

One consequence of the configuration at P4 is the nonequivalence of the two N_2 ligands in **1**. This is manifested in the preferential protonation of the less hindered N_2 ligand, as previously noted.⁵

There are significant differences in the reactivity of the A and B isomers as illustrated by (i) their reactions with acid to produce ammonia and hydrazine,⁵ (ii) addition of NEt_3 (2 mol) to a B^{13} isomer in CH_2Cl_2 solution at room temperature resulting in the immediate loss of all nitrogen as N_2 but a similar result not occurring with **2A**, and (iii) the lability of PPh_3 to exchange in **2B** but not **2A**. Presently, it is not obvious how these differences arise. One notable feature about the solid-state structure of **2B'** is the open volume above P4 in the coordination sphere.

Work is in progress to delineate this problem and understand why the B isomers favor hydrazine formation whereas the A isomers favor ammonia formation in solvents of low dielectric constant.¹⁴

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE83-05478.

Supplementary Material Available: For **2A** and **2B'**, fully numbered molecular structure projections and listings of final atomic coordinates and isotropic thermal parameters (15 pages). Ordering information is given on any current masthead page.

- (13) Carried out by using $[\text{MoCl}(\text{NNH}_2)(\text{triphos})(\text{PPhMe}_2)]\text{Cl}$.⁵
 (14) A full report of the structural data and allied chemistry will be submitted for publication in *Inorg. Chem.*

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Received December 17, 1985

Facile Substitution of NH_3 Ligands in a D diplatinum(III) Complex of 1-Methyluracil

Sir:

The degree of inertness of amine ligands in *cis*-diamineplatinum complexes and its possible relevance in biological systems, specifically with regard to the mode of action of Pt antitumor agents, still are a matter of debate. While there has been a report on the release of amine from dichloro(ethylenediamine)platinum(II) under in vivo conditions,¹ similar in vitro studies have provided no evidence for an amine labilization on binding of *cis*-diamineplatinum(II) complexes to DNA.^{2,3} On the other hand, in model systems the replacement of NH_3 or other amine ligands from platinum complexes has been shown to occur occasionally, e.g. on reaction with poly(A),⁴ during the reaction of *cis*- $(\text{NH}_3)_2\text{Pt}(\text{H}_2\text{O})_2^{2+}$ with pyrimidine nucleobases leading to "platinum blues",⁵ or in the presence of S-containing ligands such as methionine.⁶ Recently, we could demonstrate by X-ray analysis the conversion of *cis*- $[(\text{NH}_3)_2\text{Pt}(\text{MeC})\text{Cl}]\text{Cl}$ (MeC = 1-methylcytosine) into *trans*- $(\text{NH}_3)\text{Pt}(\text{MeC})\text{Cl}_2$ ⁷ and further that via this route formation of tris(nucleobase) complexes of Pt(II) is possible.⁸

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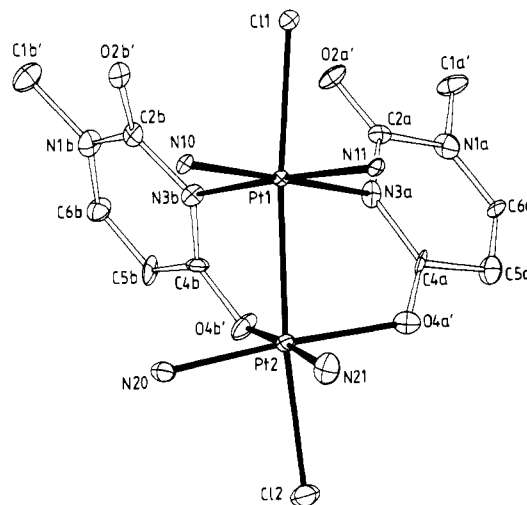


Figure 1. Molecular structure of the cation of $[\text{Cl}(\text{NH}_3)_2\text{Pt}(1\text{-MeU})_2\text{Pt}(\text{NH}_3)_2\text{Cl}]\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ (**2**).

We herewith wish to report yet another example of NH_3 replacement from a platinum coordination compound, the facile substitution of two *cis*-arranged ammonia ligands in a diplatinum(III) complex containing bridging 1-methyluracil ligands in a head-head orientation. Reaction occurs in 1 N HCl solution at room temperature or at 3 °C. Interestingly, only the two NH_3 groups trans to the two coordinating O4 oxygens of the two 1-MeU ligands are replaced by chloride, yet the NH_3 ligands trans to the N3 sites are not.

The two diplatinum(III) complexes described here were prepared via another diplatinum(III) precursor, *cis*- $[(\text{NO}_2)_2(\text{NH}_3)_2\text{Pt}(1\text{-MeU})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (head-head) (**1**),⁹ which was obtained from the diplatinum(II) complex *cis*- $[(\text{NH}_3)_2\text{Pt}(1\text{-MeU})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ (head-head)¹⁰ through oxidation with concentrated HNO_3 . The identity of **1** has been established by elemental analysis and X-ray crystallography.¹¹ **1** is unusual in the sense that it is the first structurally characterized diplatinum(III) complex with unequal coordination numbers (6 and 5) of the two Pt atoms.

cis- $[\text{Cl}(\text{NH}_3)_2\text{Pt}(1\text{-MeU})_2\text{Pt}(\text{NH}_3)_2\text{Cl}]\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ (**2**) was prepared as follows: 100 mg of **1** was dissolved in 1.5 mL of 1 N HCl; the resulting yellow solution was centrifuged from any undissolved material and then allowed to evaporate in air at 22 °C. After 24 h, 65 mg of orange cubes of **2** was collected.^{12,13} Slow evaporation (several days) of the filtrate gave other products as well, two of which (*cis*- $(\text{NH}_3)_2\text{PtCl}_4$ and neutral 1-MeUH) were identified by IR spectroscopy.

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 (12) Crystal data for **2** at -120 °C: $a = 20.813$ (5) Å, $b = 14.266$ (3) Å, $c = 17.704$ (4) Å, $\beta = 97.13$ (2)°, $V = 5216.0$ Å³, monoclinic system, space group $I2/c$, $Z = 8$, $\rho_{\text{calcd}} = 2.303$ g cm⁻³. Of the 6493 independent reflections (Phillips PW-1100 diffractometer, -120 °C, $\lambda = 0.71069$ Å, $\theta/2\theta$ technique with $\theta_{\text{max}} = 28^\circ$, L_p and empirical absorption corrections), 4700 reflections with $F_o > 2\sigma_{F_o}$ were used and gave a final $R = 0.056$. The SHELX program package was used for the calculations. The coordinates of the Pt atoms were taken from Patterson maps; the other non-hydrogen atoms were located by subsequent ΔF syntheses. All atoms, except the water oxygens, were refined anisotropically. Elemental analysis¹³ and density measurements ($\rho_{\text{obsd}} = 2.35$ in $\text{CH}_3\text{I}/\text{CH}_2\text{I}_2$) favor formulation of **2** as a 4.5-hydrate. Crystallographically, only 3.5 water molecules were found, but we cannot exclude the possibility of an additional, disordered water molecule present, e.g. at $x = 0.1885$, $y = 0.0632$, $z = 0.7324$. Although we also considered the possibility that two different modifications of **2** might be present, determinations of cell constants of several samples originating from different preparations did not confirm this assumption.
 (13) Anal. Calcd for $[\text{Cl}(\text{NH}_3)_2\text{Pt}(\text{C}_4\text{H}_5\text{N}_2\text{O}_2)]_2\text{Cl}_2 \cdot 4.5\text{H}_2\text{O}$: C, 12.89; H, 3.36; N, 12.03; O, 14.60; Cl, 15.22; Pt, 41.89. Found: C, 12.89; H, 3.27; N, 12.25; O, 14.55; Cl, 15.40; Pt, 41.9.

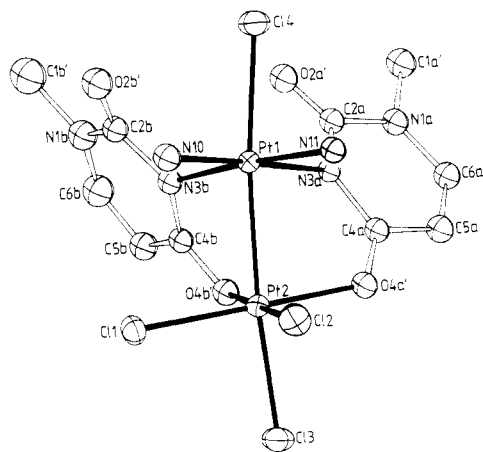


Figure 2. Molecular structure of $\text{Cl}(\text{NH}_3)_2\text{Pt}(\text{1-MeU})_2\text{PtCl}_3 \cdot 2\text{H}_2\text{O}$ (**3**).

In the course of the ^1H NMR spectroscopic characterization of **2**, we observed that on redissolving **2** in 1 N DCl, a dark red, crystalline compound (**3**) was formed. On a preparative scale, 20 mg of $\text{Cl}(\text{NH}_3)_2\text{Pt}(\text{1-MeU})_2\text{PtCl}_3 \cdot 2\text{H}_2\text{O}$ (**3**) was obtained from 40 mg of **2**, dissolved in 1.2 mL of 1 N HCl, within 2–5 days at 3 °C.^{14,15} If the solution was allowed to evaporate at 22 °C, the yield of **3** was lower, and small amounts of $(\text{NH}_4)_2[\text{PtCl}_6]$ and 1-MeUH were isolated as well.

The structure of the cation of **2** is shown in Figure 1. It is comprised of two *cis*-diammineplatinum units that are bridged by two 1-MeU ligands in a head-head arrangement and axially capped by chloro ligands. In agreement with the stoichiometry (three negative groups per Pt), the hexacoordination of each Pt, and the short Pt–Pt separation of 2.573 (1) Å, which is consistent with a Pt–Pt single bond, the oxidation state of Pt in **3** is +3.¹⁶ Pt–Cl distances are 2.459 (3) Å (Cl1) and 2.425 (4) Å (Cl2) and agree with data obtained in similar systems.¹⁷ As a consequence of the tilting of the equatorial Pt coordination planes toward each other (21.1°), the Cl–Pt–Pt–Cl unit is not exactly collinear but forms an angle about each Pt of ca. 174° (Pt1) and 172° (Pt2).

The neutral complex **3** is shown in Figure 2. The overall geometry of **3** is very similar to that of **2**, yet the two NH_3 ligands trans to the coordinating O4 donor atoms are now replaced by two chlorides. The Pt–Pt separation of 2.543 (1) Å is slightly shorter than in **2**. Pt–Cl distances in the equatorial plane of Pt2 are significantly shorter than the axial Pt–Cl distances, 2.285 (3) and 2.296 (3) Å vs. 2.465 (3) and 2.416 (3) Å. While the equatorial Pt–Cl distances are normal for mononuclear complexes of Pt(II)¹⁸ and Pt(IV),¹⁹ the considerably longer axial Pt–Cl

separations reflect the high trans influence of the Pt–Pt bond. The tilt angle between the Pt coordination planes in **3** (16°) is somewhat smaller than in **2**, in agreement with the shorter Pt–Pt distance in **3**.

A comparison of Pt– NH_3 distances trans to N3 of 1-MeU in **2** (2.05 (1) Å each) with those trans to O4 (2.02 (1), 2.00 (1) Å) does not reveal differences that might be attributed to a higher structural trans influence of O4 vs. N3.

The solution behavior of **2** and **3**, as studied by UV–visible,²⁰ ^1H NMR, and Raman spectroscopy, can be summarized as follows: (i) **2** is unstable in water. The ^1H NMR resonances of **2**, which are sharp immediately after sample preparation, become broad and unresolved with time.²¹ (ii) In 1 N HCl (DCl), **2** is converted into the transient species **3**. According to UV–visible spectroscopy, the maximum concentration of **3** at 22 °C is reached within 10–12 h; afterward decomposition of **3** occurs, with PtCl_6^{2-} and 1-MeUH identified as products. Isolated **3**, when dissolved in HCl, shows the same decomposition behavior. (iii) **2** is relatively stable (for days) in 1 N HCl in the presence of NaNO_2 (1–2 equiv/dimer). NaNO_3 (3–6 equiv/dimer) has no stabilizing effect. Consistent with this observation, **1** is stable in 1 N HCl (DCl) for days, even though its NO_2^- ligand immediately is substituted by Cl^- ²² and only gradually is it decomposed to *cis*- $(\text{NH}_3)_2\text{PtCl}_4$ (yet not PtCl_6^{2-}), 1-MeUH, and possibly other products. A direct conversion of **1** → **3** without isolation of **2** could not be achieved.

Conclusion. The facile displacement of the two *cis*-arranged NH_3 groups in **2** is surprising in that it does not follow the pattern that might be expected on the basis of the usual kinetic trans effect for Pt(II) complexes with $\text{N} > \text{O}$. While steric effects may play an important role in permitting NH_3 substitution at Pt2 yet not at Pt1 (Pt1 is, in contrast to Pt2, shielded by the two exocyclic O2' atoms of the 1-MeU rings), the fact that HNO_2 apparently prevents NH_3 substitution may suggest that the conversion **2** + HCl → **3** is coupled with a redox process.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Technische Universität München for financial support and Degussa for a loan of K_2PtCl_4 .

Supplementary Material Available: Listings of atomic coordinates and temperature factors for **2** and **3** (2 pages). Ordering information is given on any current masthead page.

(14) Anal. Calcd for $\text{Cl}(\text{NH}_3)_2\text{Pt}(\text{C}_5\text{H}_5\text{N}_2\text{O}_2)_2\text{PtCl}_3 \cdot 2\text{H}_2\text{O}$: N, 9.86; Pt, 45.78. Found: N, 10.25; Pt, 45.8.

(15) Crystal data for **3**: $a = 15.986$ (5) Å, $b = 8.856$ (3) Å, $c = 8.700$ (3) Å, $\alpha = 111.31$ (3)°, $\beta = 86.24$ (3)°, $\gamma = 112.58$ (3)°, $V = 1055.6$ Å³, space group $P\bar{1}$, $Z = 2$, $\rho_{\text{calcd}} = 2.681$ g cm⁻³, $\rho_{\text{obsd}} = 2.70$ g cm⁻³. Of the 2925 measured reflections, 2647 with $F_o > 2\sigma_{F_o}$ were used (cf. ref 13, except $\theta_{\text{max}} = 23^\circ$). $R = 0.042$, and $R_w = 0.046$ with $w^{-1} = \sigma_2^2 F + 0.0006F^2$.

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(20) UV–visible spectral data in 1 N HCl, immediately after sample preparation are as follows [λ , nm (ϵ , cm⁻¹ M⁻¹)]. For **2**: 390 (3650), 312 (27 400), 275 (23 600). For **3**: 500 (145), 400 (2200), 317 (13 800), 276 (17 700).

(21) ^1H NMR spectral data for **2** are as follows (0.1 M Pt, D₂O, pD = 2.9). Immediately after sample preparation: δ 3.49 (CH₃, s), 6.13 (H5, d, $^3J(\text{H5-H6}) = 7.3$ Hz), 7.90 (H6, d). After 20 h: δ 3.46 (CH₃, s, b), ≈ 6.1 (H5, half-width = ca. 0.6 ppm), ≈ 7.6 (H6, half-width = ca. 0.6 ppm).

(22) The Raman solution spectrum of **1** in 1 N HCl does not show the intense bands typical of diplatinum(III)-nitro complexes around 1300 and 810 cm⁻¹.

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Received September 17, 1985