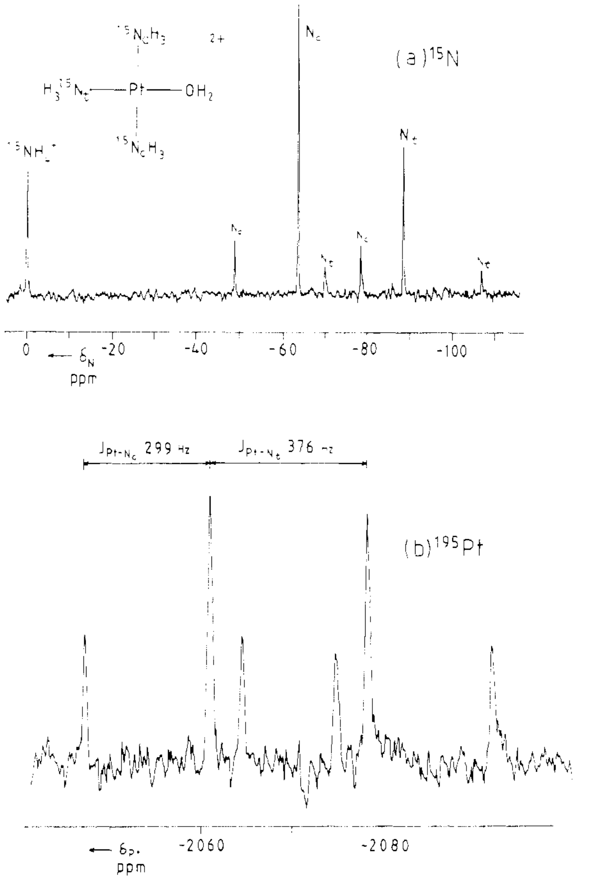

Figure 1. ^1H-decoupled NMR spectra of a solution of $[Pt(^{15}NH_3)_3(H_2O)](ClO_4)_2$ in H_2O: (a) 10.1-MHz ^{15}N; (b) 21.4-MHz ^{195}Pt.

Table IV. NMR Parameters for *cis*-Diammineplatinum(IV) Complexes, $Pt(^{15}NH_3)_2Z_2(OH)_2^{n+}$ (VII)

Z	δ_{Pt} obsd (calcd)[a]	δ_N obsd (calcd)[a]	^1J(Pt–N), Hz obsd (calcd)[a]
"H_2O"[b]	+1730	−50.9	305
OH^-	+1735 (1649)	−47.2 (−48.7)	268 (262)
Cl^-	+860 (735)	−37.9 (−37.4)	271 (268)
Br^-	+481 (367)	−29.1 (−32.5)	247 (240)
I^-	−392 (−435)	−20.9 (−28.6)	199 (187)
$^{15}NO_2^-$	+1291 (1233)	−42.2 (−40.6)	248 (249)
SCN^-	−274 (−323)	−20.9 (−24.9)	221 (214)
tu	−162 (−203)	−23.2 (−25.4)	199 (192)

[a] For calculated values, see text. [b] Protonation state uncertain.

Table V. Values of ^2J(Pt–N–H) for Diammineplatinum(II) Complexes *cis*-$Pt(^{15}NH_3)_2Z^{m+}$

Z	^1J(Pt–N), Hz	^2J(Pt–N–H), Hz	Z	^1J(Pt–N), Hz	^2J(Pt–N–H), Hz
H_2O[a]	390	71	$^{15}NH_3$	287	56
μ-OH[b]	342	66	tu	237	50
OH[c]	296	56			

[a] From ref 13. [b] Bridging hydroxide in $[Pt(^{15}NH_3)_2(\mu-OH)]_2^{2+}$. [c] Terminal hydroxide in *cis*-$Pt(^{15}NH_3)_2(OH)_2$.

in relaxation times and nuclear Overhauser effect for the different sets of ammine ligands in a compound. The ^1H-decoupled ^{195}Pt spectrum showed a doublet of triplets due to coupling with two equivalent N_c nuclei and one N_t nucleus (Figure 1b). Where the two Pt–N coupling constants are similar (e.g., $Pt(^{15}NH_3)_3(OH)^+$), the inner lines of this pattern coincided to give a 1:3:3:1 quartet. Solutions of $[Pt(^{15}NH_3)_3(ONO_2)]NO_3$ and $[Pt(^{15}NH_3)_3(H_2O)](ClO_4)_2$ showed only peaks due to $Pt(^{15}NH_3)_3(H_2O)^{2+}$. Solutions of $Pt(^{15}NH_3)_3(OSO_3)$ showed additional peaks assigned to the sulfato complex in solution in equilibrium with the aqua complex.

The ^1H-decoupled ^{15}N and ^{195}Pt spectra of *cis*-diammineplatinum(II) complexes, *cis*-$Pt(^{15}NH_3)_2Z_2^{m+}$ (V) were simpler. The ^{15}N spectrum showed a singlet with satellites and the ^{195}Pt spectrum a 1:2:1 triplet. For *cis*-$Pt(^{15}NH_3)_2YZ^{m+}$, with Y and Z different ligands, two singlets with satellites and a doublet of doublets were observed in the ^{15}N and ^{195}Pt spectra, respectively. No ^{15}N–Pt–^{15}N couplings were observed.

When Z = $^{15}NO_2^-$, additional splittings were observed in ^{15}N and ^{195}Pt spectra. An ammine nitrogen trans to nitrite gave a doublet due to small ^{15}N–Pt–^{15}N coupling, while ammines cis to nitrite did not couple (Figure 2a). The nitrite ^{15}N signals were not observed. The long relaxation times and lack of nuclear Overhauser effect for ^{15}N nuclei in such environments make their observation difficult.[25] ^{195}Pt spectra showed the expected multiplets. For example, Figure 2b shows the ^{195}Pt spectrum of $Pt(^{15}NH_3)_3(^{15}NO_2)^+$, which is a doublet of doublets of triplets (with coincidence of some peaks due to the accident that $J(Pt-N)_{NO_2^-} \approx J(Pt-N_t) + J(Pt-N_c)$).

NMR parameters were, in general, insensitive to changes in pH, except for Z = H_2O, which was converted to Z = OH^- at high pH.

^2J(Pt–N–H) may be obtained, in principle, from the ^1H-coupled ^{195}Pt spectrum of any of the complexes in Table I and II. However, because this coupling splits the ^{195}Pt signal into many lines, and nuclear Overhauser enhancement is lost, long accumulation times with concentrated samples are required. These coupling constants were therefore obtained for only a few of the more soluble diammine complexes *cis*-$Pt(^{15}NH_3)_2Z_2^{m+}$ (V), which give simpler spectra than triammine complexes (VI). These coupling constants are given in Table V.

NMR data for *mer*-triammine- and *cis*-diammineplatinum(IV) complexes are given in Tables III and IV, respectively. The ^1H-decoupled ^{15}N and ^{195}Pt spectra showed the same types of patterns as the platinum(II) complexes from which they were derived. In each case, a single set of peaks was observed: the ^1H-decoupled ^{15}N spectrum of the triammine complexes showed two singlets with satellites, with intensity ratio 2:1 (except for Z

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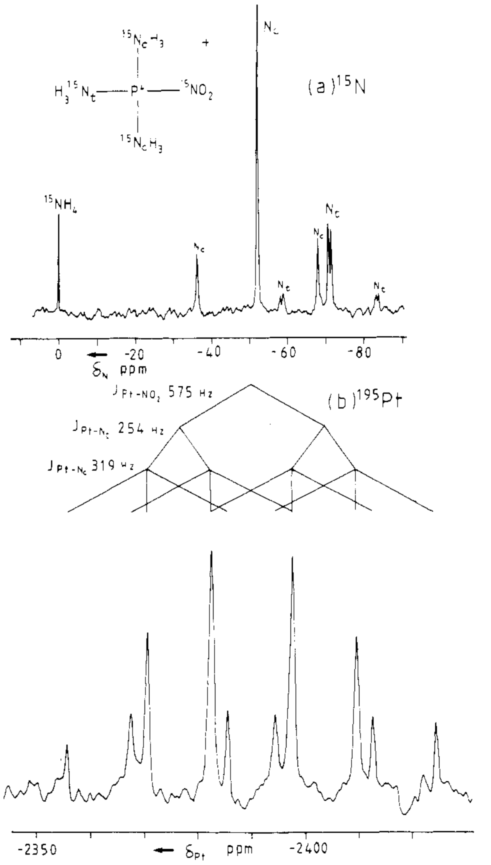
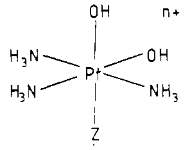
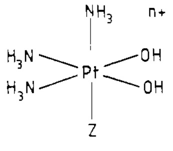


Figure 2. ^1H-decoupled NMR spectra of a solution of $[Pt(^{15}NH_3)_3(^{15}NO_2)]NO_3$ in H_2O: (a) 10.1-MHz ^{15}N (ammine region); (b) 21.4-MHz ^{195}Pt.

= I^-, mentioned below), and the ^{195}Pt spectrum a doublet of triplets. Only one isomer was therefore formed in each case. A reviewer has pointed out that these patterns do not necessarily prove that the peroxide addition is, as usual,[16,20] trans across the square plane, as isomers VIII and IX would give qualitatively



VIII



IX

similar patterns. For Z = OH^-, the *fac* isomer IX can be ruled out, since all ^{15}N nuclei would be equivalent then. For the oxidation product of $Pt(^{15}NH_3)_4{}^{2+}$, only trans addition of peroxide is possible, to give isomer VI (Z = NH_3), as only for this isomer are all ^{15}N nuclei equivalent. It is unlikely that, for the other compounds, the sole product formed would be a different isomer. The correlations between NMR parameters noted below are also consistent with geometry VI. Similarly, the observed NMR patterns do not allow isomers other than VII to be eliminated as the products of oxidation of *cis*-$P(^{15}NH_3)_2Z_2{}^{m+}$, but other isomers are unlikely. *mer*-$Pt(^{15}NH_3)_3I(OH)_2{}^+$ was unusual in that the intensity of the ^{15}N peak from the ammine trans to iodide was always less than half that from ammine cis to iodide. The intensity ratio was not altered when pulse width and pulse delay were varied and is probably due to different nuclear Overhauser enhancements.

The ^1H-decoupled ^{15}N and ^{195}Pt NMR spectra of a fresh solution of $Pt(^{15}NH_3)_2(H_2O)_2(OH)_2{}^{2+}$, obtained by peroxide oxidation of *cis*-$Pt(^{15}NH_3)_2(H_2O)_2{}^{2+}$, showed respectively a singlet with satellites and a 1:2:1 triplet. When this solution was allowed to stand, many additional peaks grew in the spectra, owing to formation of hydroxo-bridged oligomers (cf. oligomerization of *cis*-$Pt(NH_3)_2(OH)(H_2O)^+$ [7,9,13]). When the pH of a fresh solution was raised from 1.5 to 5.0, changes in the ^{15}N and ^{195}Pt spectra occurred that were consistent with deprotonation to *cis*-$Pt(^{15}NH_3)_2(OH)_4$ (Table IV). No further significant changes occurred in the spectra up to pH 13, and alkaline solutions did not change with time. A ^1H-coupled ^{195}Pt spectrum in H_2O at pH 13 showed no Pt-N-H coupling, owing to rapid exchange of ammine protons with those of solvent water. This is not surprising in view of the known acidity of ammine protons in platinum(IV) compounds.[26] Ismail et al.[27] noted that the ^1H-decoupled ^{195}Pt spectrum of *cis*-$Pt(NH_2(i\text{-}C_3H_7))_2Cl_2$ in D_2O slowly broadens as the amine protons were deuterated but that the spectrum of the platinum(IV) derivative $Pt(NH_2(i\text{-}C_3H_7))_2Cl_2(OH)_2$ does not change with time. They suggested that this was due to very slow exchange of the amine protons with solvent deuterium. In the light of our observation above, it is more likely that their platinum(IV) complex had undergone N-deuteration before their spectrum was run.

Discussion

^{195}Pt Chemical Shifts. From the ^{195}Pt chemical shifts for the series $Pt(^{15}NH_3)_3Z^{n+}$ listed in Table I, it is apparent that δ_{Pt} depends primarily on the donor atom through which Z coordinates. The order of increasing shielding is $OSO_3{}^{2-} < OH^- \leq H_2O < Cl^- < NO_2{}^- < Br^- < NH_3 < SCN^- < I^- <$ tu $< Me_2SO$-*S*, in accord with the large amount of empirical data in the literature for platinum(II) chemical shifts.[28-32]

Variations in δ_{Pt} are usually considered to be caused mainly by variations in the paramagnetic contribution to the shielding, σ_P. Using Ramsey's equations for σ_P,[33] Dean and Green[30] derived the following expression for σ_P for a platinum(II) complex of C_{2v} symmetry

$$\sigma_P = -\frac{e^2h^2}{3m^2c^2}\langle r^{-3}\rangle C_{a_{1g}}{}^2\left[8C_{a_{2g}}{}^2(E(^1A_{2g}) - E(^1A_{1g}))^{-1} + 4C_{e_g}{}^2(E(^1E_{1g}) - E(^1A_{1g}))^{-1}\right] \quad (1)$$

where $\langle r^{-3}\rangle$ is an average over the radial 5d functions used as a basis set and C_n values denote the coefficients of the platinum d orbitals to the molecular orbitals involved in the electronic transitions. They pointed out that, if there were no covalent bonding, these would be pure d orbitals ($C_{a_{1g}} = C_{a_{2g}} = C_{e_g} = 1$). σ-bonding involving the $d_{x^2-y^2}$ orbital will decrease $C_{a_{1g}}$. Donation of π-electrons from the metal to the ligands will decrease C_{e_g} and $C_{a_{2g}}$. In the series *trans*-$Pt(H)X(PEt_3)_2$, they showed that the order of increasing shielding is related to measures of covalence such as the nephelauxetic effect of X and equilibrium constants. The so-called "heavy-atom effect",[31,32] where donor atoms with high atomic weight cause pronounced shifts to higher shielding, is then seen as a consequence of a large contribution of the Pt 5d orbitals to covalent bonds with these atoms, due to favorable orbital overlap and a matching of orbital energies. Variations in the electronic excitation energies are also probably important,[34] with increases in the position of a ligand in the spectrochemical series also causing increased shielding of the metal nucleus. Variations may also occur in $\langle r^{-3}\rangle$, and in the effect of diamagnetic and paramagnetic circulation of the electrons of the donor atom,[31,32,34] but these are probably of lesser importance.

It has been shown that δ_{Pt} varies regularly with increasing substitution of one ligand Y by a second ligand X in several series of platinum(II) complexes, PtX_nY_{4-n}, although the dependence of *n* is not linear over the whole range 0-4.[34-37] It is, then, not

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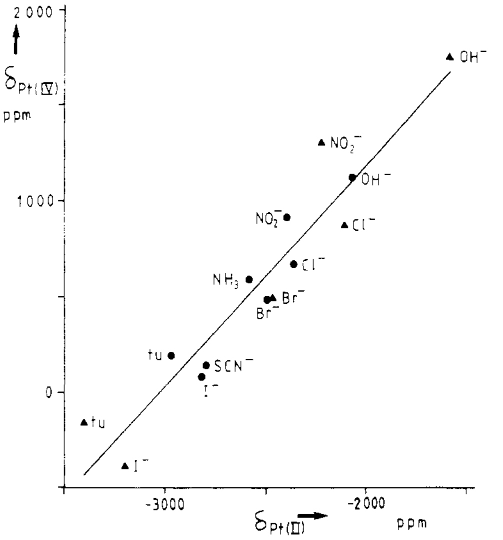


Figure 3. Plot of δ_{Pt} for platinum(IV) complexes against δ_{Pt} for corresponding platinum(II) complexes: (●) *mer*-$Pt(NH_3)_3Z(OH)_2^{n+}$ (VI) and $Pt(NH_3)_3Z^{n+}$ (IV); (▲) $Pt(NH_3)_2Z_2(OH)_2^{m+}$ (VII) and *cis*-$Pt(NH_3)_2Z_2^{m+}$ (V).

surprising that the effect of substituting two ammine ligands of $Pt(NH_3)_4^{2+}$ to give *cis*-$Pt(NH_3)_2Z_2^{m+}$ or *cis*-$Pt(NH_3)_2YZ^{m+}$ may be predicted, to a good approximation, from the shifts for $Pt(NH_3)_3Z^{n+}$ and $Pt(NH_3)_3Y^{n+}$, by assuming that the effects of the two substitutions are additive. Values of δ_{Pt} predicted on this simple basis are included in Table II, for comparison with the experimental values.

It has previously been noted[32,38] that the overall order of ligand effects on δ_{Pt} is similar for compounds of platinum(IV) and -(II). Figure 3 shows a plot of δ_{Pt} for platinum(IV) compounds against δ_{Pt} for the platinum(II) compounds from which they were derived by peroxide oxidation. The correlation is close to linear, with the slope of the line of best least-squares fit 1.15 ± 0.11. This indicates that changing one of the six ligands bound to platinum(IV) has at least as great an effect on δ_{Pt} as changing one of the four ligands bound to platinum(II).

Despite the clear overall relationship between the platinum shifts in the two oxidation states, there are some minor deviations that are worthy of comment. For example, in the series *mer*-$Pt(^{15}NH_3)_3Z(OH)_2^{n+}$ (VI) the order of increasing shielding is $OH^- < NO_2^- < Cl^- < NH_3 < Br^- <$ tu $< -SCN^- < I^-$. From comparison with the order given above for the platinum(II) series $Pt(^{15}NH_3)_3Z^{n+}$, it is evident that the halide ligands cause shifts to relatively higher shielding in the platinum(IV) series. Kerrison and Sadler[36] have previously noted the inversion of the effect of replacing chloride by nitrite on platinum(IV) shifts relative to platinum(II). It is tempting to ascribe these differences to a relatively stronger bonding interaction with the halides for platinum in the higher oxidation state.

The overall relationship illustrated in Figure 3 would appear to indicate that π-bonding effects are not very important in determining δ_{Pt} for Pt(II) complexes, as it would be expected that π-bonding to ligands such as I^- and S-donors would be much reduced in the corresponding platinum(IV) compounds.[39]

As with the platinum(II) compounds, the effect on δ_{Pt} of replacing two of the ammine ligands of *trans*-$Pt(^{15}NH_3)_4(OH)_2^{2+}$ with Z is approximately twice that of replacing one. Shifts calculated on this basis are included, with the experimental values, in Table IV.

^{15}N Chemical Shifts. As previously noted,[4] coordination of an amine to a metal causes a shift of the ^{15}N resonance to higher shielding. For platinum–ammine complexes, the ^{15}N nuclei are always more shielded than in $^{15}NH_4^+$.[6,7,9-13,16] Among the factors that will contribute to δ_N will be the influence of the same motions of the metal electrons that are responsible for the paramagnetic contribution to the chemical shift of the metal nucleus. This influence has been most thoroughly investigated, both theoretically[40,41] and experimentally for hydride complexes. At a distance of approximately 2 Å from the metal, the effect of these electron motions is to increase the hydride shielding (i.e., the opposite direction to the effect on the metal nucleus itself). When the ligand trans to hydride is varied, the major influence on δ_H comes from the variation in the effect on the hydride ligand of the metal paramagnetism. This results in an inverse linear correlation if δ_H trans to X is plotted against δ_{Pt} in a series of complexes *trans*-$Pt(H)XL_2$.[30] Because of the anisotropy of this paramagnetism, the effect of varying a ligand cis to hydride is different. Whereas for hydride trans to X the order of increasing shielding is $I < Br < Cl$, for hydride cis to X it is $Cl < Br < I$.[40,42]

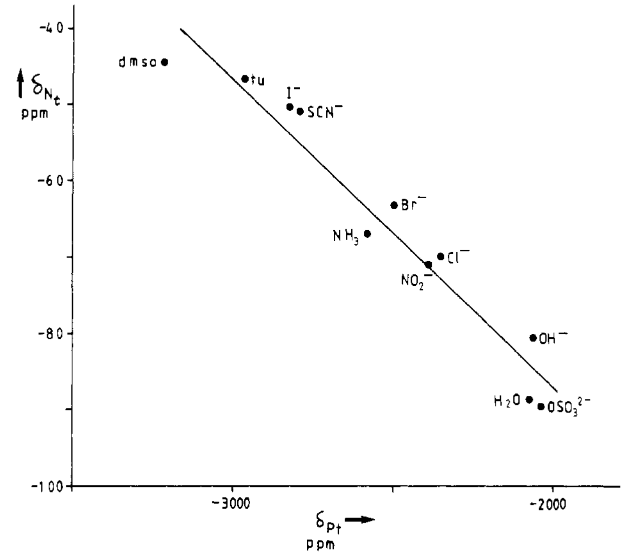
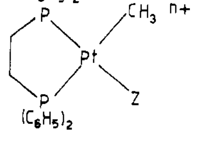


Figure 4. Plot of δ_N trans to Z (δ_{N_t}) against δ_{Pt} for the series $Pt(^{15}NH_3)_3Z^{n+}$ (IV).

For nuclei such as ^{13}C, ^{15}N, and ^{31}P similar effects would be expected to be superimposed on those arising from changes in the electronic structure of the atom under consideration. There have been no extensive series studied in which changes in δ_C or δ_P trans to a variable ligand Z are compared with variation in δ_{Pt}. However, the ordering of δ_C or δ_P within such a series usually approximates the order inverse to that expected for δ_{Pt}. For example, in the series *trans*-$Pt(CH_3)Z(P(CH_3)_2C_6H_5)_2^{n+}$, the order of increasing carbon shielding is $I^- < CN^- < Cl^- < NC_5H_5 < NO_2^-$,[43] and in the series $Pt(CH_3)Z((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)^{n+}$ (X), the shielding of the P atom trans to Z increases in the order $CN^- < I^- \approx -SCN^- < Cl^- < OH^- < NO_2^- < ONO_2^-$.[44]



X

For δ_N, Motschi et al.[3] have noted that, in the series *trans*-$PtCl_2(^{15}NH_2(CH_2)_5CH_3)L$ (II), there is an inverse linear correlation with δ_{Pt}. In our series $Pt(^{15}NH_3)_3Z^{n+}$ (IV), there is also a good inverse linear correlation between the shift for the ammine

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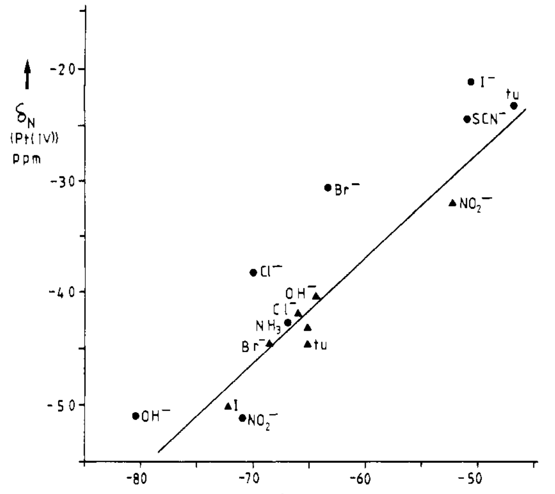

Figure 5. Plot of δ_N in *mer*-Pt($^{15}NH_3$)$_3$Z(OH)$_2^{n+}$ (VI) against δ_N in corresponding complexes Pt($^{15}NH_3$)$_3$Z^{n+} (IV): (●) N trans to Z (N_t); (▲) N cis to Z (N_c). The line drawn is the best least-squares fit ignoring points for N_t trans to halides.

N atom trans to Z (δ_{N_t}) and δ_{Pt} (Figure 4), paralleling the behavior of hydride chemical shifts. For the complexes studied, δ_{N_t} varies from −44.5 to −89.4, a range of 44.9. The range of δ_{N_c}, cis to Z, is smaller, from −52.1 to −72.2 ppm (range 20). There is no observable correlation with δ_{Pt}. It is interesting to note, however, that, with halides, the N_c shielding increases in the order $Cl^- < Br^- < I^-$, the inverse of the order for N_t. In this respect also, then, the behavior of δ_N parallels that of δ_H for transition-metal hydrides. The theory of these ^{15}N chemical shifts cannot at this stage be developed very far, but if the widely accepted general theory of hydride shifts[40,41] is correct, it will also provide the basis for dealing with δ_N in ammine complexes. δ_{N_t} is then affected by Z primarily by the extent to which platinum d orbitals are used in bonding to Z and the extent to which the ligand field of Z splits the energy levels of the metal d orbitals.

The trans and cis influence of Z on δ_N in the series Pt($^{15}NH_3$)$_3$Z^{n+} (IV) may be expressed numerically, relative to Z = NH$_3$, by the parameters $T(\delta)_Z$ and $C(\delta)_Z$, respectively, defined as

$$T(\delta)_Z = \delta_{N_t}(\mathrm{Pt(NH_3)_3Z^{n+}}) - \delta_N(\mathrm{Pt(NH_3)_4^{2+}}) \qquad (2)$$

$$C(\delta)_Z = \delta_{N_c}(\mathrm{Pt(NH_3)_3Z^{n+}}) - \delta_N(\mathrm{Pt(NH_3)_4^{2+}}) \qquad (3)$$

These values are included in Table I.

If these parameters are transferable from one complex to another, then

$$\delta_N(cis\text{-}\mathrm{Pt(^{15}NH_3)_2Z_2^{m+}}) = \delta_N(\mathrm{Pt(NH_3)_4^{2+}}) + T(\delta)_Z + C(\delta)_Z \qquad (4)$$

and

$$\delta_N(\text{trans to Y in } cis\text{-}\mathrm{Pt(^{15}NH_3)_2YZ^{m+}}) = \delta_N(\mathrm{Pt(NH_3)_4^{2+}}) + T(\delta)_Y + C(\delta)_Z \qquad (5)$$

The ^{15}N chemical shifts for diammineplatinum(II) compounds calculated by using eq 4 and 5 are included in Table II, together with the experimental values. Correspondence between the two values is generally good, within 2.6 ppm except for *cis*-Pt($^{15}NH_3$)$_2$($^{15}NO_2$)$_2$ (deviation 5.4 ppm) and ammine trans to H$_2$O in *cis*-Pt($^{15}NH_3$)$_2$(Me$_2$SO-*S*)(H$_2$O)$^{2+}$ (deviation 8.1 ppm).

For the platinum(IV) complexes the ammine nitrogen nuclei are, in general, less shielded than for the platinum(II) complexes. For the series *mer*-Pt($^{15}NH_3$)$_3$Z(OH)$_2^{n+}$, δ_{N_t} correlates inversely with δ_{Pt}, as with the platinum(II) series. Figure 5 shows a plot of the shifts (N_t and N_c) for the triammineplatinum(IV) complexes against those for the platinum(II) analogues. Most of the points lies close to a single line, but significant deviations occur for ammine groups trans to a halide (N_t is relatively less shielded in the Pt(IV) complexes). That is, the halide ions have higher trans influences in the platinum(IV) series than in the platinum(II) series. This is consistent with the increased platinum(IV) shielding in halide complexes noted above and the effect of halides on J(Pt(IV)–N_t) discussed below.

Trans- and cis-influence parameters for δ_N were defined for the platinum(IV) complexes *mer*-Pt($^{15}NH_3$)$_3$Z(OH)$_2^{n+}$ in a way similar to those for the platinum(II) series Pt($^{15}NH_3$)$_3$Z^{n+} (eq 2 and 3), but with *trans*-Pt($^{15}NH_3$)$_4$(OH)$_2^{2+}$ as the reference compound. These values are included in Table III and were used to calculate predicted ^{15}N shifts for the complexes Pt($^{15}NH_3$)$_2$Z$_2$(OH)$_2^{n+}$ (VII). These calculated values are included in Table IV, for comparison with the experimental values. As for the platinum(II) analogues, correspondence is quite close (deviation <4 ppm except for Z = I$^-$, 7.7 ppm, perhaps owing to steric crowding).

It is interesting to compare these results with the ^{15}N shifts observed for the series Co($^{15}NH_3$)$_5$Z^{n+},[45,46] for which the order of increasing shielding for ammine trans to Z is $NO_2^- < NH_3 < Br^- < Cl^- < H_2O$. Nitrite occupies a very different position in a series which is otherwise similar to that for platinum(IV). Nitrite causes significant deshielding of ammine cis to itself, as with the platinum complexes.

^{195}Pt–^{15}N Coupling Constants. One-bond coupling constants between a transition-metal nucleus and a ligand nucleus (e.g., ^{1}H, ^{13}C, ^{31}P) have usually been interpreted in terms of the dominance of the Fermi contact contribution to the coupling.[30,39,43,44,47] Pregosin et al.[1,3,4] have discussed variations in $^1J(^{195}\mathrm{Pt}\text{–}^{15}\mathrm{N})$ in terms of this theory, which, if an average singlet–triplet excitation energy, ΔE, is used, gives the simplified expression (6), where α_i^2

$$^1J(\mathrm{Pt\text{–}N}) \propto \alpha_{Pt}^2\alpha_N^2[\psi_{Pt(6s)}(0)]^2[\psi_{N(2s)}(0)]^2/\Delta E \qquad (6)$$

is the contribution of the *ns* orbital to the bonding orbital used by i and $[\psi_{i(ns)}(0)]^2$ is the *ns* electron density at the nucleus i. They showed that ^1J(Pt–N) in the series *trans*-PtCl$_2$($^{15}NH_2$(CH$_2$)$_5$CH$_3$)L (II) correlated linearly with ^1J(Pt–P) for corresponding complexes in the series *trans*-PtCl$_2$(P(*n*-C$_4$H$_9$)$_3$)L. They interepreted this as indicating that variations in both series of coupling constants are dominated by variations in α_{Pt}^2, the Pt(6s) contribution to the Pt–N or Pt–P bond.

For our series Pt($^{15}NH_3$)$_3$Z^{n+}(IV), the order of decreasing Pt–N_t coupling trans to Z (increasing NMR trans influence) is $H_2O > -OSO_3^{2-} > Cl^- > Br^- > I^- \approx OH^- \approx NH_3 > SCN^- > NO_2^- >$ Me$_2$SO-*S* ≈ tu, similar to the series obtained from Pt–H, Pt–C, and Pt–P coupling constants and consistent with the dominance of the s-orbital contribution. In this series, the total variation in ^1J(Pt–N_t), 133 Hz, is much greater than that in ^1J(Pt–N_c), cis to Z, 50 Hz. That is, the cis influence is significant but is smaller than the trans influence. The order of decreasing Pt–N_c couplings is $NO_2^- >$ Me$_2$SO-*S* $\approx OSO_3^{2-} > H_2O > OH^- > NH_3 > Cl^- \approx SCN^- >$ tu $\approx Br^- > I^-$. There is no obvious relationship between this series and the trans-influence series, and the order is quite different from that obtained from ^1J(Pt–P) cis to Z in the series VIII. However, there is a definite trend for the $^{15}N_c$ nucleus to become more shielded as ^1J(Pt–N_c) decreases in magnitude (Figure 6). Both δ_{N_c} and J(Pt–N_c) are presumably reflecting properties of the Pt–N_c bonds.

There is a much poorer correlation between ^1J(Pt–N_t) and δ_{N_t}. The overall tendency is for the N_t nucleus to become less shielded as ^1J(Pt–N_t) decreases in magnitude, but there are significant differences in the two series in detail, since the two parameters depend on different electronic effects (it is an oversimplification but is perhaps useful to consider that the coupling constant is mainly sensitive to effects of Z on the Pt(6s) orbital and δ_{N_t} is mainly sensitive to the effect of Z on the Pt(5d) orbitals). J(Pt–N) is very much less trans to hydroxide than trans to water, although δ_{N_t} hardly changes. On the other hand, ligands with heavy donor

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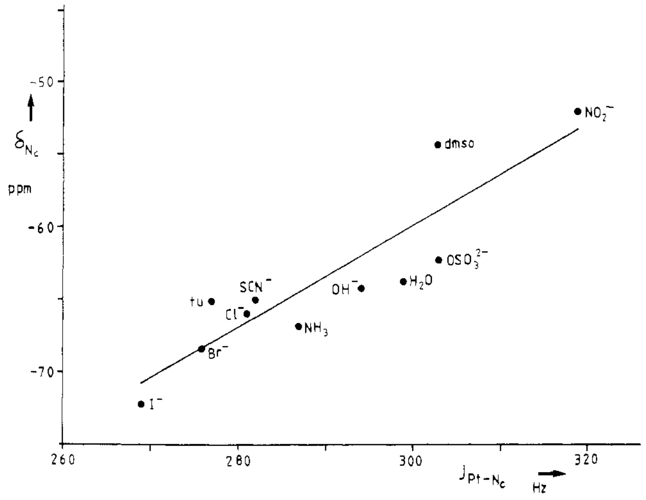

Figure 6. Plot of ^{15}N chemical shifts cis to Z (δ_{N_c}) against J(Pt–N$_c$) for the series Pt($^{15}NH_3)_3Z^{n+}$ (IV).

atoms (Br^-, I^-, S-donors) are differentiated more clearly from N-donors (NO_2^-, NH_3) by the δ_{N_t} values. Both the coupling constant and ^{15}N chemical shift are therefore independently useful in characterizing platinum–ammine complexes.

It is possible to use the coupling constants in Pt($^{15}NH_3)_3Z^{n+}$ to define trans and cis influences on J(Pt–N), $T(J)_Z$ and $C(J)_Z$, in a way similar to that for the parameters for δ_N:

$$T(J)_Z = {}^1J(\text{Pt–N}_t)_{\text{Pt(NH}_3)_3\text{Z}^{n+}} - {}^1J(\text{Pt–N})_{\text{Pt(NH}_3)_4{}^{2+}} \qquad (7)$$

$$C(J)_Z = {}^1J(\text{Pt–N}_c)_{\text{Pt(NH}_3)_3\text{Z}^{n+}} - {}^1J(\text{Pt–N})_{\text{Pt(NH}_3)_4{}^{2+}} \qquad (8)$$

These values are included in Table I. The coupling constants for *cis*-Pt($^{15}NH_3)_2Z_2^{m+}$ (V) and *cis*-Pt($^{15}NH_3)_2YZ^{m+}$ were calculated on the basis that the parameters $T(J)_Z$ and $C(J)Z$ are transferable from one complex to another, in an analogous way to the ^{15}N chemical shifts (eq 5 and 6). These predicted values are included in Table II, for comparison with the experimental values. Agreement is generally good, within a few hertz in most cases. The only serious discrepancy is for *cis*-Pt($^{15}NH_3)_2I_2$, for which the observed Pt–N coupling constant, 311 Hz, is much larger than predicted, 271 Hz. Since experimental coupling constants for *cis*-Pt($^{15}NH_3)_2I(H_2O)^+$ are close to the predicted values, the "anomaly" with *cis*-Pt($^{15}NH_3)_2I_2$ is most probably caused by steric interaction between the bulky iodide ligands. There was no significant different between experimental and predicted values for δ_N for this complex.

Figure 7 shows a plot of the Pt–N$_t$ and Pt–N$_c$ coupling constants for the series *mer*-Pt($^{15}NH_3)_3Z(OH)_2^{n+}$ (VI) against the corresponding couplings of the platinum(II) series Pt($^{15}NH_3)_3Z^{n+}$ (IV). Most of the points lie close to a straight line, indicating that the effects of Z on Pt–N couplings trans and cis to itself are generally parallel in the two oxidation states. The points for ^1J(Pt(IV)–N$_t$) trans to halide lie well below that line. This may indicate that the halides compete more effectively with ammine ligands for metal s character in the higher oxidation state. Together with the comparative effects of the halides in the two oxidation states on δ_{Pt} and δ_{N_t}, noted above, this may reasonably be interpreted as indicating relatively strongly bonding between platinum(IV) and the halides—especially the heavier halides.

Trans- and cis-influence parameters on ^1J(Pt–N) in this platinum(IV) series were calculated in a way similar to that for the values of platinum(II), from the coupling constants in the series *mer*-Pt($^{15}NH_3)_3Z(OH)_2^{n+}$ (VI) with *trans*-Pt($^{15}NH_3)_4(OH)_2^{2+}$ as the reference compound. These parameters were used to predict Pt–N coupling constants in the series Pt($^{15}NH_3)_2Z_2(OH)_2^{m+}$ (VII). The predicted and experimental coupling constants are given in Table IV. As with the platinum(II) series, agreement is good overall, with the largest variation (12 Hz) for Z = I^-, again probably for steric reasons.

Pregosin et al.[1] noted that the ratio of ^1J(Pt–N) for *cis*-PtA$_2$Cl$_2$ to that for *cis*-PtA$_2$Cl$_4$ (A = *n*-dodecylamine) is 1.41, which was compared with the value of 1.5 that would be predicted if α_{Pt}^2 changed on oxidation from $^1/_4$ to $^1/_6$, and no other variable in eq 6 changed significantly. The ratio J(Pt(II)–N)/J(Pt(IV)–N) is usually lower for our compounds. For example, for Pt($^{15}NH_3)_4^{2+}$ and *trans*-Pt($^{15}NH_3)_4(OH)_2^{2+}$ it is 1.10. With the relatively higher trans influence of chloride in Pt(IV) compounds (see above), the ratio is higher for Pt($^{15}NH_3)_3Cl^+$ and *mer*-Pt($^{15}NH_3)_3Cl(OH)_2^+$, 1.21. If two additional chloride ligands were cis to the ammine ligands, rather than hydroxide, the Pt(IV)–N couplings would be predicted to be still lower, from the cis-influence parameters in Table III.

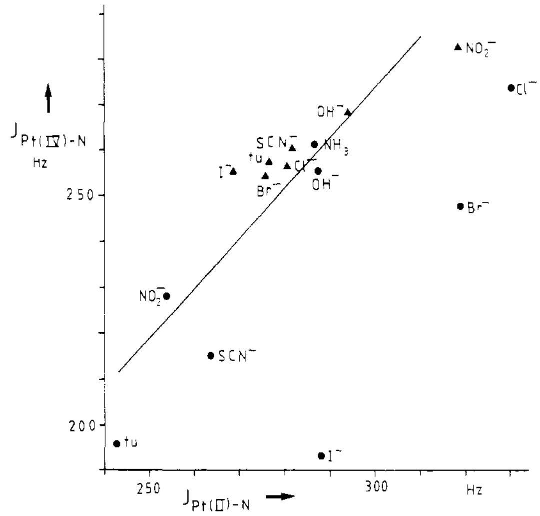

Figure 7. Plot of J(Pt–N) for platinum(IV) complexes *mer*-Pt($^{15}NH_3)_3Z(OH)_2^{n+}$ (VI) against J(Pt–N) in corresponding platinum(II) complexes Pt($^{15}NH_3)_3Z^{n+}$ (IV): (●) N trans to Z (N$_t$); (▲) N cis to Z (N$_c$). The line drawn is the best least-squares fit ignoring points for N$_t$ trans to halides.

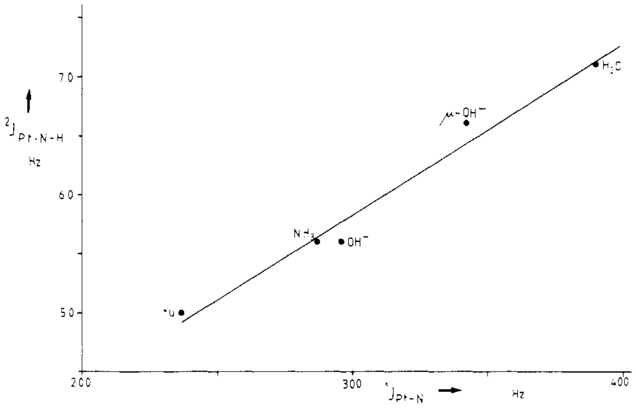

Figure 8. Plot of ^2J(Pt–N–H) against ^1J(Pt–N) for the series *cis*-Pt($^{15}NH_3)_2Z_2^{m+}$. For Z = μ-OH$^-$, the complex is [Pt($^{15}NH_3)_2(\mu$-OH)]$_2^{2+}$.

Other Coupling Constants. For the limited number of complexes of type V for which ^2J(Pt–NH$_3$) was measured, the values are given in Table V, and a plot of ^2J(Pt–NH$_3$) against ^1J(Pt–N) is shown in Figure 8. As with ^2J(Pt–CH$_3$) and ^1J(Pt–C),[43] the variation in the two-bond coupling tends to parallel that in the one-bond coupling, as would be expected if changes in hybridization at platinum are dominant in variations of both coupling constants.[49] There are insufficient data to allow finer points to be determined (e.g., is the two-bond coupling less sensitive to cis influences, as with platinum–methyl couplings?[38,50]).

The Pt–N coupling constants for the nitrite ligands are larger in magnitude than for the ammine ligands. Kerrison and Sadler[36] have shown that ^1J(Pt–N)$_{nitrite}$ decreases with increasing trans

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influence of the ligand trans to nitrite and that there is a significant cis influence which, for example, causes a regular increase in $^1J(\mathrm{Pt{-}N})$ as chloride ligands cis to nitrite are replaced by nitrite. $^1J(\mathrm{Pt{-}N})$ for nitrite trans to ammine in our platinum(II) complexes lie in the range 571-613 Hz. From comparison with the results of Kerrison and Sadler[36] and Balch and Wood,[51] the order of trans influence on this coupling constant is $\mathrm{H_2O} < \mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{NH_3} \approx \mathrm{OH^-} < \mathrm{NO_2^-}$.

It is interesting to note that, for the pair of complexes $\mathrm{Pt(^{15}NH_3)_3(^{15}NO_2)^+}$ and *mer*-$\mathrm{Pt(^{15}NH_3)_3(^{15}NO_2)(OH)_2^+}$, the ratio $^1J(\mathrm{Pt(II){-}N})/^1J(\mathrm{Pt(IV){-}N})$ is 1.11 for amine trans to nitrite, 1.13 for ammine cis to nitrite, and 1.40 for nitrite. Clearly, all of the variables in eq 1 are not affected to the same extent for the two different types of Pt-N couplings on oxidation by peroxide.

$^{15}\mathrm{N{-}Pt{-}^{15}N}$ coupling between nonequivalent nitrogen nuclei was observed only between an ammine $^{15}\mathrm{N}$ nucleus and that of a trans nitrite ligand. The coupling constant was larger in platinum(IV) complexes than in their platinum(II) analogues.

Acknowledgment. We thank the Australian Research Grants Scheme for financial support. S.F.R. is grateful for receipt of an Australian Commonwealth Postgraduate Scholarship.

Registry No. IV ($Z = {}^{15}\mathrm{NH_3}$), 98857-71-7; IV ($Z = \mathrm{H_2O}$), 98857-72-8; IV ($Z = \mathrm{OH^-}$), 98857-73-9; IV ($Z = \mathrm{OSO_3^{2-}}$), 98857-74-0; IV ($Z = \mathrm{Cl^-}$), 66752-58-7; IV ($Z = \mathrm{Br^-}$), 98857-75-1; IV ($Z = \mathrm{I^-}$), 98857-76-2; IV ($Z = {}^{15}\mathrm{NO_2^-}$), 98857-77-3; IV ($Z = \mathrm{Me_2SO}$-*S*), 66745-15-1; IV ($Z$ = tu), 98857-78-4; IV ($Z = \mathrm{SCN^-}$), 98857-79-5; V ($Y = Z = \mathrm{Cl^-}$), 78017-69-3; V ($Y = \mathrm{H_2O}$, $Z = \mathrm{Cl^-}$), 78039-62-0; V ($Y = \mathrm{OH^-}$, $Z = \mathrm{Cl^-}$), 98874-69-2; V ($Y = Z = \mathrm{Br^-}$), 98857-80-8; V ($Y = \mathrm{H_2O}$, $Z = \mathrm{Br^-}$), 98857-81-9; V ($Y = \mathrm{OH^-}$, $Z = \mathrm{Br^-}$), 98857-82-0; V ($Y = Z = \mathrm{I^-}$), 98857-83-1; V ($Y = \mathrm{H_2O}$, $Z = \mathrm{I^-}$), 98857-84-2; V ($Y = Z = {}^{15}\mathrm{NO_2}$), 98857-85-3; V ($Y = \mathrm{H_2O}$, $Z = {}^{15}\mathrm{NO_2}$), 98857-86-4; V ($Y = Z = \mathrm{SCN^-}$), 98857-87-5; V ($Y = \mathrm{H_2O}$, $Z = \mathrm{Me_2SO}$), 98857-88-6; V ($Y = Z$ = tu), 98857-89-7; VI ($Z = {}^{15}\mathrm{NH_3}$), 98857-90-0; VI ($Z = \mathrm{H_2O}$), 98857-91-1; VI ($Z = \mathrm{OH^-}$), 98839-21-5; VI ($Z = \mathrm{Cl^-}$), 98839-22-6; VI ($Z = \mathrm{Br^-}$), 98839-23-7; VI ($Z = \mathrm{I^-}$), 98839-24-8; VI ($Z = {}^{15}\mathrm{NO_2^-}$), 98839-25-9; VI ($Z = \mathrm{SCN^-}$), 98839-26-0; VI ($Z$ = tu), 98839-27-1; VII ($Z = \mathrm{H_2O}$), 98839-28-2; VII ($Z = \mathrm{OH^-}$), 98839-29-3; VII ($Z = \mathrm{Cl^-}$), 98839-30-6; VII ($Z = \mathrm{Br^-}$), 98839-31-7; VII ($Z = \mathrm{I^-}$), 98839-32-8; VII ($Z = {}^{15}\mathrm{NO_2^-}$), 98839-33-9; VII ($Z = \mathrm{SCN^-}$), 98839-34-0; VII ($Z$ = tu), 98839-35-1; $^{195}\mathrm{Pt}$, 14191-88-9; $^{15}\mathrm{N}$, 14390-96-6.

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Contribution from the Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Stereoselectivity in Electron-Transfer Reactions. Determination of the Absolute Configuration of a Nickel Oxime Imine Complex

Daniel P. Martone, Peter Osvath, Charles Eigenbrot, Mauro C. M. Laranjeira,[1a] Robert D. Peacock,[1b] and A. Graham Lappin*

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The crystal structure of the stereospecifically formed complex $[\mathrm{Ni^{II}}((S)\text{-}\mathrm{Me_2LH_2})](\mathrm{ClO_4})_2$, where $(S)\text{-}\mathrm{Me_2LH_2}$ is a chiral sexidentate bis(oxime imine) ligand, has been determined. It crystallizes in orthorhombic space group $P2_12_12_1$ (No. 19), with $Z = 4$, $a = 14.817$ (2) Å, $b = 18.864$ (2) Å, $c = 9.269$ (1) Å, and $R = 0.063$ for 2502 reflections. The absolute configuration around the metal center in $[\mathrm{Ni^{II}}((S)\text{-}\mathrm{Me_2LH_2})]^{2+}$ is ΛΔΛΛΔΛ, abbreviated Λ. In the reduction of $[\Lambda\text{-}\mathrm{Ni^{IV}}((S)\text{-}\mathrm{Me_2L})]^{2+}$ by $[\mathrm{Co(pdta)}]^{2-}$ and $[\mathrm{Co(cdta)}]^{2-}$, the products show an excess of $[\Delta\text{-}\mathrm{Co(pdta)}]^-$ and $[\Delta\text{-}\mathrm{Co(cdta)}]^-$, respectively, of approximately 10%. Comparable results have been obtained for $[\Lambda\text{-}\mathrm{Ni^{III}}((S)\text{-}\mathrm{Me_2LH})]^{2+}$ reduction. This chiral induction is explained in terms of stereoselectivity in precursor complex formation supported by ion-exchange studies which reveal that the ion pair $[\Lambda\text{-}\mathrm{Ni^{IV}L^{2+}},\Delta\text{-}\mathrm{Co(edta)^-}]$ is preferred over $[\Delta\text{-}\mathrm{Ni^{IV}L^{2+}}, \Delta\text{-}\mathrm{Co(edta)^-}]$, where $\mathrm{LH_2}$ is a nonchiral analogue of $(S)\text{-}\mathrm{Me_2LH_2}$. These stereochemical studies and kinetic studies have been used to produce a detailed picture of the electron-transfer precursor complex.

Introduction

The study of stereoselectivity in outer-sphere electron-transfer reactions between metal ion complexes in solution has the potential for yielding valuable information about the interactions between the participating species. Well-defined examples of stereoselectivity have been reported by a number of authors;[2-6] however, the data available provide no basis for predicting the extent and course of the stereochemical induction and detailed interpretation has not been possible.

The extent of chiral induction is generally small but may be measured by the detection of optical activity in the products of reaction between an optically active complex and a racemic mixture, provided proper amount is taken of the racemization of the reactants or reaction products by a self-exchange electron-transfer mechanism.[2,3] This latter problem and the fact that kinetic methods for determining stereoselectivity lack the necessary sensitivity continue to confound studies in this area.[7-13]

A useful strategy in preventing racemization by a self-exchange electron-transfer pathway involves the use of chiral ligands which complex with metal ions in a stereospecific fashion. The ligand (5*S*,12*S*)-4,7,10,13-tetraaza-3,5,12,14-tetramethylhexadeca-3,13-diene-2,15-dione dioxime, $(S)\text{-}\mathrm{Me_2LH_2}$ (**1**), is a chiral analogue of the sexidentate ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\mathrm{LH_2}$ (**2**), and complexes stereospecifically with nickel(II).[6] This can be oxidized to both nickel(III) and nickel(IV) forms, with retention of configuration.

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(1) (a) Permanent address: Department of Chemistry, Universidade Federal de Santa Catarina, Florianopolis, Santa Catarina, 88000, Brasil. (b) Permanent address: Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ Scotland, U.K.

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