

Supplementary Information

Synthesis, structural studies, kinetic stability, and oxidation catalysis of the late first row transition metal complexes of 4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]pentadecane

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Discussion of Hydrogen Bonding in Crystal Structures:

[Mn(Me₂B13N4)Cl₂]: The complexes are packed in accordance with the P2₁/c symmetry in such a way that there are a large number of C–H···Cl interactions present. One way to describe the structure is in terms of puckered sheets of complexes in the *xz* plane held together by C–H···Cl interactions, that are then further arranged into a 3-D array by AAA stacking along *b*.

[Mn(Me₂B13N4)Cl₂]PF₆ and [Co(Me₂B13N4)Cl₂]PF₆: In the solid state, the complexes are ordered in sheets in the *yz* plane by C–H···Cl interactions. These are arranged in an AAA sequence at a separation of *a*. Between the sheets are found layers of PF₆[−] anions which form C–H···F interactions to each layer.

[Co(Me₂B13N4)Cl₂]PF₆ · MeCN: The arrangement is layered; sheets of PF₆[−] anions and double sheets of [Co(Me₂B13N4)Cl₂]⁺/MeCN extend in the *xz* plane. These sheets are stacked parallel to the crystallographic *b*-axis in an ABA'B' fashion. Within the double sheets there are C–H···Cl interactions C–H···F interactions exist between the sheets.

[Cu(Me₂B13N4)Cl]Cl · 2H₂O: The crystal packing within the compound is largely unremarkable except for the location of the water. The two water molecules are engaged in hydrogen bonding to chloride, to each other and to a pair of symmetry-related counterparts. This leads to the formation of centrosymmetric, hydrogen-bonded tetramers of water which are aligned in columns parallel to the *a*-axis.

[Zn(Me₂B13N4)Cl(OH₂)₂][ZnCl₄] · CH₃CN: There are a large number of C–H···Cl contacts and C–H···N≡CMe contacts within the structure. The hydrogen-bonded dimers form into double layers that extend in the *xy* plane. Between these lie layers of [ZnCl₄]^{2−} and acetonitrile. The extensive collection of intermolecular interactions helps to bind these layers into an extended 3-D array.

[Zn(Me₂B13N4)OAc(OH₂)]PF₆: Formally this trimer can be described as R₃₆(12) using Graph Set notation [1] and it is formed by the O3···H1c hydrogen bond and an interaction between O1–H1D···O3^{*i*} (*i* = 1−*x*+*y*, 1−*x*, *z*) with O···O distance 2.705(6) Å. These trimers are arranged in stacks parallel to the *c*-direction. Between these lie the PF₆[−] anions, forming short contacts to the macrocycle indicative of C–H···F interactions. Full details of intermolecular interactions are given in **Table S1**.

Hydrogen bond	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	∠(D–H···A) / °
C3–H3A···F2 _{<i>i</i>}	0.99	2.61	3.418(9)	138.9
C7–H7B···O2	0.99	2.54	3.101(7)	115.7
C8–H8B···F3 _{<i>ii</i>}	0.99	2.55	3.490(10)	159
C12–H12A···O1	0.98	2.55	3.127(9)	117.5
C13–H13B···F2- _{<i>iii</i>}	0.98	2.37	3.344(9)	172.7
C13–H13C···O1	0.98	2.63	3.118(9)	111.1
C15–H15C···F4 _{<i>i</i>} _{<i>v</i>}	0.98	2.81	3.421(9)	121
O1–H1C···O3	0.86(5)	1.85(5)	2.669(6)	160(8)
O1–H1D···O3 _{<i>v</i>}	0.91(5)	1.82(5)	2.705(6)	166(8)

[1] J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem. Int. Ed. Engl.*, vol. 34, pp. 1555-1573, 1995.