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Platinum Amides from Platinum Nitriles: X-ray Crystal Structures of the Unbridged Dinuclear Compounds Bis[bis(1-imino-1-hydroxy-2,2-dimethylpropane)dichloroplatinum(II)] and Bis[bis(1-imino-1-hydroxy-2,2-dimethylpropane)(1-amino-1-oxo-2,2-dimethylpropane)dichloroplatinum(II)]

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Abstract: Mono- and bisnitrile platinum complexes, $[PtCl_3(NCR)]^-$ and *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = Bu^t, Me and Ph), hydrolyze to amidate amide and mixed amide–nitrile complexes. The amide ligands generally adopt the enol tautomeric form and coordinate to platinum through nitrogen. The presence of two amides cis to one another plays a critical role in favoring the association of platinum units in dimers. For example, molecules of *cis*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2]_2$, **7b**, comprise two monomeric units, placed face to face, with a Pt–Pt distance of 3.165(1) Å and four interplanar N–H···Cl hydrogen bonds. Although hydrogen bonding interactions would place the dimer in the eclipsed conformation, the compound adopts the staggered conformation which minimizes interligand steric interactions allowing a closer approach of the two platinum subunits. The driving force to shortening the intermetallic distance stems from a direct intermetallic bonding interaction. Addition of two extra amides to axial sites of **7b** gave $[PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2NC({=}O)Bu^t\}]_2$, **7c**. The axial amides differ from the equatorial ones, in both tautomeric form (keto instead of enol) and donor atom (oxygen instead of nitrogen). In spite of a very long Pt–O distance [3.229(5) Å] the axial coordination causes a considerable lengthening of the intermetallic distance (0.23 Å) and, furthermore, conversion from the staggered to the eclipsed conformation. The solution chemistry of both **7b** and **7c** is in accord with their dimeric structure. A fast rate of proton exchange, between the hydroxyl group of the amide ligands and water present in the solvent, was observed whenever two amide ligands are cis to one another. Such an exchange process could be favored by the hydrogen bonding interaction of the two cis amides with a molecule of water. Mixed amide nitrile complexes have also been prepared; one *trans*-$[PtCl_2\{HN{=}C(OH)Bu^t\}(NCBu^t)]$ proved to be the complex previously formulated as a platinum(IV) dichlorobisamidate derivative having the two amidate ligands in different tautomeric forms. The structure of **7b**·$C_2H_4Cl_2$ and **7c** have been solved by single-crystal X-ray diffraction. **7b** crystallizes as 1,2-dichloroethane solvate (1:1) in the space group $P\bar{1}$ (n° 2) with $a = 11.292(3)$, $b = 13.618(3)$, $c = 14.069(4)$ Å, $\alpha = 62.12(2)$, $\beta = 83.58(2)$, $\gamma = 76.47(2)°$, $V = 1859(1)$ Å^3, $Z = 2$. **7c** crystallizes in the space group $P\bar{1}$ (n° 2) with $a = 10.279(1)$, $b = 10.772(1)$, $c = 11.099(3)$ Å, $\alpha = 90.66(1)$, $\beta = 89.58(1)$, $\gamma = 114.27(1)°$, $V = 1120(1)$ Å^3, $Z = 1$.

Introduction

The synthetic and structural chemistry of platinum-bound nitriles which are susceptible to nucleophilic attack by alcohols, amines, and carbanions to give iminoethers, amidines, and imines is well established.[1,2] More recently the hydrolysis of platinum-bound acetonitrile and benzonitrile to give bridging[3] and terminal[2] amidates has been reported; to the best of our knowledge, the resulting complexes are the only examples of fully characterized amide complexes obtained by hydrolysis of platinum-nitrile species. Other platinum complexes have been prepared with the preformed ligand;[4–7] these include the blue complexes prepared by reaction of the aquated products of the antitumor drug *cis*-diamminedichloroplatinum(II) with a variety of cyclic and linear amides.[3–10] We now report on the hydrolysis of mono- and bisnitrile platinum(II) complexes under different experimental conditions to yield amidate, amide, and mixed amide–nitrile complexes. Two amide ligands, cis to one another, are shown to play a critical role in favoring the association of platinum units

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[†] Università di Siena.

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(1) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1. Braunstein, P.; Matt, D.; Dusausoy, Y.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1979**, 763. Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 1410. Uchiyama, T.; Takagi, K.; Matsumoto, K.; Ooi, S.; Nakamura, Y.; Kawaguchi, S. *Chem. Lett.* **1979**, 1197; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1077. Michelin, A.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Angelici, R. J. *Organometallics* **1991**, *10*, 1751. Casas, J. M.; Chisholm, M. H.; Silicia, M. V.; Streib, W. E. *Polyhedron* **1991**, *10*, 1573. Lopez, G.; Ruiz, J.; Garcia, G.; Vicente, C.; Marti, J. M.; Hermoso, J. A.; Vegas, A.; Martinez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53.

(2) Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180. Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1989**, 947. Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1019.

(3) Rochon, F. D.; Kong, P. C.; Melanson, R. *Inorg. Chem.* **1990**, *29*, 1352.

(4) Kerridge, D. H. *Chem. Soc. Rev.* **1988**, *17*, 181.

(5) Lippert, B.; Neugebauer, D.; Schubert, U. *Inorg. Chim. Acta* **1980**, *46*, L11. Lippert, B.; Schöllhorn, H.; Thewalt, U. *J. Am. Chem. Soc.* **1986**, *108*, 525. Schöllhorn, H.; Eisenmann, P.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1986**, *25*, 3384.

(6) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *22*, 4086. Laurent, J. P.; Lepage, P.; Dahan, F. *J. Am. Chem. Soc.* **1982**, *104*, 7335. Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2600. Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2605. O'Halloran, T. V.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1986**, *25*, 957.

(7) Matsumoto, K.; Takahashi, H.; Fuwa, K. *Inorg. Chem.* **1983**, *22*, 4086.

(8) Davidson, P. J.; Faber, P. J.; Fisher, R. G., Jr.; Mansy, S.; Peresie, H. J.; Rosenberg, B.; Van Camp, L. *Cancer Chemother. Rep.* **1975**, *59*, 287. Rosenberg, B. *Cancer Chemother. Rep.* **1975**, *59*, 589.

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Table I. Proton Chemical Shift [δ, Downfield from $SiMe_4$ or TSP; J(Pt–H) (in Parentheses) in Hz are Given When Assignable] of Complexes

compd	formula	solvent	O–H	N–H	C–Bu^t	C–Me	C–Ph
1	$K[PtCl_3(NCBu^t)]$	*a*			1.44		
1b	$(Et_4N)[PtCl_3\{HN{=}C(OH)Bu^t\}]$	*b*	11.16	7.06	1.16		
2	$K[PtCl_3(NCMe)]$	*a*				2.56 (13)	
2b	$(Et_4N)[PtCl_3\{HN{=}C(OH)Me\}]$	*b*	11.15	6.94		2.00	
3	$K[PtCl_3(NCPh)]$	*a*					7.89 (2H), 7.82 (1H), 7.63 (2H)
3b	$(Et_4N)[PtCl_3\{HN{=}C(OH)Ph\}]$	*b*	11.60	*d*			7.70 (2H), 7.53 (1H), 7.40 (2H)
4	*trans*-$[PtCl_2(NCBu^t)_2]$				1.43		
4b	*trans*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2]$	*b*	10.43	6.70	1.22		
5	*trans*-$[PtCl_2(NCMe)_2]$	*b*				2.52 (12)	
5b	*trans*-$[PtCl_2\{HN{=}C(OH)Me\}_2]$	*b*	10.42	6.60		2.13	
6	*trans*-$[PtCl_2(NCPh)_2]$	*b*					7.78 (2H), 7.72 (1H), 7.55 (2H)
6b	*trans*-$[PtCl_2\{HN{=}C(OH)Ph\}_2]$	*b*	10.87	*d*			7.74 (2H), 7.59 (1H), 7.48 (2H)
7	*cis*-$[PtCl_2(NCBu^t)_2]$	*b*			1.45		
7b	*cis*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2]_2$	*c*	9.97	7.00	1.22		
7c	*cis*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2N{-}C({=}O)Bu^t\}]_2$	*c*	10.20	7.0, 5.5^e	1.22, 1.19^e		
7d	*cis*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2N{-}C({=}O)Me\}]_2$	*c*	10.21	7.2, 5.7^e	1.22	2.01^e	
8	*cis*-$\{PtCl_2(NCMe)_2]$	*b*				2.48 (11)	
9	*cis*-$\{PtCl_2(NCPh)_2]$	*b*					7.78 (2H), 7.73 (1H), 7.55 (2H)
10	*trans*-$[PtCl_2\{HN{=}C(OH)Bu^t\}(NCBu^t)]$	*b*	11.06	6.90	1.20, 1.43^f		
11	*trans*-$[PtCl_2\{HN{=}C(OH)Bu^t\}(NCMe)]$	*b*	11.02	6.90	1.20	2.48 (11)	
12	*trans*-$[PtCl_2\{HN{=}C(OH)Bu^t\}(NCPh)]$	*b*	11.12	7.00			7.73 (3H), 7.53 (2H)
13	*cis*-$[PtCl_4\{HN{=}C(OH)Bu^t\}_2]$	*b*	11.84	6.64	1.33		

^{a} D_2O. ^{b} $CDCl_3$. ^{c} CD_2Cl_2. ^{d} Signal obscured by other resonance peaks. ^{e} Signal of the keto amide. ^{f} Signal of the nitrile.

in dimers, a key step in the formation of one-dimensional materials such as the already mentioned biologically active "platinum blues".[11,12] Moreover a *trans*-amidenitriledichloroplatinum(II) complex has been shown to be the controversial species previously formulated as a platinum(IV) complex with two amidate ligands having different tautomeric forms.[13]

Results and Discussion

General Description of the Reactions and Products. The hydrolysis of platinum-bound nitriles {$K[PtCl_3(NCR)]$ (R = Bu^t, **1**; Me, **2**; Ph, **3**), *trans*-$[PtCl_2(NCR)_2]$ (R = Bu^t, **4**; Me, **5**; Ph, **6**), and *cis*-$[PtCl_2(NCR)_2]$ (R = Bu^t, **7**; Me, **8**; Ph, **9**)} occurred readily under basic conditions and led to the formation of the corresponding amidate species. The reaction can be performed either in water (**1**–**3**) or in chlorinated solvents with KOH added as a powdered solid (**4**–**9**).

For **1**–**3** the reaction with base led to a solution containing the amidate species $K_2[PtCl_3\{HN{=}C(O)R\}]$ (R = Bu^t, **1a**; Me, **2a**; Ph, **3a**). Acidification of **1a**–**3a** with HCl afforded the corresponding amides $K[PtCl_3\{HN{=}C(OH)R\}]$ (R = Bu^t, **1b**; Me, **2b**; Ph, **3b**). These were isolated and characterized (hence forth **a** and **b** will denote amidate and amide species, respectively).

For **4**–**6** the isolation of the amidate compounds, $K_2\{$*trans*-$[PtCl_2\{HN{=}C(O)R\}_2]\}$ (R = Bu^t, **4a**; Me, **5a**; Ph, **6a**) was straightforward since **4a**–**6a** are sparingly soluble in dichloromethane. Complexes **4a**–**6a** were stable under dry conditions and could be stored indefinitely at room temperature. Acidification of ice-cold aqueous solutions of **4a**–**6a** afforded the corresponding amides, *trans*-$[PtCl_2\{HN{=}C(OH)R\}_2]$ (R = Bu^t, **4b**; Me, **5b**; Ph, **6b**), in quantitative yields.

For the cis complexes **7**–**9**, the isolation of both the amidate and the amide species was complicated by isomerization to the corresponding trans isomers accompanied by decomposition to blue materials. Only for **7** could the amidate species $K_2\{$*cis*-$[PtCl_2\{HN{=}C(O)Bu^t\}_2]\}$ (**7a**) be isolated by evaporation of the solvent (dichloromethane). **7a**, dissolved in cold water and treated with hydrochloric acid, afforded the corresponding amide, *cis*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2]_2$ (**7b**), in quantitative yield.

In chlorinated solvents (e.g., dichloromethane) **7b** decomposes spontaneously to the trans complex **4b**. However in dichloromethane/hexane (1:1 v/v) or in acetonitrile, in which the solubility of the platinum species is lower, it is possible to isolate an intermediate compound, $[PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2N{-}C({=}O)Bu^t\}]_2$ (**7c**), containing three amide molecules per platinum. **7c** and similar complexes having a different amide in axial positions (e.g., $[PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2N{-}C({=}O)Me\}]_2$, **7d**) can also be prepared from a solution of **7b** and free amide at 0 °C.

The lability of the *cis*-diamide complex suggested a procedure for preparing unsymmetrical complexes of platinum. Therefore, starting from **7b** and free nitrile, complexes of formula *trans*-$[PtCl_2(HN{=}C(OH)Bu^t\}(NCR)]$ (R = Bu^t, **10**; Me, **11**; Ph, **12**) were obtained in good yield. The trans structure of the complexes was confirmed by preparing **10** by reaction of the *trans*-bisnitrile complex (**4**) with sufficient base to hydrolyze only one nitrile ligand. Compound **10** proved to be the compound "II" of Brown *et al.*[13] obtained by reaction of $[PtCl_2(NCMe)_2]$ with melted *tert*-butylamide at ca. 160 °C and the exact nature of which was still a matter of debate.[14] *tert*-Butylnitrile was formally absent in the reaction performed by Brown *et al.*; however, a small amount of nitrile could either be present as an impurity in the excess amide used or be formed by thermal dehydration of the *tert*-butylamide.

^{1}H NMR Data. The following discussion will be concerned primarily with the amide and mixed amide–nitrile complexes (Table I).

The NMR spectra in chloroform of **1b**–**3b**, having one amide ligand per platinum, exhibit a rather sharp resonance between 10 and 11 ppm (1H), a very broad resonance between 6.5 and

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(9) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827. Barton, J. K.; Szalda, D. J.; Raboniwitz, H. N.; Waszcyak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434. O'Halloran, T. V.; Roberts, M. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6427. Mascharak, P. K.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6428. O'Halloran, T. V.; Mascharak, P. K.; Williams, I. D.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 1261.

(10) Sakai, K.; Matsumoto, K. *J. Am. Chem. Soc.* **1989**, *111*, 3074.

(11) Speer, R. J.; Ridgeway, H.; Hall, L. M.; Stewart, D. O.; Howe, K. E.; Lieberman, D. Z.; Newman, A. D.; Hill, J. M. *Cancer Chemother. Rep.* **1975**, *59*, 629. Hill, J. M.; Loeb, E.; MacLellan, A.; Hill, N. O.; Khan, A.; King, J. J. *Cancer Chemother. Rep.* **1975**, *59*, 647.

(12) Aggarwal, S. K.; Wagner, R. W.; Mc Allister, P. K.; Rosenberg, B. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 928. Bauer, W.; Gonias, S. J.; Kam, S. K.; Wu, K. C.; Lippard, S. J. *Biochemistry* **1978**, *17*, 1060.

(13) Brown, D. B.; Burbank, R. D.; Robin, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2895.

(14) Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2835. Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Guta, C.; Ruse, D. *Inorg. Chem.* **1980**, *19*, 1662. Johnson, A. K.; Miller, J. D. *Inorg. Chim. Acta* **1977**, *22*, 219. Barton, J. K.; Best, S. A.; Lippard, S. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 3785. Laurent, M. P.; Biscoe, J.; Patterson, H. H. *J. Am. Chem. Soc.* **1980**, *102*, 6576.

7.5 ppm (1H) and resonances of the R protons in the usual regions (TMS reference). The signal at lower field is characteristic of a hydroxyl proton, while the signal near 7 ppm is characteristic of a N-bound proton (the resonance is broadened by quadrupolar relaxation of nitrogen). Therefore, of the two tautomeric forms available for a hydrolyzed nitrile, keto [$H_2N\text{-}C(=O)R$] and enol [$HN{=}C(OH)R$], only the latter is preferred on coordination to platinum. Moreover in the series of compounds **1b**–**3b**, the NMR signal for the hydroxyl proton which was very sharp for the Bu^t derivative became increasingly broader for the methyl and phenyl analogues, respectively. This observation is consistent with an exchange process involving the hydroxyl proton and adventitious moisture. The rate of this process is expected to increase in the order **1b** < **2b** < **3b** since the acidity of the hydroxyl proton also increases in the same order.

The NMR spectra of *trans*-bisamide complexes **4b**–**6b** are very similar to those of compounds **1b**–**3b** and are in accord with N-coordinated amides in the enol tautomeric form. These results are also in complete agreement with the NMR and X-ray data reported by Brown *et al.* for compound **4b** obtained by a different procedure.[13]

In the case of compound **7b**, having two *cis-tert*-butylamide ligands, the ^1H NMR spectrum in undried CD_2Cl_2 showed, at 20 °C, only one peak at 1.2 ppm which was assignable to Bu^t. At 0 °C, a new, very broad peak arose at 7 ppm (the intensity of this signal was indicative of a single proton). At −20 °C this peak sharpened and shifted slightly to lower field, while another broad peak arose at ca. 10 ppm, the intensity of this latter signal also corresponded to one proton. At still lower temperature (−60 and −80 °C) the signal at ca. 10 ppm became increasingly sharper and shifted significantly to higher field (9.4 ppm at −80 °C), Figure 1.

The different spectral behavior of the trans (**4b**) and cis isomers (**7b**) could be explained on the basis of a different rate of proton exchange between the amide protons and the water present in the undried solvent. The rate of exchange was slow, in the NMR time scale, for **4b** and rather fast for **7b** (the exchange process involves primarily the hydroxyl proton which is the most affected). To check the validity of this hypothesis the NMR spectrum of compound **7b** was measured in carefully dried solvent. Under these experimental conditions the 20 °C spectrum showed a rather sharp resonance at ca. 10 ppm (hydroxyl proton) and a broader resonance at 7 ppm (N-bound proton) so resembling the spectrum of **4b** in undried solvent. How the cis position of the two amide ligands can promote a faster proton exchange between these and free water will be commented later in the text.

Compound **7c** contains three amide ligands per platinum. The NMR spectrum in dichloromethane showed at 0 °C two peaks at 1.19 and 1.20 ppm of relative intensity 1:2 for the alkyl protons and three broad peaks of equal intensity at 5.5, 7.0, and 10.0 ppm for the amide protons. On lowering the temperature, the peaks originally at 7 and 10 ppm became sharper, and the 10 ppm peak also shifted significantly down field. The signal at 5.5 ppm, on the other hand, split into two signals of equal intensity; these became sharper and shifted down field as the temperature was lowered (also the separation between the two peaks increased) (Figure 2).

The signals at *ca.* 7 and 10 ppm are characteristic of N–H and O–H protons, respectively, and account for two equivalent amide ligands. The values of chemical shift are nearly identical to those observed in **7b** for the spectrum recorded at 0 °C, while for the spectra at lower temperature the values are different particularly for the hydroxyl protons (10.1 for **7b** vs 10.3 for **7c** at 0 °C and 9.4 *vs* 11.4 at −80 °C). The signal which is positioned at 5.5 ppm at 0 °C and split into two peaks and shifted to 6.4 and 7.6 ppm at −80 °C is from the third amide ligand of **7c**. The values of chemical shift at 0 °C are nearly identical to those of the free amide. On the contrary those observed at low temperature and, in particular, the two peaks in the NH region, are characteristic of a O-bound amide having a keto tautomeric form with the two chemically inequivalent NH's.[15] The NH protons remain equivalent and shift only slightly to lower field in the case of free ligand at low temperature.

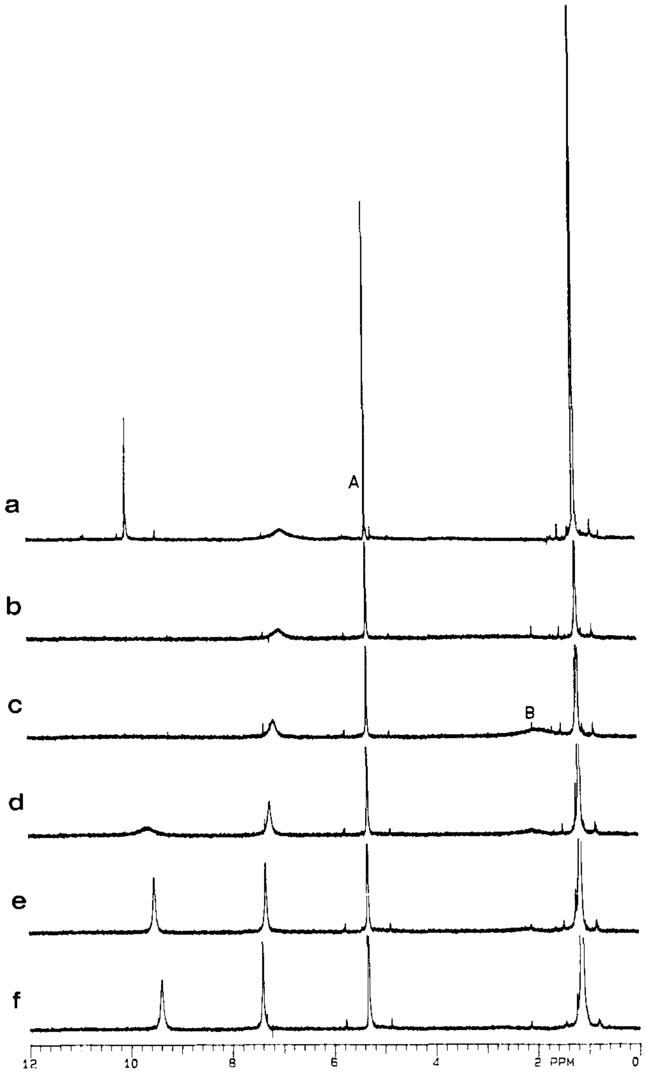

Figure 1. ^1H NMR spectra as a function of temperature for compound **7b** in CD_2Cl_2: (a) spectrum in dry solvent at 20 °C and (b–f) spectra in undried solvent at 0, −20, −40, −60 and −80 °C, respectively. A and B mark the resonances of $CHDCl_2$ and water, respectively.

Also in the case of **7c** the use of a carefully dried solvent caused a considerable sharpening of the hydroxyl signal even at 20 °C.

In summary, the 20 °C spectrum of **7c** indicates that the compound dissociates into **7b** and free amide. On the contrary, the low-temperature spectra suggest that the free amide recoordinates in the keto tautomeric form. In particular, the chemical shift difference in the hydroxyl protons for **7b** and **7c** ($\Delta\delta = 2$ ppm at −80 °C) also indicates that **7b** is distinct from **7c**.

The behavior of compound **7d** is strictly analogous to that of **7c**.

The ^1H NMR spectrum of compound **10** contains two signals for Bu^t; one signal for N–H and one for O–H protons of relative intensity 9:9:1:1. One set of signals (one Bu^t, the NH and the OH peaks) belongs to an amide ligand, the other signal in the Bu^t region belongs to a nitrile ligand. The different interpretation of this NMR spectrum (an amide and a nitrile instead of two isomeric amidate ligands[13]) is also supported by its similarity

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[15] Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 1533. Angel, R. L.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1990**, *29*, 20 and references therein.

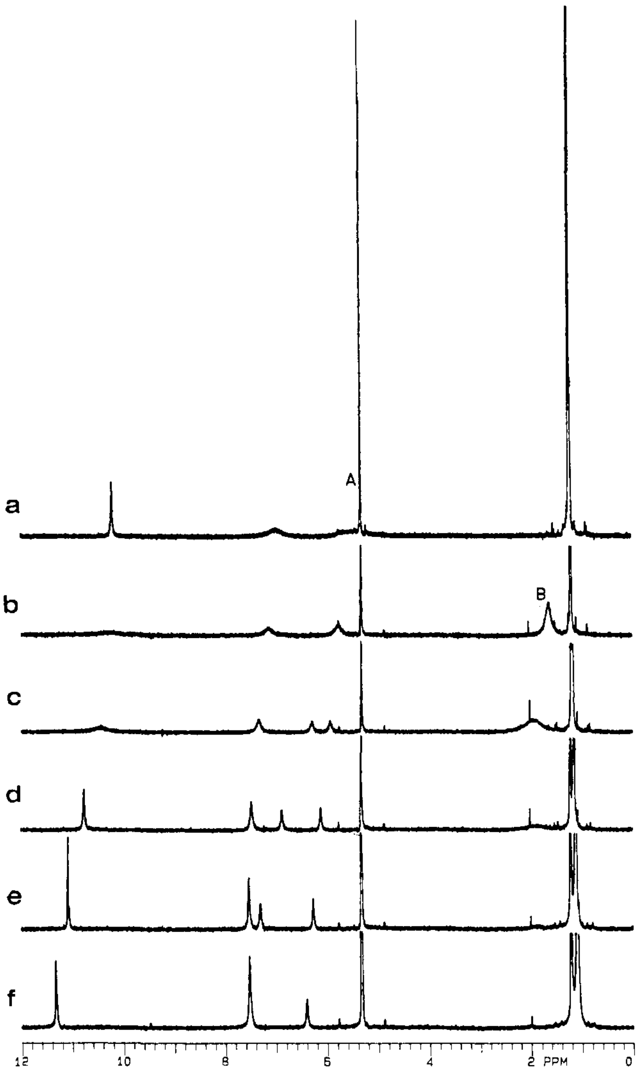

Figure 2. ^{1}H NMR spectra as a function of temperature for compound **7c** in CD_2Cl_2: (a) spectrum in dry solvent at 20 °C and (b–f) spectra in undried solvent at 0, –20, –40, –60 and –80 °C, respectively. A and B mark the resonances of $CHDCl_2$ and water, respectively.

with the spectra of **11** and **12** containing acetonitrile and benzonitrile in place of *tert*-butylnitrile.

Crystal Structures. The crystal lattice of **7b** contains discrete dimeric molecules and 1,2-dichloroethane. The coordination geometry of the two metal atoms is square pyramidal. The basal sites are occupied by two chloride and two N-bound amide ligands and the apical site by the other metal center of the dimer (Figure 3 and Tables II and III).

The four equatorial donors and the platinum are almost coplanar [maximum deviation of 0.05(3) Å for N(1A) and N(1B)]. The average bond distances, 2.326(6) Å for Pt–Cl and 2.026(19) Å for Pt–N, are in good agreement with the values usually found for platinum complexes.[16] The accuracy of the structural data does not allow a detailed description of the amide functionalities. No hydrogen atoms were located from the Fourier difference map, and the assumption of an enol tautomeric form had to rely on the NMR data. The N–C and C–O bond distances are not significantly different, although the former appears to be slightly shorter than the latter. The N–C–O and N–C–C angles are greater (122–127°) than the O–C–C angle (110–115°); this compression of the O–C–C angle lowers the interligand strain.

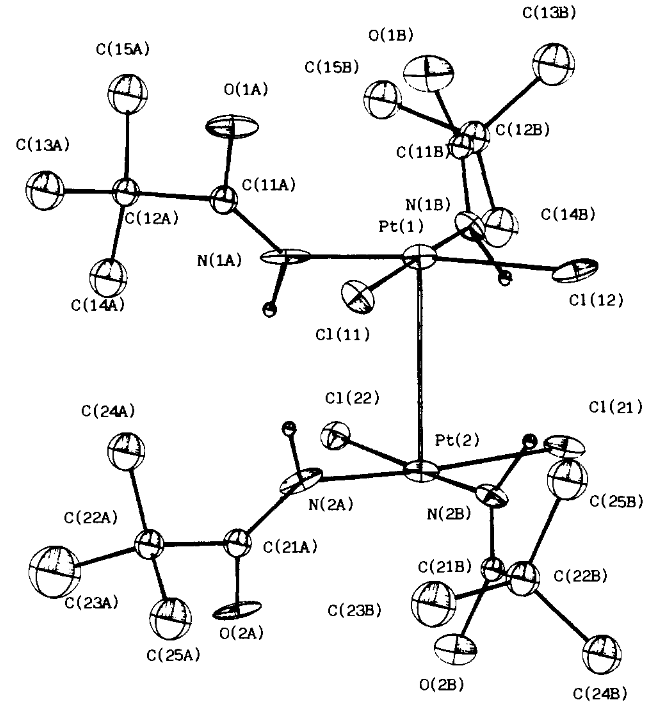

Figure 3. ORTEP drawing of the dimeric molecule of **7b**, showing also the labeling scheme. Ellipsoids enclose 30% probability. H atoms involved in the N–H···Cl bridges were set in calculated positions. Their thermal ellipsoids have an arbitrary scale.

The intermetallic distance is 3.165(1) Å, and the configuration of the complex is staggered. The amide ligands are in equivalent pairs, and a 90° rotation of the two platinum subunits about the Pt–Pt vector interchanges the ligand positions and converts the complex into its enantiomeric form. Both enantiomers are found in the crystal. Four hydrogen bonds link chlorine and nitrogen atoms of twin subunits [av N···Cl distance, 3.38(1) Å].

The Pt–Pt distance is longer compared to those observed in covalently bridged Pt^{II} dimers (2.8–3.0 Å).[17] This lengthening is a consequence of the absence of bridging ligand constraints which leaves the twin subunits free to optimize their interatomic distances. Comparable examples of unsupported Pt^{II}–Pt^{II} dimers have not been reported. The dihedral X–Pt–Pt–Y angles are close to 39.2° when X and Y donors are linked by hydrogen bonds and close to 50.8° in the other cases. Therefore hydrogen bond interactions between the two subunits would tend to place the dimer into an eclipsed conformation. This, however, is not

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(16) Faggiani, R.; Howard-Lock, H. E.; Lock, C. J. L.; Lippert, B.; Rosenberg, B. *Can. J. Chem.* **1982**, *60*, 529. Kuroda, R.; Neidle, S.; Ismail, I. M.; Sadler, P. J. *Inorg. Chem.* **1983**, *22*, 3620. Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2708. Muller, G.; Riede, J.; Beyerle-Pfnür, R.; Lippert, B. *J. Am. Chem. Soc.* **1984**, *106*, 7999. Marsh, R. E. *Inorg. Chem.* **1984**, *23*, 2363. Vollano, J. F.; Blatter, E. E.; Drabowiak, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2732. Fanizzi, F. P.; Natile, G.; Maresca, L.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1467. Natile, G.; Fanizzi, F. P.; Maresca, L.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1057. Hambley, T. W. *Acta Crystallogr.* **1986**, *C42*, 49.

(17) Bellitto, C.; Flamini, A.; Piovesana, O.; Zanazzi, P. F. *Inorg. Chem.* **1980**, *19*, 3632. Dos Remedios Pinto, H. A. F.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subiah, A.; Kuroda, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 13. Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1983**, *B39*, 280. Fackler Jr., J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1009. King, C.; Anerbach, R. A.; Fronczek, F. R.; Roundhill, D. M. *J. Am. Chem. Soc.* **1986**, *108*, 5626. Lippert, B.; Neugebauer, D.; Raudaschl, G. *Inorg. Chim. Acta* **1983**, *78*, 161. Trötscher, G.; Micklitz, W.; Schöllhorn, H.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 2541. Schöllhorn, H.; Thewalt, U.; Lippert, B. *Inorg. Chim. Acta* **1984**, *93*, 19. Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3494. Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2600. Laurent, J.-P.; Lepage, P.; Dahan, F. *J. Am. Chem. Soc.* **1982**, *104*, 7335. Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230. Lock, C. J.; Peresie, H. J.; Rosenberg, B.; Turner, G. *J. Am. Chem. Soc.* **1978**, *100*, 3371. Faggiani, R.; Lock, C. J. L.; Pollock, R. J.; Rosenberg, B.; Turner, G. *Inorg. Chem.* **1981**, *20*, 804. Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111. Lippert, B.; Neugebauer, D.; Schubert, U. *Inorg. Chim. Acta* **1980**, *46*, L11. Micklitz, W.; Riede, J.; Huber, B.; Müller, G.; Lippert, B. *Inorg. Chem.* **1988**, *27*, 1979. Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897.

Table II. Bond Distances (Å) with Estimated Standard Deviations in Parentheses for **7b**·$C_2H_4Cl_2$ and **7c**

7b·$C_2H_4Cl_2$				**7c**	
Pt(1)–Pt(2)	3.165(1)			Pt–Pt′	3.399(1)
Pt(1)–Cl(11)	2.314(7)	Pt(2)–Cl(21)	2.321(6)	Pt–Cl(1)	2.311(2)
Pt(1)–Cl(12)	2.332(6)	Pt(2)–Cl(22)	2.337(6)	Pt–Cl(2)	2.307(2)
Pt(1)–N(1A)	2.025(18)	Pt(2)–N(2A)	1.970(21)	Pt–N(A)	2.023(6)
Pt(1)–N(1B)	2.056(20)	Pt(2)–N(2B)	2.054(19)	Pt–N(B)	2.012(6)
				Pt–O(C)	3.229(5)
N(1A)–C(11A)	1.21(3)	N(2A)–C(21A)	1.25(3)	N(A)–C(1A)	1.289(9)
C(11A)–O(1A)	1.40(3)	C(21A)–O(2A)	1.32(3)	C(1A)–O(A)	1.320(9)
C(11A)–C(12A)	1.59(3)	C(21A)–C(22A)	1.53(4)	C(1A)–C(2A)	1.507(9)
C(12A)–C(13A)	1.57(4)	C(22A)–C(23A)	1.62(5)	C(2A)–C(3A)	1.56(3)
				C(2A)–C(3A)′	1.51(3)
				C(2A)–C(3A)″	1.51(3)
C(12A)–C(14A)	1.50(4)	C(22A)–C(24A)	1.46(4)	C(2A)–C(4A)	1.66(3)
				C(2A)–C(4A)′	1.62(4)
				C(2A)–C(4A)″	1.49(2)
C(12A)–C(15A)	1.60(4)	C(22A)–C(25A)	1.55(4)	C(2A)–C(5A)	1.56(4)
				C(2A)–C(5A)′	1.62(3)
				C(2A)–C(5A)″	1.65(4)
N(1B)–C(11B)	1.29(3)	N(2B)–C(21B)	1.23(3)	N(B)–C(1B)	1.311(9)
C(11B)–O(1B)	1.26(3)	C(21B)–O(2B)	1.32(3)	C(1B)–O(B)	1.313(9)
C(11B)–C(12B)	1.49(3)	C(21B)–C(22B)	1.48(4)	C(1B)–C(2B)	1.49(1)
C(12B)–C(13B)	1.55(4)	C(22B)–C(23B)	1.66(5)	C(2B)–C(3B)	1.55(1)
C(12B)–C(14B)	1.49(4)	C(22B)–C(24B)	1.55(4)	C(2B)–C(4B)	1.51(2)
C(12B)–C(15B)	1.54(4)	C(22B)–C(25B)	1.60(4)	C(2B)–C(5B)	1.49(2)
				N(C)–C(1C)	1.30(1)
				C(1C)–O(C)	1.31(1)
				C(1C)–C(2C)	1.50(1)
				C(2C)–C(3C)	1.55(2)
				C(2C)–C(4C)	1.51(1)
				C(2C)–C(5C)	1.53(1)
				HO(A)–O(A)	1.02(11)
				HN(A)–N(A)	1.23(11)
				HO(B)–O(B)	0.99(12)
				H1C(3B)–C(3B)	0.69(12)
				H2C(3B)–C(3B)	1.10(11)
				H1C(4B)–C(4B)	0.62(11)
				H1C(5B)–C(5B)	0.84(11)
				HN(C)–N(C)	0.90(11)
				H1C(4C)–C(4C)	0.83(11)
Cl(1D)–C(1D)[a]	1.80(1)				
Cl(2D)–C(2D)[a]	1.80(1)				
C(1D)–C(2D)[a]	1.54(1)				

[a] These distances were constrained during the refinement (ref 27).

attained because the two platinum subunits are forced to come closer to each other and minimize the interligand steric interactions by adopting the staggered conformation. The driving force to this closer approach of the platinum atoms can only stem from direct intermetallic bonding which can take place by mixing of the filled d_{z^2}–d_{z^2} orbitals with the higher lying p_z–p_z orbitals.[18] It is to be noted that a longer intermetallic distance [Pt···Pt = 3.259(4) Å] has been found in compounds like [Pt(dpg)$_2$](ClO$_4$) (dpg = diphenylglyoximato anion) made of an infinite chain of equidistant Pt^{III} centers. In the latter case the bond order between platinum atoms is formally $^1/_2$, and the bulk material is ESR silent.[19]

The analysis of the crystal packing reveals that molecules of **7b** are held together by hydrogen bonds involving chlorine and oxygen atoms.[20] The presence of such hydrogen bonds is in agreement with the enol tautomeric form of the amide ligands. The shortest intermolecular Pt···Pt distance is 4.169(1) Å [Pt(2)···Pt(2)($\bar{x}$, $\bar{y}$ + 1, $\bar{z}$ + 1)]. No hydrogen-bond interactions involving the Cl atoms of cocrystallized $C_2H_4Cl_2$ molecules are present.

The crystal lattice of **7c** also contains discrete dimeric molecules (Figure 4 and Tables II and III). The two metal atoms show a pseudooctahedral coordination geometry. The equatorial sites are occupied by two chloride and two N-bound amide ligands, the apical positions by the metal center of the twin unit and by the oxygen atom of the third amide ligand.

The four equatorial donors and the platinum atom are almost coplanar [maximum deviation 0.004(7) Å for N(1) and N(2)] with bond distances and angles close to the canonical values [av bond distances 2.309(2) and 2.017(6) Å for Pt–Cl and Pt–N, respectively].[16] The analysis of the crystallographic data allowed the location, from the difference Fourier map, of all the hydroxyl protons and half the N-bound protons; therefore confirming the enol tautomeric form of the equatorial amides. As already observed for **7b**, the N–C and C–O bond distances are similar within experimental error, while the N–C–O and N–C–C angles are greater (121–126°) than the O–C–C angle (112–115°); this compression of the O–C–C angle lowers the interligand strain.

An amide molecule, having a tautomeric form different from that of the equatorial ligands, is located in a nearly apical position, trans to the Pt–Pt vector [Pt–Pt–O angle of 170.91(7)°]. The Pt–O distance of 3.229(5) Å can be compared with the sum of the van der Waals radii of Pt and O of 3.2–3.3 Å.[21] The amide nitrogen is 3.870(5) Å away from platinum and is anchored, through a strong hydrogen bond, to an equatorial chloride ligand [N···Cl distance, 3.38(1) Å]. In the case of apical amides the N–C and C–O bond distances and the N–C–O, N–C–C, and O–C–C bond angles are practically identical.

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(18) Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489. Mann, K. R.; Lewis, N. S.; Williams, R. W.; Gray, H. B.; Gordon II, J. G. *Inorg. Chem.* **1978**, *17*, 828.

(19) Endres, H.; Keller, H. J.; van de Sand, H.; Dong, V. *Z. Naturforsch.* **1978**, *33B*, 843.

(20) Intermolecular hydrogen-bond interactions (esd's = 0.01 Å) in the lattice of **7b**·$C_2H_4Cl_2$ were Cl(11)···O(1A)($\bar{x}$, $\bar{y}$, $\bar{z}$ + 1), 3.07; Cl(11)···O(1B)($\bar{x}$, $\bar{y}$, $\bar{z}$ + 1), 3.18; Cl(12)···O(1B)($\bar{x}$, $\bar{y}$, $\bar{z}$ + 1), 3.55; Cl(21)···O(2B)($\bar{x}$, $\bar{y}$ + 1, $\bar{z}$ + 1), 3.54; Cl(22)···O(2A)($\bar{x}$, $\bar{y}$ + 1, $\bar{z}$ + 1), 3.04; Cl(22)···O(2B)($\bar{x}$, $\bar{y}$ + 1, $\bar{z}$ + 1), 3.10.

Table III. Bond Angles (deg) with Estimated Standrad Deviations in Parentheses for **7b**·$C_2H_4Cl_2$ and **7c**

7b·$C_2H_4Cl_2$				**7c**	
Pt(2)–Pt(1)–Cl(11)	92.7(2)	Pt(1)–Pt(1)–Cl(21)	92.8(2)	Pt′–Pt–Cl(1)	96.6(1)
Pt(2)–Pt(1)–Cl(12)	90.7(2)	Pt(1)–Pt(2)–Cl(22)	91.0(2)	Pt′–Pt–Cl(2)	95.8(1)
Pt(2)–Pt(1)–N(1A)	83.8(5)	Pt(1)–Pt(2)–N(2A)	84.5(5)	Pt′–Pt–N(A)	83.5(2)
Pt(2)–Pt(1)–N(1B)	85.1(6)	Pt(1)–Pt(2)–N(2B)	84.4(7)	Pt′–Pt–N(B)	82.4(2)
				Pt′–Pt–O(C)	170.9(1)
Cl(11)–Pt(1)–Cl(12)	92.1(3)	Cl(21)–Pt(2)–Cl(22)	91.0(2)	Cl(1)–Pt–Cl(2)	91.3(1)
Cl(11)–Pt(1)–N(1A)	89.4(6)	Cl(21)–Pt(2)–N(2A)	89.9(6)	Cl(1)–Pt–N(A)	86.7(2)
Cl(11)–Pt(1)–N(1B)	177.2(6)	Cl(21)–Pt(2)–N(2B)	176.5(6)	Cl(1)–Pt–N(B)	177.9(2)
Cl(12)–Pt(1)–N(1A)	174.4(5)	Cl(22)–Pt(2)–N(2A)	175.4(5)	Cl(2)–Pt–N(A)	177.8(2)
Cl(12)–Pt(1)–N(1B)	89.6(6)	Cl(22)–Pt(2)–N(2B)	91.2(6)	Cl(2)–Pt–N(B)	86.9(2)
N(1A)–Pt(1)–N(1B)	88.7(8)	N(2A)–Pt(2)–N(2B)	87.8(8)	N(A)–Pt–N(B)	95.2(2)
Pt(1)–N(1A)–C(11A)	127(2)	Pt(2)–N(2A)–C(21A)	130(2)	Pt–N(A)–C(1A)	126.8(5)
Pt(1)–N(1B)–C(11B)	125(2)	Pt(2)–N(2B)–C(21B)	128(2)	Pt–N(B)–C(1B)	126.4(5)
N(1A)–C(11A)–O(1A)	124(2)	N(2A)–C(21A)–O(2A)	122(2)	N(A)–C(1A)–O(A)	121.1(6)
N(1A)–C(11A)–C(12A)	125(2)	N(2B)–C(21A)–C(22A)	124(2)	N(A)–C(1A)–C(2A)	124.0(6)
O(1A)–C(11A)–C(12A)	110(2)	O(2A)–C(21A)–C(22A)	113(2)	O(A)–C(1A)–C(2A)	114.9(6)
C(11A)–C(12A)–C(13A)	107(2)	C(21A)–C(22A)–C(23A)	111(3)	C(1A)–C(2A)–C(3A)	110(1)
				C(1A)–C(2A)–C(3A)′	115(1)
				C(1A)–C(2A)–C(3A)″	108(1)
C(11A)–C(12A)–C(14A)	111(2)	C(21A)–C(22A)–C(24A)	113(2)	C(1A)–C(2A)–C(4A)	110(1)
				C(1A)–C(2A)–C(4A)′	104(1)
				C(1A)–C(2A)–C(4A)″	111(1)
C(11A)–C(12A)–C(15A)	108(2)	C(21A)–C(22A)–C(25A)	106(2)	C(1A)–C(2A)–C(5A)	105(1)
				C(1A)–C(2A)–C(5A)′	107(1)
				C(1A)–C(2A)–C(5A)″	105(1)
C(13A)–C(12A)–C(14A)	107(2)	C(23A)–C(22A)–C(24A)	103(3)	C(3A)–C(2A)–C(4A)	100(2)
C(13A)–C(12A)–C(15A)	110(2)	C(23A)–C(22A)–C(25A)	112(3)	C(3A)–C(2A)–C(5A)	126(2)
C(14A)–C(12A)–C(15A)	114(2)	C(24A)–C(22A)–C(25A)	112(2)	C(4A)–C(2A)–C(5A)	105(2)
N(1B)–C(11B)–O(1B)	123(2)	N(2B)–C(21B)–O(2B)	123(2)	N(B)–C(1B)–O(B)	121.5(7)
N(1B)–C(11B)–C(12B)	122(2)	N(2B)–C(21B)–C(22B)	127(2)	N(B)–C(1B)–C(2B)	126.1(7)
O(1B)–C(11B)–C(12B)	115(2)	O(2B)–C(21B)–C(22B)	110(2)	O(B)–C(1B)–C(2B)	112.3(6)
C(11B)–C(12B)–C(13B)	108(2)	C(21B)–C(22B)–C(23B)	113(3)	C(1B)–C(2B)–C(3B)	108.8(7)
C(11B)–C(12B)–C(14B)	114(2)	C(21B)–C(22B)–C(24B)	112(2)	C(1B)–C(2B)–C(4B)	108.9(8)
C(11B)–C(12B)–C(15B)	110(2)	C(21B)–C(22B)–C(25B)	109(2)	C(1B)–C(2B)–C(5B)	112.4(8)
C(13B)–C(12B)–C(14B)	109(3)	C(23B)–C(22B)–C(24B)	109(3)	C(3B)–C(2B)–C(4B)	109.8(9)
C(13B)–C(12B)–C(15B)	108(2)	C(23B)–C(22B)–C(25B)	107(3)	C(3B)–C(2B)–C(5B)	110.6(8)
C(14B)–C(12B)–C(15B)	108(2)	C(24B)–C(22B)–C(25B)	107(3)	C(4B)–C(2B)–C(5B)	106.4(9)
				N(C)–C(1C)–O(C)	119.6(7)
				N(C)–C(1C)–C(2C)	122.1(8)
				O(C)–C(1C)–C(2C)	118.3(7)
				C(1C)–C(2C)–C(3C)	111.7(8)
				C(1C)–C(2C)–C(4C)	108.0(8)
				C(1C)–C(2C)–C(5C)	111.3(8)
				C(3C)–C(2C)–C(4C)	107.4(9)
				C(3C)–C(2C)–C(5C)	109.5(8)
				C(4C)–C(2C)–C(5C)	108.8(8)
Cl(1D)–C(1D)–C(2D)	96(5)				
Cl(2D)–C(2D)–C(1D)	100(3)				

Four interplanar hydrogen bonds link the N and Cl atoms of twin subunits [av N···Cl distance 3.41(1) Å]. The distance between the two symmetry related Pt atoms is 3.399(1) Å (sum of the van der Waals radii of Pt atoms 3.4–3.6 Å),[21] and the conformation of the two platinum subunits is eclipsed with an average value of the torsion angles about the Pt–Pt vector of 2.0°.

The lengthening of the Pt–Pt distance (0.23 Å), and the switch from staggered to eclipsed conformation, on passing from **7b** to **7c**, has to be attributed entirely to the presence, in the latter complex, of two extra ligands in the axial sites. In spite of the long Pt–O distance, an electron charge donation from the apical amides into the empty p*z* orbitals of the platinum atoms takes place which contravenes the metal–metal interaction. The unwinding of the two platinum subunits, while the two platinum atoms are moving apart, confirms that interligand bonds alone place the dimer into the eclipsed conformation.

In the crystal the dimeric molecules of **7c** are linked to each other by just one significant hydrogen bond, namely Cl(1)···N(C)($\bar{x}$ + 1, $\bar{y}$, $\bar{z}$ + 1) = 3.37 Å.

Conclusions

Different modes of coordination of amides to platinum have been proposed, both on experimental and theoretical grounds. They include oxygen and nitrogen coordination of both the keto and enol tautomers.[22] This work has shown that the N-coordination of the enol form is preferred. Only in one case (apical amides in **7c**) we had evidence for a O-bound keto form; however, the resulting interaction appeared to be very weak, and the metal–ligand bond distance was comparable to the sum of the van der Waals radii. The preference for the N-coordination stems from the greater affinity of platinum(II) for the nitrogen as compared with the oxygen atom. The N-coordination favors the shift of one proton from the nitrogen to the oxygen atom so stabilizing the enol tautomer. On the contrary, O-coordination, which is preferred in complexes of "class a" metal ions such as cobalt(III), stabilizes the keto tautomer;[15] the separate NMR signals observed for the NH_2 protons evidence an increased polarization of the amide function upon coordination [$H_2N{=}CR{-}O{-}M$]. The N-coordination becomes the stable form also in complexes of "class a" metal ions when the amide ligand is deprotonated to form an amidate anion.

Why the apical amides in **7c** have chosen a different mode of coordination to platinum needs to be explained. It might be that

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[21] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[22] Johnson, A. K.; Miller, J. D. *Inorg. Chim. Acta* **1977**, *22*, 219. Kerrison, J. Y. S.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 61. Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230. Lippert, B. *Inorg. Chem.* **1981**, *20*, 4326. Arrizabalaga, P.; Castan, P.; Laurent, J. P. *Inorg. Chim. Acta* **1982**, *66*, L9. *Inorg. Chim. Acta* **1984**, *92*, 203.

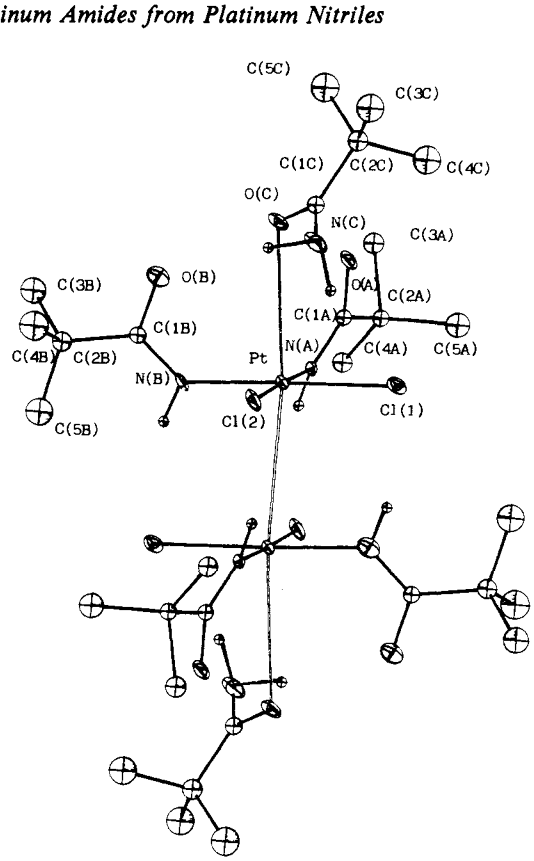

Figure 4. ORTEP drawing of the dimeric molecule of **7c**, showing the labeling scheme. H atoms involved in the N–H⋯Cl bridges were included in the figure; that bound to N(B) and one of those bound to N(C) were set in calculated positions since the difference Fourier synthesis was unable to reveal them. The ellipsoids of all the H atoms have an arbitrary scale.

a crucial role in the anchoring of the axial amides is played by the strong hydrogen bond formed between the nitrogen atom and an equatorial chloride ligand. Once the nitrogen atom is engaged in hydrogen-bonding, only the oxygen atom is available for coordination to platinum, and the amide assumes the keto form as always observed for O-coordinated amides.

A fast rate of proton exchange, between the hydroxyl group of the amide ligands and water present in the solvent, was observed in **7b**, **7c**, and also in *cis*-$[PtCl_4\{HN{=}C(OH)Bu^t\}_2]$ (**13**), all having two amide ligands in cis positions. It is proposed that such an exchange is favored by the interaction, through hydrogen bonding, of a water molecule with the two *cis*-amides. In particular compound **13** crystallizes with a water molecule which does not appear to be just an interstitial molecule from the IR spectrum (the X-ray characterization of $\mathbf{13}\cdot H_2O$ is underway).

The special role of the amide ligands in favoring the association of platinum monomers in dimers requires a comment. The geometry of the amide ligands in the enol tautomeric form appears to be ideal for favoring the formation of interfacial hydrogen bonds. Moreover the amide ligands have an empty π^* orbital which could draw electron charge from filled *d* orbitals of the metal and so stabilize the intermetallic interaction between the two platinum(II) units.

The cis position of two equatorial amides also plays a critical role in favoring the association of platinum units in dimers [compare the structure of **7b** with that of **4b** (ref 25)]. The explanation we can offer is that in the staggered conformation the contacts, between twin units, involve ligands of the same type (both chlorides or both amides) in only two cases out of eight if the configuration about platinum is cis, in four cases out of eight if the configuration is trans. Therefore cis units can approach one to the other with minor interligand strain than trans units, and this difference appears to be sufficient for the intermetallic bonding interaction to be seen only in the former case. The constant value of the N⋯Cl distances in **7b** and **7c** indicates that interfacial hydrogen bonds have equal strength in the staggered and eclipsed conformations, and $Pt^{II}\cdots Pt^{II}$ intermetallic interaction is responsible for the closer approach of the two metal atoms and for the staggered conformation of **7b**. The absence of bridging ligands constraints allows the 3.16 Å distance to be considered a genuine value for two interacting Pt^{II} units.

The dimeric nature of **7b** and **7c** does not pertain only to the solid state but also to the solution chemistry. For instance **7b** reacts instantaneously with chlorine to give the corresponding Pt^{III} dimer,[23] and it is well established that species of this type can be obtained by oxidation of Pt^{II} compounds already having a dimeric structure.[24] The corresponding trans isomer (**4b**), which has a monomeric structure,[25] gives exclusively the monomeric Pt^{IV} complex upon addition of chlorine. For **7c** the NMR spectra have shown that at room temperature the compound dissociates the apical amides to give **7b** and free amide. On lowering the temperature, however, the apical amides recoordinate (shifting and splitting of the NH_2 signal), and the observation that in solution as well as in the solid two amides are in the enol and one in the keto form suggests a similar structure for the complex in the two states.

The remarkable shift with temperature observed for the NMR signals of the hydroxyl protons of the equatorial amides (this had an opposite trend in compounds **7b** and **7c**) could be correlated with the stabilization, at low temperature, of the staggered conformation for **7b** and of the eclipsed conformation for **7c**, as observed in the solid. In the case of **7c** a contribution to the change in chemical shift could also come from the anchoring of the extra amides in the apical positions.

Materials and Methods

Starting Materials. Commercial reagent grade chemicals were used without further purification. The complexes *trans*-$[PtCl_2(NCR)_2]$ (R = Me, **5**; Ph, **6**) and *cis*-$[PtCl_2(NCR)_2]$ (R = Me, **8**; Ph, **9**) were prepared by the procedures reported in ref 2.

$K[PtCl_3(NCR)]$ (R = Bu^t, 1; Me, 2; Ph, 3). Potassium tetrachloroplatinate(II) (0.40 g, 1 mmol) dissolved in water (10 mL) and the nitrile (3–4 mmol) were stirred at 70 °C for 10–20 min until appearance of a yellow precipitate of the neutral disubstituted product. The reaction mixture was either filtered (R = Me) or extracted with CH_2Cl_2 (R = Bu^t, Ph) to remove the neutral species, the water solvent was evaporated under reduced pressure, and the solid residue was extracted with methanol. The methanolic solution, by evaporation of the solvent, afforded a yellow solid of $K[PtCl_3(NCR)]$ (yield: 65%, **1**; 80%, **2**; 30%, **3**). Anal. Calcd for $C_5H_9Cl_3KNPt$ (**1**): C, 14.2; H, 2.1; Cl, 25.1; N, 3.3. Found: C, 14.2; H, 2.1; Cl, 25.0; N, 3.3. Anal. Calcd for $C_2H_3Cl_3KNPt$ (**2**): C, 6.3; H, 0.8; Cl, 27.9; N, 3.7. Found: C, 6.6; H, 0.9; Cl, 27.6; N, 3.8. Anal. Calcd for $C_7H_5Cl_3KNPt$ (**3**): C, 18.9; H, 1.1; Cl, 24.0; N, 3.1. Found: C, 19.2; H, 1.2; Cl, 24.2; N, 3.1.

***trans*-$[PtCl_2(NCBu^t)_2]$, 4.** Potassium tetrachloroplatinate(II) (0.5 g, 1.2 mmol) dissolved in water (12 mL) and *tert*-butylnitrile (1.5 g, 18 mmol) were stirred at 75 °C for 20 h. The aqueous phase turned from red to pale yellow and a yellow precipitate, imbued with *tert*-butylnitrile, separated out. The mixture was extracted with dichloromethane, and the organic phase was reduced to small volume and treated with *n*-hexane. The yellow precipitate which separated out was a mixture of *cis*- and *trans*-$[PtCl_2(NCBu^t)_2]$ (yield 90%). The separation of the two isomers

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(23) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Am. Chem. Soc.* **1991**, *113*, 7805.

(24) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761. Barton, J. K.; Caravana, C.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 7269. Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253. Bellitto, C.; Flamini, A.; Gastaldi, L.; Scaramuzza, L. *Inorg. Chem.* **1983**, *22*, 444. O'Halloran, T. V.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1986**, *25*, 957. Bellitto, C.; Bonamico, M.; Dessy, G.; Fares, V.; Flamini, A. *J. Chem. Soc., Dalton Trans.* **1986**, 595. Schöllhorn, H.; Eisenmann, P.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1986**, *25*, 3384. Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 763. Bancroft, D. P.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 4022. Kuyper, J.; Vrieze, K. *Trans. Met. Chem.* **1976**, *1*, 208. Steel, B. R.; Vrieze, K. *Trans. Met. Chem.* **1977**, *2*, 169.

(25) Brown, D. B.; Robin, M. B.; Burbank, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 5621.

Table IV. Experimental Details for the Crystallographic Analyses

	7b·$C_2H_4Cl_2$	**7c**
formula	$C_{22}H_{48}N_4O_4Cl_6Pt_2$	$C_{30}H_{66}N_6O_6Cl_4Pt_2$
M	1035.5	1138.8
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
unit cell determination	25, randomly selected, high θ reflections	
a, Å	11.292(3)	10.279(1)
b, Å	13.618(3)	10.772(1)
c, Å	14.069(4)	11.099(3)
α, deg	62.12(2)	90.66(1)
β, deg	83.58(2)	89.58(1)
γ, deg	76.47(2)	114.27(1)
V, Å^3	1859(1)	1120(1)
Dc, g cm^{-3}	1.850	1.688
Z	2	1
$F(000)$	996	1120
cryst dimens, mm	0.12 × 0.37 × 0.60	0.50 × 0.25 × 0.25
μ(Cu-K$_\alpha$), cm^{-1}	183.64	142.34
diffractometer	Philips PW1100	Enraf-Nonius, CAD4
λ, Å	1.5418, graphite monochromatized	
scan range, deg	$5 \leq 2\theta \leq 110$	$8 \leq 2\theta \leq 114$
scan type	$\omega/2\theta$	$\omega/2\theta$
ω scan width, deg	$0.90 + 0.15 \tan\theta$	$0.80 + 0.14 \tan\theta$
scan speed, deg s^{-1}	0.06	0.06
reflcns collected	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
std reflcns periodically measd, 2 h	$(2\,1\,\bar{2}, 3\,1\,\bar{2}, \bar{2}\,\bar{1}\,2)$	$(\bar{6}\,4\,\bar{3}, 4\,5\,\bar{3})$
no. of data collected at 22 °C	4543	3530
data reduction	Lorentz–polarization effects	
no. of independent obsd reflcns with $F > 3\sigma(F)$	2460	3160
$R = \sum \lvert F_o - \lvert F_c \rvert\rvert / \sum F_o$	0.0623	0.0435
$R_w = \sum \sqrt{w} \lvert F_o - \lvert F_c \rvert\rvert / \sum F_o \sqrt{w}$	0.0651	0.0490
weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/[\sigma^2(F) + 0.0047F^2]$
no. of params refined	224	194

was accomplished by chromatography on an open column of silica gel using dichloromethane as eluant. The first eluted fraction contained *trans*-[$PtCl_2(NCBu^t)_2$] which was obtained crystalline by evaporation of the solvent (62% yield). The second eluted fraction contained *cis*-[$PtCl_2(NCBu^t)_2$] which was obtained crystalline by evaporation of the solvent and trituration of the oily residue with ethanol (12% yield). The initial water solution was taken to dryness, and the residue was extracted with methanol. The alcoholic solution, after evaporation of the solvent, afforded K[$PtCl_3(NCBu^t)$] (10% yield). Anal. Calcd for $C_{10}H_{18}Cl_2N_2Pt$ (**4**): C, 27.8; H, 4.2; Cl, 16.4; N, 6.5. Found: C, 27.6; H, 4.2; Cl, 16.4; N, 6.4.

***cis*-[$PtCl_2(NCBu^t)_2$], 7.** Potassium tetrachloroplatinate(II) (0.5 g, 1.2 mmol) dissolved in water (12 mL) and *tert*-butylnitrile (0.3 g, 3.6 mmol) were stirred at 75 °C for 4 h. The aqueous phase turned from red to pale yellow and a yellow precipitate, imbued with *tert*-butylnitrile, separated out. The mixture was extracted with dichloromethane, and the organic extract, after removal of the solvent and trituration of the oily residue with ethanol, afforded a yellow solid of *cis*-[$PtCl_2(NCBu^t)_2$] (48% yield). The surnatant ethanol solution contained a small amount of the cis isomer and the trans isomer formed in the reaction; the initial water solution contained KCl, unreacted K_2PtCl_4, and a small amount of K[$PtCl_3(NCBu^t)$]. Anal. Calcd for $C_{10}H_{18}Cl_2N_2Pt$ (**7**): C, 27.8; H, 4.2; Cl, 16.4; N, 6.5. Found: C, 27.7; H, 4.1; Cl, 16.7; N, 6.4.

Preparation of Complexes. K[$PtCl_3\{HN{=}C(OH)R\}$] (R = Bu^t, 1b; Me, 2b; Ph, 3b). K[$PtCl_3(NCR)$] (1 mmol) dissolved in the minimum volume of water (4–6 mL) and cooled to 0 °C was treated with KOH in slight excess (1.2 mmol). The solution was stirred for 1 h at 0 °C and then treated with 3 M HCl until pH = 3. The solvent was evaporated under reduced pressure, and the solid residue was extracted with MeOH. The alcoholic solution, after evaporation of the solvent, afforded a yellow solid of K[$PtCl_3\{HN{=}C(OH)R\}$] (yield 70, 85, and 95% for **1b**, **2b**, and **3b**, respectively). Anal. Calcd for $C_5H_{11}Cl_3KNOPt$ (**1b**): C, 13.6; H, 2.5; Cl, 24.1; N, 3.2. Found: C, 13.5; H, 2.4; Cl, 24.3; N, 3.2. Anal. Calcd for $C_2H_5Cl_3KNOPt$ (**2b**): C, 6.0; H, 1.3; Cl, 26.6; N, 3.5. Found: C, 5.5; H, 1.1; Cl, 26.3; N, 3.2. Anal. Calcd for $C_7H_7Cl_3KNOPt$ (**3b**): C, 18.2; H, 1.5; Cl, 23.0; N, 3.0. Found: C, 18.7; H, 1.6; Cl, 22.8; N, 3.0.

K_2\{*trans*-[$PtCl_2\{HN{=}C(O)R\}_2$]\} (R = Bu^t, 4a; Me, 5a; Ph, 6a). These compounds were prepared by addition of potassium hydroxide to the corresponding *trans*-[$PtCl_2(NCR)_2$] complexes. In a typical experiment one mmol of *trans*-[$PtCl_2(NCR)_2$] was dissolved in the minimum volume of dichloromethane, and then a large excess of KOH (1.12 g, 20 mmol) and a small amount of methanol (0.3 mL) were added. The mixture was left under stirring for 2 h at 25 °C; in the meanwhile a yellow solid separated out. This was collected by filtration of the mother liquor, washed with dichloromethane, to remove traces of unreacted nitrile complex, and with ethanol, to remove excess KOH, and then dried in a stream of dry air and stored under dry conditions (yield 90%). Anal. Calcd for $C_{10}H_{20}Cl_2K_2N_2O_2Pt$ (**4a**): C, 22.1; H, 3.7; Cl, 13.0; N, 5.1. Found: C, 21.3; H, 3.8; Cl, 13.4; N, 4.8. Anal. Calcd for $C_4H_8Cl_2K_2N_2O_2Pt$ (**5a**): C, 10.4; H, 1.7; Cl, 15.4; N, 6.1. Found: C, 10.3; H, 2.0; Cl, 15.1; N, 5.5. Anal. Calcd for $C_{14}H_{12}Cl_2K_2N_2O_2Pt$ (**6a**): C, 28.8; H, 2.1; Cl, 12.1; N, 4.8. Found: C, 28.3; H, 2.1; Cl, 11.9; N, 4.7.

***trans*-[$PtCl_2\{HN{=}C(OH)R\}_2$] (R Bu^t, 4b; Me, 5b; Ph, 6b).** The amide species were obtained by protonation of the corresponding amidate complexes **4a–6a**. In a typical experiment the potassium salt of the amidate complex (1 mmol) was dissolved in the minimum volume of ice cold water and treated with an excess of hydrochloric acid (10 mL, 6 M), meanwhile a yellow precipitate separated from the solution. This was collected by filtration of the mother liquor, washed with ice cold water, and dried in a stream of dry air. The isolated compound might be contaminated by a blue material and require a further purification. Compound **4b** can be purified by chromatography using an open column of silica gel and dichloromethane as eluant; compound **5b** by crystallization from chloroform: yields 80%. Anal. Calcd for $C_{10}H_{22}Cl_2N_2O_2Pt$ (**4b**): C, 26.6; H, 4.7; Cl, 15.1; N, 6.0. Found: C, 26.2; H, 4.7; Cl, 15.0; N, 5.8. Anal. Calcd for $C_4H_{10}Cl_2N_2O_2Pt$ (**5b**): C, 12.5; H, 2.6; Cl, 18.5; N, 7.3. Found: C, 12.5; H, 2.6; Cl, 18.3; N, 7.1. Anal. Calcd for $C_{14}H_{14}Cl_2N_2O_2Pt$ (**6b**): C, 33.1; H, 2.8; Cl, 13.9; N, 5.5. Found: C, 33.0; H, 2.7; Cl, 13.8; N, 5.9.

***cis*-[$PtCl_2\{HN{=}C(OH)Bu^t\}_2$]$_2$, 7b.** The same reaction pathway used for the preparation of the corresponding trans isomers can be employed for the preparation of the cis complexes; however, additional problems arose from the instability of the intermediate amidate species and from the easy isomerization of the cis complexes to the corresponding trans isomers. In a typical experiment, 1 mmol of *cis*-[$PtCl_2(NCBu^t)_2$] (**7**) was dissolved in 15 mL of dichloromethane, and the solution was treated with an excess of powdered potassium hydroxide (1.12 g, 20 mmol). After stirring for 10 min at 25 °C the solvent was evaporated under vacuum, and the solid residue, containing the amidate species and the excess potassium hydroxide, was dissolved in water and filtered. The ice cold solution was then treated with an excess of HCl (10 mL, 3 M) which caused the precipitation of the amide complex as a deep green solid. The solid was collected by filtration of the mother liquor, dried in a stream of dry air, quickly washed with small portions of benzene and then with hexane, dried again, and stored at 0 °C: yield 60%. Anal. Calcd for $C_{20}H_{44}Cl_4N_4O_4Pt_2$ (**7b**): C, 25.6; H, 4.7; Cl, 15.1; N, 6.0. Found: C, 26.0; H, 4.9; Cl, 15.3; N, 6.0. This compound is unstable in solvents such as benzene, dichloromethane, etc. in which it undergoes a series of transformations which inevitably leads to the formation of the trans isomer as a final product. An intermediate product of the transformation is the triamide complex [$PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2NC({=}O)Bu^t\}$]$_2$, **7c**.

[$PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2NC({=}O)Bu^t\}$]$_2$, 7c. Compound **7b** was dissolved in the minimum volume of dichloromethane, and the solution was covered with a surnatant layer of *n*-hexane and left on standing at room temperature. In a few hours yellow needles of a crystalline product separated out. These were collected and dried in a stream of dry air. Anal. Calcd for $C_{30}H_{66}Cl_4N_6O_6Pt_2$ (**7c**): C, 31.6; H, 5.8; Cl, 12.4; N, 7.4. Found: C, 31.8; H, 5.9; Cl, 12.7; N, 7.1.

[$PtCl_2\{HN{=}C(OH)Bu^t\}_2\{H_2NC({=}O)Me\}$]$_2$, 7d. Compound **7b** (0.2 g, 0.2 mmol) was dissolved in the minimum volume of acetonitrile (2 mL) and treated with a solution of acetamide (0.05 g, 0.8 mmol) in the same solvent (1 mL) at 0 °C. In a few minutes a green solid separated from the solution; this was collected, washed with ice-cold acetonitrile, and dried in a stream of dry air: yield 70%. Anal. Calcd for $C_{24}H_{54}Cl_4N_6O_6Pt_2$ (**7d**): C, 27.3; H, 5.2; Cl, 13.4; N, 8.0. Found: C, 27.3; H, 5.2; Cl, 13.3; N, 7.9.

***trans*-[$PtCl_2\{HN{=}C(OH)Bu^t\}(NCR)$] (R = Bu^t, 10; Me, 11; Ph, 12).** *cis*-[$PtCl_2\{HN{=}C(OH)Bu^t\}_2$]$_2$ (**7b**) (0.32 mmol) dissolved in 1,2-dichloroethane (60 mL) and the nitrile (2.5 mmol) were stirred for 16 h at 75 °C. The solvent was then evaporated, and the solid residue was chromatographed on a open column of silica gel using dichloromethane as eluant. The first eluted fraction contained *trans*-[$PtCl_2\{HN{=}C(OH)$-

$\mathrm{Bu}^t\}_2]$ (**4b**), the second fraction the product *trans*-[$\mathrm{PtCl_2\{HN{=}C(OH)Bu^t\}(NCR)}$] (0.1 mmol). Anal. Calcd for $C_{10}H_{20}Cl_2N_2OPt$ (**10**): C, 26.7; H, 4.5; Cl, 15.7; N, 6.2. Found: C, 26.7; H, 4.6; Cl, 15.3; N, 6.2. Anal. Calcd for $C_7H_{14}Cl_2N_2OPt$ (**11**): C, 20.6; H, 3.4; Cl, 17.4; N, 6.9. Found: C, 20.7; H, 3.7; Cl, 17.0; N, 6.7. Anal. Calcd for $C_{12}H_{16}Cl_2N_2OPt$ (**12**): C, 30.6; H, 3.4; Cl, 15.1; N, 5.9. Found: C, 30.0; H, 3.4; Cl, 15.4; N, 5.9.

Compound **10** was also prepared by reaction of **4** with equimolar amount of KOH. Compound **4** (0.66 mmol) was dissolved in the minimum volume of dichloromethane and treated with powdered potassium hydroxide (0.70 mmol). After stirring for 1 h, the solvent was evaporated under vacuum, and the solid residue was washed with small portions of ethyl ether and then dissolved in water. The solution was filtered, cooled to 0 °C, and acidified with 3 M HCl affording a yellow precipitate of **10**. This was collected and dried, yield 40%. Anal. Found: C, 26.2; H, 4.3; Cl, 15.6; N, 6.0.

***cis*-[$\mathbf{PtCl_4\{HN{=}C(OH)Bu^t\}_2}$], 13.** A solution of **7b** (0.5 mmol) in dichloromethane (3 mL) was treated with a saturated solution of chlorine in carbontetrachloride (4 mL). As the reaction proceeded a yellow precipitate separated out, this was collected on a glass filter, washed with carbontetrachloride and dried, yield 80%. Anal. Calcd for $C_{10}H_{24}Cl_4N_2O_3Pt$ (**13**·H_2O): C, 21.5; H, 4.3; Cl, 25.4; N, 5.0. Found: C, 21.6; H, 4.4; Cl, 25.2; N, 5.0. When the same reaction was carried out in the dark, it led to the formation of a $\mathrm{Pt^{III}}$ dimer described in ref 23.

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. ^{1}H NMR spectra were obtained with Varian XL 200 and Bruker AM 300 spectrometers.

X-ray Crystallography. Crystals of **7b**·$C_2H_4Cl_2$ and **7c**, grown from $C_2H_4Cl_2$ and CH_2Cl_2/hexane, respectively, were selected for the X-ray analyses. Crystallographic data for the two compounds are listed in Table IV. Unit cell parameters were obtained by least-squares refinement of the values (in the range 9–15°) of 25 carefully centered reflections chosen from different regions of the reciprocal space. The structure amplitudes were obtained after the usual Lorentz–polarization reduction. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 2460 (**7b**·$C_2H_4Cl_2$) and 3160 (**7c**) independent reflections with $F > 3\sigma(F)$. A correction for absorption effects was applied (DIFABS).[26]

Pt, Cl, O, and N atoms of **7b** were treated anisotropically, and all the C atoms and the Cl atoms of the co-crystallized $C_2H_4Cl_2$, isotropically. Owing to the disorder found for the solvent molecule, the C–C and C–Cl bond distances were constrained to 1.54 ± 0.03 and 1.80 ± 0.03 Å, respectively.[27]

Pt, Cl, O, and N atoms of **7c** were refined anisotropically, and all other atoms were treated isotropically. The Fourier-difference maps revealed three sets, of three carbon atoms each, around C(2A) and the positions of nine H atoms. The nine carbon atoms around C(2A) were refined isotropically with the occupancy fixed to 1/3. The thermal parameters were freely refined to reasonable values [U in the range 0.0266(49)–0.0662(115) Å^2]. This kind of disorder was not found for the other two amide molecules of the asymmetric unit. The H atoms were included in the full-matrix least-squares cycles with isotropic thermal parameters; U was fixed at 0.06 Å^2.

All the calculations were carried out on Vax11/750 computer using the SHELX-86 and SHELX-76 systems of crystallographic computer programs.[28] The scattering factors were those of SHELX-86, SHELX-76, and of ref 29.

Final atomic coordinates for the two compounds are listed in Tables SI and SII; thermal parameters are given in Tables SIII and SIV; observed and calculated structure factors are given in Tables SV and SVI (supplementary material). Bond distances and angles are reported in Tables II and III, respectively.

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Supplementary Material Available: Listings of atomic coordinates (Tables SI and SII) and thermal parameters (Tables SIII and SIV) (4 pages); listing of observed and calculated structure factors (Tables SV and SVI) (29 pages). Ordering information is given on any current masthead page.

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(26) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(27) Allen, F. H.; Kennard, O.; Wason, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1.

(28) Sheldrick, G. M. *SHELX-86, Program for Crystal Structure Determination*; University of Gottingen, Germany, 1986. Sheldrick, G. M. *SHELX-86, Program for Crystal Structure Determination*; University of Cambridge, U.K., 1976.

(29) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.