Electronic Supplementary Information for Dalton Transactions

The structure of *N,N′*-bis(2-hydroxyethyl)ethane-1,2-diamine and its complexes with Zn(II) and Cd(II)

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Supplementary Information

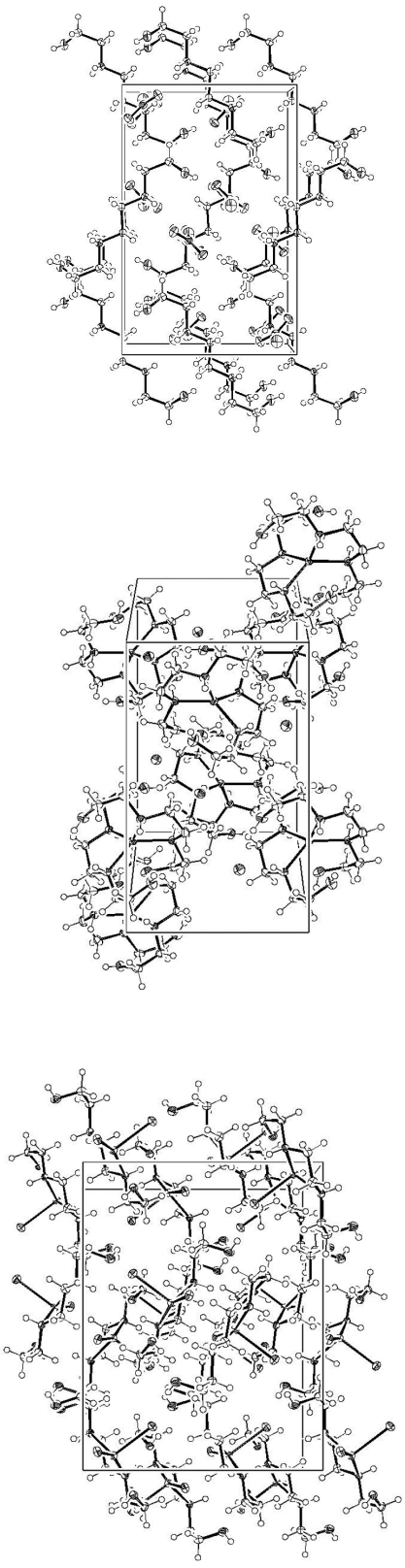

Figure S1. *ORTEP-3* diagrams of the unit cell (viewed along the (1 0 0) direction), from the top, of $(H_2BHEEN)(NO_3)_2$, $[Zn(BHEEN)_2]Cl_2$ and $[(\mu\text{–}Cl)_2(Cd(BHEEN)Cl)_2)]$.

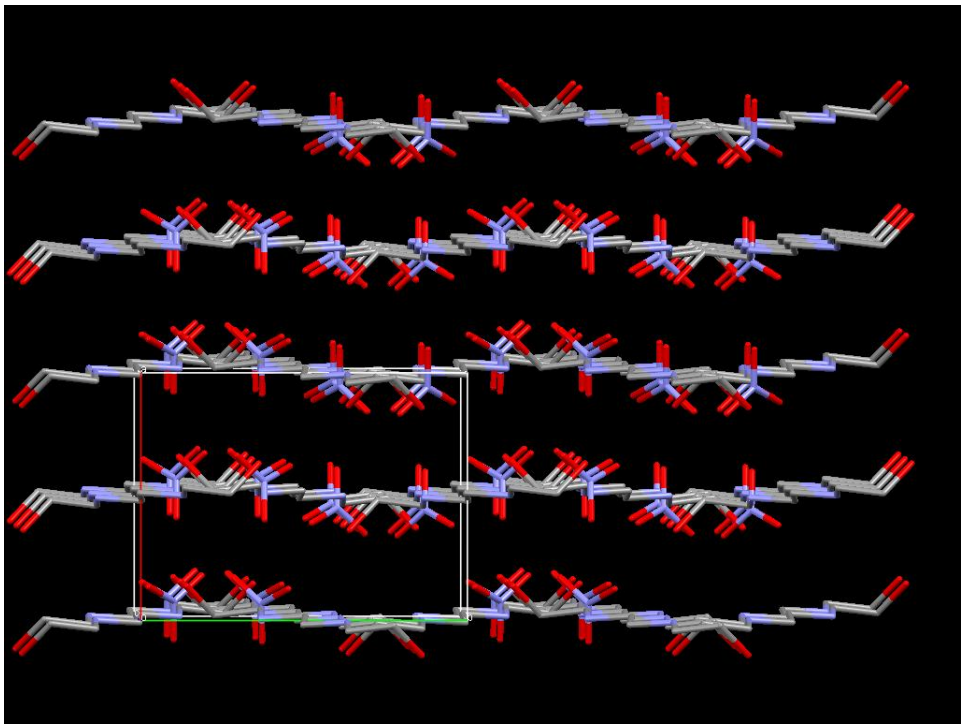

Figure S2. The layered packing of $(H_2BHEEN)(NO_3)_2$ viewed (slightly offset, and with H atoms omitted for clarity) along the crystallographic *c* axis.

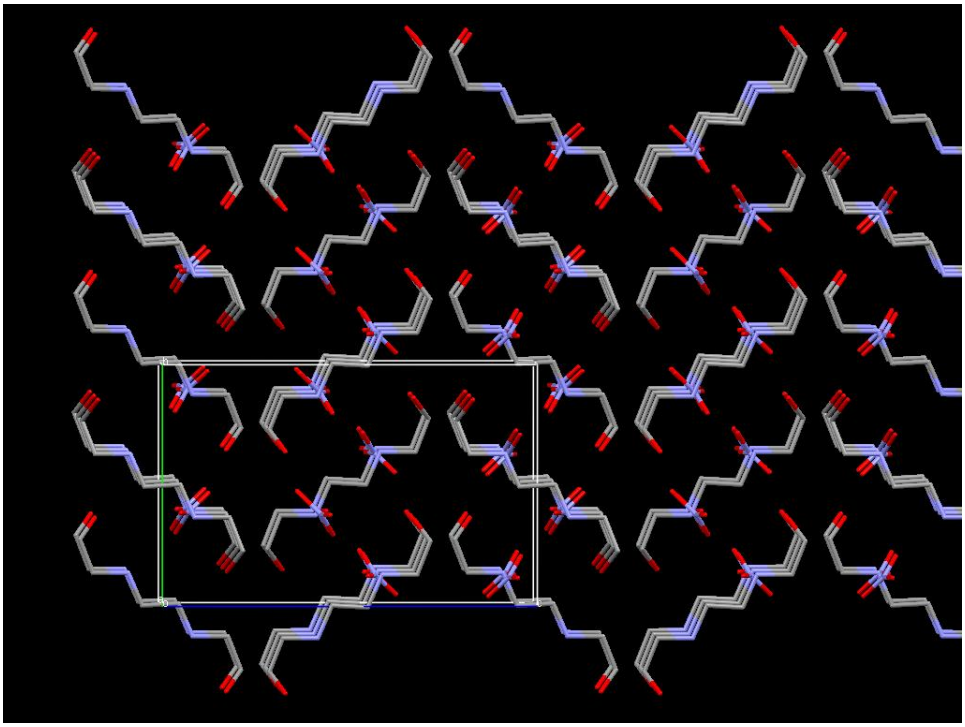

Figure S3. The herring-bone packing of $(H_2BHEEN)(NO_3)_2$ viewed (slightly offset) along the crystallographic *a* axis.

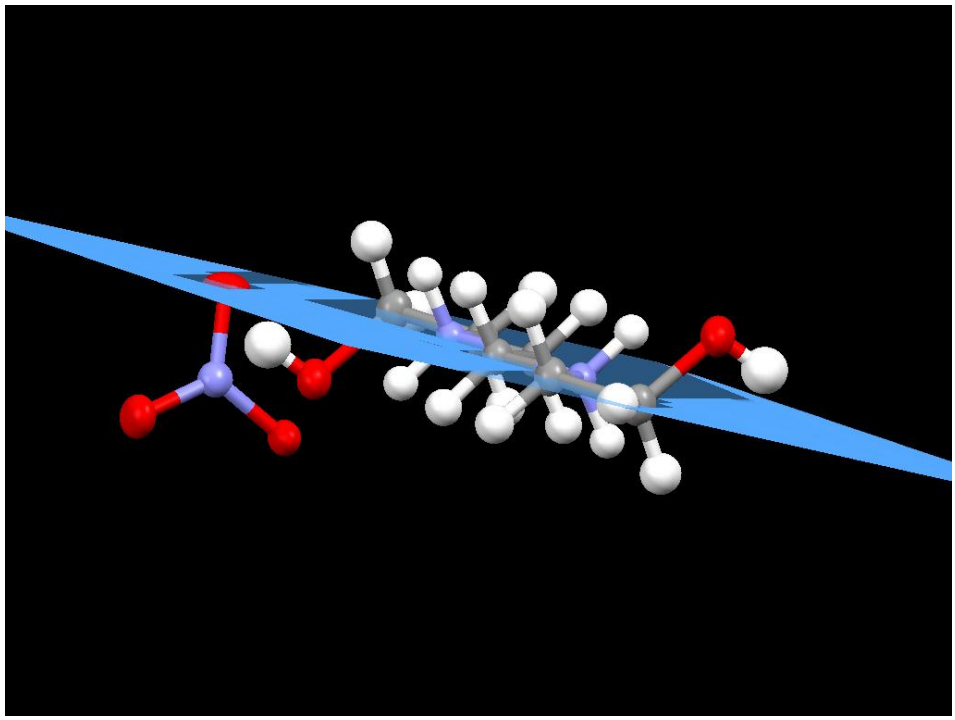

Figure S4. The C and N atoms of $(H_2DHEEN)^{2+}$ lie along a plane with the two hydroxyl groups above and below the plane, respectively.

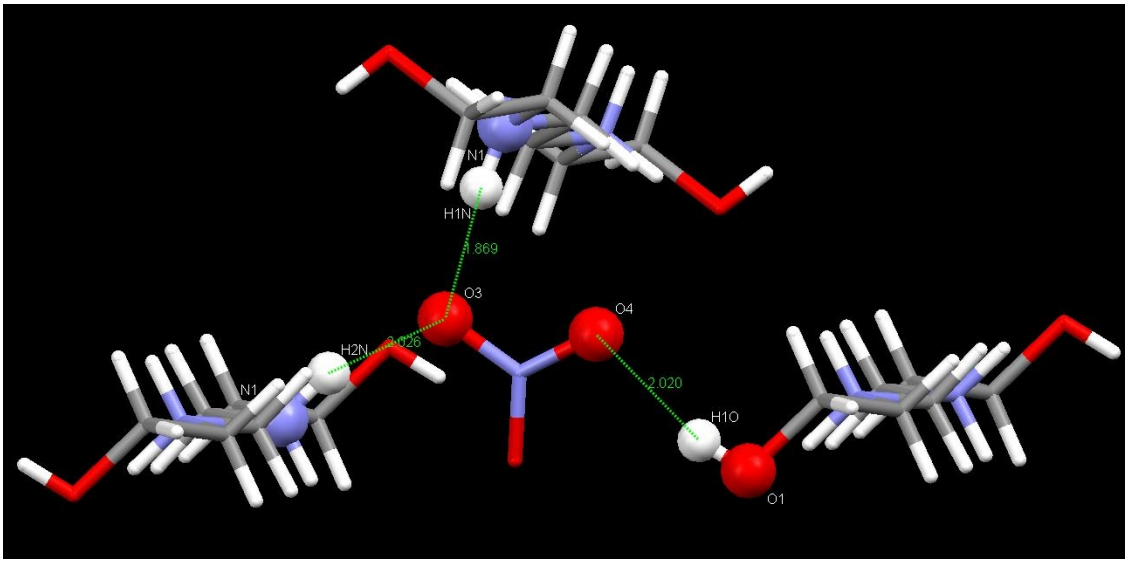

Figure S5. The H-bonding in the crystal structure of $(H_2BHEEN)(NO_3)_2$.

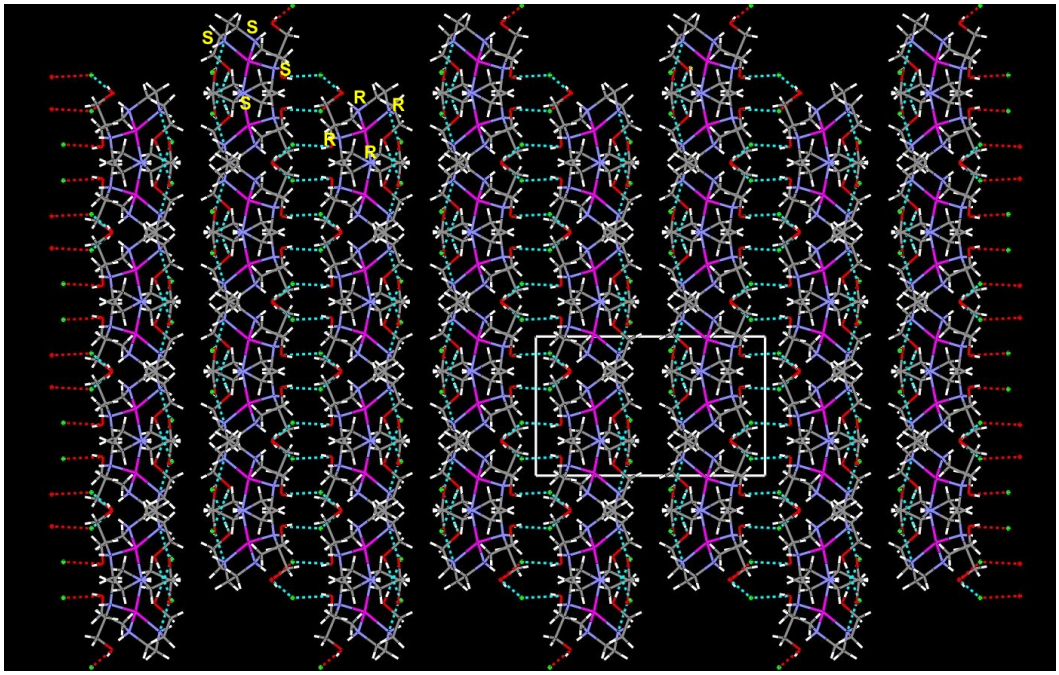

Figure S6. The packing of $[Zn(BHEEN)_2]Cl_2$ in alternating layers of bis-*trans*-*R,R* and the bis-*trans*-*S,S* isomers, viewed along the crystallographic *c* axis.

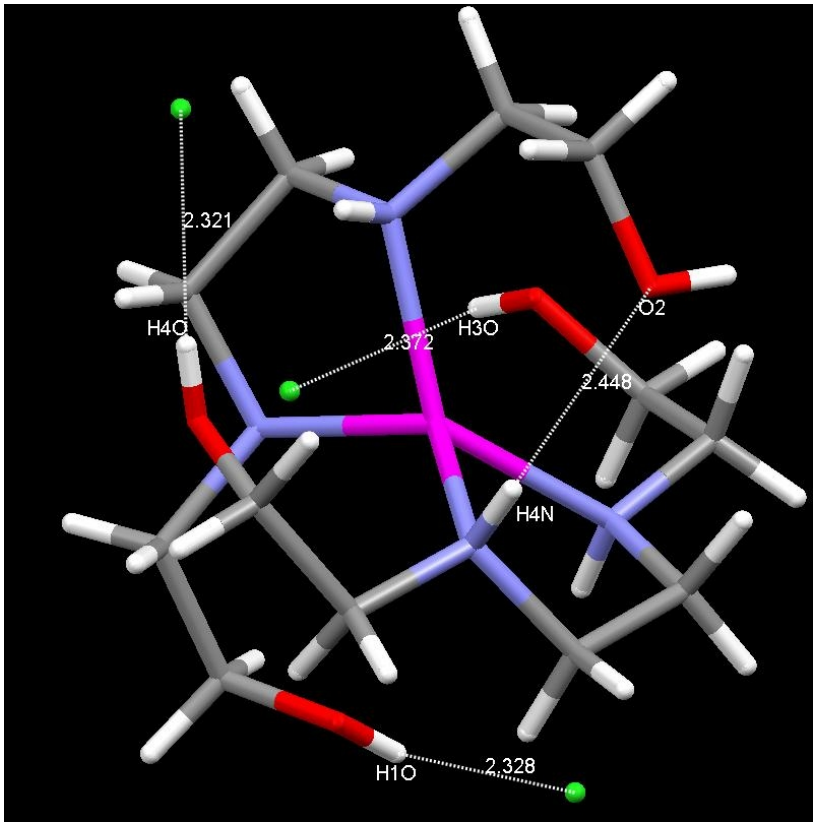

Figure S7. Hydrogen bonding in $[Zn(BHEEN)_2]Cl_2$

Figure S8. The crystal structure (white) and the DFT structure (yellow) of $[Zn(BHEEN)_2]^{2+}$ overlaid at the 5-membered chelate ring in the plane of the picture.

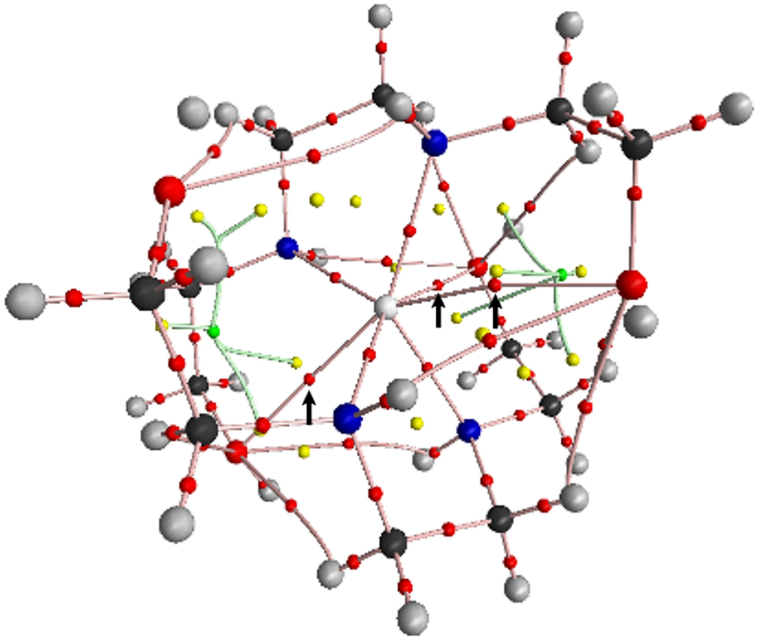

Figure S9. The molecular graph of $[Zn(BHEEN)_2]^{2+}$ at the crystal structure geometry analysed using AIM2000 from a wavefunction generated by a DFT calculation with the TZVP basis set on Zn, cc-pVTZ for all H atoms, and aug-cc-pVTZ for all other atoms. A bond path between Zn(II) and three of the O atoms of the pendent hydroxyethyl groups is observed (arrows indicate the bond critical points).

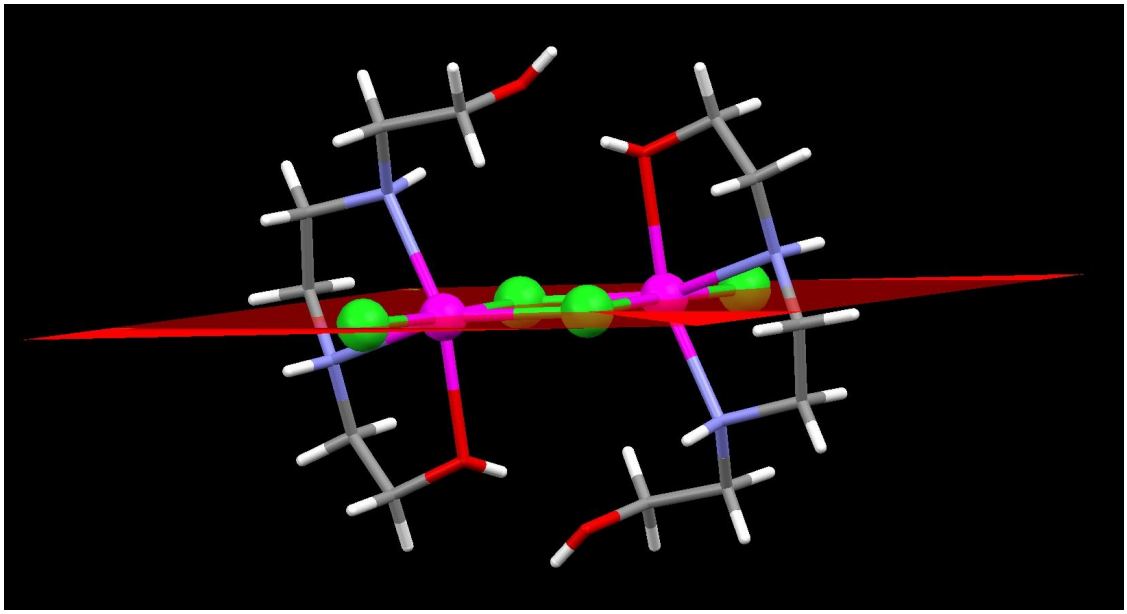

Figure S10. The four chloride ligands and the two metal ions in [(μ–$Cl)_2$(Cd(BHEEN)$Cl)_2$)] are coplanar. A centre of inversion is located at the intersection of the vectors connecting the two Cd(II) ions and the two bridging chloride ligands, respectively.

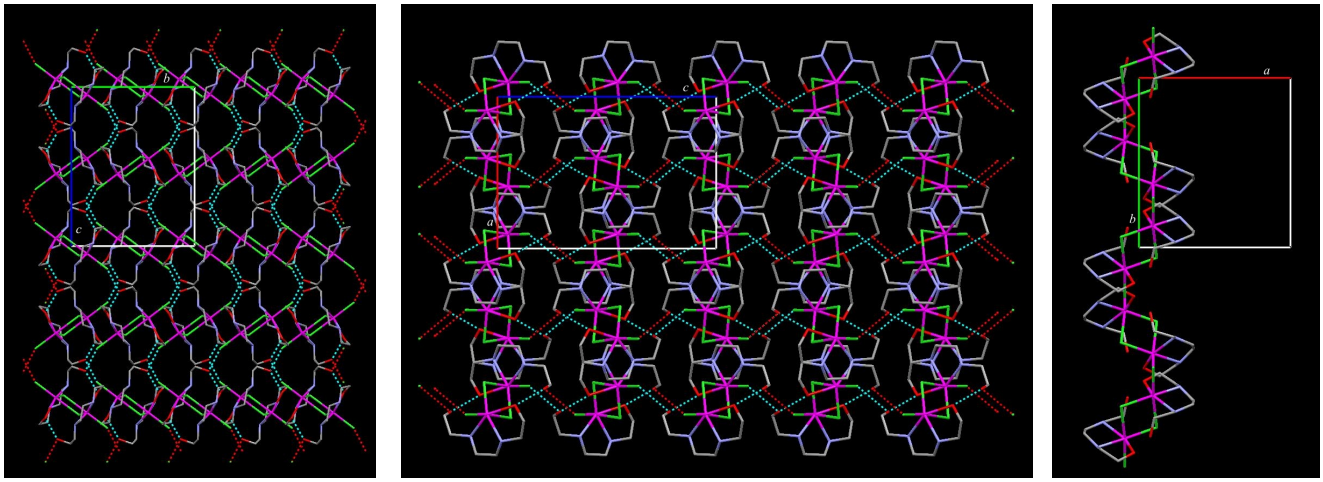

Figure S11. The packing of [(μ–$Cl)_2$(Cd(BHEEN)$Cl)_2$)]. When viewed along the *a* and *b* crystallographic axes, the compound packs in a layered structure with layers connected by hydrogen bonding between a terminal Cl^- ligand and the uncoordinated OH group of a molecule in the neighbouring layer (Cl···O = 2.411 Å). A two-fold screw axis is evident along the *c* axis.

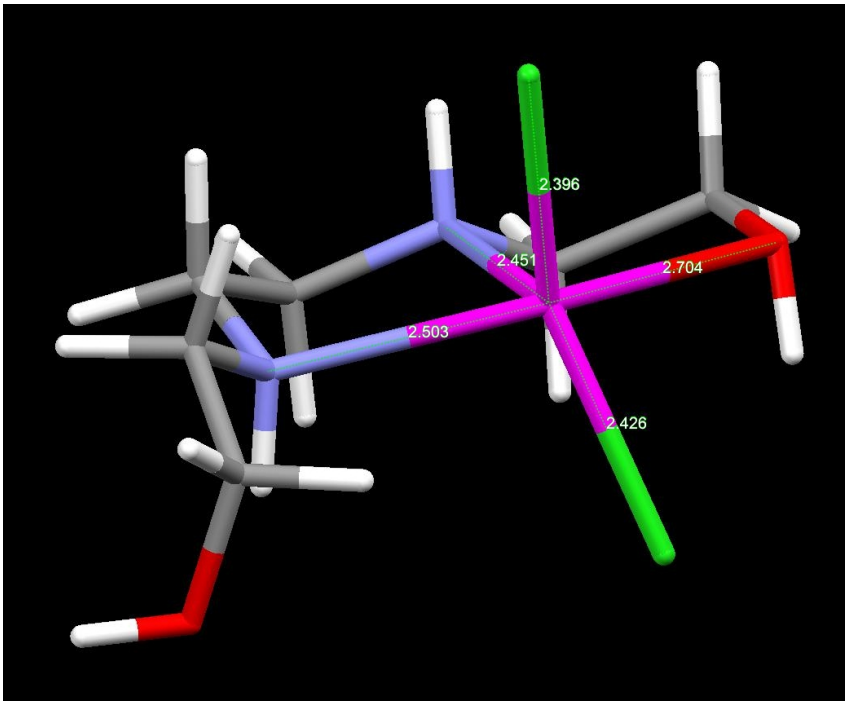

Figure S12. The DFT structure of the monomer, [Cd(BHEEN)Cl_2]

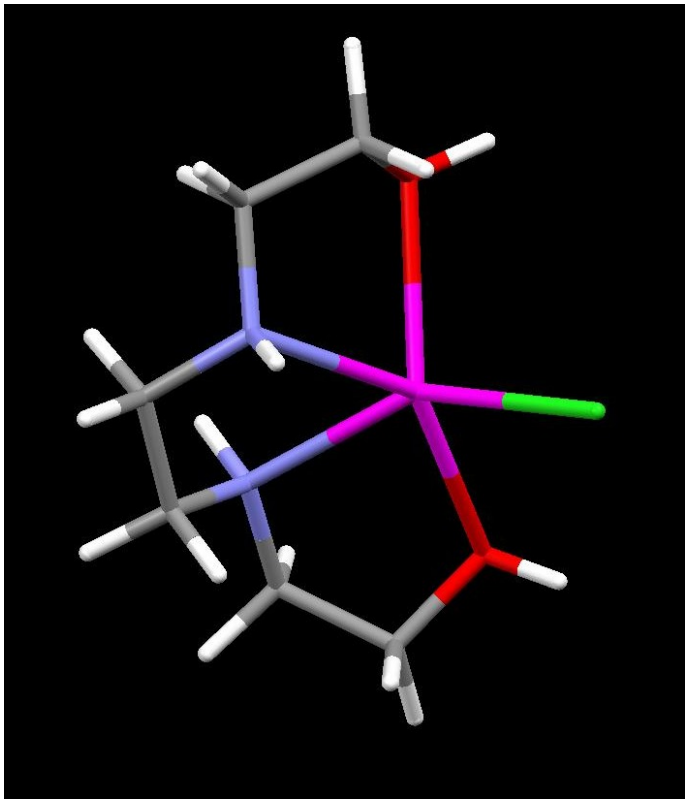

Figure S13. The DFT structure of $[Cd(BHEEN)Cl]^+$

Table S1. Comparison of structural parameters in $[Zn(BHEEN)_2]^{2+}$ determined crystallographically and calculated using DFT at the B3LYP/TZVP/cc-pVTZ/aug-cc-pVTZ level of theory

Bond lengths				
X	Y	Bond length /Å		
		Obs	Calc	Obs-Calc
C1	C2	1.503	1.513	-0.010
C1	O1	1.423	1.439	-0.016
C10	C9	1.515	1.522	-0.007
C10	N4	1.481	1.489	-0.008
C11	C12	1.506	1.513	-0.007
C11	N4	1.481	1.488	-0.007
C12	O4	1.420	1.488	-0.068
C2	N1	1.482	1.522	-0.040
C3	C4	1.506	1.489	0.017
C3	N1	1.486	1.488	-0.002
C4	N2	1.484	1.487	-0.003
C5	C6	1.498	1.513	-0.015
C5	N2	1.480	1.439	0.041
C6	O2	1.420	1.439	-0.019
C7	C8	1.501	1.513	-0.012
C7	O3	1.421	1.439	-0.018
C8	N3	1.485	1.487	-0.002
C9	N3	1.484	1.488	-0.004
N1	Zn1	2.068	2.103	-0.035
N2	Zn1	2.058	2.092	-0.034
N3	Zn1	2.071	2.092	-0.021
N4	Zn1	2.072	2.103	-0.031
Average Deviation				
C-C				***-0.005(11)***
C-N				***-0.003(22)***
C-O				***-0.030(25)***
Zn-N				***-0.030(6)***

Bond Angles						
			Angle /deg			
X	Y	Z	Obs	Calc	Obs-Calc	|Obs-Calc|
C1	C2	N1	110.8	112.9	-2.1	2.1
C10	C9	N3	109.8	110.7	-0.8	0.8
C10	N4	C11	110.2	112.0	-1.7	1.7
C10	N4	Zn1	106.0	104.3	1.7	1.7
C11	C12	O4	109.0	110.0	-1.0	1.0
C11	N4	Zn1	119.6	122.2	-2.6	2.6
C12	C11	N4	110.9	112.9	-2.0	2.0
C2	C1	O1	109.5	110.0	-0.6	0.6
C2	N1	C3	110.9	112.0	-1.1	1.1
C2	N1	Zn1	119.7	122.2	-2.5	2.5

C3	C4	N2	108.9	110.7	-1.8	1.8
C3	N1	Zn1	106.2	104.3	1.9	1.9
C4	C3	N1	110.8	110.6	0.2	0.2
C4	N2	C5	112.5	112.1	0.3	0.3
C4	N2	Zn1	106.4	105.0	1.4	1.4
C5	C6	O2	111.1	109.8	1.3	1.3
C5	N2	Zn1	118.9	121.1	-2.2	2.2
C6	C5	N2	109.1	112.4	-3.3	3.3
C7	C8	N3	110.5	112.4	-2.0	2.0
C8	C7	O3	108.9	109.7	-0.9	0.9
C8	N3	C9	111.3	112.1	-0.9	0.9
C8	N3	Zn1	120.2	121.1	-0.9	0.9
C9	C10	N4	110.5	110.6	-0.1	0.1
C9	N3	Zn1	106.1	105.0	1.1	1.1
N1	Zn1	N2	85.8	86.7	-0.9	0.9
N3	Zn1	N4	86.1	86.7	-0.6	0.6
N1	Zn1	N3	114.8	112.5	2.3	2.3
N2	Zn1	N4	117.6	112.5	5.1	5.1
N3	Zn1	N2	131.1	134.2	-3.1	3.1
N1	Zn1	N4	126.9	130.7	-3.8	3.8

Average deviation	
N-Zn-N	***2.6(1.7)***
C-N-Zn	***1.8(6)***
All other angles	***1.3(9)***

Table S2. Thermochemical data from DFT energy-minimised structures of Cd(II) and BHEEN. All values in Hartrees, T = 298.15 K, P = 1 atm.

		[Cd(BHEEN)Cl$_2$]	**[Cd(BHEEN)Cl]$^+$**	**Cl$^-$**
Zero point correction	ZPE	0.238671	0.239475	0
Correction to internal energy	$E_{corr} = E_t + E_r + E_v + E_e$	0.256530	0.25473	0.001416
Thermal correction to enthalpy	$H_{corr} = E_{tot} + k_B T$	0.257474	0.255674	0.00236
Thermal correction to Gibbs energy	$G_{corr} = H_{corr} - TS_{tot}$	0.189676	0.194742	-0.015023
Total Electronic energy	E_o	-1586.791496	-1126.28851	-460.310516
Sum of electronic and zero point energies	$E' = E_o + ZPE$	-1586.552825	-1126.049032	-460.310516
Sum of electronic and thermal energies	$E = E_o + E_{corr}$	-1586.534966	-1126.033777	-460.309099
Sum of electronic and thermal enthalpies	$H = E_o + H_{corr}$	-1586.534022	-1126.032832	-460.308155
Sum of electronic and thermal Gibbs energies	$G = E_o + G_{corr}$	-1586.601820	-1126.093765	-460.325538
Excluding low frequency vibrational modes (<625 cm^{-1})				
Zero point correction	ZPE	0.238671	0.239475	
Correction to internal energy	$E_{corr} = E_t + E_r + E_v + E_e$	0.227734	0.229033983	
Thermal correction to enthalpy	$H_{corr} = E_{tot} + k_B T$	0.228678	0.229978229	
Thermal correction to Gibbs energy	$G_{corr} = H_{corr} - TS_{tot}$	0.191561	0.193320825	
Total Electronic energy	E_o	-1586.791496	-1126.28851	
Sum of electronic and zero point energies	$E' = E_o + ZPE$	-1586.552825	-1126.049032	
Sum of electronic and thermal energies	$E = E_o + E_{corr}$	-1586.563762	-1126.059473	
Sum of electronic and thermal enthalpies	$H = E_o + H_{corr}$	-1586.562818	-1126.058529	
Sum of electronic and thermal Gibbs energies	$G = E_o + G_{corr}$	-1586.599935	-1126.095186	