Supporting Information

Metal Ion Complexes of *N,N′*-Bis(2-Pyridylmethyl)-*trans*-1,2-Diaminocyclohexane-*N,N′*-Diacetic Acid, H_2bpcd; Cis/Trans Isomerization Equilibria

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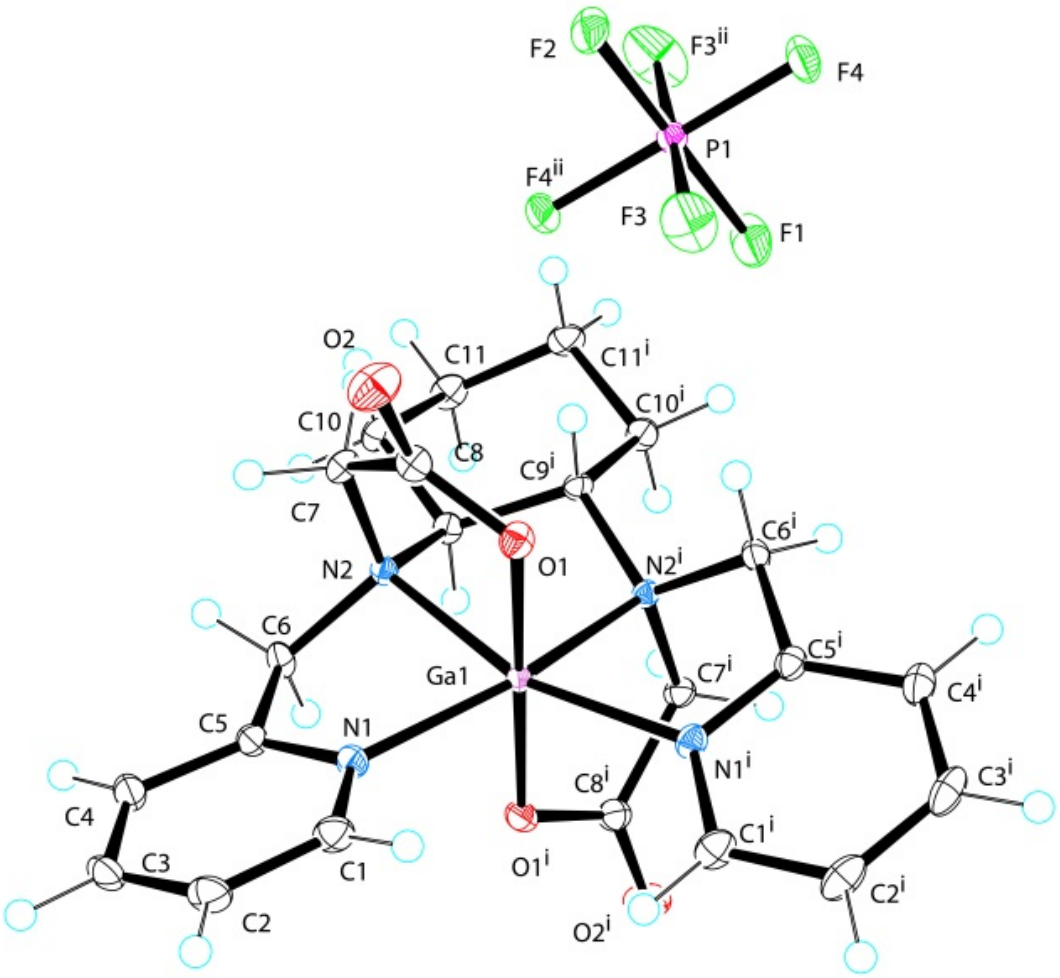
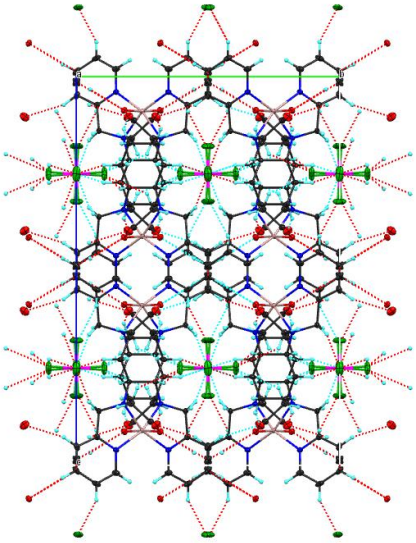
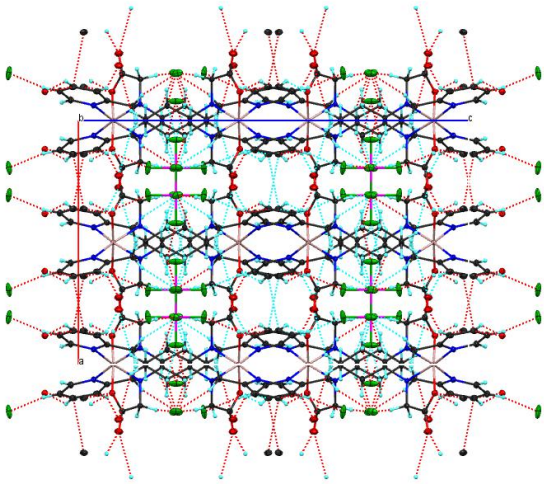


Figure S1. Thermal displacement plot (50%) of the [Ga(bpcd)]PF_6. H atoms are shown as circles of arbitrary size. i. Symmetry code: 1-*x*, ½ - *y*, *z*.

a)



b)



c)

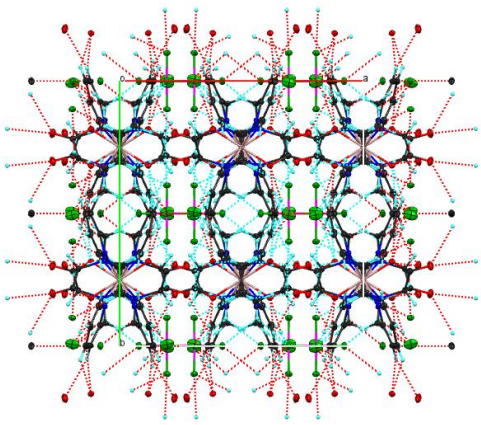


Figure S2. Packing diagrams of [Ga(bpcd)]PF_6 shown along a) *a*, b) *b*, and c) *c*. Short interactions inside the unit cell are shown in cyan.

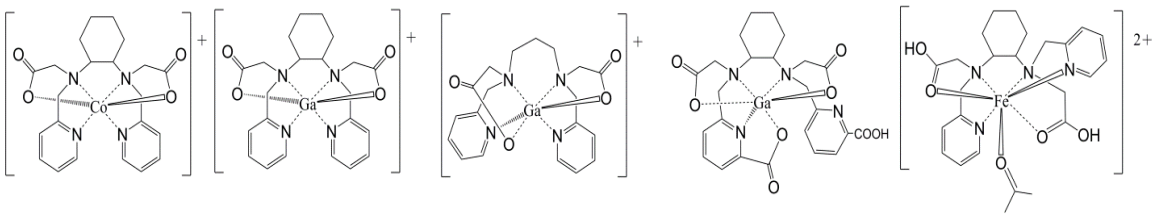


Figure S3. Species represented in Tables S1 and S2.

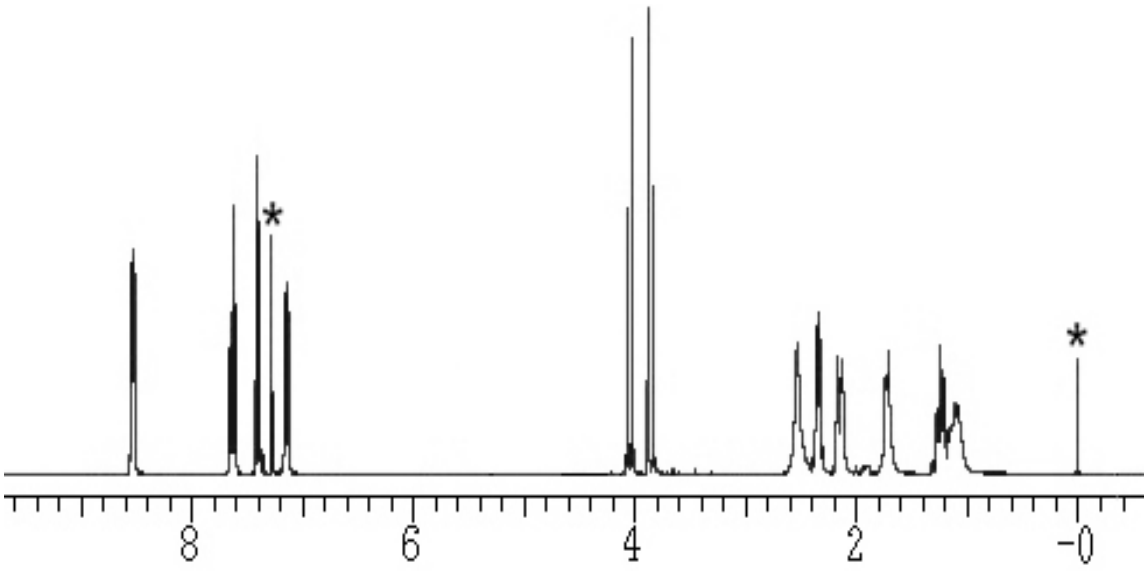


Figure S4. ^{1}H NMR spectrum for *N,N'-bis*(2-pyridylmethyl)-1,2-diaminocyclohexane, bpmdac, in $CDCl_3$ at 25 ^{o}C.

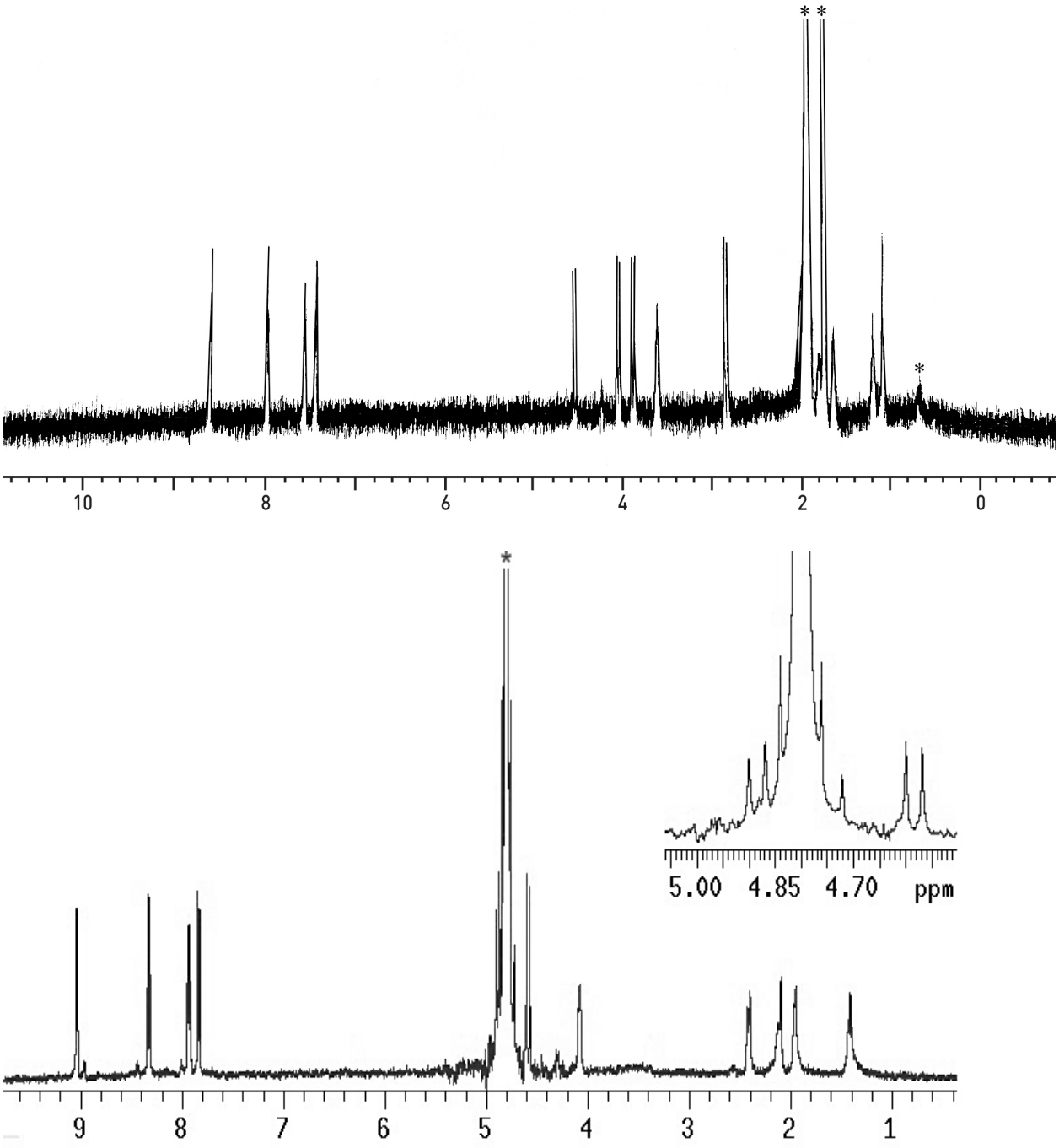


Figure S5. ^{1}H NMR spectra of $[Co(bpcd)]^{+}$ in CD_3CN (top) and D_2O (bottom) at 25 ^{o}C, the * indicates solvent or an impurity. The insert expands the region around the solvent signal. Signals centered at 2.85 and 3.90 ppm $\Delta\nu_{AB}/J$ = 28.7), and 4.07 and 4.57 ppm ($\Delta\nu_{AB}/J$ = 16.8) in the CD_3CN spectrum (top) have relative intensity four and are assigned as the methylene *AX* quartets.

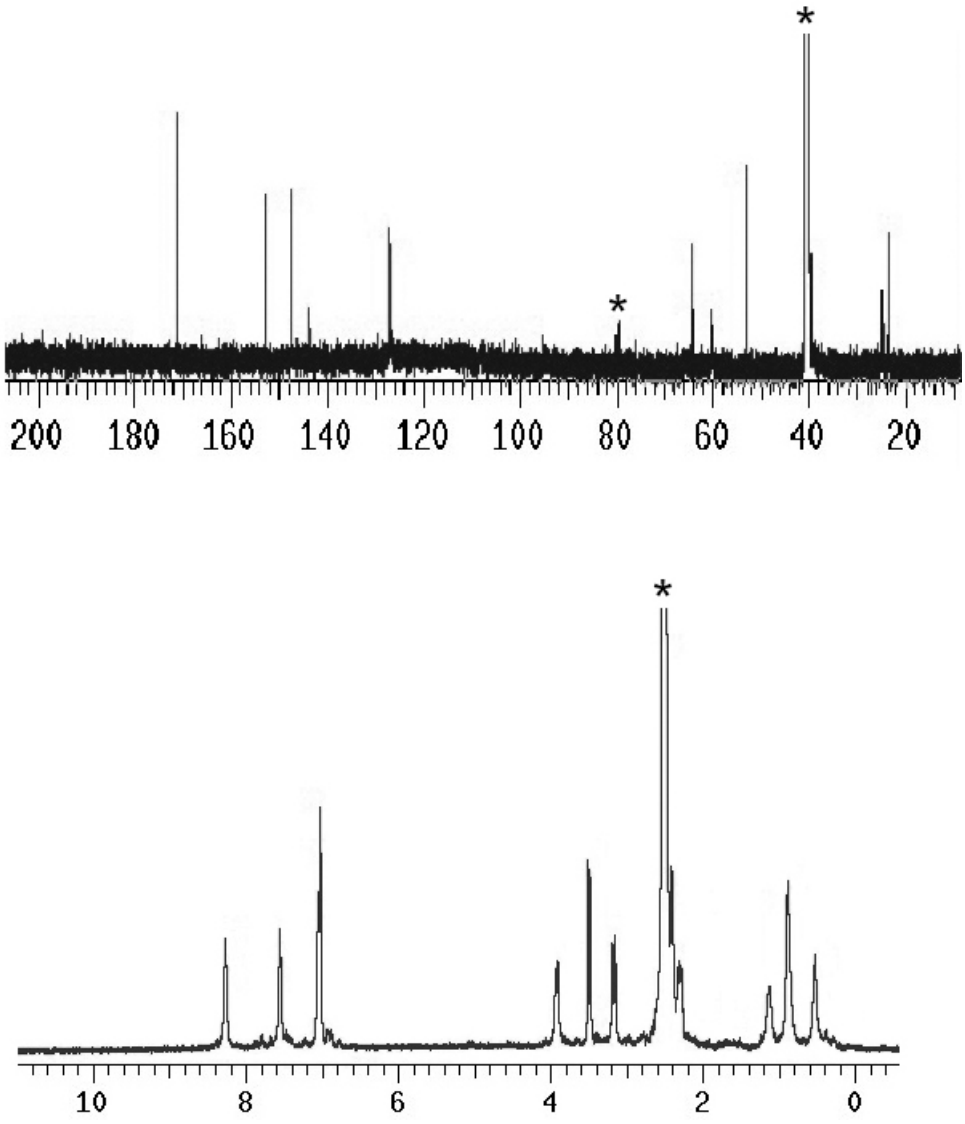


Figure S6. ^{13}C NMR spectrum (top) and ^{1}H NMR spectrum (bottom) of $[Ga(bpcd)]^{+}$ in DMSO-d_6 at 25 ^{o}C, the * indicates solvent or an impurity. The signals in the ^{1}H NMR spectrum centered at Signals centered at 2.30 and 3.49 ppm, and 3.17 and 3.92 ppm are assigned as the pendant arm methylene *AX* quartets.

Table S1. Bond Distances (Å) and Experimental Data for $Co(bpcd)^{+}$, $Ga(bpcd)^{+}$, $Ga(bppd)^{+}$, Ga(H*CHX*octapa), and $[Fe^{II}(H_2bpcd)(C_3H_6O)]^{2+}$. Structures are show in Figure S3.

Bond (Å)	$Co(bpcd)^{+a}$	$Ga(bpcd)^{+b}$	$Ga(bppd)^{+c}$	Ga(H*CHX*octapa)^{d}	$[Fe^{II}(H_2bpcd)(C_3H_6O)]^{2+e}$
$M–O_{ac1}$	1.8868 (8)	1.9343 (9)	1.9459 (15)	1.953 (3)	2.293 (2)
$M–O_{ac2}$	*	1.9344 (9)**	1.8956 (14)	1.894 (3)	2.288 (2)
$M–N_{am}1$	1.9548 (9)	2.0866 (10)	2.0673 (16)	2.152 (4)	2.309 (3)
$M–N_{am}2$	*	*	2.1061 (17)	2.174 (3)	2.300 (3)
$M–N_{py}1$	1.9448 (9)	2.0574 (10)	2.0156 (17)	1.999 (3)	2.162 (3)
$M–N_{py}2$	*	2.0575 (10)**	2.1377 (17)	***	2.163 (3)
$C–O_{ac1}$	1.3029 (13)	1.3025 (15)	1.286 (3)	1.293 (5)	1.308 (6)
$C=O_{ac1}$	1.2212 (14)	1.2151 (15)	1.211 (3)	1.216 (5)	1.226 (4)
$C–O_{ac2}$	*	*	1.287 (3)	1.319 (5)	1.297 (6)
$C=O_{ac2}$	*	*	1.208 (3)	1.208 (5)	1.235 (5)
$M–O_{ac3\ of\ py}$				1.959 (3)	
$C–O_{ac3\ of\ py}$				1.301 (5)	
$C=O_{ac3\ of\ py}$				1.215 (5)	
$M–O_{acetone}$					2.172 (2)
M above N/N/N/*X* plane	0****	0****	0.0387 (9)	0.136***	*****
Temp, K	100	100	296	100	150

[a]McLauchlan et al.[16] [b]This work. [c]Kissel et al.[15] [d]Ramogida et al.[8] with values from deposited data, not as reported in manuscript. [e]Oddon et al.[10] *N/A. Symmetry equivalent. ** Symmetry equivalent, but a difference in the distances is noted in the refinement output file. *** N/A. N_3O_3 donor set. This plane is closest to the plane that would contain the cyclohexyl unit, i.e. it contains the two N_{am}, 1 N_{pyr}, and $O_{ac3\ of\ py}$. **** Special position. ***** N/A. Not a relevant descriptor for 7-coordinate geometry. Reference numbers refer to the numbering in the main manuscript

Table S2. Selected Bond Angles (°) for $Co(bpcd)^{+}$, $Ga(bpcd)^{+}$, $Ga(bppd)^{+}$, Ga(H*CHX*octapa), and $[Fe^{II}(H_2bpcd)(C_3H_6O)]^{2+}$ Structures. Structures are show in Figure S3.

Angle (deg)	$Co(bpcd)^{+a}$	$Ga(bpcd)^{+b}$	$Ga(bppd)^{+c}$	Ga(H*CHX*octapa)^{d}	$[Fe^{II}(H_2bpcd)(C_3H_6O)]^{2+\ e}$
O_{ac1}–M–O_{ac2}	176.08 (5)	176.56 (5)	91.83 (7)	92.89 (13)	152.23 (8)
N_{am1}–M–N_{am2}	89.33 (5)	85.30 (5)	96.47 (7)	81.92 (12)	76.96 (10)
N_{pyr1}–M–N_{py2}	106.74 (5)	114.95 (6)	90.80 (6)	**	177.41 (11)
N_{am1}–M–N_{py1}	82.17 94)	80.51 (4)	81.46 (7)	79.77 (14)	75.64 (11)
N_{am2}–M–N_{py2}	*	*	80.39 (7)	**	76.50 (11)
N_{am1}–M–O_{ac1}	87.84 (4)	85.36(4)	83.59 (7)	82.94 (12)	70.27 (10)
N_{pyr1}–M–O_{ac1}	89.92 (4)	91.19 (4)	99.41 (7)	89.13 (13)	99.00 (11)
O=C–O_{ac}	124.95 (10)	125.09 (12)	125.0 (3)	124.9 (4)	124.26
	*	*	123.5 (2)	125.1 (4)	124.32
				114.3 (4)	
C(O)–O_{ac}–M	114.57 (7)	115.26 (8)	117.81 (15)	117.6 (3)	112.54
	*	*	114.77 (14)	117.4 (3)	111.65
				116.9 (3)	

[a]McLauchlan et al.[16] [b]This work. [c]Kissel et al.[15] [d]Ramogida et al.[8] with values from deposited data, not as reported in manuscript. [e]Oddon et al.[14] *N/A. Symmetry equivalent. ** N/A. N_3O_3 donor set. Reference numbers refer to the numbering in the main manuscript