On the Heterogeneous Nature of Cisplatin-1-Methyluracil Complexes: Coexistence of Different Aggregation Modes and Partial Loss of NH$_3$ Ligands as Likely Explanation

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Table S1. Selected bond lengths (Å) and bond angles (°) for compound 1a'.

| Bond | Length/Angle      |
|------|-------------------|
| Pt1–N10       | 2.011(7)          |
| Pt1–N11       | 2.104(7)          |
| Pt1–N3        | 2.050(8)          |
| Pt1–I1        | 2.5887(9)         |
| N1–C1         | 1.469(13)         |
| N1–C2         | 1.431(12)         |
| N1–C6         | 1.341(12)         |
| C2–N3         | 1.326(12)         |
| C2–O2         | 1.242(11)         |
| N3–C4         | 1.381(12)         |
| C4–O4         | 1.243(11)         |
| C4–C5         | 1.416(14)         |
| C5–C6         | 1.33(2)           |
Table S2. Selected bond lengths (Å), bond angles (°), and selected hydrogen bond lengths (Å) for compound 10.

| Bond          | Length (Å) | Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|---------------|------------|
| Pt1–N11       | 2.036(8)   | N11–Pt1–N3    | 178.1(4)   | Pt1–N3        | 2.048(8)   |
| Pt1–N3        | 2.048(8)   | N11–Pt1–I2    | 87.8(2)    | Pt1–I2        | 2.602(1)   |
| Pt1–I2        | 2.595(1)   | N3–Pt1–I2     | 91.3(2)    | N1–C1         | 1.461(14)  |
| N1–C1         | 1.461(14)  | N3–Pt1–I1     | 90.0(2)    | N1–C2         | 1.387(13)  |
| N1–C2         | 1.387(13)  | I2–Pt1–I1     | 177.82(3)  | N1–C6         | 1.37(2)    |
| N1–C6         | 1.37(2)    | C6–N1–C2      | 120.2(9)   | C2–N3         | 1.347(13)  |
| C2–N3         | 1.347(13)  | C6–N1–C1      | 119.3(10)  | C2–O2         | 1.233(12)  |
| C2–O2         | 1.233(12)  | C2–N1–C1      | 120.6(10)  | N3–C4         | 1.374(14)  |
| N3–C4         | 1.374(14)  | O2–C2–N3      | 123.3(10)  | C4–O4         | 1.252(12)  |
| C4–O4         | 1.252(12)  | O2–C2–N1      | 117.8(10)  | C4–C5         | 1.409(14)  |
| C4–C5         | 1.409(14)  | N3–C2–N1      | 118.9(9)   | C5–C6         | 1.36(2)    |
| C5–C6         | 1.36(2)    | C2–N3–C4      | 122.5(9)   | Pt2–N21       | 2.029(8)   |
| Pt2–N21       | 2.029(8)   | C2–N3–Pt1     | 119.2(7)   | Pt2–N22       | 2.034(7)   |
| Pt2–N22       | 2.034(7)   | C4–N3–Pt1     | 118.1(7)   | O4–C4–N3      | 119.0(9)   |
|               |            | O4–C4–C5      | 123.0(10)  |               |            |
| N11⋯O4$_2$    | 3.047(12)  | O4–C4–C5      | 123.0(10)  |               |            |
| N11⋯O1w$_3$   | 3.011(14)  | N3–C4–C5      | 118.0(9)   |               |            |
| N11⋯O2w$_4$   | 3.172(13)  | C6–C5–C4      | 119.8(10)  |               |            |
| N21⋯O4        | 2.956(13)  | C5–C6–N1      | 120.6(10)  |               |            |
| N21⋯O2$_5$    | 3.009(12)  | N21–Pt2–N21$_1$ | 179.1(5) |               |            |
| N21⋯O2w$_4$   | 3.131(13)  | N21–Pt2–N22$_1$ | 91.2(4)  |               |            |
| N22⋯O4        | 3.010(13)  | N21–Pt2–N22   | 88.8(4)    |               |            |
| N22⋯O2$_6$    | 3.033(12)  |               |            |               |            |
| N22⋯O2w$_7$   | 3.189(14)  |               |            |               |            |

Symmetry transformations used to generate equivalent atoms:

$\bar{1}$: $x+1, y, -z+1/2$

$\bar{2}$: $x+3/2, y+1/2, -z+3/2$

$\bar{3}$: $x+3/2, y+1/2, -z$

$\bar{4}$: $x, -y+1, z+1/2$

$\bar{5}$: $x+3/2, y+1/2, -z+3/2$

$\bar{6}$: $x+1, y+1/2, z$

$\bar{7}$: $-x+1, -y+1, -z+1$
Table S3. Selected bond lengths (Å) and bond angles (°) for compound 11.

| Bond          | Length (Å)   | Bond          | Angle (°)   |
|---------------|--------------|---------------|-------------|
| Pt1–N1        | 2.094(5)     | N1–Pt1–S1     | 175.1(2)    |
| Pt1–S1        | 2.222(2)     | N1–Pt1–I2     | 86.1(2)     |
| Pt1–I1        | 2.6057(7)    | S1–Pt1–I2     | 90.74(6)    |
| Pt1–I2        | 2.6099(7)    | N1–Pt1–I1     | 87.9(2)     |
| S1–O1         | 1.472(6)     | S1–Pt1–I1     | 95.43(6)    |
| S1–C11        | 1.769(5)     | I2–Pt1–I1     | 173.20(2)   |
| S1–C12        | 1.765(9)     | O1–S1–C12     | 107.2(4)    |
|               |              | O1–S1–C11     | 107.8(4)    |
|               |              | C12–S1–C11    | 97.2(4)     |
|               |              | O1–S1–Pt1     | 114.0(3)    |
|               |              | C12–S1–Pt1    | 116.2(2)    |
|               |              | C11–S1–Pt1    | 112.9(3)    |
Figure S1. Hydrogen bond network of 1a' along the z axis. Based on the original molecule A, B is generated with the symmetry operation -x+1, -y+1, -z and C with -x+1, y, -z+0.5. H bond length are: N10...O2 2.91(1) Å, N10...O4 2.87(1) Å, N11...O4 2.95(1) Å.
Figure S2. $^1$H-NMR resonance of CH$_3$ signal of freshly prepared sample of 1a in D$_2$O at 3.36 ppm, with $^{13}$C satellites (*, $^1J$ 140 Hz) and impurity of cis-[Pt(NH$_3$)$_2$(1MeU-N3)$_2$] (2) with its CH$_3$ resonance at 3.26 ppm. The intensity of 2 corresponds to ca. half of each $^{13}$C satellite, hence to ca. 0.25% of 1a. The amount of 2 thus is approximately 0.13% of that of 1a.
Figure S3. Possible trinuclear self-condensation products of 1b and products formed upon cyclization or additional dimerization. \( U = 1\text{MeU-N3}; -\text{U} \rightarrow = \mu-1\text{MeU-N3,O4}; a = \text{NH}_3. \)
Figure S4. Feasible association patterns of neutral [Pt(NH$_3$)(1MeU)Cl] entities to account for the m/z 767 signal (as Na$^+$ adducts) in ESI-mass spectrum. A mixed µ-U, µ-Cl species is feasible only following an isomerization of one of the two units with a and U ligands becoming cis to each other (not shown).
Figure S5. H5 NMR resonances of sample of 1a (D2O, 0.025 M, ambient temperature) treated with 1.12 equiv. of AgNO3: (a) 24 h after start, AgCl not removed; the sample contains largely 1b, and smaller amounts of (1aAg)x, 3, and 4; (b) after 4 d; (c) after 3 weeks. Apart from 1b, 3, and 4, a number of very minor H5 doublets, e.g. at 5.99, 5.845, 5.795, and 5.60, are present as shown in the inset in spectrum (c)). Doublets at 5.51 and 5.86 ppm (partly overlapped by resonances of 4) are due to 13C satellites of main resonance of 1b.
Figure S6. H5 NMR resonances of sample of 1a treated with 0.8 equiv. of AgNO₃ in H₂O (4 days, room temperature), then centrifuged from AgCl, allowed to evaporate in air to dryness, and then re-dissolved in D₂O: (a) Immediately after sample preparation; (b) after 3 weeks. Relative signal intensities in (b) are 1b (44%), 3 (25%), unreacted 1a (11%), 2 (10%), and 4 (9%), corresponding to a mole ratio of 44:12.5:11:5:4.5 of the respective species.
Figure S7. a) $^1$H NMR spectrum (0.1 M, D$_2$O) of pump-evaporated sample of 1a treated with 1 equiv. of AgNO$_3$ and centrifugation of AgCl with multiple weak H6 and CH$_3$ resonances in inserts. b) Enlarged H5 and H6 resonances of the unknown species “X”. 
Figure S8. DOSY spectrum of pump-evaporated sample of 1a treated with 1 equiv. of AgNO₃, following centrifugation of AgCl ([Pt] = 0.1 M, D₂O).
Figure S9. ESI-mass spectra of sample (I) (1a + 1.2 AgNO₃), and of sample (II) (1a + 0.8 AgNO₃), redissolved in H₂O.
Figure S10. ESI-mass peak centered at m/z 446, possibly due to species "X" seen in $^1$H-NMR spectrum. The simulation is based on a proposed composition $[\text{Pt}^{IV}(\text{NH}_3)_2(\text{MeU})(\text{NO})(\text{NO}_3)]^+$. 
Figure S1. Comparison of $m/z$ 690-770 signals seen in the ESI-mass spectra of (a) sample I, and (b) sample III.
Figure S12. Proposed structure for species with m/z 973.
Figure S13. Observed peaks and simulations for heteronuclear Pt,Ag(1MeU) complexes: (a) $\{\text{Pt}^{\text{II}}\text{Ag (NH}_3\text{)(1MeU)(OH)(OH}_2\text{)}\}^{+}$ and (b) $\{\text{Pt}^{\text{II}}\text{Ag (NH}_3\text{)}_2(\text{1MeU})(\text{OH})(\text{OH}_2\text{})\}^{+}$.
Figure S14. Stereo view of the hydrogen bond network of the [Pt(NH$_3$)$_4$]$^{2+}$ cation in 10 with the trans-[Pt(NH$_3$)(1MeU-N3)I$_2$]$^{-}$ anion and water of crystallization. Hydrogen bond lengths are given in Table S2.

Figure S15. (a) View of trans-[Pt(NH$_3$)(DMSO-S)I$_2$] (11) with atom numbering scheme. Ellipsoids are drawn at the 50% probability level. (b) Hydrogen bond network involving the NH$_3$ ligand of one complex and the oxygen atom of two symmetry related molecules (x+0.5, -y+0.5, z+0.5: 3.059(8) Å; -x+1.5, -y+0.5, -z+1: 3.169(11) Å).
Figure S16. Signals (o) emerging with time from internal DSS reference compound in a mixture of 1b and cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ (1:1; 3 month room temperature). The new resonances are downfield relative to DSS and occur at 0.14, 0.74, ca. 1.80 and 2.92 ppm.