Solution Structure of a Pentachromium(II) Single Molecule Magnet from DFT Calculations, Isotopic Labelling and Multinuclear NMR Spectroscopy

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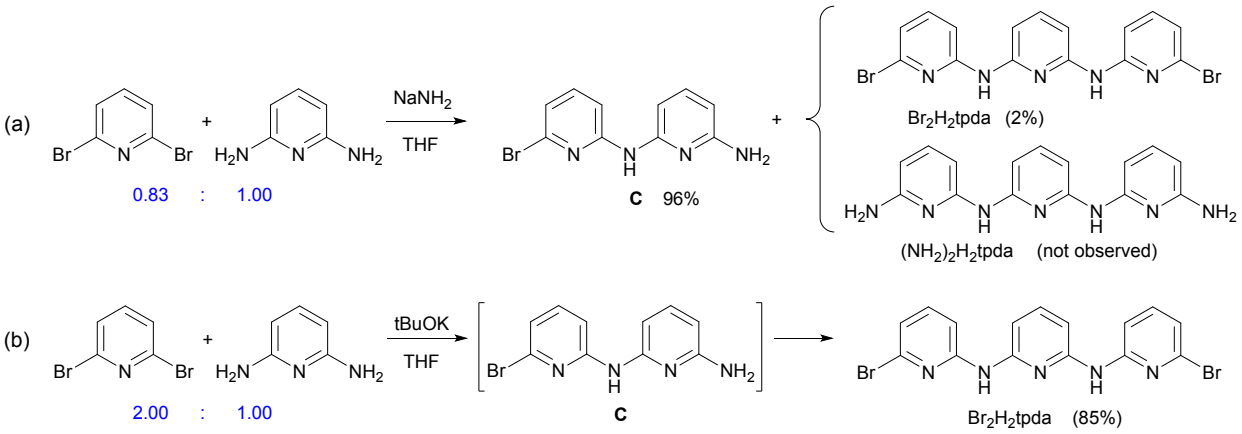
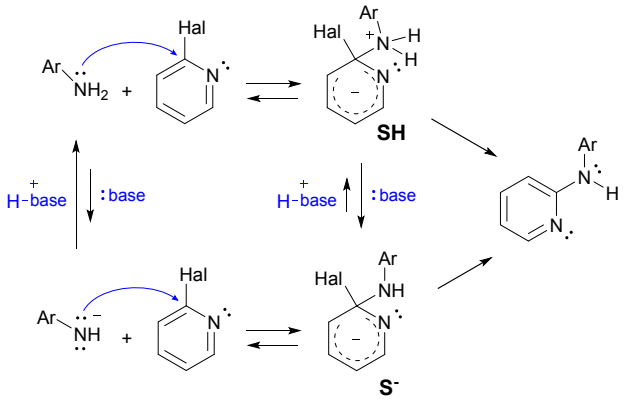
Electronic Supplementary Information



Scheme S1. Reactivity of mixtures of 2,6-dibromopyridine and 2,6-diaminopyridine. In reaction (a),[S1] an understoichiometric amount of 2,6-dibromopyridine affords very high yields of **C** but no $(NH_2)_2H_2$tpda as a consequence of the low electrophilicity of **C**. In reaction (b),[S2] a 2:1 ratio of the reactants gives Br_2H_2tpda in high yields owing to the high nucleophilicity of **C**. The dibromide Br_2H_2tpda is formed only in trace amounts in reaction (a). Br_2H_2tpda could in principle be converted to H_2tpda through metal-catalyzed hydro-dehalogenation.[S3]

Supplementary Note 1. A wealth of theoretical and experimental data support an addition-elimination mechanism for S_NAr, with the formation of an intermediate cyclohexadienyl anion with broken benzenoid resonance.[S4] Either the formation or the decomposition of this intermediate, also known as a σ-complex (**SH** or $\mathbf{S^-}$ in Scheme S2) may be rate determining. However, its stability is a major predictor of overall substitution rate, due to the structural and energetic similarity to the involved transition states.[S5,S6] The interaction of neutral nucleophiles such as amines on deactivated rings such as halopyridines likely encompasses the formation of a zwitterionic σ-adduct (**SH** in Scheme S2), consistent with the observation of base catalysis of its decomposition.[S7,S8]

The nature of the nucleophile greatly influences the features of the σ-complex and the mobility of the halide leaving group, depending on the relative energy of the transition states of formation vs. decomposition of **SH**. When the formation of **SH** is rate determining, the halogen nucleofugality order F > Cl ≈ Br is often encountered; conversely, when C-Hal bond is broken in the rate determining step, the opposite reactivity order is found to prevail (I > Br > Cl > F).[S9] Therefore, the case under study best fits with a rate determining formation of **SH**.



Scheme S2. S_NAr mechanism in the case of neutral and anionic nucleophiles.

Other factors, including the nature of the solvent and of the added base, may also play a pivotal role and revert the small energetic advantage of decomposition vs formation of **SH**.[S10] Overall, due to the interaction between its components, the system stands on a faint balance, where narrow concentration ranges of the constituents give optimal efficiency. Polar aprotic solvents should result in increased stabilization of **SH**, while protic (hydrogen donor) solvents often adversely affect the overall rate, possibly due to excessive solvation of the nucleophile. Moreover, a too strong base would cause undesired side-reactions on halopyridines (e.g. $S_{RN}1$).[S11] Investigations of S_NAr involving amine nucleophiles in aprotic solvents have revealed a complex base catalysis behaviour that could be rationalized by supposing the initial formation of a molecular charge-transfer complex between the nucleophile and the electrophilic aromatic ring.[S12-S14] Notwithstanding these considerations, the crucial role played by pyridine in the case under study is at present unexplained.

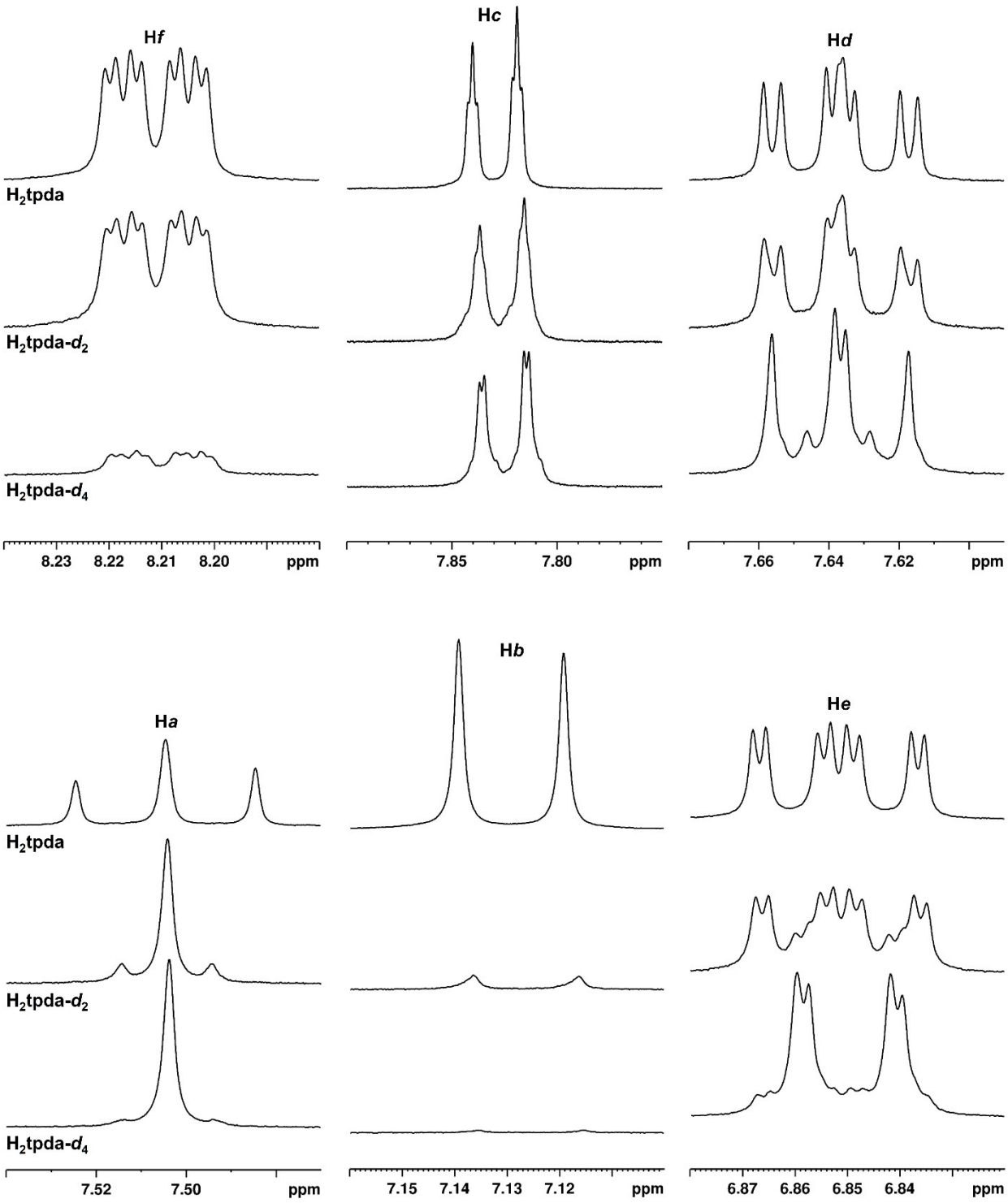


Figure S1. Scale-expanded proton NMR spectra of H_2tpda, H_2tpda-d_2, and H_2tpda-d_4 (solvent = DMSO-d_6). For the labelling scheme, see Scheme 1 in main text.

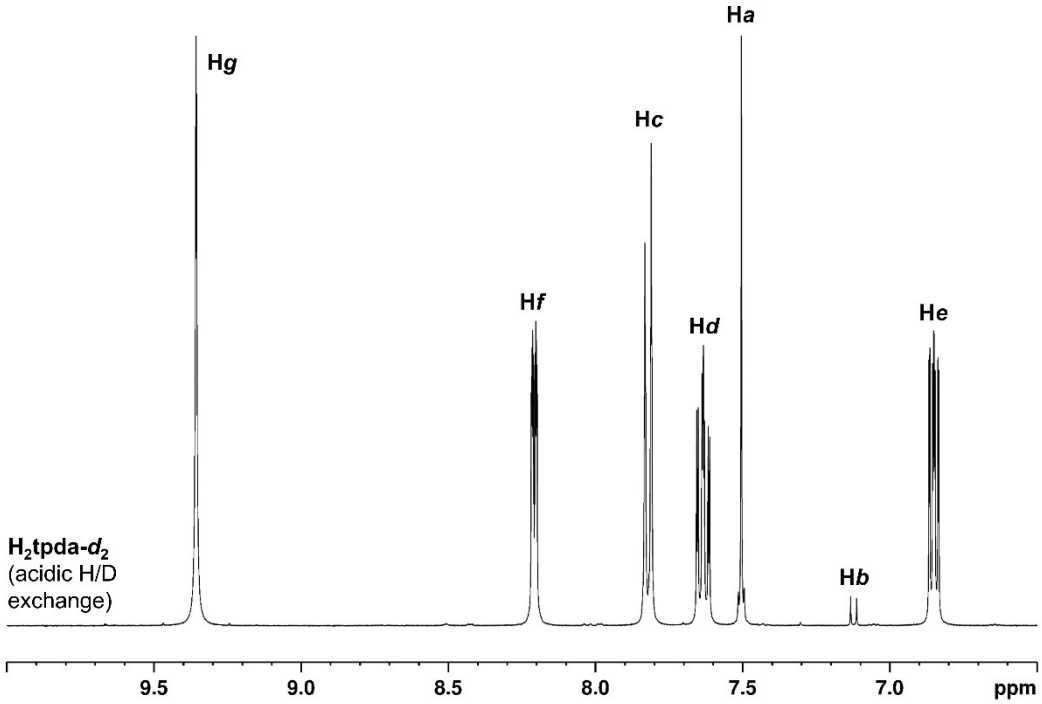


Figure S2. Proton NMR spectrum of H_2tpda-d_2 obtained by acidic H/D exchange (solvent = DMSO-d_6). For the labelling scheme, see Scheme 1 in main text.

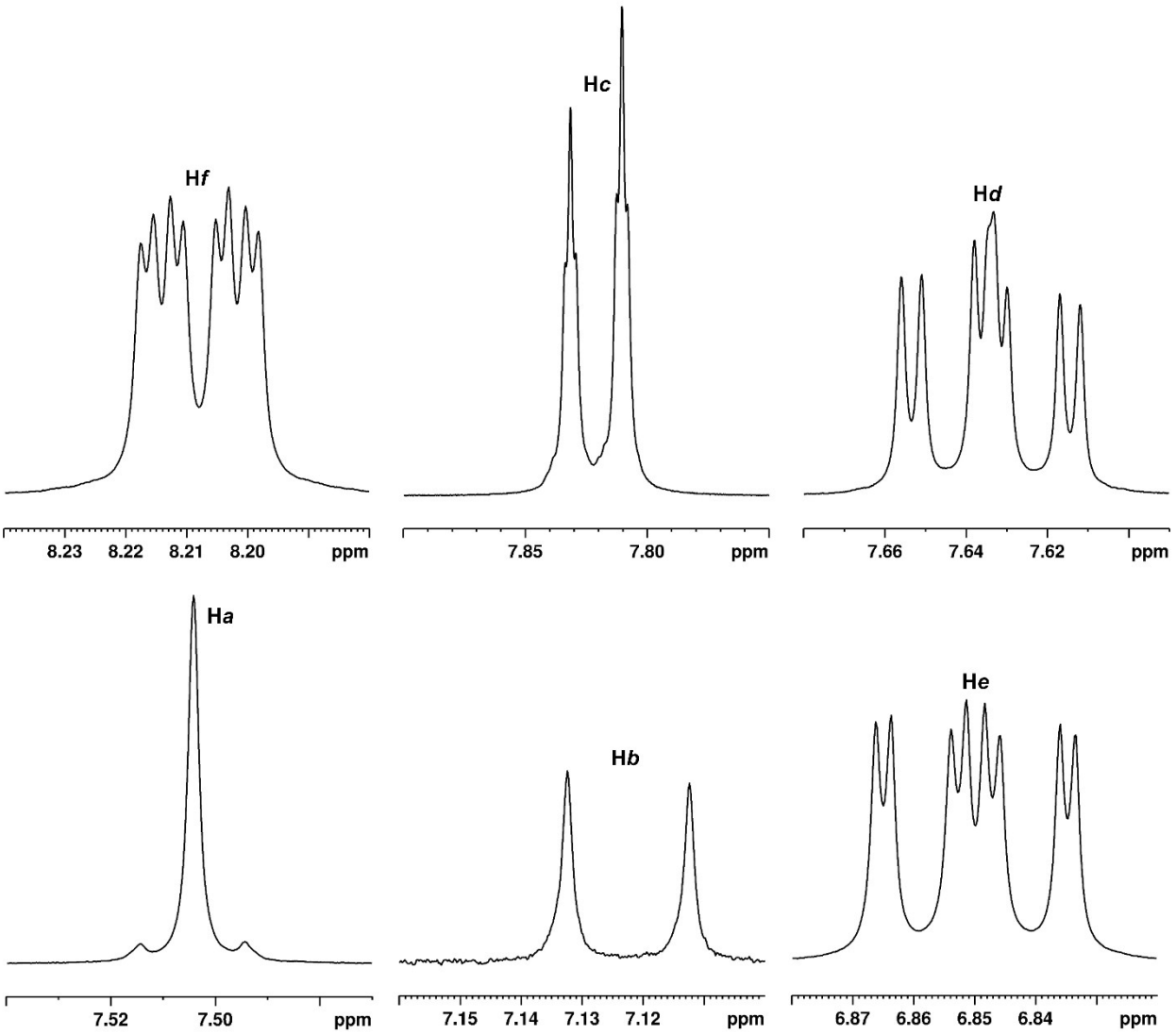


Figure S3. Scale-expanded proton NMR spectra of H_2tpda-d_2 obtained by acidic H/D exchange (solvent = DMSO-d_6). For the labelling scheme, see Scheme 1 in main text.

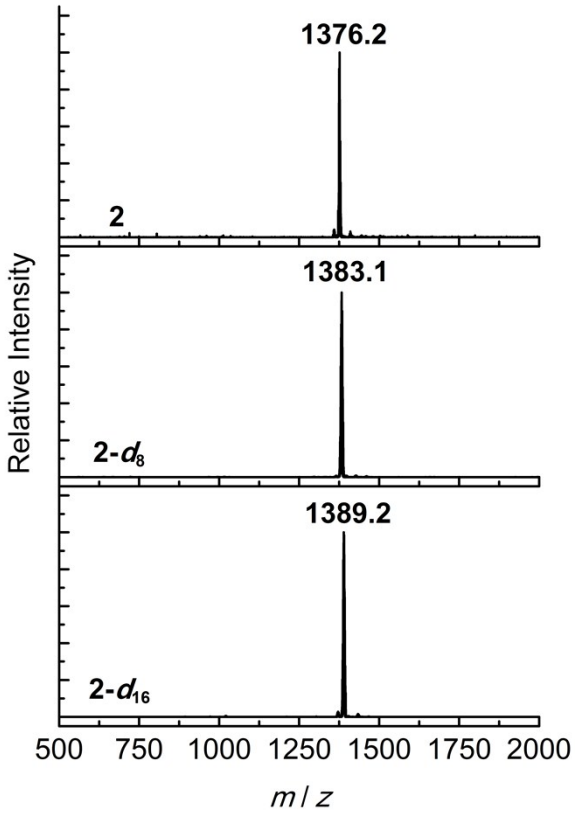


Figure S4. Full-range ESI-MS spectra of **2**, **2**-d_8 and **2**-d_{16} (direct infusion, CH_2Cl_2, positive ion mode).

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