

Table S1. Variation of the N_{ax} -M- N_{ax} angle for six-coordinated Ni(II) and Co(III)

complexes as a function of the cavity size of the macrobicyclic L.

L	Complex	N_{ax} -M- N_{ax} angle/degree	Reference
N,N'-Me ₂ [2 ⁵]adz	[Ni(L)(acac)] ⁺	161.6(1)	42
[2 ⁴ .3 ¹]adz	[Ni(L)(H ₂ O) ₂] ²⁺	168.43(5)	43
	[Ni(L)(η ² -NO ₂)] ⁺	170.3(3)	43
	[Ni(L)(η ² -NO ₃)] ⁺	170.14(9)	43
N,N'-Me ₂ [2 ² .3 ² .2 ¹]adz	[Ni(L)(acac)] ⁺	174.6(1)	42
	[Ni(L)(H ₂ O) ₂] ²⁺	175.39(5)	42
[(2.3) ² .2 ¹]adz	[Ni(L)(H ₂ O) ₂] ²⁺	176.77(5)	38
[3 ⁵]adz	[Ni(L)(η ² -NO ₃)] ⁺	176.5(2)	44
	[Ni(L)(η ² -ClO ₄)] ⁺	177.34(10)	44
Me ₂ [2 ⁵]adz	[Co(L)Cl ₂] ⁺	168.8(4)	39
[2 ⁴ .3 ¹]adz	[Co(L)Cl ₂] ⁺	173.5(3)	38
[3 ⁵]adz	[Co(L)(η ² -CO ₃)] ⁺	176.8(3)	45
	[Co(L)(η ² -HCO ₃)] ²⁺	177.7(4)	45
	[Co(L)(η ² -SO ₄)] ⁺	176.02(15)	45

Table S2. Variation of the N_{ax} -M- N_{ax} angle for six-coordinated complexes,

$M(L)X_2^{z+}$, as a function of the radius of the central ion for $L = Me_2[2^5]adz$.

M	radius/ppm ^a	N_{ax} -M- n_{ax} /degree	Reference
Mn(II) ^b	97	144.0(2)	47
Fe(II) ^b	92	145.78(7)	47
Zn(II) ^b	88.0	148.30(8)	39
Co(II) ^b	88.5	149.81(9)	42
Cu(II) ^c	87	164.85(13)	42
Ni(II) ^d	83	161.58(13)	42

^aRadii for octahedral coordination (high spin in the case of Mn(II), Fe(II) and

Co(II)) complexes have been taken from reference 46. ^bX = Cl. ^cX = MeCN. ^dX₂

= acac⁻.