Articles

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Reaction of the *cis*-Diamminediaquaplatinum(II) Cation with *N*-Acetylglycine

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cis-$Pt(NH_3)_2(H_2O)_2^{2+}$ with *N*-acetylglycine ($acglyH_2$) gives initially *cis*-$Pt(NH_3)_2(acglyH\text{-}O)(H_2O)^+$, which then undergoes chelate ring closure to $Pt(NH_3)_2(acglyH\text{-}N,O)^+$. Deprotonation results in precipitation of $Pt(NH_3)_2(acgly\text{-}N,O)\cdot 2H_2O$. These compounds represent the first reported complexes in which acetylglycine acts as an N,O-chelating ligand. Acid dissociation constants for the deprotonation have been determined by NMR in H_2O (2.6 ± 0.1) and D_2O (3.4 ± 0.3). In strongly alkaline solution, *cis*-$Pt(NH_3)_2(acgly\text{-}N)(OH)^-$ is formed, while, in strongly acidic solution, the acetylglycine ligand is completely dissociated. Solutions near pH 2, which were exposed to light, slowly developed blue colors.

Introduction

The coordination behavior of *N*-acetylglycine, $MeCONHCH_2CO_2H$ ($acglyH_2$), might be expected to show some similarities to that of the O-terminal end of peptides and proteins. There has consequently been considerable interest in the reactions of this ligand with a wide range of metal ions.[1] Although there are three potential donor sites, viz., carboxyl oxygen, nitrogen, or acetyl oxygen, in all complexes previously characterized only carboxyl oxygen has been involved in coordination. This prompted Sigel and Martin[1] to state that "*N*-acetylglycine acts only as a unidentate ligand through the carboxylate group". Platinum and palladium have not, however, been included in the metal ions studied. As part of our continuing study of the reactions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ (**1**) with amino acids[2-4] and related ligands,[5,6] we now report the results of an investigation of the reactions of **1** with *N*-acetylglycine.

Experimental Section

Starting Materials. $(^{15}NH_4)_2SO_4$ (99% ^{15}N, Cambridge Isotopes) was supplied by Novachem (Melbourne). *N*-Acetylglycine (Sigma) was used without further purification. cis-$Pt(NH_3)_2(ONO_2)_2$ (with either ^{14}N or ^{15}N in the ammine ligands) was prepared as previously described.[7,8] Samples of *cis*-$Pt(ND_3)_2(ONO_2)_2$ were prepared by allowing a solution of *cis*-$Pt(NH_3)_2(ONO_2)_2$ in D_2O to stand for several days, followed by evaporation over silica gel in a vacuum desiccator.

NMR Measurements. The 10.1-MHz ^{15}N, 21.4-MHz ^{195}Pt, 25.05-MHz ^{13}C, and 100-MHz ^1H NMR spectra were run on a JEOL FX-100 instrument with a 10-mm tunable probe (a 5-mm tube was used for ^1H spectra). An internal lock on the deuterium of the solvent D_2O was used for ^{13}C and ^1H spectra. ^{15}N and ^{195}Pt spectra were run in H_2O with a ^7Li external lock. The 100.5-MHz ^{13}C spectra were run on a JEOL GX-400 instrument, with a 10-mm tunable probe. Details of spectrum accumulation were as previously described.[2-4,8]

Unless otherwise stated, spectra of nuclei other than ^1H were ^1H-decoupled. Chemical shifts are positive to lower shielding. ^{15}N chemical shifts (±0.1 ppm) are relative to $^{15}NH_4^+$ in a coaxial capillary containing 5 M $^{15}NH_4{}^{15}NO_3$ in 2 M HNO_3. ^{195}Pt–^{15}N coupling constants were measured, whenever possible, from the ^{15}N spectra, which, because of narrower line widths, gave more accurate values (±1 Hz) than ^{195}Pt spectra. Because of the negative nuclear Overhauser effect for ^{15}N directly bound to protons, the ^{15}N spectra are actually emission spectra but are presented in a conventional absorption mode for convenience. ^{195}Pt shifts are relative to a separate sample of Na_2PtCl_6 (0.5 g) in H_2O (2 mL). 3-(Trimethylsilyl)propanesulfonate (TSS) was used as internal reference for ^1H spectra, and ^{13}C spectra were referenced to internal dioxane, taken as 67.73 ppm.

Other Instrumentation. IR spectra were run as Nujol mulls with a Mattson Sirius 100 FT-IR spectrophotometer. For pH measurements for the determination of acid dissociation constants, a TPS 1852-mV digital pH meter with an Ionode electrode was used. Meter readings in D_2O were adjusted to pD values by adding 0.40.[9] Other pH measurements were made by using narrow-range indicator strips supplied by Merck or Riedel-de-Haen.

Preparation of $Pt(NH_3)_2(acgly\text{-}N,O)\cdot 2H_2O$. *cis*-$Pt(NH_3)_2(ONO_2)_2$ (0.50 g, 1.42 mmol) was dissolved by warming and stirring in 2 mL of water. The solution was filtered through a cotton wool plug, and solid *N*-acetylglycine (0.17 g, 1.42 mmol) was added slowly with stirring. After the solid dissolved, the pH was adjusted to 3–4 with 1 M NaOH solution, and the solution was allowed to stand in the dark for 24 h. Over this period, the pH fell to 2–2.5, and some white solid deposited. More alkali was then added to restore the pH to 3–4, and the mixture was left in the dark for a further 24 h. The white solid was then collected on a sintered-glass funnel, washed with 2 × 3 mL of cold water and 2 × 3 mL of ethanol, and then dried in air. The crude yield was 27%. A further crop of solid could be obtained by evaporating the filtrate to near dryness in a stream of air. The combined solid was recrystallized from boiling water, with filtration and drying as before. The yield was 12.5%. The relatively low yields indicate that, even when concentrated solutions were used, significant quantities of product remained in solution. IR spectra and microanalytical results indicated the presence of water of crystallization, $[Pt(NH_3)_2(acgly\text{-}N,O)]\cdot 2H_2O$. Anal. Calcd for $C_4H_{15}N_3O_4Pt$: C, 12.6; H, 4.0; N, 11.1. Found (microanalytical service, this department): C, 13.0; H, 3.8; N, 10.7.

Results and Discussion

^{195}Pt and ^{15}N NMR data are presented in Table I, and ^{13}C and ^1H NMR data in Table II.

***cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ with Acetylglycine.** A solution of *cis*-$Pt(^{15}NH_3)_2(H_2O)_2^{2+}$ (**1**) in H_2O (pH ~2) was prepared by dissolving solid *cis*-$Pt(NH_3)_2(ONO_2)_2$ in water. The ^{195}Pt NMR spectrum showed the characteristic 1:2:1 triplet from coupling with two equivalent ^{15}N nuclei ($J(^{195}Pt\text{–}^{15}N)$ 391 Hz, ^{195}Pt, $I = {}^1/_2$, 34% abundance) at −1580 ppm, and the ^{15}N spectrum the characteristic sharp singlet with "satellites" at −85.8 ppm.[7,8] Solid *N*-acetylglycine (0.8 mol equiv) was added slowly with shaking to facilitate dissolution. The pH was then approximately 1.0. After 18 min, two new singlets, with satellites, were detected, which were assigned to *cis*-$Pt(^{15}NH_3)_2(acglyH\text{-}O)(H_2O)^+$ (**2**, Scheme I; Table I). The observed shifts are consistent only with ammine trans to O-donors.[10] The ^{195}Pt spectrum of this species showed, overlapping with the triplet from **1**, the expected doublet of doublets (from coupling of ^{195}Pt with two nonequivalent ^{15}N nuclei, with splittings corresponding to the coupling observed in the ^{15}N

(1) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 185.
(2) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 673.
(3) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Aust. J. Chem.* **1986**, *39*, 1347.
(4) Appleton, T. G.; Connor, J. W.; Hall, J. R. *Inorg. Chem.* **1988**, *27*, 130.
(5) Appleton, T. G.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* **1986**, *25*, 720.
(6) Appleton, T. G.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* **1986**, *25*, 726.
(7) Boreham, C. J.; Broomhead, J. A.; Fairlie, D. P. *Aust. J. Chem.* **1981**, *34*, 659.
(8) Appleton, T. G.; Berry, R. D.; Davis, C. A.; Hall, J. R.; Kimlin, H. A. *Inorg. Chem.* **1984**, *23*, 3514.
(9) Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188.
(10) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 4685.

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Table I. ^{195}Pt and ^{15}N NMR Data

compd[a]	struct	pH	δ_{Pt}[b]	^{15}N(ammine) δ_N	^{15}N(ammine) J(Pt–N), Hz	ligand trans to NH_3
$Pt((NH_3)_2(acglyH\text{-}O)(H_2O)^+$	**2**	1.5	−1583 dd	−85.1	353	acglyH carboxyl
				−87.3	392	H_2O
$Pt(NH_3)_2(acglyH\text{-}N,O)^+$	**3**	1.5	−2026 br	−65.6	296	acglyH N
				−83.8	333	acglyH carboxyl
$Pt(NH_3)_2(acgly\text{-}N,O)$	**6**	6.0	−2022 br	−64.1	269	acgly N
				−87.5	319	acgly carboxyl
$Pt(NH_3)_2(acgly\text{-}N)(OH)^-$	**7**	>9	−2018 br	−65.1	248	acgly N
				−79.0	291	OH^-

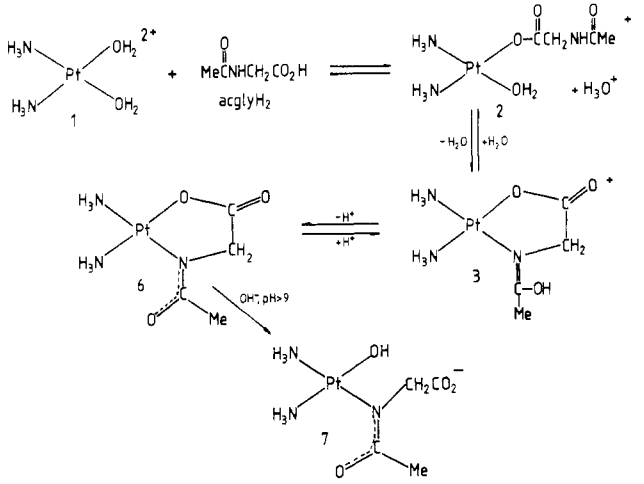
[a] All compounds contain ^{15}N-substituted ammine and are cis. [b] Abbreviations: dd, doublet of doublets; br, broad.

Table II. ^1H and ^{13}C NMR Data

compd[a]	struct	pD	methylene group δ_C	methylene group δ_H	methylene group J(Pt–H)	methyl group δ_C	methyl group δ_H	carboxyl δ_C	C(O), acetyl, δ_C
$acglyD_2$		2.5		3.96			2.05		
$acglyD^-$		4.0	43.2			22.9		176.1	175.6
$Pt(ND_3)_2(acglyD\text{-}O)(D_2O)^+$	**2**	3.0	43.6	3.88	≤2	22.2	2.03	179.7	175.6
$Pt(ND_3)_2(acglyD\text{-}N,O)^+$	**3**	1	*b*	4.23	23.7	*b*	2.12	*b*	*b*
$Pt(ND_3)_2(acgly\text{-}D,O)$	**6**	6.0	56.2	4.11	24.2	22.6	1.92	190.6	180.7

[a] All coordination complexes cis. [b] ^{13}C spectrum not measured.

Scheme I



spectrum). The observed chemical shift corresponded to a PtN_2O_2 complex.[10] The NMR parameters for **2**, listed in Table I, may be compared with those for the O-bound glycine complex, *cis*-$Pt(^{15}NH_3)_2(glyH\text{-}O)(H_2O)^{2+}$ (δ_{Pt} −1582; δ_N trans to carboxylate −82.6, J(Pt–N) = 358 Hz; δ_N trans to H_2O −87.2, J(Pt–N) = 392 Hz).[2] The coordination of carboxyl oxygen to the metal is not surprising, as the carboxyl group of $acglyH_2$ is the most readily deprotonated, and the carboxyl oxygen is then the most basic atom present. This corresponds to the coordination mode that has usually been observed for *N*-acetylglycine complexes.[1]

Peaks due to **2** continued to grow in the ^{15}N spectra over several hours, but after 3 h, two new singlets with satellites had appeared, which continued to grow over several days until they became the strongest peaks in the spectrum, although significant concentrations of **1** and **2** were still clearly present (Figure 1). One of these peaks, near −65 ppm, with J(Pt–N) 290 Hz, must correspond to ammine trans to nitrogen. The other, near −84 ppm, with a Pt–N coupling constant of 333 Hz, must correspond to ammine trans to carboxylate.[10] In the ^{195}Pt spectrum a broad peak corresponding to the same species appeared at −2026 ppm, in the region expected for a PtN_3O complex.[10] The broadening of the ^{195}Pt signal is expected when platinum is bound to one or more ^{14}N atoms and is due to partial decoupling of ^{195}Pt from ^{14}N as the latter nucleus undergoes relatively rapid quadrupole-induced relaxation.[11] These data, together with those reported below for other nuclei, indicate

(11) Ismail, I. M.; Kerrison, S. J. S.; Sadler, P. J. *Polyhedron* **1982**, *1*, 57.

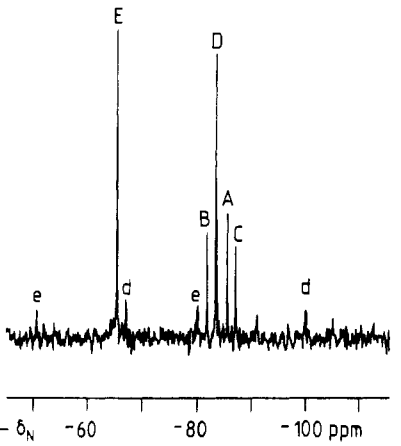
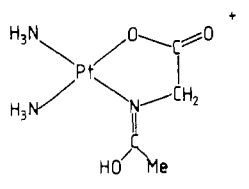
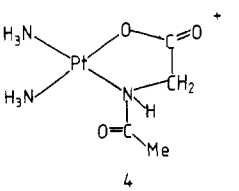
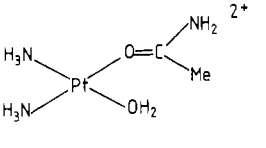


Figure 1. 10.1-MHz ^{15}N NMR spectrum of a solution obtained from *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](NO_3)_2$ and *N*-acetylglycine in H_2O, pH 2, 2 days after mixing. Lower case letters indicate "satellites". Labels: A, *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ (**1**); B, *cis*-$Pt(NH_3)_2(acglyH\text{-}O)(H_2O)^+$ (**2**), ammine trans to carboxylate; C, **2**, ammine trans to H_2O; Dd, $Pt(NH_3)_2(acglyH\text{-}N,O)^+$ (**3**), ammine trans to carboxylate; Ee, **3**, ammine trans to N(acglyH).

that acetylglycine is coordinated as an N,O-chelate. As described below, there are changes in the spectra corresponding to a deprotonation reaction when the pH of the solution is increased, so that the complex retains an acid proton. The complex is therefore formulated as $Pt(^{15}NH_3)_2(acglyH\text{-}N,O)^+$. Either acetyl oxygen (**3**) or the coordinated nitrogen atom (**4**) could carry this proton.







On the basis of the chemical shift data presented later, we propose that **3** is the tautomer present.

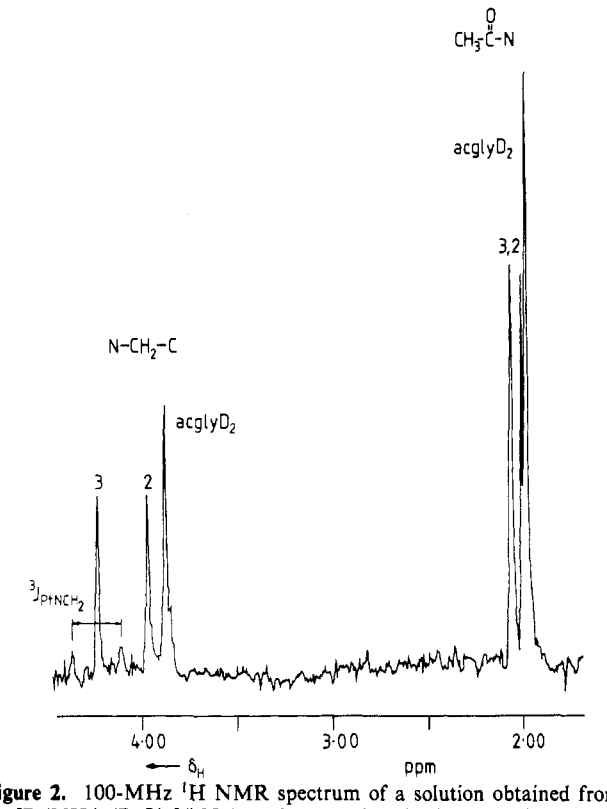


Figure 2. 100-MHz ^1H NMR spectrum of a solution obtained from *cis*-$[Pt(NH_3)_2(D_2O)_2](NO_3)_2$ and *N*-acetylglycine in D_2O, pD 2, 2 days after mixing. Labels on peaks correspond to those on structures in Scheme I.

The NMR parameters for **3** given in Table I may be compared with those for the complex in which glycinate acts as an N,O-chelate, $Pt(^{15}NH_3)_2$(gly-*N*,*O*)$^+$ (δ_{Pt} −2129; δ_N trans to glycinate N −64.9, J(Pt–N) = 301 Hz; δ_N trans to glycinate O −84.9, J(Pt–N) = 331 Hz).[2]

The formation of **3** is of interest in that it is, to our knowledge, the first compound in which *N*-acetylglycinate acts as a chelating ligand. It is also a rare example of the coordination to platinum of a neutral amide. Kerrison and Sadler[12] have shown by ^{15}N and ^{195}Pt NMR spectroscopy that acetamide coordinates through oxygen to platinum in complex **5**. The behavior of acetylglycine differs from that of glycine under comparable conditions, in that the formation of the N,O-chelate complex is much slower for acetylglycine and does not go to completion.

The reaction of $acglyH_2$ with **1** was also monitored by ^1H NMR spectroscopy, using a solution of *cis*-$Pt(^{14}ND_3)_2(ONO_2)_2$ in D_2O. When $acglyH_2$ was added, the spectrum initially showed only the two sharp singlets from the methyl and methylene protons of the free ligand. Peaks due to **2** slowly grew, and then those from **3** (Figure 2, Table I) appeared. No couplings with ^{195}Pt were resolved for **2**. Similarly, no platinum coupling was observed for the methylene protons of *cis*-$Pt(ND_3)_2$(glyD-*O*)$(D_2O)^{2+}$.[2] The methyl protons of the N,O-chelate complex **3** did not show any observable coupling to platinum, but the methylene protons showed a relatively large Pt–N–CH_2 coupling of 23.7 Hz (cf. 32.0 Hz for $Pt(ND_3)_2$(gly-*N*,*O*)$^{+2}$).

The ^{13}C NMR spectrum of free acetylglycine in D_2O was recorded for comparison with the spectra of the platinum complexes. Shifts at pD 4, where the carboxyl group is deprotonated, are listed in Table II. Our chemical shifts in D_2O are in reasonable agreement with those reported by Newmark and Hill[13] for a DMSO solution. It was difficult to obtain ^{13}C spectra of good quality from the solutions obtained by addition of acetylglycine to **1**, as, over the long spectrum accumulation times required, reactions occurred that changed the pD of the solutions. This caused broadening of peaks whose chemical shifts were sensitive to pD. Buffering of solutions was not possible, as, in our experience, potential buffers all tend to react with the platinum complexes. Since the spectrum of **2** is not affected by a pD up to 6, it was possible to measure the shifts of the carbon peaks (Table II) for this complex, but the signal to noise ratio obtained did not allow satellite peaks to be discerned clearly. The carboxyl carbon resonance shifted by 3.6 ppm to lower shielding, compared with $acglyH^-$, but the resonance frequencies of other carbon nuclei were scarcely affected (Table II).

Deprotonation of $Pt(NH_3)_2$(acglyH-*N*,*O*)$^+$. When dilute NaOH solution (or NaOD/D_2O) was added to solutions containing $Pt(NH_3)_2$(acglyH-*N*,*O*)$^+$ (**3**) (Tables I and II), changes occurred in the ^{15}N and ^1H spectra that corresponded to deprotonation of the coordinated ligand to give $Pt(NH_3)_2$(acgly-*N*,*O*) (**6**), and most of this compound precipitated as a white solid. Both the methyl and methylene ^1H resonances shifted to higher shielding as a result of this deprotonation, but the shift was greater for the methyl protons ($\Delta\delta$ −0.28 ppm) than for the methylene protons ($\Delta\delta$ −0.15 ppm). This result is consistent with the site of protonation being acetyl oxygen, as in **3**, rather than amide nitrogen, as in **4**. Similar reasoning has been used by Rabenstein[14] in establishing the protonation sites in a bis(diglycinato)cobalt(III) complex. It has been well established from study of numerous peptide complexes[1,15] that protonation occurs first at the peptide oxygen, because of its greater basicity, rather than at the peptide nitrogen.

^{15}N NMR parameters are usually more sensitive to changes in the ligand trans to ammine than in the cis ligand.[10] It is therefore not surprising that the decrease in J(Pt–N) trans to amide nitrogen on deprotonation (27 Hz) is greater than that in J(Pt–N) trans to carboxylate (14 Hz). The lower Pt–N coupling constants are indicative of stronger coordination to the metal of the deprotonated ligand.[10] While, however, the ^{15}N nucleus trans to the amide nitrogen shifted slightly to lower shielding on deprotonation ($\Delta\delta$ +1.5 ppm), as expected if the bonding is stronger,[10] the ^{15}N nucleus trans to carboxylate oxygen shifted by a greater amount, and to higher shielding ($\Delta\delta$ −3.7 ppm). To account for this "anomaly", it may be noted that the latter ammine group is closer "through space" to the amide group, and so may be affected directly by the deprotonation reaction, rather than predominantly via an inductive effect through bonds. It may be noted that the hydrogen atoms of this ammine ligand are well placed to form hydrogen bonds to the amide oxygen in the deprotonated complex **6**. Protonation to **3** would weaken or destroy these hydrogen bonds.

The ^{195}Pt NMR spectrum of a solution of **6** showed a broad triplet at −2022 ppm, not significantly shifted from the shift for the protonated complex **3**. Platinum shifts are determined primarily by donor atoms and are frequently relatively insensitive to ligand protonations.[7]

The ^{15}N and ^1H NMR shifts at the normal probe temperature, 28 °C, were plotted as a function of pH or pD. Results are shown in Figures 3 and 4. For the ^{15}N measurements, which required 20–45 min each, there was usually some change in pH during the run, as some of the complex containing O-bound ligand, **2**, was converted to the N,O-chelate and as some of the deprotonated chelate complex, **6**, precipitated. This caused some broadening of peaks, especially the central singlet for ammine trans to carboxylate in the chelate complex (whose shift is most sensitive to the deprotonation reaction). The pH was measured immediately before and after each run, and the average value was used. This problem was much less evident for the ^1H measurements, for which accumulation times were much shorter.

A derivation from the Henderson–Hasselbach equation[16] gives eq 1, where δ is the measured chemical shift, δ_A is the chemical

$$pK_a = pH + \log [(\delta - \delta_B)/(\delta_A - \delta)] \quad (1)$$

(12) Kerrison, S. J. S.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 61.
(13) Newmark, R. A.; Hill, J. R. *J. Magn. Reson.* **1976**, *21*, 1.
(14) Rabenstein, D. L. *Can. J. Chem.* **1971**, *49*, 3767.
(15) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257.
(16) Edward, J. T.; Leane, J. B.; Wang, I. C. *Can. J. Chem.* **1962**, *40*, 1521.

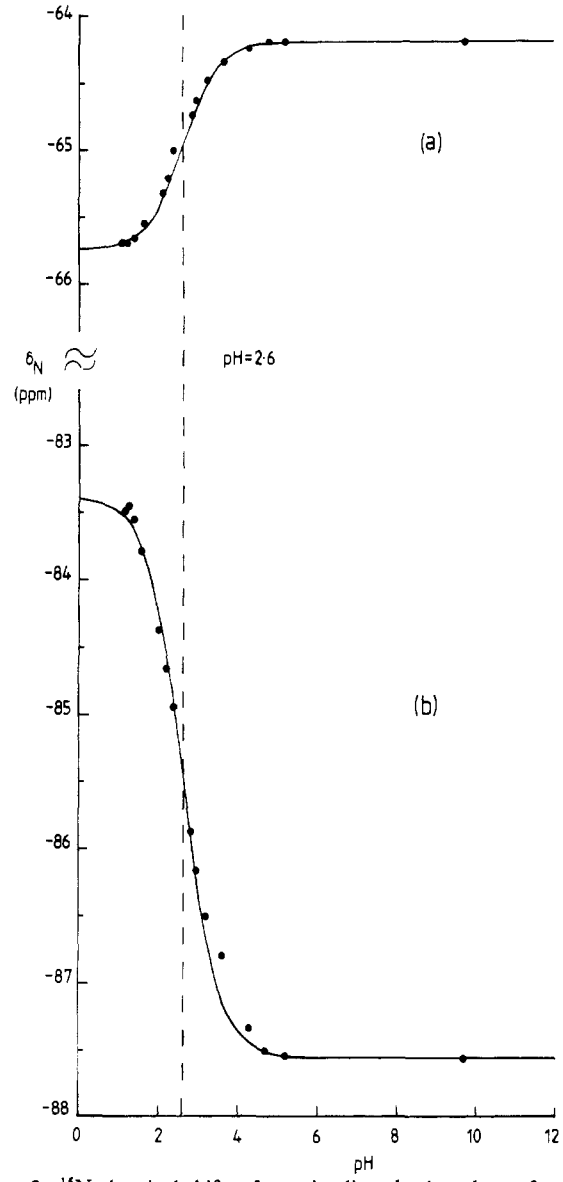


Figure 3. ^{15}N chemical shifts of ammine ligands plotted as a function of pH as NaOH solution was added to a solution of $Pt(^{15}NH_3)_2(acglyH\text{-}N,O)^+$ (**3**): (a) ammine trans to nitrogen; (b) ammine trans to oxygen. The points shown are experimental points. The curves are theoretical curves calculated from eq 1 with $pK_a = 2.6$.

shift in acid, and δ_B is the chemical shift in base. Provided the chemical shifts of the acid and base forms, δ_A and δ_B, do not change significantly with pH, this equation may be used to determine a value for pK_a from the measured chemical shift. An average value of pK_a was calculated from data corresponding to points on the "steep" parts of the curve (i.e., $pH = pK_a \pm 1.5$), and the theoretical curve based on this value of pK_a is shown, along with the experimental points, in each plot. From the ^{15}N data in H_2O, the pK_a for **3** was 2.6 ± 0.1, and from the ^1H data in D_2O, the value was 3.4 ± 0.3. According to Martin,[17] the effect of deuteration on pK_a may be expressed by eq 2, where a and b are

$$pK_a^D - pK_a^H = a + b(pK_a^H) \quad (2)$$

constants that depend on the acid concerned. Values of a and b corresponding to a coordinated amide group are not known, but an increase in the value of pK_a in the deuterated solvent is expected.[17] These values may be compared with those determined for deprotonation of a coordinated peptide group in palladium(II) complexes of glycinamide (2.47) and diglycine (3.76).[18]

(17) Martin, R. B. *Science* **1963**, *139*, 1198.
(18) Lim, M. C. *J. Chem. Soc., Dalton Trans.* **1977**, 15.

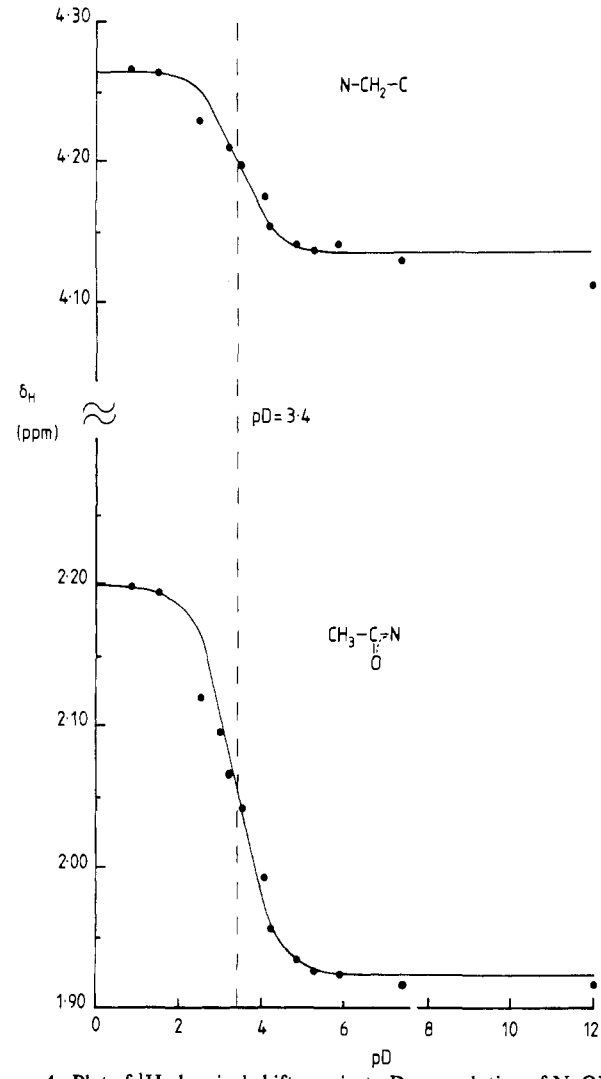


Figure 4. Plot of ^1H chemical shifts against pD as a solution of NaOH in D_2O was added to a D_2O solution of $Pt(ND_3)_2(acglyD\text{-}N,O)^+$ (**3**). The points shown are experimental points. The curves are theoretical curves calculated from eq 1 with $pK_a(D_2O) = 3.4$.

At pD 6, most of the complex had precipitated as $Pt(ND_3)_2(acgly\text{-}N,O)\cdot 2D_2O$, but a sufficient amount of the complex remained in solution to allow the major ^{13}C peaks to be observed (but not satellites from coupling to platinum). Since all of the complex in solution was now present as **6**, there was no change in pD with time, and peaks were relatively sharp. It is clear from the data in Table II that, compared with those in **2**, all carbon nuclei in **6** except the methyl carbon are significantly less shielded. Of particular interest is the very low shielding of the carboxyl carbon atom (δ_C 190.6). While coordination of a carboxyl group to a metal usually causes deshielding of the carboxyl carbon nucleus, such a low shielding is characteristic of a carboxylate group incorporated into a five-membered chelate ring. Thus, the carboxyl carbon in $Pt(NH_3)_2(gly\text{-}N,O)^+$ with a five-membered ring occurs at 190.0 ppm,[2] while the β-alanine analogue, with a six-membered chelate ring, gave a carboxyl resonance at 181.1 ppm.[3] An analogous deshielding is observed for phosphorus nuclei when a phosphonate group is incorporated in a five-membered chelate ring.[5,6] The low shielding of the carboxyl carbon therefore provides good evidence that the acetylglycine complex is, in fact, a chelate complex, rather than, e.g., a complex in which acetylglycine bridges between two metal ions.

The IR spectra of Nujol mulls of $acglyH_2$ and $Pt(NH_3)_2(acgly\text{-}N,O)\cdot 2H_2O$ are shown in Figure 5. While $acglyH_2$ showed a moderately sharp peak at 1720 cm^{-1} from –COOH and a broad, split peak at 1582 and 1549 cm^{-1} from the acetyl carbonyl, **6** showed a peak at 1640 cm^{-1} assignable to coordinated carboxylate[19] and a peak at 1555 cm^{-1} from the amide group. Bands

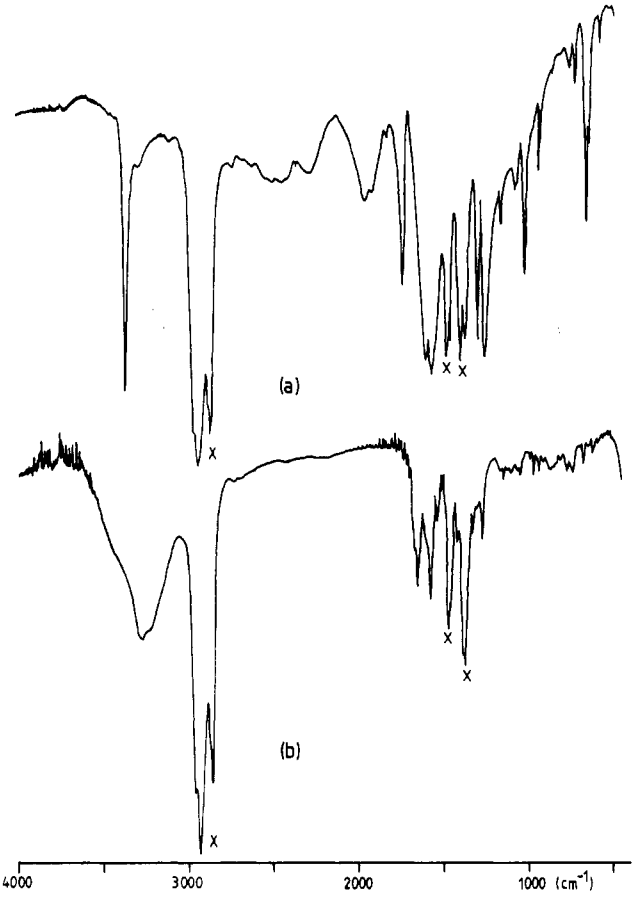


Figure 5. IR spectra of Nujol mulls: (a) *N*-acetylglycine; (b) Pt-$(NH_3)_2$(acgly-*N*,*O*)·$2H_2O$. The peaks due to Nujol are marked ×.

from $\delta(NH_3)$ and $\delta(OH_2)$ would also be expected to occur in this region, although weaker. The spectrum of $Pt(ND_3)_2$(acgly-*N*,-*O*)·$2D_2O$, however, still showed strong bands at 1630 and 1550 cm^{-1}, indicating that they are mainly due to C=O stretching vibrations. The spectra did not show any peaks assignable to nitrate ion.

Other Reactions. When alkali was added to a solution of $Pt(^{15}NH_3)_2$(acgly-*N*,*O*) (**6**) to increase pH above 9.0, peaks slowly grew that could be assigned to *cis*-$Pt(^{15}NH_3)_2$(acgly-*N*)$(OH)^-$ (**7**). Although carboxylate oxygen is displaced by OH^- in strongly alkaline solution, the deprotonated amide nitrogen is too strongly coordinated to be displaced as readily.

Solid $Pt(^{15}NH_3)_2$(acgly-*N*,*O*)·$2H_2O$ was only sparingly soluble in water, but it dissolved readily in acid, to give initially ^{15}N peaks corresponding to $Pt(^{15}NH_3)_2$(acgly-*N*,*O*)$^+$. In weakly acid solution (pH 1.5–3) the equilibrium solution containing **1**, **2**, and **3**/**6** was slowly established. At pH <0.5, the ligand is eventually displaced totally from the metal. This reaction probably proceeds initially by acid attack on the coordinated amide group, weakening its coordination. Dissociation of the amide end of the chelate ligand gives **2**, and subsequent acid attack on the Pt–carboxylate bond causes dissociation of the whole ligand. By contrast, reaction of a platinum glycinate chelate ring with strong acid causes cleavage of the carboxyl but not the amine group from the metal, to form Pt–NH_2CH_2COOH.[20]

In none of our NMR spectra was there any sign that acetylglycine, coordinated or free, was hydrolyzing to acetate and glycine. The various changes that occurred in the NMR spectra as pH was changed were all reversible.

If a solution containing the acetylglycine complexes was allowed to stand under fluorescent lighting at pH ~2.0, the solution slowly became an intense blue. In the dark, a pale brown color slowly developed, which may be due to traces of products from condensation reactions. No solid deposited from the solutions. Amides are known to readily form "blues" when allowed to react with **7** in the presence of air.[21,22] Crystal structure determinations (e.g., of the α-pyridone blues[23]) have shown that these compounds are tetramers with pairs of platinum atoms bridged by PtO–C–N–Pt bridges and an average metal oxidation state of 2.25. The blue color will be due to the formation of such compounds, probably in relatively small concentrations. Initiation by light of reactions to form "blues" has been previously observed (e.g., "blues" from phosphate and *cis*-$Pt(NH_2Me)_2(H_2O)_2^{2+}$[8]). Ultimately, platinum metal deposits from these solutions after lengthy standing.

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