Electronic Supplementary Information for Dalton Transactions

Supporting Information

The Role of Bridging Ligands in Determining DNA-binding ability and Cross-linking Patterns of Dinuclear Platinum (II) Antitumor Complexes

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Synthesis of {[*cis*-Pt$(NH_3)_2$Cl$]_2$L2}$(NO_3)_2$ (2)

The *cis*-[Pt$(NH_3)_2$Cl(DMF)](NO_3), which was used as starting material to prepare the complex **2**, was obtained by stirring $AgNO_3$ and *cis*-[Pt$(NH_3)_2Cl_2$] in dimethylformamide (DMF) overnight and filtering off AgCl precipitate, as previously described.[1] The DMF solution of linker L2 (30.00 mg, 0.22 mmol) was added dropwise to the solution of *cis*-[Pt$(NH_3)_2$Cl(DMF)](NO_3) (0.47 mmol) with stirring, then the resultant mixture was stirred overnight in the dark at room temperature. After precipitation, filtration, condensation and vacuum dry, light yellow solids of complex **2** were obtained (yield 85 mg, 43%).

The purity of complex **2** was characterized by ^{1}H NMR and ESI-MS. In the ^{1}H NMR spectrum (Fig. S1A), only one set of signals of methylene and phenyl (3.91 ppm, –CH_2; 7.60 ppm, –Ph–H) was observed, shifting significantly to lower field compared to those of free L2, which suggested both amine groups of L2 bind to Pt(II) equivalently (Fig. S1B). In the ESI-MS spectru, a major peak was observed at *m/z* 332.1, which corresponds to the positively doubly charged species $\{[Pt(NH_3)_2Cl]_2L2\}^{2+}$. The isotopic distribution pattern of this peak matched perfectly with the simulated one.

Elemental analysis of complex **2**, found (calcd.) for $Pt_2C_8H_{24}Cl_2N_8O_6$ (%): C, 12.17 (12.03); H, 3.04 (3.16); N, 14.20 (14.53).

Computational Methods

The starting geometry for each optimization was generated with the Q-Chem electronic structure calculation suite of programs.[2] Bond lengths of 2.31 Å for Pt-Cl[3] and 2.03 Å for Pt-amine[4] were used. All N-Pt-N angles were started at 90º. The electrostatic potential used in the RESP charge fitting[5] was calculated at the HF/6-31G** level using the Gaussian 03 program.[6] Computational results of the geometry-optimized structures of complexes 1 and 2 are shown in the Fig. S2.

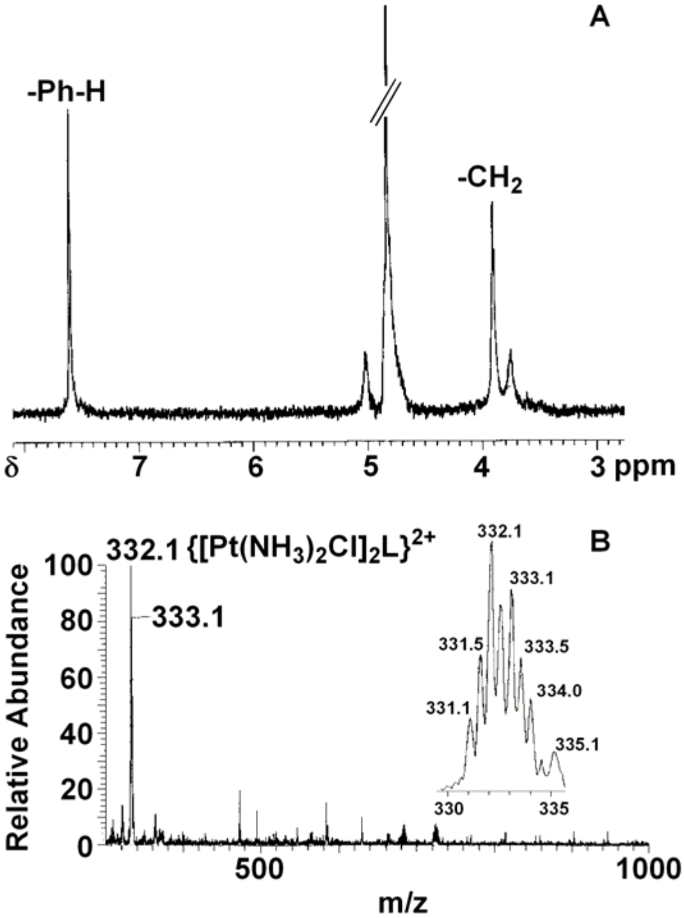

Fig. S1 The ^{1}H NMR (A, D_2O, 298 K) and electrospray mass spectrometry (B, methanol, positive mode) spectra of complex **2**.

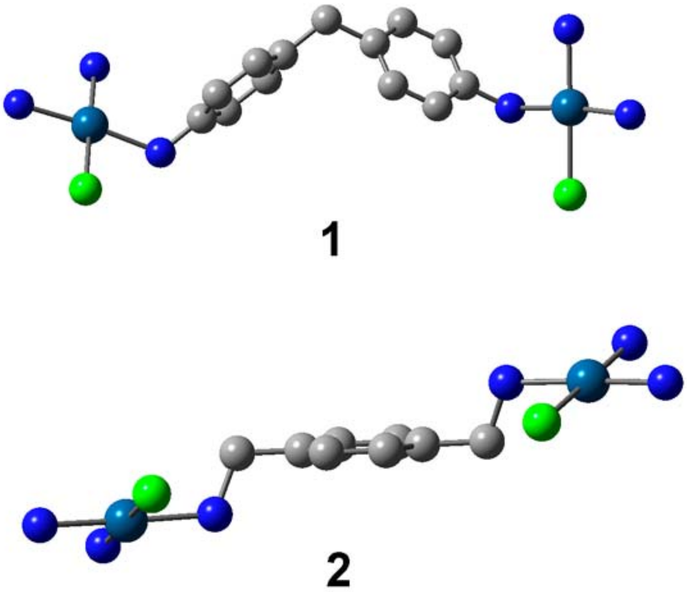

Fig. S2 Calculated structures of complexes **1** and **2**. Hydrogen atoms are omitted for clarity.

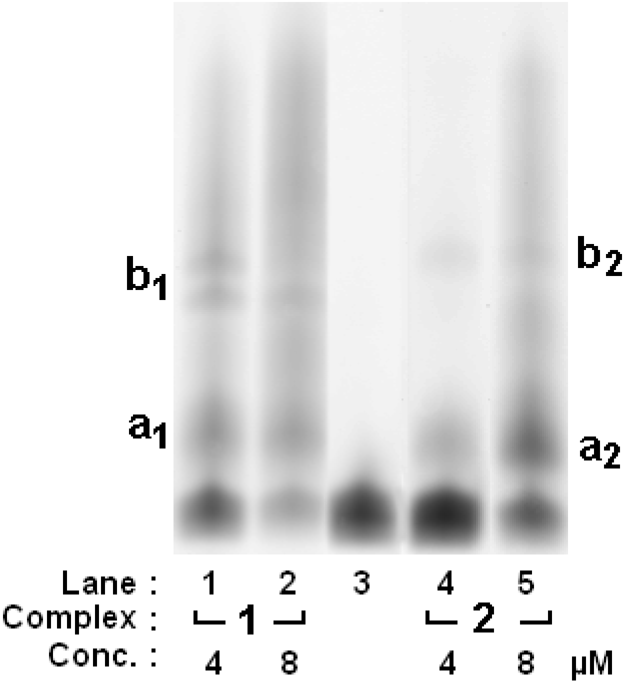

Fig. S3 Fluorescence image of a 20% polyacrylamide denaturing gel of DNA adducts of complex **1** and **2** induced in duplex **N2**. Lane 1 and 2: complex **1**; lane 3, unplatinated duplex **N2**; lane 3 and 4: complex **2**.

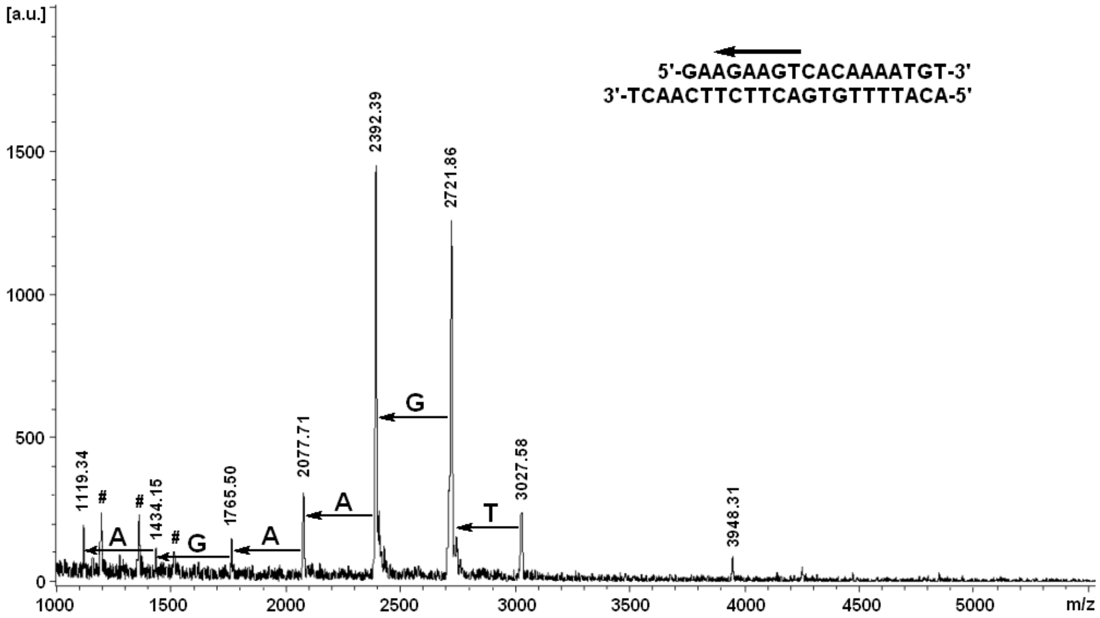

Fig. S4 MALDI-TOF mass spectra of Exo III digests of duplex **N3**. The arrows indicate the cleavage direction and location along the sequence. The peaks corresponding to doubly charged ions are marked with #.

References

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