Oxygen versus Nitrogen Coordination of a Urea to (Diethylenetriamine)platinum(II)

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Syntheses and properties of isomeric (diethylenetriamine)platinum(II) complexes of 1,1-dimethylurea (DMU) bound through oxygen or nitrogen are reported. Isomers were distinguished by a combination of NMR (^{1}H, ^{13}C) and IR spectroscopy, acidity and reactivity measurements, and an isomer selective synthetic route. The oxygen-bonded DMU compound, $[dienPtOC(NH_2)NMe_2]^{2+}$, is the kinetically preferred product from the stoichiometric reaction of DMU with $[dienPtOH_2]^{2+}$ in acetone. This oxygen-bonded form then rearranges ($t_{1/2} \sim 18$ min, 22 °C) to the slightly more thermodynamically stable nitrogen-bonded linkage isomer (K_{NO} = [N-isomer]/[O-isomer] ~ 3). The reverse isomerization from N-bonding to O-bonding was also detected. NMR (^{1}H, ^{13}C) and IR spectroscopy proved that the N-bonded DMU complex, which was also independently and selectively synthesized through base hydrolysis of the cyanamide precursor $[dienPtN{\equiv}CNMe_2]^{2+}$, exists in solution and in the solid state as the unusual *amide* tautomer $[dienPtNH_2COR]^{2+}$ (R = NMe_2), rather than the *imidol* tautomer $[dienPtNH{:}C(OH)R]^{2+}$ observed for acetamide (R = Me). The N-bonded DMU ligand was much more acidic (pK_a 5.6, H_2O, 20 °C) than the O-bonded DMU linkage isomer ($pK_a \geq 11$(est)), indicating greater resonance stabilization for the deprotonated urea of $[dienPtNHCONMe_2]^+$ versus $[dienPtOC(NMe_2)NH]^+$, but less acidic than the N-bonded acetamide of $[dienPtNH{:}C(OH)Me]^{2+}$ (pK_a 3.8), where the acidic proton is on oxygen instead of nitrogen. Both the ~50-fold faster solvolysis of the N-bonded DMU versus the N-bonded acetamide (R = NMe_2, $k = 5 \times 10^{-4}$ s^{-1}; R = Me, $k = 1 \times 10^{-5}$ s^{-1}; H_2O, pH 2.5, 40.0 °C) and the ~100-fold rate difference in linkage isomerization from O-bonding to N-bonding DMU (R = NMe_2, $k = 6.4 \times 10^{-4}$ s^{-1}; R = Me, $k = 6.8 \times 10^{-6}$ s^{-1}; acetone, 22 °C) are attributed to the requirement for proton migration between *imidol* and *amide* tautomers of the N-bonded form. Both isomerization and solvolysis likely proceed via the amide tautomer only. The O-bonded DMU ligand is displaced much faster (water, DMSO; $t_{1/2} < 1$ min, 22 °C) than the N-bonded DMU ligand from platinum by coordinating solvents.

Introduction

Urea is an ambident nucleophile which can coordinate to metal ions through either nitrogen or oxygen atoms.[1-6] It selectively protonates on oxygen[7] but can diprotonate in super acids (e.g. FSO_3/SbF_6).[8]

$$NH_2CONH_2 \xrightarrow{H^+} NH_2{=}C(OH)NH_2^+ \xrightarrow{H^+} NH_3C(OH)NH_2^{2+}$$

Its coordination to "hard" metal ions (M = Co(III),[1,2] Cr(III),[3] Ru(III)[4]) has previously been examined, and in each case the oxygen-bonded linkage isomer $[(NH_3)_5MOC(NH_2)_2]^{3+}$ was kinetically preferred and thermodynamically more stable (acetone, sulfolane, water) than the N-bonded urea $[(NH_3)_5MNH_2CONH_2]^{3+}$. Recently a chelating ligand, incorporating a pyridine and urea group, was coordinated through the pyridine-N as well as a urea *nitrogen* to Ni(II) and Cu(II) to form a five-membered ring but via the pyridine-N and a urea *oxygen* to Zn(II) producing a six-membered ring.[6] The present work reports the binding of a monodentate urea, free from the steric constraints and entropic influence of chelate formation, to a soft metal and compares the solution structures and reactivity for "soft" versus "hard" metals.

Although dienPt^{II} has polarizing power comparable to that of the hard $(NH_3)_5M^{III}$ moieties (Table I), its softer nature was expected to favor coordination of the urea nitrogen. While very few Pt(II) complexes containing neutral O-donor ligands have been previously isolated,[9] the soft Pt(II) usually forms stable complexes with N-donor ligands.

Nitrogen-bonded urea complexes are quite unstable for hard metal ions,[1,2,4,5] either decomposing to free urea or ammonia and carbon dioxide[5,10,11] or alternatively rearranging to the oxygen-bonded urea isomer.[1-5] We found previously that tautomerism between MNH_2COR and $MNH{=}C(OH)R$ can be important in controlling the reactivity of amide complexes.[4,12]

In another context Ni(II) is present in the enzyme urease, which hydrolyzes urea to ammonia and carbon dioxide.[13] Being in the same group, Pt(II) offered a chance to examine urea coordination to an inert soft metal. We now report the syntheses and properties of dienPt^{II} complexes of a urea, bound to the metal through nitrogen or oxygen.

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Table I. Comparison of Acidities (pK_a's) of Ligands (L) in Metal Complexes in Water at 25 °C

	L		
metal	OH_2	NH:C(OH)Me	NH_2CONMe_2
$(NH_3)_5Co^{III}$	6.2 [14]	3.0 [15]	2.9 [1]
$(NH_3)_5Cr^{III}$	5.2 [16]		
$(NH_3)_5Ru^{III}$	4.1 [17]	2.0 [18]	1.8[b,4]
$(NH_3)_5Rh^{III}$	6.4 [19]		3.9[b,5]
$(dien)Pt^{II}$	6.1 [20]	3.8[a,9]	5.6[a,c]

[a] 20 °C. [b] Urea, not dimethylurea. [c] This work.

Experimental Section

NMR spectra were measured in the indicated deuterated solvents (Aldrich) using a 300-MHz Varian Gemini spectrometer, and tabulated chemical shifts are relative to TMS as reference. Infrared spectra were recorded with a Perkin-Elmer 1600FT spectrophotometer. A Varian Cary 3 spectrophotometer was used to monitor acid–base and solvolysis reactions. Elemental analyses were conducted commercially by Chemical & Microanalytical Services, North Essendon, Australia.

Synthesis. Solvents and reagents were AR grade. 1,1-Dimethylurea (NH_2CONMe_2) is abbreviated as DMU. $[dienPtOH_2](CF_3SO_3)_2$ and $[dienPtNCNMe_2](CF_3SO_3)_2$ were prepared, isolated, and characterized as described elsewhere.[21]

$[dienPtNH_2CONMe_2](CF_3SO_3)_2$. 1,1-Dimethylurea (0.4 g) was added to a solution of $[dienPtOH_2](CF_3SO_3)_2$ in acetone (0.5 g in 40 mL), and the mixture was stirred for 30 min at 30 °C. Although DMU was not appreciably soluble in acetone, some clearly dissolved on reaction. After cooling in ice, the supernatant was decanted from insoluble DMU, diethyl ether (200 mL) was added to the solution, and the resulting oily precipitate was dried by vacuum evaporation. The oil was redissolved in acetone and filtered, and diethyl ether was slowly added to the filtrate until the solution just became cloudy. Cooling at 0 °C for 3 days gave colorless crystals. These were filtered off, washed with diethyl ether (5 × 10 mL), and air-dried. Isolated yield = 0.2 g. Other fractions may also be collected; the overall yield is ~90%. Anal. Calcd for $PtN_5C_9F_6S_2O_7H_{21}$: C, 15.78; H, 3.07; N, 10.23; S, 9.35. Found: C, 15.74; H, 3.06; N, 10.21; S, 9.38. IR (ν, cm^{-1}; Nujol): 3204, 3138 (NH stretches); 1725 (s, C=O); 1254 (s), 1164 (s), 1077 (w), 1032 (s, sharp), 788 (w), 721 (w), 638, 606, 575, 516 (all s, sharp). Absorption spectrum: ϵ_{236} (shoulder) = 5029 for $[dienPtNHCONMe_2](CF_3SO_3)$ in water pH 8 versus ϵ_{236} = 643 for $[dienPtNH_2CONMe_2](CF_3SO_3)_2$ in water pH 1.

$[dienPtNHCONMe_2](CF_3SO_3)$. NaOH (0.68 mL, 1 M) was added to an aqueous solution of $[dienPtN{\equiv}CNMe_2](CF_3SO_3)_2$ (0.45 g in 5 mL). After 30 min at 20 °C water was removed by vacuum evaporation and the resulting solid was copiously washed with diethyl ether and acetone. The product (yield 0.19 g) was identified by NMR (^1H, ^{13}C) spectroscopy.

$[dienPtOC(NH_2)NMe_2](CF_3SO_3)_2$. $[dienPtOH_2](CF_3SO_3)_2$ (0.5 g) dissolved in cold acetone (10 mL, 0 °C) was mixed with 1,1-dimethylurea (0.1 g), and the mixture was stirred (15 min). The mixture was poured into diethyl ether, and the oily precipitate was washed copiously with cold diethyl ether (5 × 25 mL), redissolved in acetone (0 °C), and reprecipitated by adding cold diethyl ether. The resulting microcrystalline product was air-dried and gave correct analyses for $[dienPtOC(NH_2)NMe_2](CF_3SO_3)_2$. Anal. Calcd: C, 15.78; H, 3.07; N, 10.23; S, 9.35. Found: C, 15.66; H, 3.15; N, 10.08; S, 9.21. However NMR spectroscopy (d^6-acetone) showed contamination by the analytically identical N-bonded DMU isomer, formed through fast O- to N-linkage isomerization. It is thus preferable to generate the complex in situ and use immediately before isomerization ensues.

pK_a Determination. Absorbance changes for $[dienPtNH_2CONMe_2](CF_3SO_3)_2$ at 20 °C, recorded on a Cary 3 spectrophotometer, were used to determine the pK_a. pH was measured with an Activon 210 pH meter and Activon BJ411 combination glass electrode (Ag/AgCl reference) standardized to $[H^+]$ scale with appropriate buffers over separate pH ranges. Aqueous buffers (0.05 M solutions; pH 8–11, Tris-HCl; pH 5–7.5, Mes-NaOH; pH 3.5–4.5, NaOAc-HCl; pH < 1.0, CF_3SO_3H) were diluted with aqueous platinum solutions to I = 0.025 M. Absorbances were measured for dilute solutions ([Pt] = 1.71×10^{-4} M) of $[dienPtNH_2CONMe_2](CF_3SO_3)_2$ at 236 nm, the absorbance maximum for the deprotonated N-bonded DMU complex.

Kinetic Measurements. Rearrangements were monitored by ^1H and ^{13}C NMR spectroscopy using d^6-acetone as solvent. Kinetic data was obtained by ^{13}C-NMR measurements of the changes with time of the dien resonances for each isomer at 22 °C. Data were fitted to a first-order rate equation and had standard deviations of <±4%. Solvolyses (H_2O, DMSO) were followed by absorbance/time traces at 200 nm. Solid platinum complexes were typically dissolved in aqueous acid (0.1 or 0.01 M $HClO_4$, I = 1.0 M ($NaClO_4$)), preequilibrated at 40.0 °C, and measured in a 1-cm cuvette thermostated to ±0.3 °C in a Cary 3 spectrophotometer. The temperature of the cell block was regulated as described.[9] Data were collected over 5 half-lives and obeyed strictly a first-order rate law. First-order rate constants were determined by computer-fitting curves to a single exponential equation by standard least-squares procedures.

Results and Discussion

Isomer Synthesis. We chose to study the reaction of $[dien-PtOH_2]^{2+}$ with 1,1-dimethylurea, $OC(NH_2)NMe_2$, rather than urea because of the advantage of an extra ^1H and ^{13}C NMR feature (NMe_2) that would facilitate monitoring of reactions. Also this substitution was anticipated to sterically reduce the prospect of forming platinum dimers containing a bridging urea ligand, and we also expected to be able to access the N-bonded dimethylurea complex via an independent, isomer-selective synthesis using base hydrolysis of the dimethylcyanamide complex (R = NMe_2):[21]

$$[dienPtN{\equiv}CR]^{2+} + OH^- \rightarrow [dienPtNHCOR]^+$$

Although this was not a useful synthesis of the urea (R = NH_2) complex because of deprotonation of the corresponding cyanamide ligand[22]

$$[MN{\equiv}CNH_2]^{n+} + OH^- \rightarrow [MN{=}C{=}NH]^{(n-1)+}$$

it was successful for the selective synthesis of the N-bonded *dimethylurea*, providing an independent means of isomer assignment.

When $[dienPtOH_2](CF_3SO_3)_2$ was dissolved at 22 °C in d^6-acetone containing 1.03 stoichiometric equiv of NH_2CONMe_2, two complexes were detected (Figure 1). Within the first few minutes only one carbonyl (A, 164 ppm) and two dien resonances (B, 56.1; C, 51.1 ppm) were observed by ^{13}C-NMR spectroscopy. The carbonyl was not due to free dimethylurea (161 ppm). Within 20 min this intermediate had converted into a significant amount of a product characterized by carbonyl (E, 158 ppm) and dien (F, 55.0; G, 51.4 ppm) resonances (Figure 1a). After 1 h (22 °C) product signals had become dominant (Figure 1b), and equilibrium was achieved within 2 h (Figure 1c). The equilibrium favored product over intermediate by ~3:1 (see F + G versus B + C, Figure 1c).

Trace signals in Figure 1a were due to unreacted $[dienPtOH_2]^{2+}$ and DMU, excess DMU (>2 equiv) being required to complex all the platinum. The product was isolated by crystallization, and its solid-state and solution structure was established as $[dienPtNH_2CONMe_2]^{2+}$, **1**, rather than alternatives $[dienPtOC-(NH_2)NMe_2]^{2+}$, **2**, or $[dienPtNH{=}C(OH)NMe_2]^{2+}$, **3**, by infrared and NMR (^1H, ^{13}C) spectroscopy.

Infrared Spectra. The infrared spectrum for **1** (Figure 2b) in Nujol exhibited $\nu_{C=O}$ 1725 cm^{-1} typical of a short C=O bond and distinct from the strong and sharp twin amide signals (1660, 1609 cm^{-1}) exhibited by free 1,1-dimethylurea (Figure 2a). $\nu_{C=O}$ of O-bonded ureas is typically ~1660 cm^{-1} in metal complexes,[1,2,4,5] whereas N-bonded urea[5] on $(NH_3)_5Rh^{III}$ has $\nu_{C=O}$ 1740 cm^{-1} and N-bonded pyridylureas on Cu^{2+} and Ni^{2+} have $\nu_{C=O}$ 1700–1750 cm^{-1}.[6] Isolated samples of the O-bonded DMU complex here gave intense absorption at ~1660 cm^{-1}, along with a trace signal at ~1725 cm^{-1} for the N-isomer. Figure 2b shows no absorbance near 1660 cm^{-1}, consistent with assignment as $[dienPtNH_2CONMe_2]^{2+}$. The higher energy carbonyl is con-

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(22) The cyanamide complex $[dienPtN{\equiv}CNH_2]^{2+}$ deprotonates to a species which is unreactive to hydroxide, as observed for $[(NH_3)_5CoN{\equiv}CNH_2]^{3+} \rightarrow [(NH_3)_5CoN{=}C{=}NH]^{2+}$ (see ref 1 and: Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 625–631). The synthesis, characterization, and reaction of $[dienPtN{\equiv}CR]^{2+}$ with nucleophiles will be reported separately.

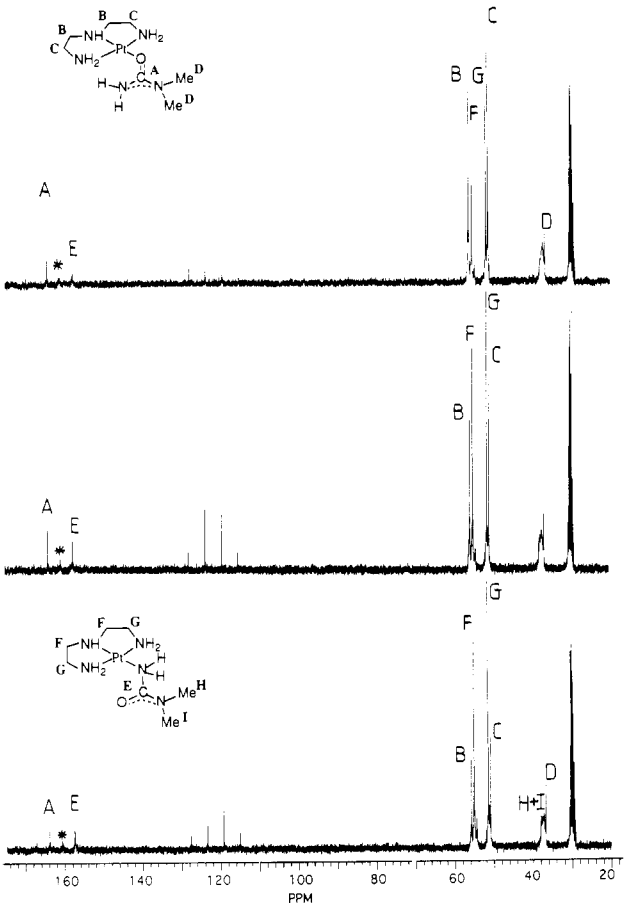


Figure 1. ^{13}C NMR spectra for $[dienPt(OH_2)](CF_3SO_3)_2$ (244 mg, 4 × 10^{-4} mol) in d^6-acetone (1 mL) with added NH_2CONMe_2 (36 mg, 4.1 × 10^{-4} mol) at 22 °C, scanned at the following intervals after mixing: 5–20 min (a, top); 64–79 min (b, middle); 135–150 min (c, bottom). An asterisk indicates free dimethylurea.

sistent with $[dienPtNH_2CONMe_2]^{2+}$, where π density is localized in the $-C(=O)NMe_2$ component of the DMU ligand. The peak at 1032 cm^{-1} (Figure 2b) is characteristic of uncoordinated triflate anion.

Selective Synthesis and Acidity of the N-Isomer. The solution identity of **1** was firmly established as the N-coordinated linkage isomer by its independent synthesis via base hydrolysis[1] of **4**:

$$\underset{\mathbf{4}}{[dienPtN{\equiv}CNMe_2]^{2+}} + OH^- \rightarrow \underset{\mathbf{5}}{[dienPtNHCONMe_2]^{+}}$$

$$\underset{\mathbf{5}}{[dienPtNHCONMe_2]^{+}} + H^+ \rightarrow \underset{\mathbf{1}}{[dienPtNH_2CONMe_2]^{2+}}$$

This selective synthesis can only give the *N-bonded* deprotonated urea complex **5**. Subsequent protonation gave a product (**1**) with NMR and infrared spectra identical to those of the crystals isolated from $[dienPtOH_2]^{2+}$ mixed with 1,1-dimethylurea in acetone. Both independently prepared samples of **1** underwent reversible deprotonation in basic/acidic water or d^6-DMSO, a feature typical of an acidic N-bonded urea isomer.[1,2] Oxygen-bonded urea complexes are much less acidic ($pK_a \sim 13$).[1,3,5]

The pK_a of **1** was determined from pH-dependent absorbance changes (Table II, supplementary material) in the UV spectrum (236 nm). The plot of absorbance–pH (Figure 3) has typical sigmoidal shape. The flat regions either side of the incline are important, indicating that both protonated and deprotonated forms of the N-bonded DMU complex were sufficiently stable to make reliable measurements. For example the protonated form is unstable with respect to displacement of DMU by coordinating solvents (H_2O, DMSO). The acidity of complexed DMU (pK_a = 5.6; 20 °C, I = 0.025 M; Figure 3) is 8 orders of magnitude

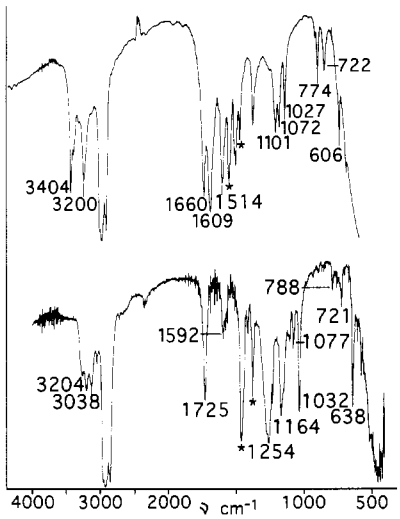


Figure 2. Infrared spectra for NH_2CONMe_2 (a, top) and $[dienPt-NH_2CONMe_2](CF_3SO_3)_2$ (b, bottom) in Nujol. An asterisk indicates Nujol.

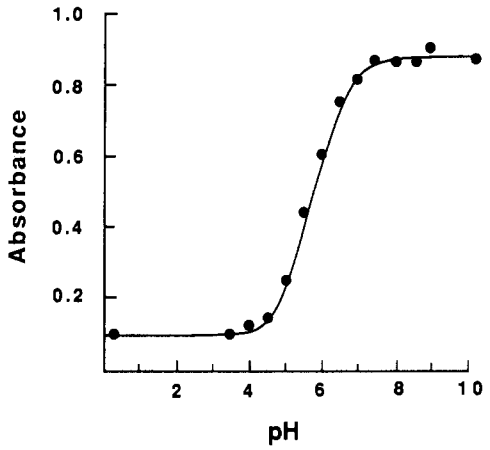


Figure 3. Variation in absorbance at 236 nm versus pH for $[dienPt-NH_2CONMe_2](CF_3SO_3)_2$ (0.171 mM) in aqueous buffers (pH 8–11, Tris-HCl; pH 5–7.5, Mes/NaOH; pH 3.5–4.5, NaOAc-HCl; pH < 1.0, CF_3SO_3H) at 20 °C with $I \sim 0.025$ M. (Data are in Table II, supplementary material.)

greater than for free DMU ($pK_a \sim 14$)[1] but similar to that for bound water, as well as N-bonded acetamide, on $dienPt^{II}$ (Table I). N-bonded dimethylurea is however 2–3 pK units less acidic on $dienPt^{II}$ than when bound to $(NH_3)_5Co^{III}$, $(NH_3)_5Rh^{III}$, or $(NH_3)_5Ru^{III}$.[1] This may be because $dienPt^{II}$ is less able to stabilize anionic DMU in the conjugate base, $[dienPtNHCONMe_2]^+$.

Ureas are ~10 orders of magnitude more acidic[1-5] when N-bonded (pK_a 2–3) than when O-bonded (pK_a 13) to hard metals, and a similar difference is exhibited for the $dienPt^{II}$ complexes as well. We were unable to quantitatively measure the acidity of the O-bonded DMU ligand here because of its high lability shown by very fast substitutions of DMU by solvent (H_2O, DMSO). This is consistent with the estimated[23] rate of exchange of water on Pt^{II} (~1 s^{-1}). However, we were able to identify a qualitatively large difference between the acidity of the N-bonded (pK_a 5.6) and O-bonded (pK_a estimated >11) DMU on $dienPt^{II}$, and this served well in isomer characterization.

NMR Spectra. Table III summarizes the NMR (^1H, ^{13}C) characteristics of 1,1-dimethylurea and its N- and O-bonded platinum complexes. In the ^1H-NMR spectrum the urea NH resonance shifted to higher frequency from 5.2 ppm in uncom-

(23) Exchange rate for water in *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$: Glass, G. E.; Schwabacher, W. B.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 2471.

Table III. NMR (^{1}H, ^{13}C) Spectral Data[a] for 1,1-Dimethylurea and Its (Diethylenetriamine)platinum(II) Complexes[b]

	^{1}H-NMR shifts					^{13}C-NMR shifts		
	dien			urea			urea	
complex	CH	NH_2	NH	NMe_2	NH/NH_2	dien CH	NMe_2	C=O
$OC(NH_2)NMe_2$	*c*			2.68		*c*	35.9	161.2
	d			2.79	5.60	*d*	35.7	160.8
	e			2.84	5.22	*e*	36.6	159.3
$[dienPtNHCONMe_2]^+$	2.5–2.9[c]			2.58		53.2,[c] 50.5	36.9	167.4
	2.5–3.0[e]	5.44	6.33	3.33	3.73	54.2,[e] 51.4	37.5	166.8
		5.32						
$[dienPtNH_2CONMe_2]^{2+}$	2.5–3.1[c]			2.74[f]		54.2,[c] 50.4	36.8[f]	158.1
	2.8–3.4[d]	5.54	6.83	3.00[f]	7.07	55.0,[d] 51.4	37.7, 37.1	157.7
		5.29						
	2.5–3.0[e]	5.38	7.22	3.08[f]	7.36			
		5.17						
$[dienPtOC(NH_2)NMe_2]^{2+}$	2.8–3.4[d]	5.5	6.70	3.02	6.81	56.1,[d] 51.1	36.8	164.1
		5.4						
$[dienPtOS(CD_3)_2]^{2+}$	2.7–2.9[e]	6.10	7.62			52.9,[e] 50.0		
		6.15						
$[dienPtOH_2]^{2+}$	2.7–3.3[d]	5.56	6.99	(7.35)[g]		56.4,[d] 51.2, 50.9		
		5.42	6.80					

[a] δ ppm downfield of TMS. [b] Trifluoromethanesulfonate salts. [c] D_2O. [d] d^6-Acetone. [e] d^6-DMSO, dioxane as internal reference (δ 66.50 ppm). [f] Broad signal. [g] H_2O ligand.

plexed DMU to 3.7 ppm upon coordination to dienPt^{II} as an anionic N-bonded ligand. This shielding is characteristic of a deprotonated urea N-bonding mode,[1,2] whereas the neutral dimethylurea ligand has a δ_{NH_2} ~7 ppm when either N- or O-bonded to dienPt^{II}. Neither the NH_2 nor NMe_2 components of DMU in any of the platinum complexes gave split ^{1}H-NMR signals, which were expected for restricted rotation about the C=N bond rendering NH_2 (or NMe_2) protons inequivalent. A feature of the spectra was the appearance for each compound of two dien-NH_2 resonances which are separated by up to 0.25 ppm in the extreme case of $[dienPtNH_2CONMe_2]^{2+}$. Solvolysis of either N- or O-bonded DMU complexes in d^6-DMSO gave very distinctive ^{1}H-NMR signals for the dien of $[dienPtSO(CD_3)_2]^{2+}$, particularly the low-field (deshielded) dien-NH proton trans to sulfur.

The ^{13}C-NMR spectra (Table III) were especially useful for distinguishing between the complexes and for following their reactions. In the case of $[dienPtNH_2CONMe_2]^{2+}$ (but no other DMU complex) in d^6-acetone, the NMe_2 signal split into two distinct Me resonances due to restricted rotation about the partial C=NMe_2 bond. Their relatively small separation in the ^{13}C spectrum is consistent with lack of splitting (broad resonances) in the ^{1}H-NMR spectrum where the chemical shift range is smaller. In D_2O the Me resonance was too broad to identify two separate Me peaks even by ^{13}C-NMR spectroscopy.

The separation between the two dien ^{13}C resonances was greater for the O-isomer (~5 ppm) than for deprotonated (~2.8 ppm) or protonated (~3.6 ppm) forms of the N-isomer, thus enabling their distinction.

The carbonyl chemical shift varied by up to 10 ppm in the following order: $[dienPtNHCONMe_2]^+$ > $[dienPtOC(NH_2)NMe_2]^{2+}$ > NH_2CONMe_2 > $[dienPtNH_2CONMe_2]^{2+}$. This difference permitted identification of acid/base forms of the N-bonded isomer (D_2O, d^6-DMSO), as well as the isomerizations (d^6-acetone) and solvolyses of isomers (D_2O, d^6-DMSO).

The results all support a structure for **1** as $[dienPtNH_2CONMe_2]^{2+}$ rather than its tautomer **3**, $[dienPtNH{=}C(OH)R]^{2+}$, which prevails for acetamide.[9] Structure **3** requires separate resonances for OH and NH protons which should exchange with added acid/water.[12] Neither separate signals nor exchange behavior was observed initially when R = NMe_2.

Linkage Isomerization. During the synthesis of **1**, $[dienPtNH_2CONMe_2]^{2+}$, from 1,1-dimethylurea mixed with $[dienPtOH_2](CF_3SO_3)_2$ in acetone, a reactive intermediate (**2**) containing dimethylurea was identified by ^{13}C-NMR spectroscopy (Figure 1). Resonances for intermediate **2** (Figure 1a) can be unambiguously assigned to $[dienPtOC(NH_2NMe_2](CF_3SO_3)_2$ for the following reasons. First, the dien signals were symmetric, eliminating a dimer formulation (e.g. $PtOC(NMe_2)NH_2Pt^{4+}$, $PtOC(NH_2)NMe_2Pt^{4+}$, or $PtNH_2CONMe_2Pt^{4+}$). Second, both ^{1}H and ^{13}C resonances were consistent with a urea ligand; vide infra. Third, a product isolated rapidly from cold acetone solution gave elemental analyses consistent with $[dienPt(DMU)](CF_3SO_3)_2$, but when redissolved in cold (0 °C) d^6-acetone, it still gave the same NMR characteristics as the intermediate (**2**) observed in situ. Upon aging in acetone, the spectrum changed to that for **1**, $[dienPtNH_2CONMe_2](CF_3SO_3)_2$. Since **1** gave C, H, N, S analyses identical to that of **2**, the intermediate must be an isomer of $[dienPtNH_2CONMe_2](CF_3SO_3)_2$.

By ^{1}H-NMR spectroscopy, the formation of the intermediate O-bonded DMU complex was complete within a few minutes in d^6-acetone and was followed by a slower conversion to $[dienPtNH_2CONMe_2](CF_3SO_3)_2$ (Figure 1). This process was thus established as an O- to N-linkage isomerization. We monitored this strictly first-order reaction at 22 °C by ^{13}C-NMR spectroscopy and determined the first-order rate constant, k = 6.4×10^{-4} s^{-1}. This is ~2 orders of magnitude faster than the corresponding rearrangement ($k = 6.8 \times 10^{-6}$ s^{-1}, 22 °C) recently observed between $[dienPtOC(NH_2)Me]^{2+}$ to $[dienPtNH{=}C(OH)Me]^{2+}$ in d^6-acetone.[9] For acetone (Figure 1), we now estimate the equilibrium constant $K_{N/O}$ ~ 3 (R = NMe_2; 22 °C), compared with $K_{N/O}$ ~ 30 (R = Me).[9]

$$\underset{\mathbf{2}}{[dienPtOC(NH_2)R]^{2+}} = \underset{\mathbf{1}}{[dienPtNH_2COR]^{2+}} \qquad K_{N/O}$$

To verify the equilibrium constant, we examined $[dienPtNH_2CONMe_2](CF_3SO_3)_2$ in d^6-acetone. Figure 4 shows that **1** (Figure 4, top) converts to **2** within hours (Figure 4, bottom). The final ratio **1**:**2** was ~3:1, agreeing with the value obtained after the reverse (**2** → **1**) rearrangement from a solution of equimolar $[dienPtOH_2]^{2+}$ and DMU in acetone (Figure 1c).

Solvolysis. While both O- and N-bonded linkage isomers of DMU on dienPt^{II} were relatively stable in the weak coordinating solvent acetone, only the N-isomer was stable in water or DMSO. Solvolysis of $[dienPtOC(NH_2)NMe_2]^{2+}$ was essentially complete within 1 min of mixing, so we estimate $k_{sol} > 10^{-1}$ s^{-1}. There was no detectable decomposition of the urea ligand; only $[dienPt(solvent)]^{2+}$ and DMU were produced. On the other hand ^{1}H and ^{13}C resonances were detectable for $[dienPtNH_2CONMe_2]^{2+}$ in water at 22 °C for several hours.

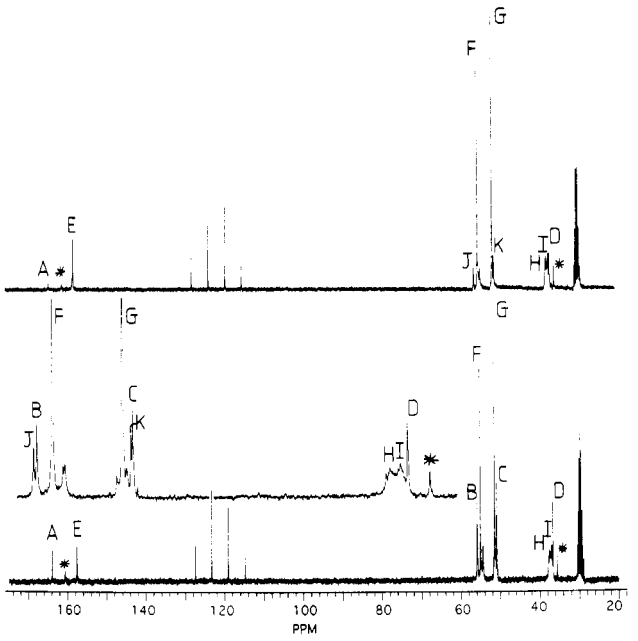


Figure 4. ^{13}C NMR spectra (15-min accumulations) for [dienPt-(OH_2)]$(CF_3SO_3)_2$ (30.4 mg, 4.94 × 10^{-5} mol; signals J + K) in d^6-acetone (0.75 mL) with excess NH_2CONMe_2 (17.6 mg, 2 × 10^{-4} mol) at 22 °C recorded 17 min (top) and 4.5 h (bottom) after mixing. An asterisk indicates free dimethylurea. See Figure 1 for the identity of signals A–I.

A kinetic study of the aquation of [dienPtNH_2CONMe_2]-$(CF_3SO_3)_2$ gave an average first-order rate constant of 4.98 × 10^{-4} s^{-1} at 40.0 °C. The aquation was independent of $[H^+]$ at 0.01–0.1 M (I = 1.0 M, NaClO4), ruling out a second protonation site for the urea ligand under these conditions. The measured rate of aquation is ~50-fold faster than for [dienPtNH=C-(OH)Me]$^{2+}$ under the same conditions. This may reflect the position of the tautomeric equilibrium. The urea complex is present in the tautomeric form which is expected to be more reactive, while the acetamide may have to tautomerize prior to dissociation. The observed difference in rate may reflect the value of K_T for acetamide.

$$[\text{dienPtNH}_2\text{COR}]^{2+} = [\text{dienPtNH=C(OH)R}]^{2+} \quad (K_T)$$

$$[\text{dienPtNH}_2\text{COR}]^{2+} \rightarrow [\text{dienPt(solvent)}]^{2+} + \text{NH}_2\text{COR}$$

Isomeric Equilibria for Metal–Urea Complexes. Table IV summarizes kinetic and thermodynamic data for linkage isomeric metal complexes of amides and ureas. For all these metal complexes, amides and ureas initially coordinate via oxygen to the metal under kinetic control. This kinetic preference appears to be related to the capture of the more basic oxygen nucleophile by the electrophilic metal in a primarily electrostatic interaction. The hard/soft character of the metal does not influence which amide/urea site is initially captured.

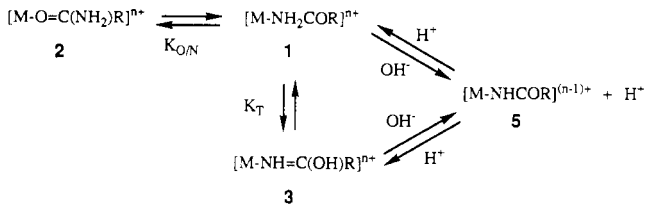
However, the thermodynamic preferences are sensitive to the hard/soft nature of the coordinated metal. Thus, on the soft dienPt^{II} unit, both amides and ureas slowly rearrange in acetone from the initially captured oxygen-bound form to the thermodynamically more stable nitrogen-bonded linkage isomers. By contrast the O-bonded ureas and amides are thermodynamically preferred for the harder pentaamminecobalt(III), pentaammineruthenium(III), and pentaamminechromium(III) moieties, while pentaamminerhodium(III) has approximately equal preference for the O- and N-termini of ureas. Surprisingly the quite soft pentaammineruthenium(II) center still has a thermodynamic preference for the oxygen atom of amides (Table IV).

Table IV. Comparison of Isomer Equilibria (K) and Rates (k, s^{-1}) of Linkage Isomerization in Metal Complexes of N-Bonded and O-Bonded Amides at 25.0 °C in Water (Or As Specified)

		kinetic and equilibr data[a]			
metal	amide	$k_{O\rightarrow N}$	$k_{N\rightarrow O}$	$K_{O/N}$	ref
dienPt^{2+}	$HCONH_2$[b]	1.1×10^{-5}	($<4 \times 10^{-7}$)	~0.03	9
	$MeCONH_2$[b]	6.8×10^{-6}	($<2 \times 10^{-7}$)	~0.03	9
	NH_2CONMe_2[b]	6.4×10^{-4}	($\sim 2 \times 10^{-4}$)	0.3	this work
$(NH_3)_5Co^{3+}$	$HCONH_2$	N.D.[c]	3.7×10^{-5}	$\geq 10^2$	12
	$MeCONH_2$	N.D.[c]	N.D.[d]	$\geq 10^2$	12
	NH_2CONMe_2	6×10^{-6}	1.8×10^{-2}	2830	2
	NH_2CONH_2	1.3×10^{-5}	3.1×10^{-3}	246	2
$(NH_3)_5Rh^{3+}$	NH_2CONH_2	6.7×10^{-5}	6.1×10^{-5}	~1	5
$(NH_3)_5Cr^{3+}$	$HCONH_2$	($\ll 10^{-3}$)	(>0.4)	($>10^4$)	3
	NH_2CONH_2	$\ll 10^{-5}$	>0.4	($>10^5$)	3
$(NH_3)_5Ru^{3+}$	NH_2CONH_2	1.1×10^{-3}	9.0×10^{-3}	8.6	4
$(NH_3)_5Ru^{2+}$	$HCONH_2$[e]	N.D.	($>10^2$)	≥10	24

[a] Data in parentheses are estimates only. $k_{O\rightarrow N}$ = rate constant (s^{-1}) for O- to N-isomerization; $k_{N\rightarrow O}$ = rate constant (s^{-1}) for N- to O-isomerization; $K_{O/N}$ = [O-isomer]/[N-isomer]. [b] Acetone solutions, 22 °C. [c] N.D. = not determined due to much faster competing solvolysis. [d] Precise value could not be determined because of fast subsequent reaction (solvolysis of O-bonded acetamide complex). [e] Formamide solution, 20 °C.

The chemistry of the urea and amide complexes in Table IV can be summarized by the following scheme:



The isomer equilibrium ($K_{O/N}$ = [**2**]/[**1**] = k_{12}/k_{21}) likely involves *direct* rearrangement between **1** and **2** only. However, the tautomeric equilibrium (K_T) *indirectly* affects $K_{O/N}$ and the rate of rearrangements. Thus if tautomer **1** is dominant over **3**, as in the case of [dienPtNH_2CONMe_2]$^{2+}$, the observed isomer equilibrium $K_{O/N}^{obsd}$ is measured by $K_{O/N}$. However if **3** is dominant over **1**, and K_T is defined as [**3**]/[**1**], then the observed isomer equilibrium constant will be reduced by K_T; i.e., $K_{O/N}^{obsd}$ = $K_{O/N}/K_T$. This is the case for [dienPtNH=C(OH)Me]$^{2+}$ and for analogous amide complexes (R = H, alkyl, aryl) of metal ions,[12,24] where K_T is estimated at ≥10 favoring **3** over **1**.

Thus for [dienPt(acetamide)]$^{2+}$, $K_{O/N}$ = $K_T \cdot K_{O/N}^{obsd}$ = (≥10)(3 × 10^{-2}) = ≥0.3. This is comparable to the value of $K_{O/N}^{obsd}$ measured here for the isomers of [dienPt(DMU)]$^{2+}$, where $K_{O/N}$ = $K_{O/N}^{obsd}$ since only tautomer **1** is present. The effect of the tautomeric equilibrium K_T could therefore account entirely for the observed difference in thermodynamic preference for O- and N-termini of ureas versus amides.

Both $K_{O/N}$ and K_T are also influenced[1,2,4] by the solvent pH because of selective deprotonation of the N-bonded ureas/amides (**1**, **3**) in the pH range 3–11. The O-bonded ureas do not deprotonate until pH ≥ 11, whereas the N-bonded isomers are appreciably acidic ($pK < 6$, Table I). The consequence of this dependence is that isomerization from O-bonding to N-bonding can be thermally driven at pH ≥ 6 even for systems where the O-bonded urea/amide complex is thermodynamically more stable (e.g. $(NH_3)_5Co^{III}$, $(NH_3)_5Ru^{III}$).[2,4] The deprotonated urea/amide complex **5** is kinetically inert and provides a thermodynamic sink for the linkage isomerization.

Supplementary Material Available: A listing of absorbance changes for the determination of pK_a (Table II) (1 page). Ordering information is given on any current masthead page.

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