

Synthesis and Crystal Structure of a *trans*-Diaquabis(amidato) Complex of Platinum(II)

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Introduction

Platinum(II) complexes with terminal aqua and/or hydroxo groups are generally assumed to occur in aqueous solution.^{1–3} Moreover hydrolysis of the first chloro ligand appears to be the rate-limiting step in the complexation to DNA of dichlorobis-(amine)platinum complexes which are of particular interest because of their remarkable antitumor activity.⁴

Only a few crystallographic studies of compounds containing platinum(II) or palladium(II) complexes with one water molecule coordinated directly to the metal ion have been published.^{5–8} In addition to this an X-ray absorption edge and EXAFS study has been performed on the tetraaqua cation [Pt(H₂O)₄]²⁺.⁹

In the course of our systematic studies on complexes of platinum with amides^{10,11} and iminoethers^{12,13} which are related to platinum–ammine complexes and are of particular interest because of the remarkable antitumor activity of some of them with features that violate the “classical” structure–activity relationships,¹⁴ we have obtained crystals of *trans*-[Pt{HN=C(O)Bu^t}₂(H₂O)₂]·¹/₃H₂O in which two amidato ligands and two water molecules are coordinated to platinum.

This appears to be the first diaquaplatinum(II) species to have been structurally characterized.

Table 1. Crystallographic Data for Compound 5·¹/₃H₂O

mol formula	C ₁₀ H ₂₄ N ₂ O ₄ Pt· ¹ / ₃ H ₂ O
mol wt	437.36
cryst syst	trigonal
space group	R3
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)
a, Å	12.752(2)
α, deg	114.96(2)
V, Å ³	1165(1)
Z	3
D _{calcd} , g cm ⁻³	1.871
F(000)	634
cryst dimens, mm	0.17 × 0.23 × 0.27
linear abs, cm ⁻¹	90.43
R ^a	0.0257
R _w ^b	0.0314

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}.$$

Experimental Section

Starting Materials. Commercial reagent grade chemicals were used without further purification. The complexes *trans*-[PtCl₂{HN=C(OH)R}₂] (R = Me, **1**; Bu^t, **2**, and Ph, **3**) were prepared by hydrolysis of the corresponding nitriles by the reported procedures.¹¹

Preparation of Complexes. *trans*-[Pt{HN=C(O)R}₂(H₂O)₂] (R = Me, **4**; Bu^t, **5**, and Ph, **6**). *Trans*-[PtCl₂{HN=C(OH)R}₂] (1 mmol), suspended in 10 mL of water, was treated with KOH (0.6 g, 10.7 mmol). The reaction mixture was stirred for 12 h at 45 °C and then filtered to obtain a clear solution. The solvent was evaporated under reduced pressure and the solid residue was treated with absolute ethanol; the resulting solution was filtered, to separate KCl, the solvent was evaporated and the residue, containing the complex K₂{*trans*-[Pt(OH)₂{HN=C(O)R}₂]}, was washed carefully with pentane and dried (yield 80%). The compound (0.3 g), dissolved in 1 mL of water, was treated with HNO₃ 1 N at 0 °C until neutral pH, and a white precipitate formed that was collected by filtration of the mother liquor, washed with water, and dried. Yield: 70%. Anal. Calcd for C₄H₁₂N₂O₄Pt (**4**): C, 13.8; H, 3.5; N, 8.1. Found: C, 13.5; H, 3.5; N, 8.1. Calcd for C₁₀H₂₄N₂O₄Pt (**5**): C, 27.8; H, 5.6; N, 6.5. Found: C, 27.8; H, 5.6; N, 6.5. Calcd for C₁₄H₁₆N₂O₄Pt (**6**): C, 35.7; H, 3.4; N, 5.9. Found: C, 36.0; H, 3.4; N, 5.9.

Physical Measurements. IR spectra in the range 4000–400 cm⁻¹ were recorded as KBr pellets; spectra in the range 400–200 cm⁻¹ were recorded as polythene pellets on Perkin-Elmer 283 and FT 1600 spectrophotometers. ¹H NMR spectra were obtained with Varian XL 200 and Bruker AM 300 spectrometers. The pK_a of the amide ligands in **1** were determined according to the method of Albert and Serjeant in aqueous solution in the presence of 10⁻² M KCl to suppress solvolysis; pH measurements were performed with a CRISON micropH 2002.¹⁵

X-ray Crystal Structure Determination of *trans*-[Pt{HN=C(O)Bu^t}₂(H₂O)₂]·¹/₃H₂O (5**·¹/₃H₂O).** Crystals of **5** suitable for X-ray diffraction analysis were grown from methanol/water. The crystallographic data are summarized in Table 1. Data were collected at room temperature on a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo Kα radiation and the ω/2θ scan mode. All reflections with θ in the range 3–27° were measured; of 1715 independent reflections, 1539, having I > 2σ(I), were considered observed and used in the analysis. The individual profiles have been analyzed according to Lehmann and Larsen.¹⁶ The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability; no significant change in the measured intensities was observed during the data collection. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.000 and 0.742.¹⁷ Only the observed reflections were used in the structure solution and refinement.

(15) Albert, A.; Serjeant, E. P. *Ionization Constants of Acids and Bases*; Methuen: London, 1962; pp 1–42.

(16) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.

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- (1) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; p 169 and references therein.
- (2) Elding, L. I. *Inorg. Chim. Acta* **1978**, *28*, 255.
- (3) Lim, M. C.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1911.
- (4) Prestayko, A. W. In *Cis-platin—Current Status and New Developments*; Crooke, S. T., Carter, S. K., Eds.; Academic Press: New York 1980, pp 1–527.
- (5) Britten, J. F.; Lippert, B.; Lock, C. J. L.; Pilon, P. *Inorg. Chem.* **1982**, *21*, 1936.
- (6) Meinema, H. A.; Verbeek, F.; Marsman, J. W.; Bulten, E. J.; Dabrowiak, J. C.; Krishnan, B. S.; Spek, A. L. *Inorg. Chim. Acta* **1986**, *114*, 127.
- (7) Rochon, F. D.; Melanson, R. *Inorg. Chem.* **1987**, *26*, 989.
- (8) Castan, P.; Jaud, J.; Wimmer, S.; Wimmer, F. *J. Chem. Soc., Dalton Trans.* **1991**, 1155.
- (9) Hellquist, B.; Bengtsson, L. A.; Holmberg, B.; Hedman, B.; Persson, I.; Elding, L. I. *Acta Chem. Scand.* **1991**, *45*, 449.
- (10) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Am. Chem. Soc.* **1991**, *113*, 7807.
- (11) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Am. Chem. Soc.* **1993**, *115*, 5123.
- (12) Cini, R.; Caputo, P. A.; Intini, F. P.; Natile, G. *Inorg. Chem.* **1995**, *34*, 1130.
- (13) Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1989**, 947.
- (14) Coluccia, M.; Nassi, A.; Loseto, F.; Boccarelli, A.; Mariggiò, M. A.; Giordano, D.; Intini, F. P.; Caputo, P.; Natile, G. *J. Med. Chem.* **1993**, *36*, 510.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^4$) Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor, for the Non-Hydrogen Atoms of the Compound $5 \cdot 1/3 \text{H}_2\text{O}$

atom	x/a	y/b	z/c	U
Pt	5000	0	5000	373(3)
O(1)	4200(4)	-18(4)	6065(4)	552(36)
O(2)	2013(5)	-3154(4)	3927(5)	694(43)
N(1)	3497(5)	-2493(4)	3395(5)	502(37)
C(1)	2318(6)	-3600(5)	3098(6)	507(41)
C(2)	1291(7)	-5465(6)	1794(7)	719(58)
C(3)	1469(13)	-6001(9)	2643(11)	1139(106)
C(4)	1841(14)	-5809(8)	970(11)	1434(138)
C(5)	-576(11)	-6476(11)	489(14)	1550(107)
O(3)	0	0	0	2270(88) ^a

^a Isotropic Thermal Parameter ($\text{\AA}^2 \times 10^4$).

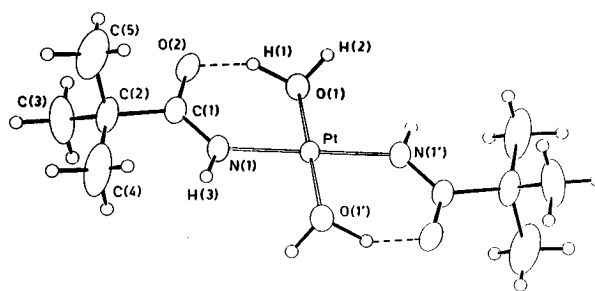
The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non hydrogen atoms, excepting for the water of crystallization, lying on the $\bar{3}$ symmetry site. The hydrogen atoms of the coordinated water molecules and of the amidato groups were found in the final ΔF map and refined isotropically, those of the Bu^t group were placed at their geometrically calculated positions ($\text{C}-\text{H} = 0.96 \text{\AA}$) and refined "riding" on the corresponding carbon atoms, whereas those of the water of crystallization were not introduced being disordered. The final cycles of refinement were carried out on the basis of 81 variables; after the last cycles, no parameters shifted by more than 0.85 esd. The biggest remaining peak in the final difference map was equivalent to about $0.37 \text{ e/\AA}^3$. In the final cycles of refinement a weighting scheme, $w = 1/[\sigma^2(F_o) + gF_o^2]$, was used with $g = 0.0024$. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 18.

All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffattometrica del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.¹⁹ The final atomic coordinates for the non-hydrogen atoms are given in Table 2. The atomic coordinates of the hydrogen atoms are given in Table SI and the thermal parameters in Table SII.

Results and Discussion

Synthesis and Solution Behavior. The diaquabisamidato platinum(II) compounds described in this paper have been synthesized by base hydrolysis of the corresponding dichlorobis-(amide) species. Under basic conditions, beside deprotonation of the amides to amidato anions, also substitution of hydroxide for chloride ions takes place. Most probably the reaction proceeds through aquation and subsequent deprotonation of the solvato species. Neutralization with nitric acid affords the sparingly soluble diaquabisamidato complexes. The molecular formula would also be in agreement with a bis(hydroxo) complex containing two amide ligands; however, previous workers have proved that coordinated amides are rather acidic ligands, probably more acidic than coordinated water molecules.^{3,5,20,21}

A solution of $\text{trans-[PtCl}_2\{\text{HN}=\text{C}(\text{OH})\text{Me}\}_2]$, **1**, was titrated with 1 and 2 equiv of base to give $\text{trans-[PtCl}_2\{\text{HN}=\text{C}(\text{O})\text{Me}\}\{\text{HN}=\text{C}(\text{OH})\text{Me}\}]^-$ and $\text{trans-[PtCl}_2\{\text{HN}=\text{C}(\text{O})\text{Me}\}_2]^{2-}$, respectively. The pK_a 's for the deprotonation of the first and second coordinated amide ligands were determined as 3.8 and

**Figure 1.** Perspective view of the molecular structure of the complex $\text{trans-[Pt}\{\text{HN}=\text{C}(\text{O})\text{Bu}^t\}_2(\text{H}_2\text{O})_2]$ showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

5.8, respectively. Values in the same range were found for other amide complexes such as $[\text{Co}(\text{NH}_3)_5\{\text{HN}=\text{C}(\text{OH})\text{Me}\}]^{3+}$ and $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)\{\text{HN}=\text{C}(\text{OH})\text{Me}\}]^{2+}$.^{22,23}

Deprotonation of the N-coordinated iminol ligands could be favored by the delocalization of the electron charge accumulated on the oxygen upon the $\text{N}=\text{C}=\text{O}$ moiety, X-ray data support this conclusion (*vide infra*). O-bonded amides have a much lower acidity, with a pK_a of 11.6 as compared to 3.0.²³

The region about 1600 cm^{-1} was very diagnostic for distinguishing between amide and amidato complexes.^{24,25} The amide complexes **1–3** were characterized by having intense IR absorption bands above 1600 cm^{-1} (at 1645, 1630, and 1630 cm^{-1} for **1**, **2** and **3**, respectively; $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ solution). In contrast, the corresponding amidato species **4–6** gave intense IR absorption bands below 1600 cm^{-1} (at 1570, 1560, and 1550 cm^{-1} for **4**, **5**, and **6**, respectively; KBr pellets). Both type of complexes gave rather sharp and intense bands in the region between 3300 and 3400 cm^{-1} assignable to N–H stretching (at 3330, 3350, and 3340 cm^{-1} for **1**, **2**, and **3**, respectively; $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ solution; at 3340, 3400, and 3380 cm^{-1} for **4**, **5**, and **6**, respectively, KBr pellets). Amide complexes gave also rather broad and intense bands in the region between 3000 and 3100 cm^{-1} assignable to O–H stretching (at 3040, 3070, and 3060 cm^{-1} for **1**, **2**, and **3**, respectively, $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ solution). The low solubility of the diaquabisamidato species prevented a NMR study of these compounds.

Crystal Structure of $\text{trans-[Pt}\{\text{HN}=\text{C}(\text{O})\text{Bu}^t\}_2(\text{H}_2\text{O})_2] \cdot 1/3 \text{H}_2\text{O}$ ($5 \cdot 1/3 \text{H}_2\text{O}$). In the crystals, $\text{trans-[Pt}\{\text{HN}=\text{C}(\text{O})\text{Bu}^t\}_2(\text{H}_2\text{O})_2]$ complexes, having a crystallographically imposed C_i symmetry with platinum lying on the inversion center and water molecules of crystallization, lying on the $\bar{3}$ site symmetry, are present, separated by van der Waals contacts only. The structure of the complex is shown in Figure 1 together with the atomic numbering scheme; bond distances and angles are given in Table 3. The square planar coordination around platinum involves two N atoms from the amidato ligands [$\text{Pt}-\text{N} = 2.006(4) \text{\AA}$] and two O atoms from water molecules [$\text{Pt}-\text{O} = 2.016(7) \text{\AA}$], which are trans to each other. The four coordinated atoms and the Pt atom are coplanar for symmetry restrictions. The Pt–O bond distances are very similar to those found for Pt–O bonds trans to oxygen donor ligands in other platinum complexes (in the range 1.99–2.01 $\text{\AA}$ in nitrate, squarate and oxalato complexes).^{26–28} The calculated value for this bond in the tetraqua cation $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ (X-ray absorption edge and

- (17) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, 39, 158.
- (18) Ugozzoli, F. *Comput. Chem.* **1987**, 11, 109.
- (19) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
- (20) Sheldrick, G. M. SHELX-76 Program for crystal structure determination. University of Cambridge, U. K., 1976; SHELXS-86 Program for the solution of crystal structures, University of Göttingen, 1986.
- (21) Jensen, K. A. Z. *Anorg. Allg. Chem.* **1939**, 242, 87.
- (22) Perumareddi, J. R.; Adamson, A. W. *J. Phys. Chem.* **1968**, 72, 414.

- (22) Buckingham, D. A.; Keene, R. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, 95, 5649.
- (23) Woon, T. C.; Fairlie, D. P. *Inorg. Chem.* **1992**, 31, 4069.
- (24) Kerridge, D. H. *Chem. Soc. Rev.* **1988**, 17, 181.
- (25) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen and Co. Ltd.: London, 1975; pp 231–262.
- (26) Elding, L. I.; Oskarsson, A. *Inorg. Chim. Acta* **1985**, 103, 127.
- (27) Kobayashi, A.; Sasaki, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1979**, 52, 3862.
- (28) Simonsen, O.; Toftlund, H. *Inorg. Chem.* **1981**, 20, 4044.

Table 3. Bond Distances (Å) and Angles (deg) for Compound $5 \cdot 1/3 \text{H}_2\text{O}$

Pt—O(1)	2.016(7)	Pt—N(1)	2.006(4)
O(2)—C(1)	1.272(11)	N(1)—C(1)	1.293(9)
C(1)—C(2)	1.527(8)	C(2)—C(4)	1.511(22)
C(2)—C(3)	1.496(18)	C(2)—C(5)	1.534(14)
O(1)—H(1)	1.11(7)	O(1)—H(2)	0.98(17)
N(1)—H(3)	0.86(12)		
O(1)—Pt—N(1)	91.7(2)	Pt—N(1)—C(1)	129.6(4)
O(2)—C(1)—N(1)	120.7(8)	N(1)—C(1)—C(2)	121.5(6)
O(2)—C(1)—C(2)	117.8(5)	C(4)—C(2)—C(5)	111.7(11)
C(1)—C(2)—C(5)	107.0(6)	C(3)—C(2)—C(5)	106.9(8)
C(1)—C(2)—C(4)	112.5(6)	C(3)—C(2)—C(4)	109.5(8)
C(1)—C(2)—C(3)	109.0(8)		
Pt—N(1)—H(3)	115(6)	C(1)—N(1)—H(3)	115(8)
Pt—O(1)—H(2)	104(8)	Pt—O(1)—H(1)	104(7)
H(1)—O(1)—H(2)	99(10)		
Hydrogen Bonds			
O(1)···O(2)	2.484(6)	O(1)···O(2) ^a	2.588(9)
H(1)···O(2)	1.46(10)	H(2)···O(2) ^a	1.70(16)
O(1)—H(1)···O(2)	150(8)	O(1)—H(2)···O(2) ^a	149(14)

^a Symmetry: (i) $z, x, y + 1$.

EXAFS) was 2.01(1) Å.⁹ Longer Pt—O bond distances have been observed in other aqua platinum complexes in which the water molecules were *trans* to a nitrogen-donor ligand: 2.052–(8) Å in *cis*-[Pt(NH₃)₂(1-methylcytosine-*N*³)(H₂O)](NO₃)₂·H₂O,⁵ 2.099(5) Å in [Pt{1,1-bis(aminomethyl)cyclohexane}(H₂O)-(SO₄)]₂·H₂O,⁶ and 2.078(6) Å in [Pt{*N,N'*-dimethylethylenediamine}(H₂O)(SO₄)]₂·H₂O,⁷ thus indicating a larger ground-state *trans*-influence for nitrogen than for oxygen atoms.

The Pt—N bond distances are shorter than those found in amine complexes *trans* to other amine ligands, which usually are *ca.* 2.06 Å.²⁹ This is due to the sp^2 hybridization of the amidic nitrogen and to the possibility of back-bonding from filled metal d-orbitals to empty π^* -orbitals of the amidato, which might further shorten the bond.

The planarity of the amidato group is preserved upon coordination [the maximum deviation from the mean plane being 0.01(1) Å]. The value of the Pt—N(1)—C(1) angle, 129.6(4)°, is larger than expected (120°) and is a common feature of amidato ligands. A large angle was also observed in *trans*-[Pt(NH₃)₂(N≡CMe){HN=C(O)Me}]⁺ [132.1(12)°],³⁰ in [PtCl{HN=C(Ph)N(Bu^t)CH₂CH₂NHBu^t}{HN=C(O)Ph}] [131.3(7)°],³¹ and in [Co(NH₃)₅{HN=C(O)Me}]²⁺ [131.0(7)°].³²

The N(1)—C(1) and C(1)—O(2) bond distances, 1.293(9) and 1.272(11) Å respectively, are comparable and denote a double bond delocalization over the N=C=O moiety which contributes to the releasing of the formal negative charge accumulated on the oxygen atom as a consequence of its deprotonation. This could contribute to increasing the acidity of the coordinated amide ligands.³¹ The mean plane of the amidato ligand is tilted by only 7.7(2)° with respect to the coordination plane. This is an unusual feature since normally ligands which extend in a plane prefer to assume a conformation with the ligand plane at roughly a right angle to the square coordination plane. The preference for an upright position appears to stem from steric rather than electronic reasons since such a conformation minimizes the interligand steric interactions with *cis* ligands.³³ In the present case the almost in-plane orientation of the amidato ligands is dictated by the strong intramolecular hydrogen bonds

they form with the adjacent water molecules. The O(1)···O(2) distance is as short as 2.484(6) Å, and the O(1)—H(1)···O(2) angle is as large as 150(8)°. This very strong H bond is favored by the geometry and the in plane orientation of the amidato ligand and the disposition of the water proton [displacements of H(1) from the planes through Pt, N(1), and O(1) and H(3), N(1), C(1), and O(2) atoms of 0.37(11) and 0.11(11) Å, respectively] and does not require any narrowing of the N—Pt—O angle which is 91.7(2)°. There appears to be a relationship between the strength of the hydrogen bond and the coplanarity of the interacting ligands as measured by the dihedral angle between the plane through the amidato anion and that of coordination. The hydrogen bond between the amidato and the ammine ligands observed in *trans*-[Pt(NH₃)₂(N≡CMe){HN=C(O)Me}]⁺ was weaker than that observed in the present case [N···O distance of 2.94(2) Å] and the dihedral angle was of 40.8(7)° to be compared with the 7.7(2)° observed in the present study.³⁰ A rather similar situation was that observed in [Co(NH₃)₅{HN=C(O)Me}]²⁺ [N···O distances of 2.988(10) and 2.900(10) Å and dihedral angles of 49.9(3)° and 40.3(3)°].³² An intermediate situation was that of [PtCl{HN=C(Ph)N(Bu^t)CH₂CH₂NHBu^t}{HN=C(O)Ph}] with a shorter N···O distance [2.789(11) Å] and a smaller dihedral angle [16.1(4)°].³¹

It has been postulated that stable aqua complexes require the formation of two strong hydrogen bonds in which the water molecule donates its protons. This was observed in the structures we have referred to in the introduction.^{5–8} Such a requirement is adequately fulfilled in the present compound. In fact, beside the H(1) atom which is involved in a very strong H-bond with the amidato ligand, the H(2) hydrogen atom is also involved in a strong H bond with the O(2) atom of another molecule with a O(1)···O(2) ($z, x, y + 1$) distance of 2.588(9) Å and an O(1)—H(2)···O(2) angle of 149(14)°.

It is noteworthy that in the packing of the complexes the hydrophobic Bu^t groups are orientated in such a way to leave large channels into which water molecules of crystallization are inserted (Figure 2, of Supporting Information).

Conclusions

The first X-ray structure of a platinum(II) diaqua species is reported. Accurate values of Pt—O [2.016(7) Å] and Pt—N distances [2.006(4) Å] indicate that water oxygen exerts a smaller ground state *trans*-influence than amine nitrogen. Extensive electron delocalization upon the N=C=O moiety stabilizes the amidato anion contributing substantially to the high acidity of coordinate amide ligands. A very strong H bond between *cis* amidato and water ligands is responsible for the in-plane orientation of the amidato ligand [dihedral angle between the plane through the amidato anion and the platinum coordination plane of 7.7(2)°]. Analogous interactions between *cis* amidato and amine ligands appear to be significantly weaker and, consequently, the dihedral angles between amidato and metal-coordination planes are bigger.

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Supporting Information Available: Coordinates for the hydrogen atoms (Table SI), anisotropic thermal parameters for the non-hydrogen atoms (Table SII), crystallographic data (Table SIII), and crystal packing (Figure 2) (4 pages). Ordering information is given on any current masthead page.

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- (29) Lock, C. J. L.; Zvagulis, M. *Inorg. Chem.* **1981**, *20*, 1817.
 (30) Erxleben, A.; Mutikainen, I.; Lippert, B. *J. Chem. Soc., Dalton Trans.* **1994**, 3667.
 (31) Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180.
 (32) Schneider, M. L.; Ferguson, G.; Balahura, R. *J. Can. J. Chem.* **1973**, *51*, 2180.
 (33) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.