Amide Complexes of (Diethylenetriamine)platinum(II)

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The coordination of acetamide and formamide to dienPt^{II} is described. Both O- and N-bonded amide complexes are stable and have been isolated. As oxygen donor ligands for dienPt^{II}, the binding affinity of amides lies between water and the very weakly coordinating acetone. The O-bonded amide complexes $[dienPtOC(R)NH_2]^{2+}$ are the kinetically preferred isomers in acetone but they rearrange very slowly ($t_{1/2} \sim 30$ h, 20 °C) and intramolecularly to the thermodynamically more stable N-bonded amide complexes ($K = [N]/[O] \sim 30$). This is the reverse of relative amide affinities for harder metal ions (e.g. $(NH_3)_5M^{3+}$, M = Co(III), Cr(III), Ru(III)) despite comparable polarizing power for dienPt^{II}. The N-bonded amide isomers exist in solution (acetone, DMSO, water) as the imidol, $[dienPtNH{=}C(OH)R]^{2+}$, rather than the amide tautomer, $[dienPtNH_2COR]^{2+}$, whereas the opposite has been observed for N-bonded ureas. The N-bonded amides adopt only one of the two possible geometric isomers which could result from restricted rotation about the amide N=C bond, and they are appreciably acidic (pK_a 3.8, 20 °C, H_2O, $I = 0.1$ M; R = Me). Complexes of both O- and N-bonded amides are unstable in coordinating solvents ($t_{1/2} < 1$ min, O-isomers; $t_{1/2} > 40$ h, N-isomers; 20 °C, H_2O), but no decomposition of the amide ligands was detected during solvolysis (amide release) in either DMSO or water, nor was the Pt(II) susceptible to aerial oxidation as reported for mixtures of amides with *cis*-diammineplatinum(II). Coordination preferences of amides to "soft" versus "hard" metals are compared.

Introduction

Amides of carboxylic acids are usually considered to be N-donor ligands for metal ions[1] despite the fact that they are known[2] to protonate on the carbonyl oxygen rather than the nitrogen atom. Indeed a similar *kinetic* preference for coordination via the amide oxygen to Lewis acid metal ions (M) has now been observed for the "hard" $(NH_3)_5M^{III}$ ions

$$RCONH_2M^+ \leftarrow RCONH_2 + M^+ \rightarrow RC(OM){=}NH_2^+$$

(M = Co,[3] Cr,[4] Ru,[5] Rh[6]). The softer Pt(II) on the other hand usually exhibits only weak affinity for O-donor ligands,[7] so we were interested to see if initial amide capture would occur at nitrogen under kineticaly controlled conditions. Despite several reports of dinuclear platinum complexes containing bridging amides,[8,9] no Pt(II) complex with a monodentate oxygen-bonded amide has been isolated before.

For the hard $(NH_3)_5M^{III}$ ions above, the oxygen-bonded amide complexes were *thermodynamically* as well as kinetically more stable than the nitrogen-bonded amide complexes. Although we had expected that the nitrogen-bonded amide would be thermodynamically prefered for the soft dienPt^{II} entity, amide coordination to Pt(II) has previously been somewhat controversial[10-12] due in part to the complication of subsequent oxidation to colored amide complexes containing Pt(III). An important feature in the case of capture of the amide nitrogen is the issue of tautomerism:[13]

$$\underset{\text{amide}}{[RCONH_2M]^{2+}} = \underset{\text{imidol}}{[RC(OH){=}NHM]^{2+}} \quad K_T$$

N-bonded amides generally adopt the imidol tautomeric form,[1,3] but we have previously demonstrated that this equilibrium can be shifted by changes to the substituent R,[3,13-17] the metal M,[13] or the solvent system.[14,18] This issue therefore needs to be examined closely here.

Since the dienPt^{II} group has polarizing power comparable to that of the $(NH_3)_5M^{III}$ moieties above (e.g. $(NH_3)_5CoOH_2^{3+}$, pK_a 6.2;[19] $dienPtOH_2^{2+}$, pK_a 6.1),[20] we chose to examine its reactivity with simple monodentate amides ($RCONH_2$, R = H, Me) with the expectation that the soft versus hard comparison might give some insight into the kinetic versus thermodynamic selectivity for amide coordination to metal ions. The synthesis, identification, and properties of linkage isomeric amide complexes of dienPt^{II} are now described for the first time, and their solution structures as well as kinetic and thermodynamic stabilities are clearly established.

Results

Synthesis and Isomer Characterization. Amide complexes were prepared from $[Pt(dien)(OH_2)](CF_3SO_3)_2$, which is freely soluble in the solvents used (acetone, water, formamide, DMSO) and can be readily characterized by NMR (^1H, ^{13}C) spectroscopy.[21] In the weakly coordinating O-donor solvent acetone, the bound

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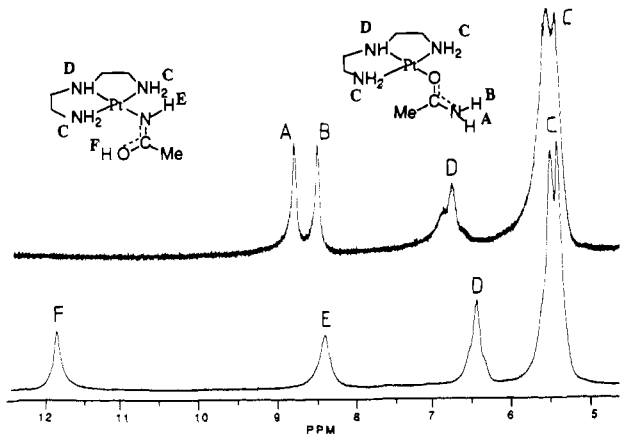

Figure 1. 300-MHz ^{1}H NMR spectra (NH/OH region only) for $[dienPtOC(NH_2)Me](CF_3SO_3)_2$ and $[dienPtNH{=}C(OH)Me](CF_3SO_3)_2$ in d^6-acetone at 22 °C.

Table I. ^{13}C NMR Data[a] for $[dienPt(ligand)](CF_3SO_3)_2$ in d^6-Acetone

ligand	C=O	dien			Me
$-OH_2$		56.2	51.2	50.9[b]	
$-N{\equiv}CMe$	121.5	55.3	51.2		3.1
$-OCHNH_2$	173.8	56.0	50.9		
-NHCHO	170.4	54.1	52.0		
$-NH{=}C(OH)H$	168.7	54.8	52.0		
$HCONH_2$[c]	166.1				
$-OC(NH_2)Me$	182.6	56.0	51.1		21.9
-NHCOMe	178.4	54.2	51.9		25.3
$-NH{=}C(OH)Me$	177.4	54.7	51.9		21.4
$MeCONH_2$[c]	174.6				22.2

[a] δ in ppm downfield of TMS. [b] Three signals represent mixture of $[dienPtOH_2]^{2+}$ and $[dienPt(acetone)]^{2+}$ caused by rapid partial exchange of bound water with solvent.[21] [c] Free ligand (~50 mM).

water molecule is rapidly exchanged for acetamide or formamide, using slightly more than 1 equiv of amide to ensure complete displacement of the equilibrium to the right:

$$[dienPtOH_2]^{2+} + RCONH_2 = [dienPtOC(NH_2)R]^{2+} + H_2O \quad K_1$$
1

On the basis of ^{1}H NMR observations, we estimate the formation constant (R = Me) in acetone as $K_1 \sim 7$.

The initial products of this synthesis were quickly isolated and definitively characterized by ^{1}H and ^{13}C NMR spectroscopy, and by their reactions, as the *oxygen*-bonded amide complexes. The formation constant implies[21] that as O-donor ligands for dienPt^{II}, the relative order of affinities is $H_2O > RCONH_2$ (R = H, Me) > acetone. The acetamide complex (R = Me) exhibits separate ^{1}H NMR signals for the diastereotopic amide-NH_2 protons (Figure 1, signals A, B) due to restricted rotation about the C=N bond. This separation is comparable to that for free acetamide. On coordination to dienPt^{II} the amide-NH_2 and -Me signals both shifted (1.7, 0.27 ppm, respectively) downfield of the corresponding free ligand signals. There was also a noticeable splitting of the NH and NH_2 resonances for dien. These oxygen-bonded amide complexes were much more reactive and much less acidic than their nitrogen-bound amide isomers; vide infra.

The N-bonded amide complexes were synthesized by two methods. As described in the next section, they were isolated from aged acetone solutions of O-bonded amide complexes. Also, the nitrogen-bonded acetamide complex was independently obtained through base hydrolysis of the acetonitrile complex[22] in water:

$$[dienPtN{\equiv}CCH_3]^{2+} + OH^- \rightarrow [dienPtNHCOCH_3]^+$$
2

The N-bonded amide complex **2** was then protonated in water by addition of CF_3SO_3H. The isolated product was clearly **3**

$$[dienPtNH{=}C(OH)CH_3]^{2+} \leftarrow [dienPtNHCOCH_3]^+ \rightarrow [dienPtNH_2COCH_3]^{2+}$$
3 **2** **4**

rather than **4** since its ^{1}H NMR spectrum in d^6-acetone (Figure 1) shows two separate low-field, single proton resonances (E, F) that can be assigned to NH and OH, respectively. Since the lowest field signal shifts upfield on addition of H_2O (with which it exchanges) and increases in intensity, while the 8 ppm signal remains constant in intensity and position with added H^+ or H_2O, **3** rather than **4** must be the structure of the protonated N-bonded amide complex.[3] A single 2 H signal for equivalent amide-NH_2 protons of **4** was not observed. Like the formamide complex below, signals F and E both diminish in intensity with time due to eventual exchange with solvent. Note that the ratio F:E:D:F in Figure 1 is 1:1:1.3:5.2 indicating that some exchange (~23%) had taken place by this time.

Tables I and II summarize NMR (^{13}C, ^{1}H) data for the respective amide complexes of dienPt^{II}. For both formamide and acetamide complexes there are some distinct features that aid in isomer identification. For example the ^{13}C NMR data (Table I) show $\delta_{C=O}$ increasing in the order $NH_2COR < [dienPtNH{=}C(OH)R]^{2+} < [dienPtNHCOR]^+ < [dienPtOC(NH_2)R]^{2+}$ for both R = H, CH_3. $\delta_{C=O}$ for the amide shifts 2–10 ppm to lower field upon coordination to dienPt^{II}. Also the dien signals are diagnostically useful since the separation between the two ^{13}C resonances for each compound varies according to the amide (or other) donor ligand in $[dienPtL]^{n+}$ as L = OH_2, $OC(NH_2)R$ (~5 ppm), N≡CR (~4 ppm), NH=C(OH)R (2.8 ppm), and $NHCOR^-$ (2.0–2.5 ppm). This feature alone appears useful in distinguishing O- from N-bonded donor ligands on dienPt^{II}.

Table II shows the ^{1}H NMR data which are also diagnostic of the amide bonding mode. Both the amide and dien signals are distinct for each compound, although the former differ more between the complexes. For example, both the free amides and the O-bonded amide complexes exhibit separate low-field signals for each amide NH proton; those for the O-bonded amide complex resonate ~2 ppm to lower field of the free amides. The O-bonded formamide complex exhibits a characteristic splitting pattern[3] (doublet of doublets) for the formyl proton due to its separate coupling with the formamide NH protons trans (J_{CH-NH} = 14 Hz) and cis (J_{CH-NH} = 3 Hz) arising from restricted rotation about the C=N bond. The deprotonated N-bonded amide isomers show only the one amide NH proton ca. 5–6 ppm, and this shifts to ~8.5 ppm upon protonation due to increased anisotropy resulting from the change from PtNH–C to PtNH=C. This NH resonance remains one proton in intensity, and there is an accompanying single proton resonance for the OH of $[dienPtNH{=}C(OH)R]^{2+}$ at lower field (~12 ppm) which shifts to higher field in the presence of water with which it exchanges.

O- to N-Linkage Isomerizations. Further evidence for the O-bonding versus N-bonding assignments derives from the observed

(21) When analytically pure crystals of $[dienPtOH_2](CF_3SO_3)_2$ were dissolved in d^6-acetone (millimolar [Pt]), the ^{13}C NMR spectrum showed three dien resonances (50.9, 51.2, 56.4 ppm) and the ^{1}H NMR spectrum showed two sets of dien-NH (7.00, 6.80 ppm; 1:1 ratio) and dien-NH_2 (5.57, 5.55, 5.50, 5.42 ppm) resonances. The splitting was not seen in other solvents (D_2O, DMSO) and was removed by addition of water to the acetone. Using these signals, we determined $K \sim 0.1$ for the following: $[dienPtOH_2]^{2+}$ + acetone = $[dienPt(acetone)]^{2+} + H_2O$. This indicates that the acetone is weakly coordinating and a much poorer ligand than water.

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Table II. ^{1}H NMR Data[a] for Complexes of $RCONH_2$ (R = Me, H)

complex	solvent	δ(dien) CH_2	δ(dien) NH_2	δ(dien) NH	δ(amide) R	δ(amide) $NH_{1/2}$	δ(amide) OH
$[dienPtNHCOMe]^+$	*b*	2.2–3.2	5.33, 5.44	6.39	1.77	5.22	
$[dienPtNH{=}C(OH)Me]^{2+}$	*b*	2.3–3.3	5.40, 5.58	6.92	2.17	8.57	13.08
	c	2.2–3.2	4.92, 5.10	6.12	1.97		
	d	2.5–3.5	5.43, 5.52	6.49	2.27	8.46	12.00
$[dienPtOC(NH_2)Me]^{2+}$	*d*	2.5–3.5	5.42, 5.51	6.75	2.21	8.49, 8.93	
$OC(NH_2)Me$	*b*				1.78	6.74, 7.36	
	d				1.94	6.67, 7.27	
$[dienPtNHCHO]^+$	*b*	2.5–3.5	5.3, 5.4	6.4	8.18[e]	5.20	
$[dienPtNH{=}C(OH)H]^{2+}$	*d*	2.5–3.5	5.55, 5.60	6.59	8.38[e]	8.82	12.65
$[dienPtOC(NH_2)H]^{2+}$	*d*	2.5–3.5	5.5, 5.7	6.8	8.14[f]	8.90[g]	
$OC(NH_2)H$	*d*				8.16[h]	6.9, 7.1	

[a] ppm downfield of TMS. [b] d^6-DMSO. [c] D_2O. [d] d^6-Acetone. [e] Doublet, J_{CH-NH} = 3 Hz. [f] Doublet of doublets; $J_{CH-NH(cis)}$ = 3 Hz; $J_{CH-NH(trans)}$ = 14 Hz. [g] Multiplet (br) (cf. ref 3). [h] Doublet, $J_{CH-NH(trans)}$ = 12 Hz.

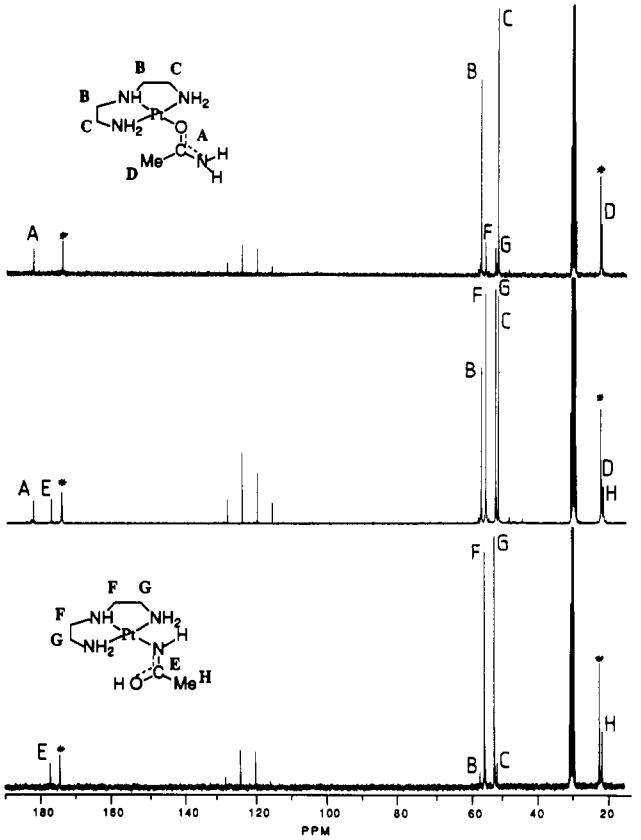


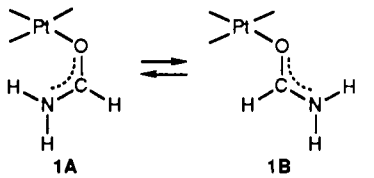
Figure 2. ^{13}C NMR spectra for $[dienPt(OH_2)](CF_3SO_3)_2$ (56 mg) mixed with excess (~15 mg) acetamide (*) in d^6-acetone at 22 °C after (top to bottom) (A) 3 h, (B) 25 h, and (C) 70 h.

reactivities in acetone. The ^{13}C NMR spectra (Figure 2) demonstrate that $[dienPt(acetamide\text{-}O)](CF_3SO_3)_2$ transforms in d^6-acetone to $[dienPt(acetamide\text{-}N)](CF_3SO_3)_2$. The N-bound acetamide product was unequivocally identified by comparison with the analogous ^{13}C spectrum for the acidified product formed through base-catalyzed hydration of $[dienPtN{\equiv}CMe](CF_3SO_3)_2$ in water.[22] Clearly this latter independent and selective synthesis of the N-bonded acetamide complex, which gave ^{1}H and ^{13}C NMR data identical to that of the product formed (Figure 2C) from the O-bonded acetamide complex (Figure 2A) in acetone, establishes that the reaction in acetone is an O- to N-linkage isomerization:

$$[dienPtO{=}C(NH_2)R]^{2+} \xrightarrow{k} [dienPtNH{=}C(OH)R]^{2+} \quad K_2$$

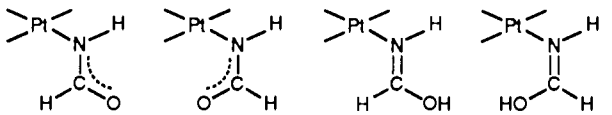
We determined the rate of this pseudo-first-order reaction by ^{1}H NMR spectroscopy ($k = 6.8 \times 10^{-6}$ s^{-1}, $t_{1/2} \sim 28$ h, 22 °C, R = Me) and found a comparable O- to N-isomerization for the formamide analogue ($k = 1.1 \times 10^{-5}$ s^{-1}, $t_{1/2} \sim 17$ h, 22 °C, R = H) as well. No side products were detected in either case, but after 20 half-lives a small amount of O-isomer still remained thus permitting determination of the isomer equilibrium constant, which was the same ($K_2 = 30$) for both cases (R = H, CH_3). We conclude that on dienPt^{II}, the N-bonded amide isomer is thermodynamically more stable than the O-bonded amide isomer by 8.3 kJ mol^{-1} ($\Delta G° = -RT \ln K$). This is the reverse of the situation for the "hard" metal ions (see Table V and Discussion), which have a comparable (reverse) coordinating preference for the alternative amide oxygen over the amide nitrogen.

Solution Structures. To determine the solution structure of the O-bonded amide complexes as **1A** or **1B**, we performed a



1A **1B**

nuclear Overhauser experiment. Unfortunately no coupling was detected between the amide-NH_2 and dien-NH_2 protons, but since the NMR data indicated only one isomer in acetone, we anticipate that it is **1B** by analogy[22] with $[(NH_3)_5CoOCHNH_2]^{3+}$. Steric hindrance from the dien ligand likely prevents **1A** from persisting in solution. We have already shown by ^{1}H NMR spectroscopy that the N-bonded amide complexes exist in acetone as the imidol (**3**) rather than amide (**4**) tautomer. However, there are two possible geometric isomers for the imidol (**3A,B**); both were observed[3] for $[(NH_3)_5CoNH{=}C(OH)H]^{3+}$ irrespective of solvent. Two isomers are also possible for the deprotonated form **2**, $[dienPtNHCHO]^+$:



2A **2B** **3A** **3B**

Since the coupling constant for **2** and **3** ($J_{CH-NH} \sim 6$ Hz) was too small for trans coupling ($J_{CH-NH} \sim 12$ Hz; **2A**, **3A**), we conclude that both deprotonated and protonated N-bonded amide complexes (R = H) exist only in the cis forms (**2B**, **3B**) since only one species was detected in each case.

One complication in the analysis of the solution structures concerned apparent H/D exchange with acetone. For example, Figure 3 shows a ^{1}H NMR spectrum of the formyl region of $[dienPtOCHNH_2](CF_3SO_3)_2$ in d^6-acetone after 11 h at 22 °C. At this stage some O- to N-isomerization has occurred (~35%) and two formyl ^{13}C resonances, as well as two sets of dien signals, were seen in the ^{13}C NMR spectrum (e.g. Figure 2B). However the two formyl ^{1}H NMR signals, assigned to O-bonded formamide (~8.1 ppm) and N-bonded formamide (~8.3 ppm), are

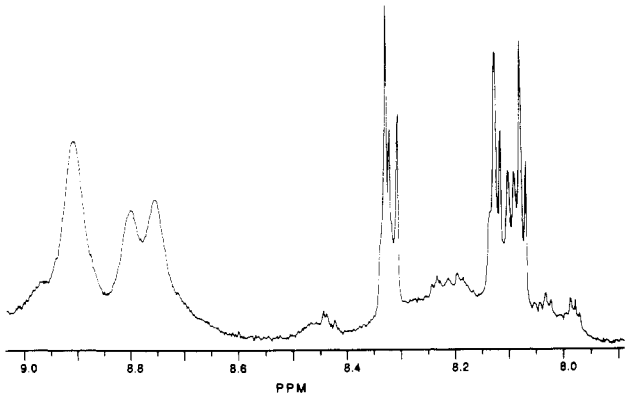


Figure 3. 300-MHz ^{1}H NMR spectrum (amide region only) of $[dienPtOCHNH_2](CF_3SO_3)_2$ in d^6-acetone after ~11 h at 22 °C.

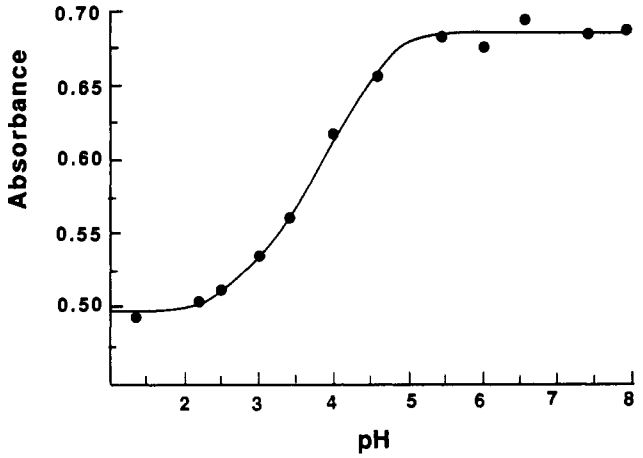
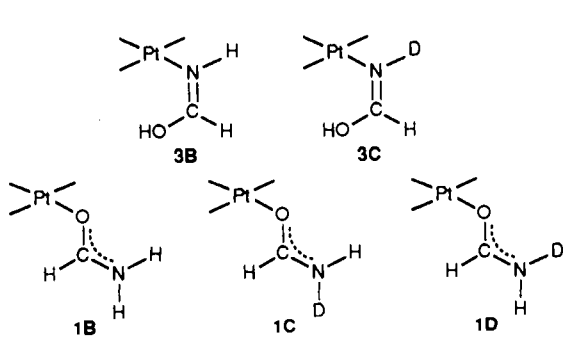


Figure 4. Absorbance–pH plot for determination of pK_a for $[dienPtNH{=}C(OH)Me](CF_3SO_3)_2$ in H_2O (20 °C).

complex multiplets (Figure 3) that each change shape and line intensities with time. If the solution is aged, the signal centered ~8.3 ppm grows while that centered ~8.1 ppm decreases and disappears, and ultimately the resonance at ~8.3 ppm decouples to a singlet. The corresponding ^{13}C spectra (Figure 2) indicate almost complete O- to N-isomerization.

Our interpretation is that the signal at ~8.3 ppm is a mix of **3B** (doublet, J_{CH-NH} = 6 Hz) and **3C** (singlet), while the resonance



~8.1 ppm is a combination of **1B** (doublet of doublets), **1C** (doublet, J_{CH-NH} = 14 Hz), **1D** (doublet, J_{CH-NH} = 6 Hz), and Pt–OCHND$_2$ (singlet). Consistent with exchange with d^6-acetone, an H^6-acetone signal grows in intensity during the isomerization process.

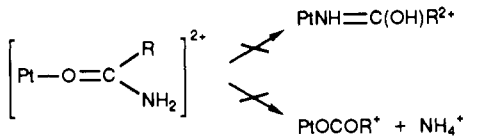
Isomer Acidity. The pK_a was determined for $[dienPtNH{=}C(OH)Me](CF_3SO_3)_2$ in aqueous buffers at 20 °C using the difference in UV absorption spectra for the acid and base forms of the complex. The absorbance–pH data obtained (recorded in Table III, supplementary material) are plotted in Figure 4 and give pK_a = 3.75. This is not too different from other dienPt^{II} complexes (Table IV) and similar to that for the $(NH_3)_5$-Co^{III} complex of N-bonded acetamide,[23] which also exists as the imidol tautomer[3] $[(NH_3)_5CoNH{=}C(OH)Me]^{3+}$. Table IV also shows other comparisons of acidities of selected molecules attached to either dienPt^{II} or $(NH_3)_5Co^{III}$.

Table IV. Comparison of Acidities of Amides and Other Molecules Coordinated to Pt(II) versus Co(III)

complex	pK_a	ref
$[dienPtNHC(OH)Me]^{2+}$	3.8	
$[(NH_3)_5CoNHC(OH)Me]^{3+}$	3.0	23
$[dienPtNH_2CONMe_2]^{2+}$	5.6	22
$[(NH_3)_5CoNH_2CONMe_2]^{3+}$	2.9	24
$[dienPtOC(NH_2)Me]^{2+}$	>10	estimate
$[(NH_3)_5CoOC(NH_2)Me]^{3+}$	11.6	25
$[dienPtOH_2]^{2+}$	6.1	20
$[(NH_3)_5CoOH_2]^{3+}$	6.2	19

From these data the polarizing powers of dienPt^{II} and $(NH_3)_5$-Co^{III} are evidently similar, yet it will be seen ahead in Table V that the thermodynamic affinities for N- and O-termini of acetamide are opposite. Factors which control these affinities are discussed ahead in relation to previous work with amide complexes of other metal ions.

Reactivity in Coordinating Solvents. When the $[dienPtOC(NH_2)R](CF_3SO_3)_2$ complexes were dissolved in either D_2O or d^6-DMSO, the amide ligand was rapidly displaced by the solvent. Solvolysis was complete within 5 min for both amide complexes at 20 °C in both solvents as assessed by NMR measurements. We can only estimate that $t_{1/2} \leq 1$ min for both amide complexes in either solvent. No side products were detected by NMR (^{1}H, ^{13}C) spectroscopy indicating no significant competition from the possible alternative linkage isomerization or amide decomposition pathways:



The isomerization reaction was observed only in acetone because, unlike water or DMSO, there was no significant competing solvolysis. The decomposition of O-bonded amides on pentaamminecobalt(III) to ammonium ion has previously been observed.[25,26] We did not detect formate/acetate, NH_4^+, N-bonded amide isomer, nor formato or acetato complexes of dienPt^{II}. Solvolysis is therefore faster in water and DMSO than either O- to N-isomerization or ligand fragmentation.

The N-bonded amide complexes were kinetically inert, although they reacted slowly with water or DMSO with release of the amide ligand (e.g. $k_1 = 1.37 \times 10^{-5}$ s^{-1}, 40.0 °C, H_2O, pH 2.5, R = Me). No side products were detected by NMR (^{1}H, ^{13}C) spectroscopy. This rate of amide displacement is comparable to that[3] observed for $[(NH_3)_5CoNH{=}C(OH)Me]^{3+}$ under similar conditions.

Discussion

We found no evidence for reaction between amides and $[dienPtOH_2]^{2+}$ in water (pH 4–7) at 20 °C over 24 h. Even in the poor coordinating solvent acetone, the equilibrium has to be

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(24) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 4038.
(25) Angus, P. M.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.*, submitted for publication.
(26) Buckingham, D. A.; Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726.

Table V. Equilibrium Constants for Metal Complexes of $RCONH_2$ in Water at 25 °C (R = Me, NH_2)

complex	K (=[O]/[N])	ref	complex	K (=[O]/[N])	ref
$(NH_3)_5Cr^{III}$	$>10^5$	4	$(NH_3)_5Ru^{II}$	≥ 10	5
$(NH_3)_5Co^{III}$	$\geq 10^2$	3	$(NH_3)_5Rh^{III}$	~ 1	6
$(NH_3)_5Ru^{III}$	~ 10	5	dienPt^{II} [a]	$\sim 3 \times 10^{-2}$	this work

[a] For acetone as solvent, lower limit when water is solvent.

forced to $[dienPt(amide\text{-}O)]^{2+}$

$$[dienPtOH_2]^{2+} + RCONH_2 = [dienPtOC(NH_2)R]^{2+} + H_2O$$

by using slightly more than 1 equiv of amide. In water the amide dissociates (equilibrium lies to the left) from Pt(II), irrespective of the binding mode (N or O) of the amide to Pt, but this process is much faster for the O-bonded than N-bonded amide complexes. These results contrast with the interpretation[11] of transient acetamide O-bonding to *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ *in water*. Those observations,[11] which were based solely on an ^{15}N and ^{195}Pt NMR experiment, were complicated by ensuing oxidation of Pt(II), yet it is conceivable that *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ does show the implied very different affinity and ligand dynamics for the amide than observed here for dienPt^{II}.

Preferential capture of the amide oxygen by the soft dienPt^{II} electrophile mirrors the similar preference of free amides for *protonation* of this site. Metal complexes evidently have a kinetic preference for the amide oxygen over the amide nitrogen irrespective of the hard/soft nature of the complexing metal system. This kinetic preference seems to primarily reflect the charge interaction between the polarizing cation and the more electronegative amide site rather than any hard/soft properties of the metal or amide.

However while the amide O-bonding mode is kinetically preferred for the dienPt^{II} moiety, amide N-bonding is thermodynamically preferred (K = [N]/[O] ~ 30). This contrasts with other metal ions in Table V for which the amide O-isomer was both kinetically and thermodynamically favored over the N-bonded amide complex. The linkage isomer equilibrium can then be considered as a molecular switch:

$$[MNH_2COR]^{n+} = [MO{=}C(NH_2)R]^{n+}$$

The position of the switch can be influenced by substituent (R),[14-17] tautomeric equilibrium (K_T),[5,13] solvent,[14] pH, and oxidation state[5] of the metal. The influence of pH is due to the large difference in acidities between the linkage isomers; typically N-bonded amides have a $pK_a \sim 3$ whereas O-bonded amides have $pK_a \sim 11$. Thus, between pH ~ 3–11 the N-bonded amide is selectively deprotonated, and this drives the equilibrium to the left when otherwise it might be to the right, as in the case for example of Co(III).[16,27]

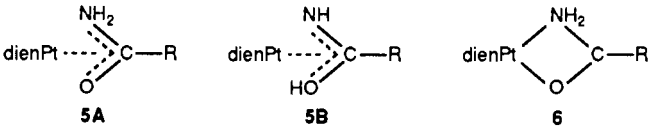
The new observations here for dienPt^{II}, when combined with the data in Table V, demonstrate that the position of the switch is also influenced by the nature of the metal (M). Clearly the hard versus soft nature of the metal ion receptor, modified by its ligand environment, is important in determining the thermodynamic affinity for the amide nucleophile. Yet the polarizing effects of these electrophilic metal ions are comparable on the basis of a comparison of the pK_a of attached ligands like water, urea, and acetamide, so the charge interaction is less important.

An intriguing feature of these isomerizations is that they are invariably intramolecular—there is no invervention by solvent during the isomerization. We have confirmed the intramolecular nature of the O- to N-isomerization here by doping solutions as in Figure 2A with other amides. No amide scrambling was observed during the isomerization thus eliminating the possibility of intermolecular amide exchange.[28] How then is the rearrangement facilitated without permitting solvent entry to the first coordination sphere of the metal? The driving force is clearly energetic; the ground-state structure of the N-bonded amide is 8.3 kJ mol^{-1} more stable than the O-bonded amide. This stabilization seems unlikely to originate from proton migration to the stable imidol tautomer (**4** → **3**), since a similar energy difference is observed on dienPt^{II} for ureas,[22] where O- to N-isomerization (**1** → **4**) also occurs, but only the amide tautomer **4** is involved.

$$[dienPtO{=}C(R)NH_2]^{2+} = [dienPtNH_2COR]^{2+} = [dienPtNH{=}C(OH)R]^{2+}$$
1 **4** **3**

For acetamide and formamide no evidence was found for the amide tautomer **4**, and only **3** was detected. However, the O- to N-isomerization (**1** → **3**) observed here very likely involves formation of **4** as a transient intermediate en route to **3**, and proton migration (**4** → **3**) consequently must be fast (since no buildup of **4** was observed).

The observation by ^1H NMR spectroscopy that the N-bonded amide isomer, produced from the rearrangement, adopts the isomeric form **3B** (with the amide oxygen syn to dienPt^{II} may reflect the geometry of a transition state in which both N and O of the amide are equally predisposed toward nucleophilic attack on Pt(II):



Whether one of these two extremes (π-intermediate **5** or 5-coordinate associative intermediate **6**) is involved in the isomerization process remains to be determined. However, there is increasing evidence from other intramolecular linkage isomerizations that a high degree of associative character is involved in these isomerization mechanisms—bond making is important even for metal complexes known to undergo dissociative intermolecular ligand substitution.[13,18,29] These intramolecular processes may therefore be able to play an important role in probing the mechanism of ligand substitution in metal complexes in general.

Summary. The synthesis, characterization, and reactivity of one of the few examples of an O-bonded ligand on Pt(II) have been demonstrated. Although unstable thermodynamically toward O- to N-rearrangement and to solvolysis, it is relatively kinetically inert in acetone, a poorer coordinating solvent than water for Pt(II). N-bonded amide complexes were also prepared. They are acidic ($pK_a \sim 4$) unlike O-bonded amide isomers (estimated $pK_a > 11$) and adopt the imidol tautomeric form rather than the amide tautomer that predominates for a urea analogue.[22] ^1H and ^{13}C NMR spectroscopy in combination permitted structure assignments of the linkage isomers and monitoring of their reactivity. Amide complexes of several metals were compared to identify effects of "soft" versus "hard" properties on their kinetic versus thermodynamic stabilities.

Experimental Section

NMR solvents were obtained in 0.5-mL ampules from Aldrich to ensure that each measured solution was dry. NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer (probe temperature 22 °C)

(27) Fairlie, D. P.; Jackson, W. G. *Inorg. Chim. Acta* **1990**, *175*, 203.

(28) A similar result has now been confirmed by ^{15}N NMR spectroscopy by doping the solution (e.g. Figure 2) with ^{15}N-acetamide.

(29) Jackson, W. G.; Sargeson, A. M. Rearrangements in Coordination Complexes. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 273.

using TMS as an internal standard. Infrared spectra were measured on a Perkin-Elmer 1600FT spectrophotometer. Cary 3 and 210 UV–vis spectrophotometers were used to observe acid/base and solvolysis reactions. Analyses (C, H, N, S) were conducted commercially by Chemical & MicroAnalytical Services, Melbourne, Australia. [dienPt(OH$_2$)](CF$_3$SO$_3$)$_2$ and [dienPtN≡CMe](CF$_3$SO$_3$)$_2$ were prepared as described elsewhere.[22] Amides, acetone, diethyl ether, and DMSO were AR grade.

pK_a Determination. The acidity of the N-bonded acetamide complex in water at 20.0 °C was determined spectrophotometrically over a range of pH values (1–10). The pH of aqueous buffers (Tris, Mes, acetate, Gly) was determined using an Activon 210 pH meter and combination glass electrode (Ag/AgCl reference) standardized for each pH range. The pK_a was determined from a plot (Figure 4) of absorbance at 240 nm versus pH; detailed data are reported in Table III (supplementary material).

Kinetic Studies. Kinetic data were obtained from absorbance/time traces at a specific wavelength or by monitoring NMR spectral changes with time. Solid platinum complexes were dissolved in acidified aqueous solution (pH 2.52) preequilibrated at 40.0 °C in a 1-cm cuvette inserted in a Cary 3 spectrophotometer. The solution temperature (40.0 ■ ≤0.3 °C) was regulated by heating the cell block with a Peltier electrothermal device. Data was collected over 5 $t_{1/2}$, fitted to nonlinear least-squares analysis, and rate constants are means of ≥2–3 determinations with standard deviations ≤±3%. The rate of solvolysis at 40.0 °C of [dienPtNH=C(OH)Me](CF$_3$SO$_3$)$_2$ was determined from first-order absorbance/time changes at 237 nm. The O- to N-bonded amide isomerizations were monitored by NMR (^{1}H, ^{13}C) spectroscopy using ^{13}C resonances of dien to determine rate constants.

Syntheses. [dienPt(OCNH$_2$Me)](CF$_3$SO$_3$)$_2$. To a solution of [dienPt(OH$_2$)](CF$_3$SO$_3$)$_2$ (120 mg) in acetone (5 mL) was added acetamide (17 mg, 1.5 equiv) followed within 2 min by diethyl ether (25 mL). The resulting oily precipitate was separated by decanting off the supernatant, and the residue was washed with chloroform (5 × 10 mL). It was then redissolved in acetone and precipitated slowly over several hours (0 °C) by gradual dropwise addition of diethyl ether. The product was collected by vacuum filtration and dried at room temperature by vacuum evaporation. Anal. Calcd for PtC$_8$H$_{18}$N$_4$O$_7$F$_6$S$_2$: C, 14.65; H, 2.75; N, 8.54; S, 9.76. Found: C, 14.35; H, 2.60; N, 8.46; S, 9.47.

[dienPt(NHCOMe)](CF$_3$SO$_3$). A solution of [dienPt(OH$_2$)](CF$_3$SO$_3$)$_2$ (0.4 g) in acetonitrile (3 mL, dried over sieves) was allowed to stir for 10 min before adding diethyl ether (15 mL) to precipitate the platinum product. The supernatant was decanted, and the oil was washed several times with diethyl ether before drying (40 °C, rotary evaporator). To the oil in water (2 mL) was added NaOH (0.56 mL, 1.0 M), and the solution was then precipitated with chloroform, followed by copious washing with diethyl ether and vacuum drying. Yield: 0.2 g. It was recrystallized from ethanol/chloroform. Anal. Calcd for PtC$_7$H$_{17}$N$_4$O$_4$F$_3$S: C, 16.62; H, 3.36; N, 11.08; S, 6.33. Found: C, 16.47; H, 3.45; N, 10.88; S, 6.42.

[dienPt(NH=C(OH)Me)](CF$_3$SO$_3$)$_2$. Method A. To a solution of [dienPt(NHCOMe)](CF$_3$SO$_3$) (0.1 g) in water (2 mL) was added CF$_3$SO$_3$H until pH < 1. Chloroform was then used to wash the compound until free of water, and then the solid was washed with diethyl ether and vacuum dried. Yield: 95%. Anal. Calcd for PtC$_8$H$_{18}$N$_4$O$_7$F$_6$S$_2$: C, 14.65; H, 2.75; N, 8.54; S, 9.76. Found: C, 14.68; H, 2.78; N, 8.37; S, 9.70.

Method B. [dienPt(OCNH$_2$Me)](CF$_3$SO$_3$)$_2$ (60 mg) was left in acetone over 3 weeks at room temperature or heated for 4 h at 60 °C. Diethyl ether was then added to the cooled solution until all the platinum had oiled out. This was washed several times by decantation with ether and crystallized from ethanol/chloroform. Yield: 90%.

[dienPt(OCHNH$_2$)](CF$_3$SO$_3$)$_2$. [dienPt(OH$_2$)](CF$_3$SO$_3$)$_2$ (0.1 g) was dissolved in acetone at 22 °C, and formamide (20 mg) was added to the mixture. The mixture was quickly treated with cold diethyl ether to produce an oily precipitate, which was washed copiously by decantation with diethyl ether before drying under vacuum. The resulting solid was washed with chloroform (5 × 10 mL) and crystallized from acetone/ether. As with the other formamide complexes below, the product was hygroscopic despite washing/crystallization procedures used in an attempt to remove traces of formamide or acid. The complexes were not analyzed for elemental composition for this reason; their purity was instead established by ^{1}H and ^{13}C NMR spectroscopy. No impurities were detected for any of the formamide complexes using NMR spectroscopy.

[dienPt(NHCHO)](CF$_3$SO$_3$). A solution of [dienPt(OH$_2$)](CF$_3$SO$_3$)$_2$ (0.2 g) in formamide (3 mL, dried over sieves) was allowed to stir for 10 min before adding diethyl ether (15 mL) to precipitate the platinum product. The supernatant was decanted, and the oil was washed several times with diethyl ether before vacuum drying (40 °C, rotary evaporator). To the oil in water (2 mL) was added NaOH (0.34 mL, 1.0 M), and after 10 min the water was removed by vacuum evaporation. The pale yellow solid was copiously washed by decantation with diethyl ether and vacuum dried (30 °C, 5 h). The product was slightly hygroscopic.

[dienPt(NH=C(OH)H)](CF$_3$SO$_3$)$_2$. Method A. To a solution of [dienPt(NHCHO)](CF$_3$SO$_3$) (0.1 g) in water (2 mL) was added CF$_3$SO$_3$H until pH < 1. Chloroform was then used to wash the compound until free of water, and then the solid was washed copiously be decantation with diethyl ether and vacuum dried. Yield: 95%.

Method B. [dienPt(OCHNH$_2$)](CF$_3$SO$_3$)$_2$ (60 mg) was left in acetone over 3 weeks at room temperature. To the cooled solution was then added diethyl ether to oil out the platinum. This was washed several times by decantation with ether and crystallized from ethanol/chloroform. Yield: 90%. The product was hygroscopic.

Supplementary Material Available: A table of absorbance–pH data (Table III) (1 page). Ordering information is given on any current masthead page.