Electronic Supplementary Material (ESI) for Dalton Transactions.

Syntheses of Polypyridyl Metal Complexes and Studies of their Interaction with Quadruplex DNA

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Supplementary Information

1. ^{1}H-^{1}H COSY NMR

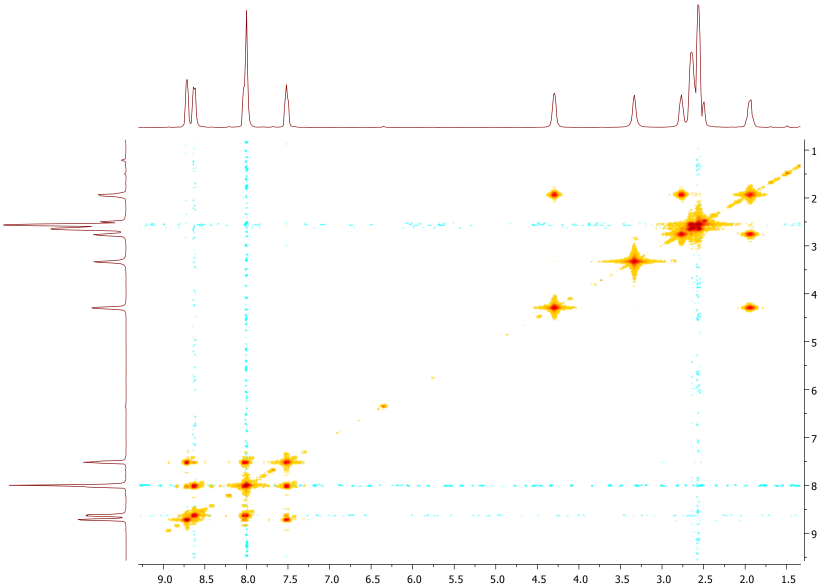

Fig. S1 ^{1}H-^{1}H COSY NMR of **L⁴** in d^6-DMSO.

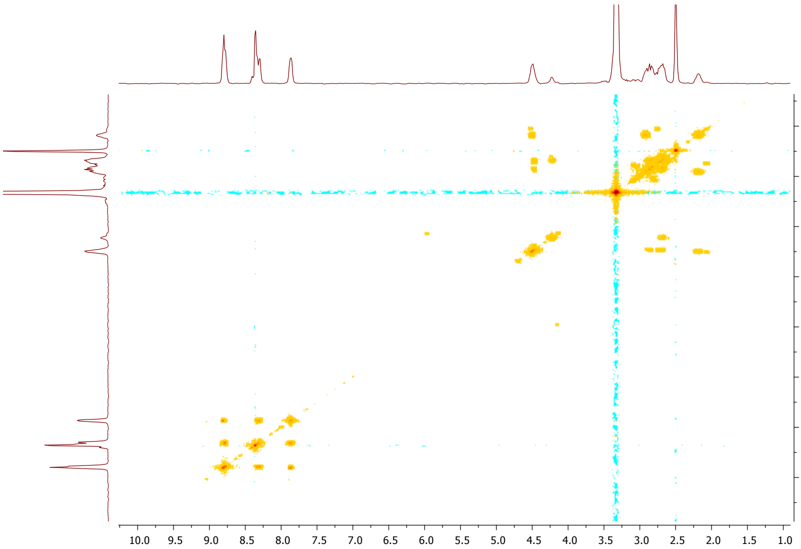

Fig. S2 ^{1}H-^{1}H COSY NMR of **8** in d^6-DMSO.

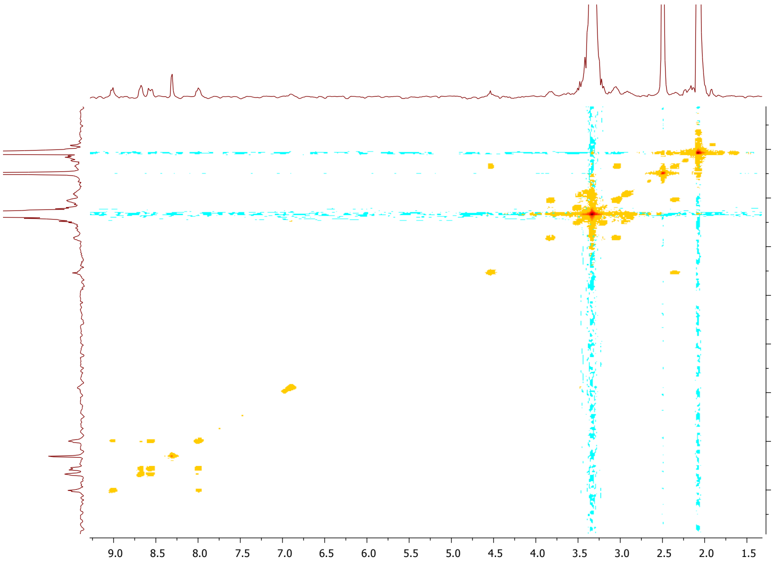

Fig. S3 ^{1}H-^{1}H COSY NMR of **11** in d^6-DMSO.

2. X-ray crystallography

X-ray crystal structure of 5. The N(22)–H hydrogen atom in the structure of **5** (Fig. S4) was located from a Δ*F* map and refined freely subject to an N–H distance constraint of 0.90 Å. Both of the two included methanol solvent molecules were found to be disordered and in each case two orientations were identified, of *ca*. 75:25 and 88:12% occupancy for the O(30)- and O(40)-based molecules respectively. The geometries of all four orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically). The O–H hydrogen atoms were included in calculated positions using the SHELXL HFIX 147 command with an O–H separation of 0.90 Å.

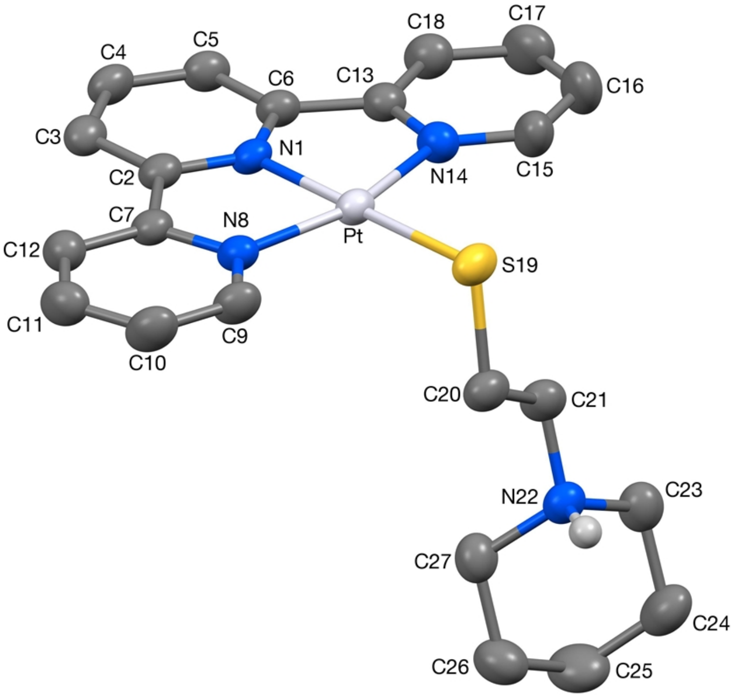

Fig. S4 The structure of the di-cationic complex present in the crystal of **5** (50% probability ellipsoids).

X-ray crystal structure of 8. The structure of **8** was found to contain two crystallographically independent cationic complexes (**8-A** and **8-B**, shown in Figs. S5 and S6 respectively), one $ZnCl_4$ di-anion, one acetone solvent molecule, and four water molecules. The three N–H hydrogen atoms in each complex [on N(26), N(29) and N(32)] were located from ΔF maps and refined freely subject to N–H distance constraints of 0.90 Å. The $ZnCl_4$ anion was found to be disordered, and two orientations of *ca*. 92 and 8% occupancy were identified. The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The O(70)- and O(80)-based water molecules were found to be disordered, and in each case two positions for the oxygen atoms were identified of *ca*. 77 and 23% occupancy. (The proximity of the two molecules means that the disorder of the two molecules is linked.) In both instances the thermal parameters of the two orientations were restrained to be similar, and only the major occupancy atoms were refined anisotropically (the minor occupancy atoms were refined isotropically).

None of the hydrogen atoms of the four water molecules were located, and so the atom list for the asymmetric unit is low by 8H, and that for the unit cell by 16H.

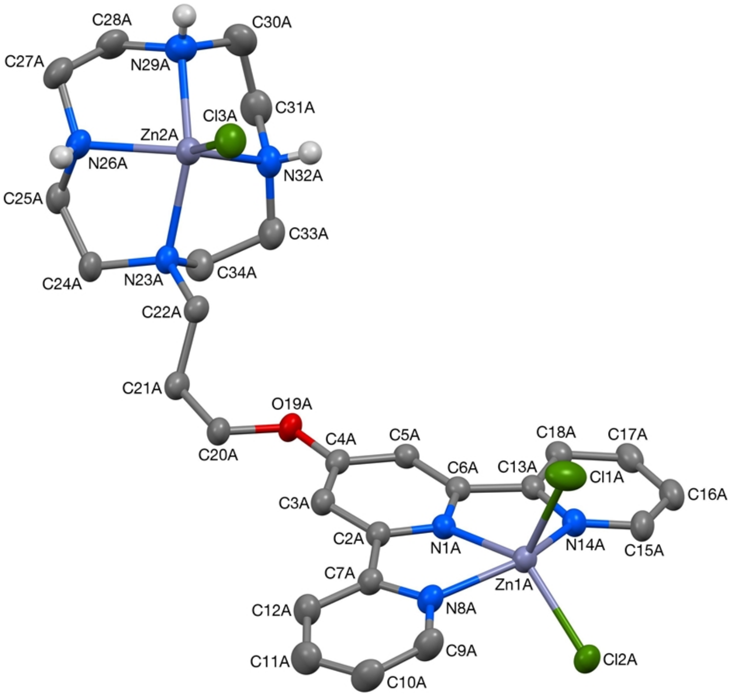

Fig. S5 The structure of one (**8-A**) of the two independent cationic complexes present in the crystal of **8** (50% probability ellipsoids).

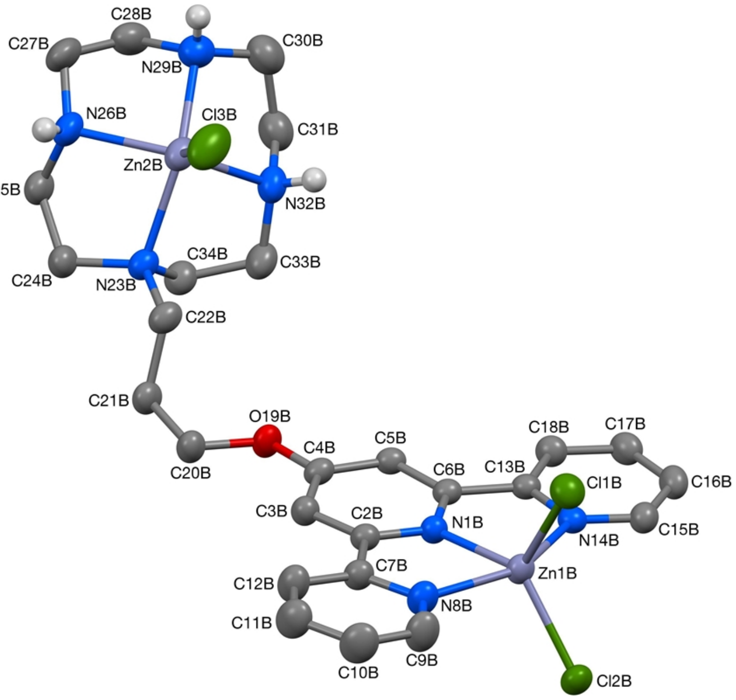

Fig. S6 The structure of one (**8-B**) of the two independent cationic complexes present in the crystal of **8** (50% probability ellipsoids).

X-ray crystal structure of 9. The crystals of **9** were very thin and fragile, and the intensity of their X-ray scattering was weak, especially at high angles; even with a trimmed down data collection lasting 158 hours the final data set for the crystal studied had a mean I/σ of only 3.8. It was thus no surprise to find extensive disorder in the structure, both in the cationic complex and the included solvent. The latter was handled by using the SQUEEZE routine of PLATON.[1] This suggested a total of 659 electrons per unit cell, equivalent to approximately 82.4 electrons per asymmetric unit. The expected chloride anion is presumed to be hidden amongst the disordered solvent, and so accounts for 17 of these electrons, leaving 65.4 electrons for the solvent. The crystal was grown from a mixture of acetone [C_3H_6O, 32 electrons] and water [H_2O, 10 electrons], and before the use of SQUEEZE the electron density distribution was a series of isolated sites that most resembled multiple water molecules. 6.5 water molecules corresponds to 65 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by Cl + 6.5(H_2O) = $H_{13}O_{6.5}Cl$ (and that for the unit cell low by $H_{105}O_{52}Cl_8$) compared to what is actually presumed to be present.

The –$(CH_2)_3$-$C_8H_{19}N_4CuCl$ portion of the cationic complex was found to be severely disordered (Fig. S8). Two orientations were identified of *ca*. 60 and 40% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and the non-hydrogen atoms of the major occupancy orientation, and the copper and chlorine atoms of the minor occupancy orientation, were refined anisotropically (the remaining atoms of the minor occupancy orientation were refined isotropically). The three N–H hydrogen atoms of each orientation were included in idealised positions at N–H distances of 0.90 Å.

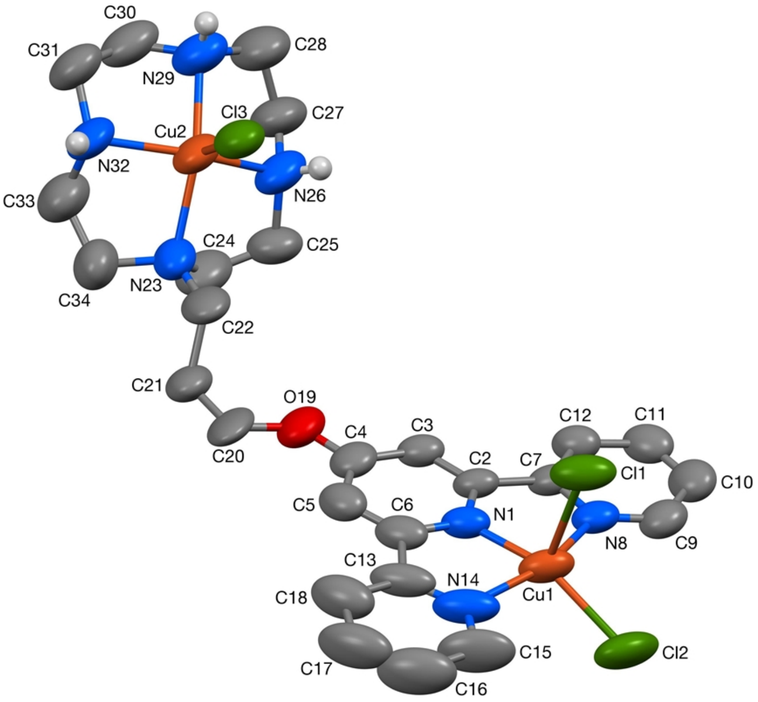

Fig. S7 The structure of the cationic complex present in the crystal of **9** (50% probability ellipsoids).

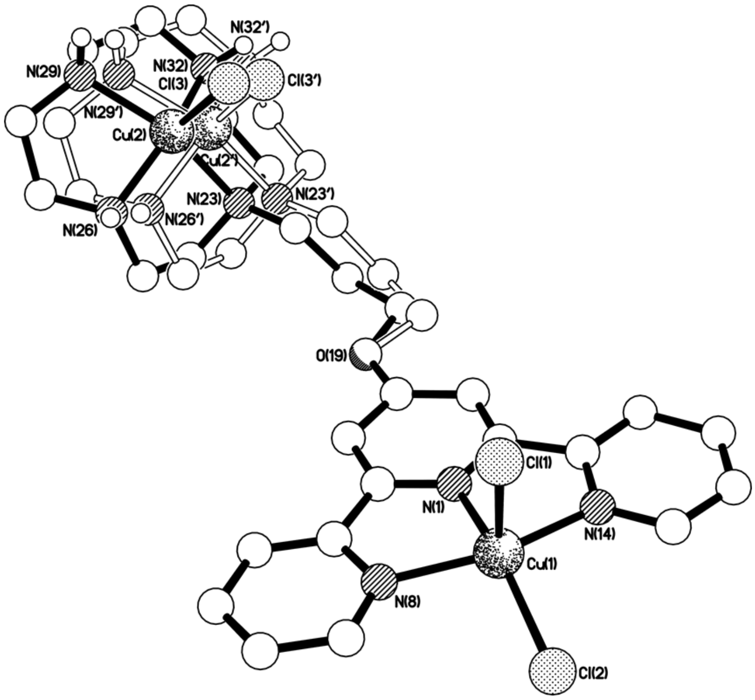

Fig. S8 The disorder in the structure of **9**.

References

1 A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.