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Supporting Information — X-Ray Crystallography

Manuscript: Structural, hemilabile and reversible carbon monoxide binding properties of Fe(II), Co(II) and Ni(II) complexes containing a new tridentate P–S–N ligand

Authors: Christopher W. Tate, Ramon Vilar Compte, Andrew deMello, Antony D. Gee, Steven Kealey, Andrew J.P. White and Nicholas J. Long

The X-ray crystal structure of **2**

The cationic complex in the structure of **2** has C_i symmetry with the iron atom sitting on the inversion centre. The N–H protons were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

The X-ray crystal structure of **3**

Complex **3** crystallised with two independent molecules (**3-A** and **3-B**, see Fig. 2 in the paper and Fig. S3 in the supporting information) in the asymmetric unit, each of which has a centre of symmetry at the cobalt atom. The four N–H protons could not be reliably located from ΔF maps and so were instead added in idealised positions and allowed to ride on their parent nitrogen atoms subject to an N–H distance constraint of 0.90 Å. Both of the two unique BF_4 anions were found to be disordered. In each case three partial occupancy orientations were identified of *ca.* 45:33:22 and 41:32:27% occupancy for the B(10)- and B(20)-based anions respectively. The geometries of all six orientations were optimised, the thermal parameters of adjacent equivalent atoms of the three orientations of each anion were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically in each case (the others were refined isotropically). The N(30)-based included acetonitrile solvent molecule was found to be disordered, and two orientations of *ca.* 70 and 30% occupancy were identified. The geometries of both orientations were optimised, the thermal parameters of adjacent equivalent atoms of the two orientations were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the others were refined isotropically).

The X-ray crystal structure of **4**

The cationic complex in the structure of **4** has C_i symmetry with the nickel atom sitting on the inversion centre. The N–H protons were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

Figures

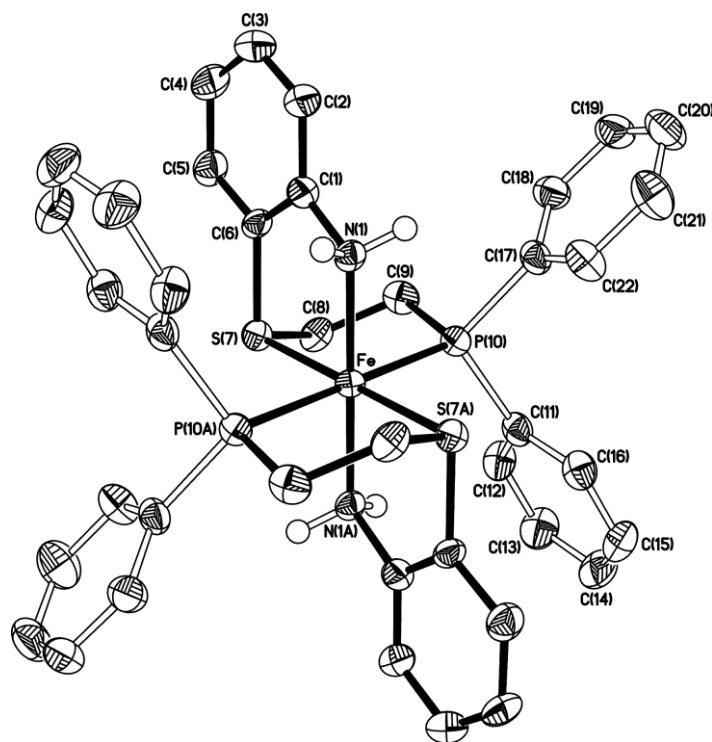


Fig. S1 The molecular structure of the C_i -symmetric cation present in the crystals of **2** (50% probability ellipsoids).

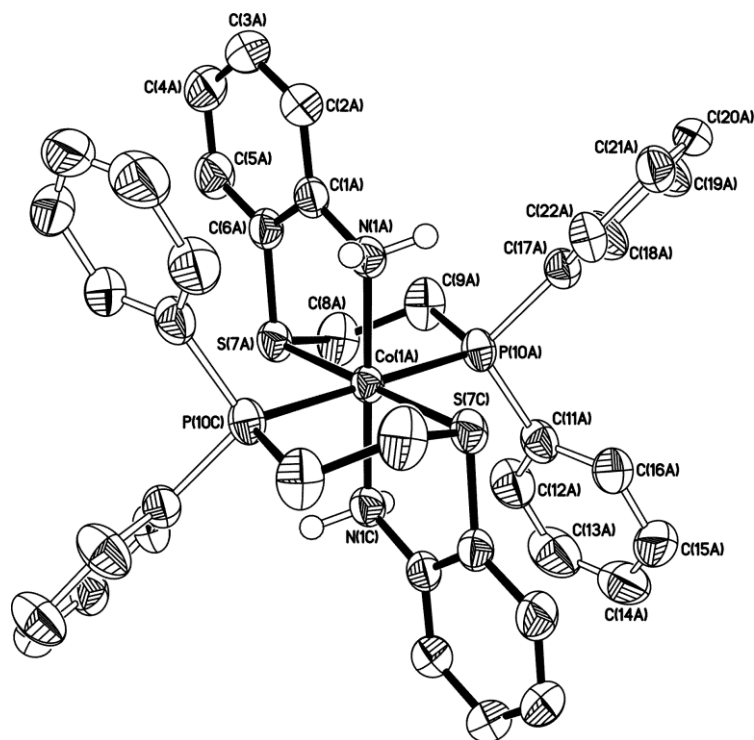


Fig. S2 The molecular structure of one (**3-A**) of the two crystallographically independent C_i -symmetric cations present in the crystals of **3** (50% probability ellipsoids).

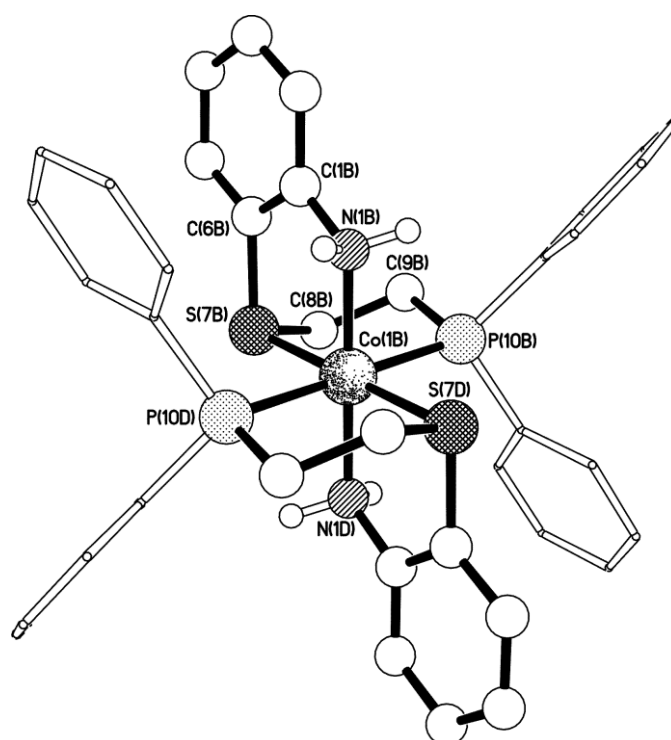


Fig. S3 The molecular structure of one (**3-B**) of the two crystallographically independent C_i -symmetric cations present in the crystals of **3**.

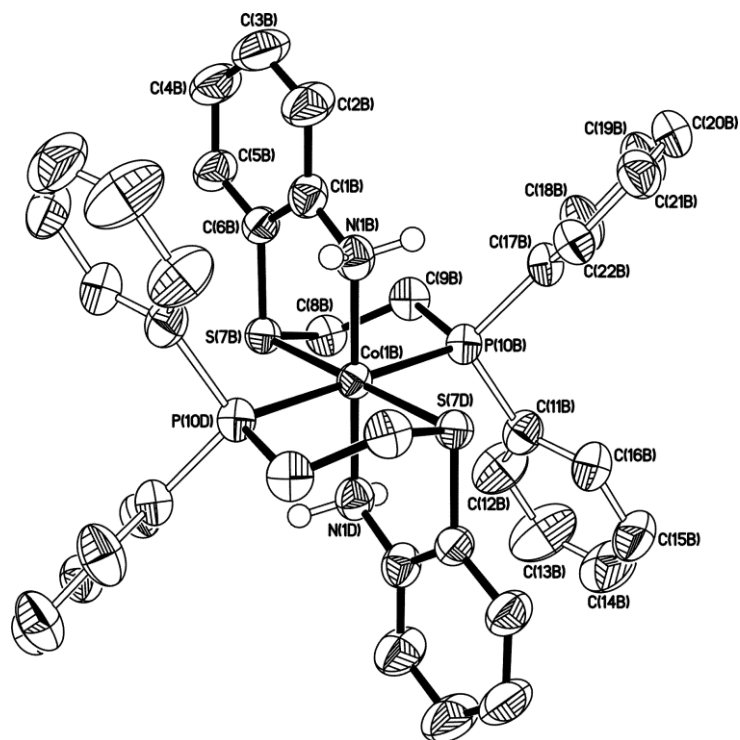


Fig. S4 The molecular structure of one (**3-B**) of the two crystallographically independent C_1 -symmetric cations present in the crystals of **3** (50% probability ellipsoids).

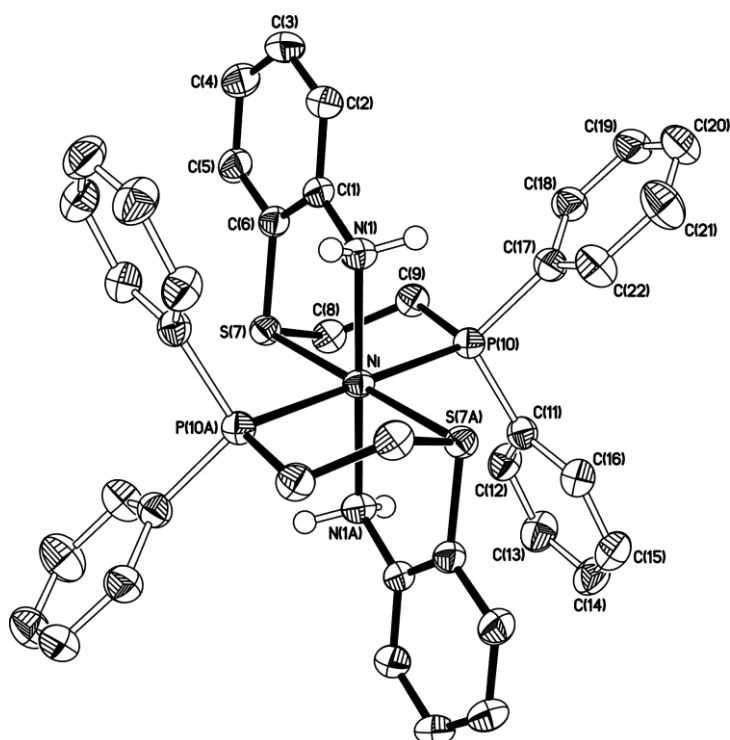


Fig. S5 The molecular structure of the C_1 -symmetric cation present in the crystals of **4** (50% probability ellipsoids).