

## Supplementary Material

### Synthesis, Structure, and Biological Assays of Novel Trifluoromethyldiazepine-Metal Complexes

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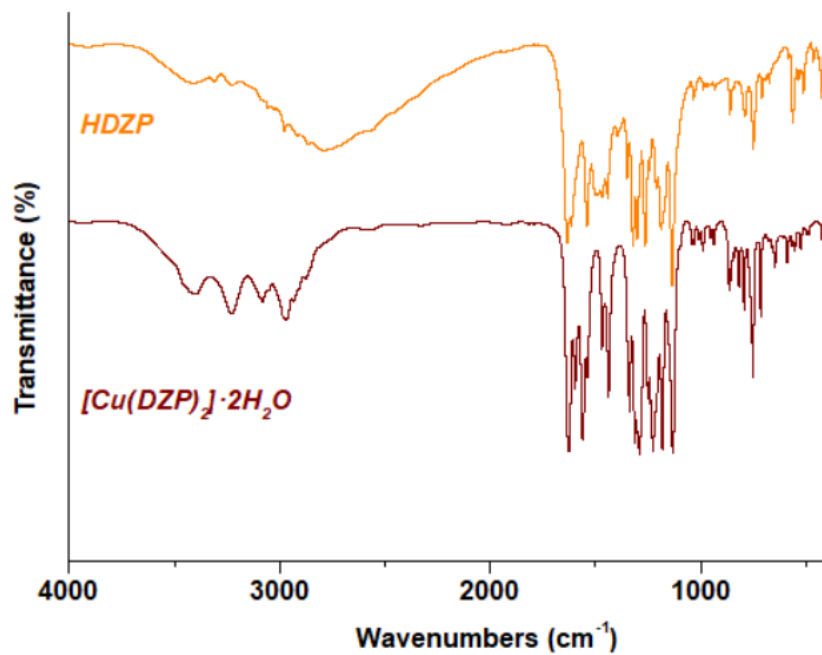
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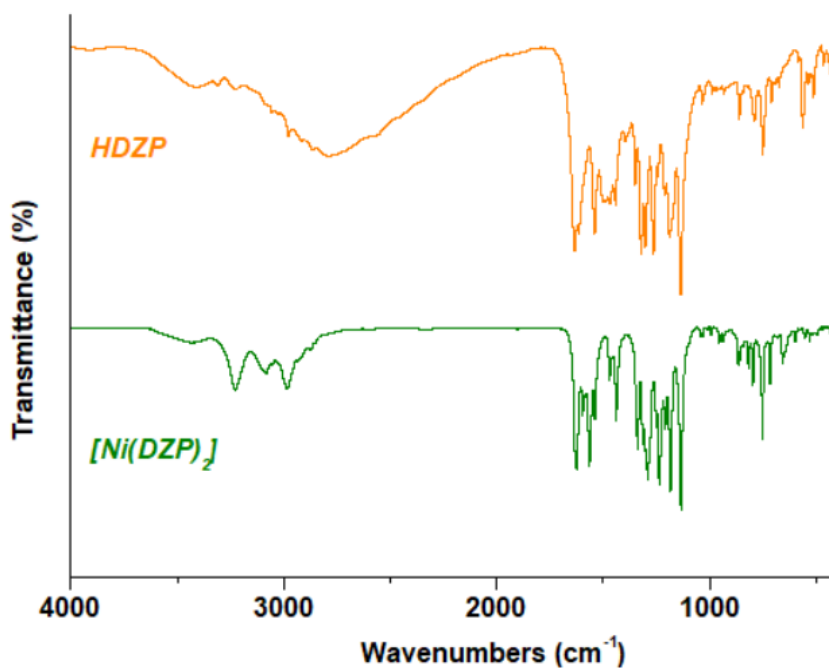
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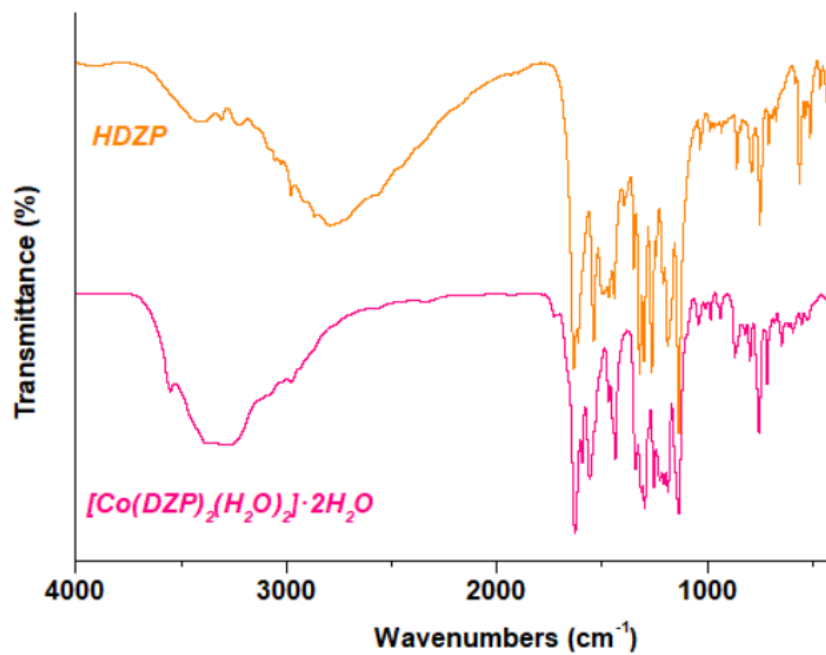
**Figure S1:** IR spectra of HDZP and  $[\text{Cu}(\text{DZP})_2] \cdot 2\text{H}_2\text{O}$



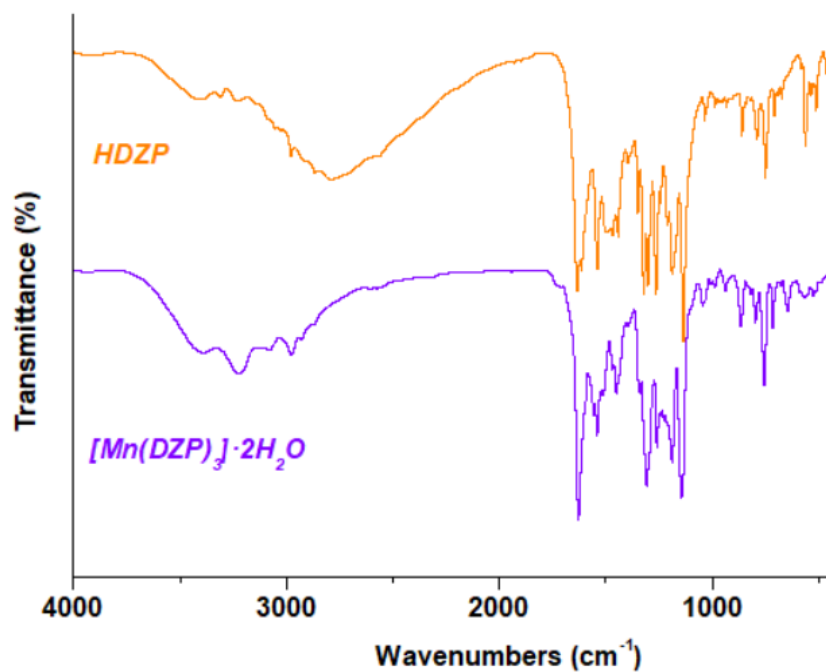
**Figure S2:** IR spectra of HDZP and  $[\text{Ni}(\text{DZP})_2]$ .



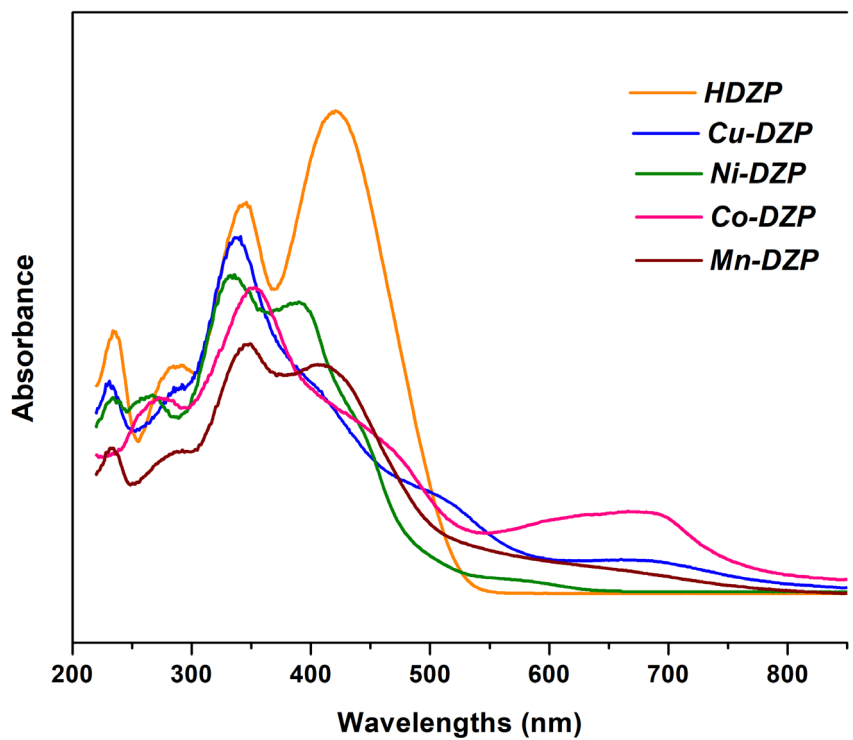
**Figure S3:** IR spectra of HDZP and  $[\text{Co}(\text{DZP})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ .



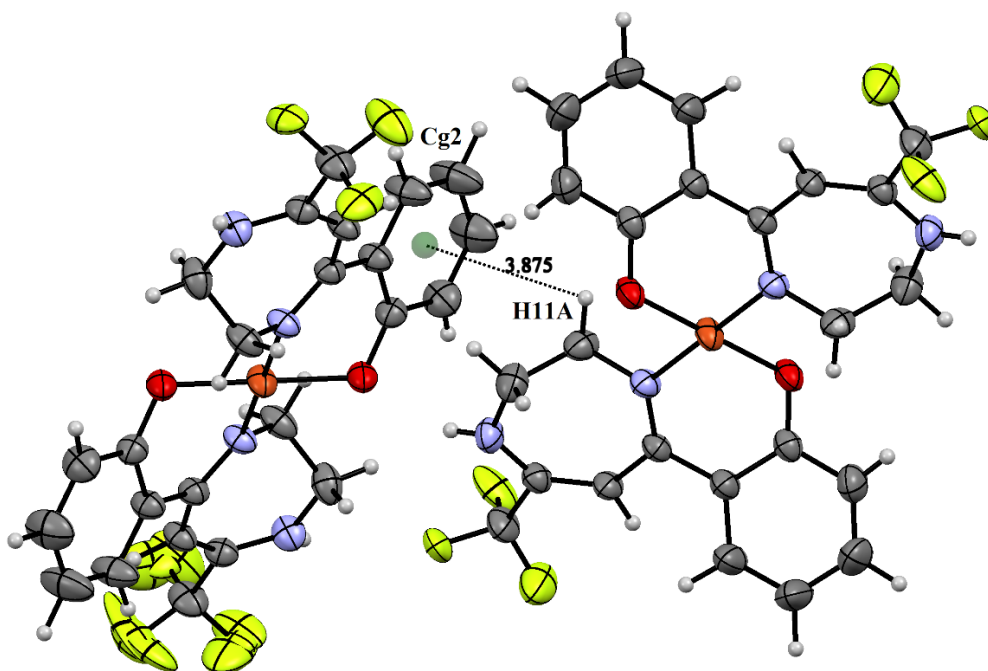
**Figure S4:** IR spectra of HDZP and  $[\text{Mn}(\text{DZP})_3] \cdot 2\text{H}_2\text{O}$ .



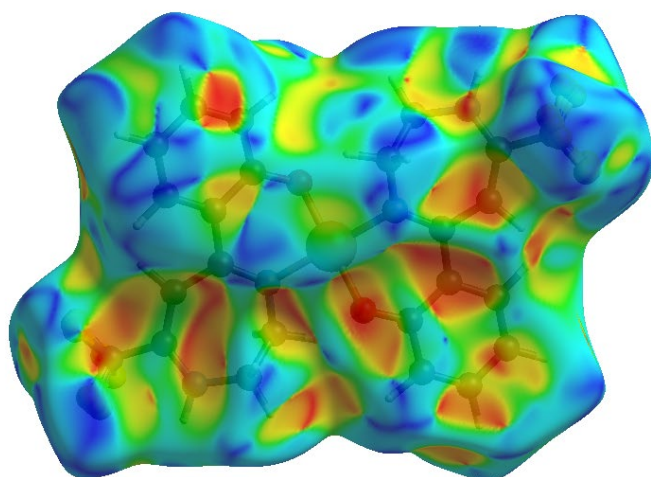
**Figure S5:** Electronic spectra (in solid state) of HDZP ligand and Cu-DZP, Ni-DZP, Co-DZP and Mn-DZP complexes.



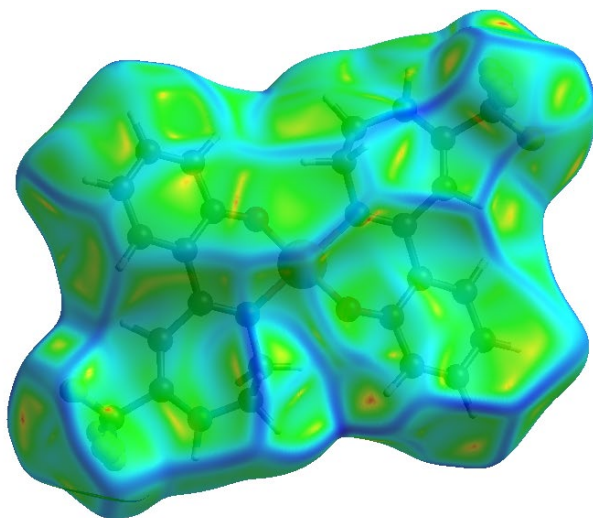
**Figure S6:** Crystal packing of  $[\text{Cu}(\text{DZP})_2]$  showing  $\text{C-H}\cdots\pi$  interactions.



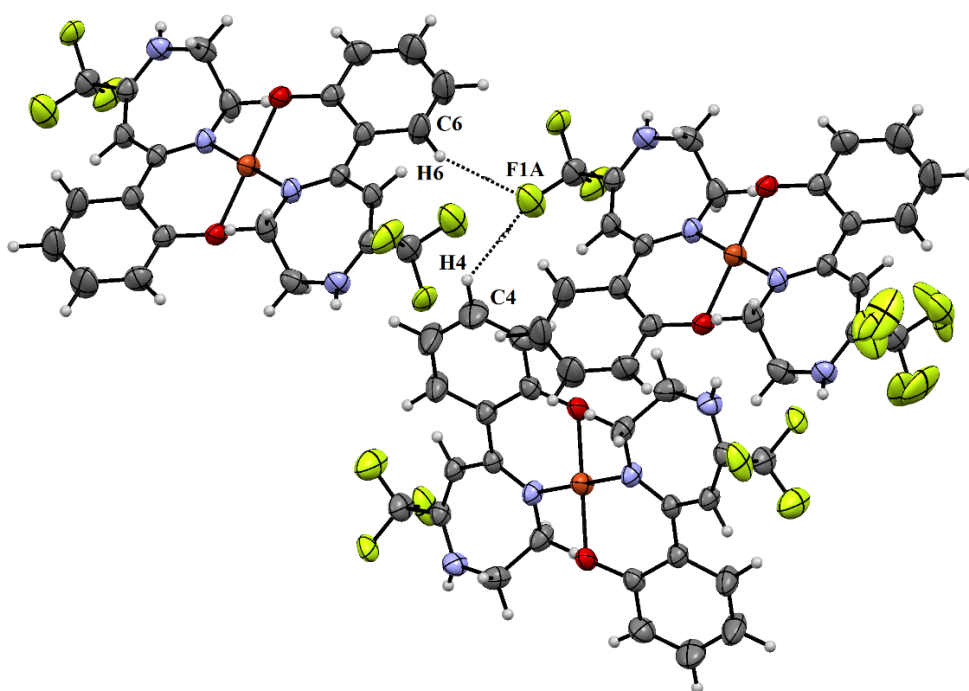
**Figure S7:** Hirshfeld surface mapped over shape index for  $[\text{Cu}(\text{DZP})_2]$ .



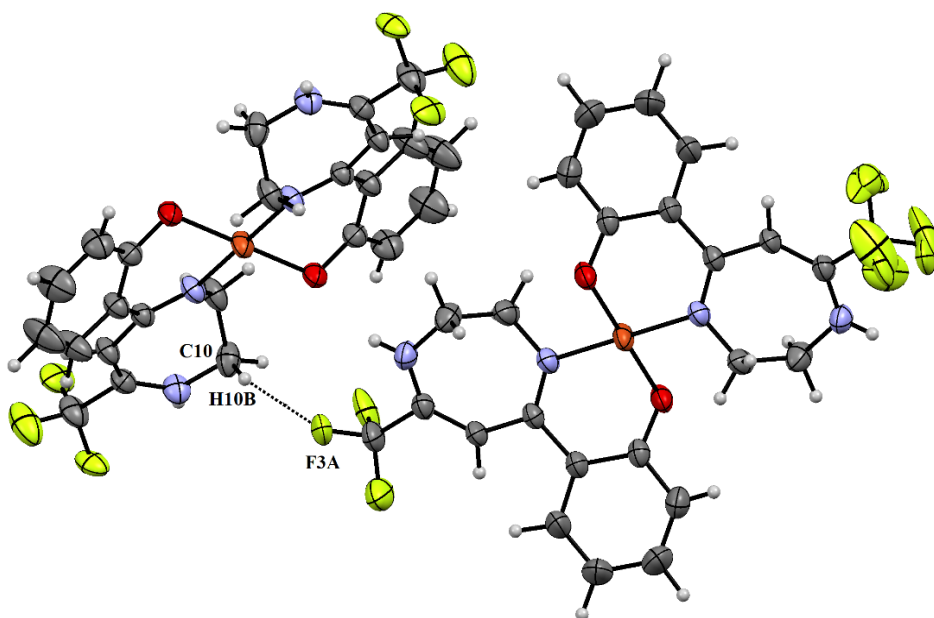
**Figure S8:** Hirshfeld surface mapped over curvedness for [Cu(DZP)<sub>2</sub>].



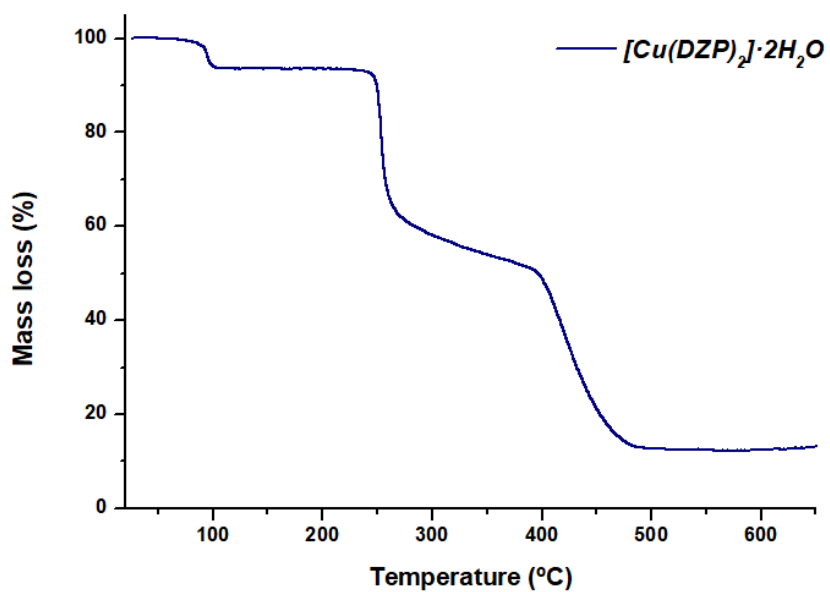
**Figure S9:** Crystal packing of [Cu(DZP)<sub>2</sub>] showing C-H...F interactions.



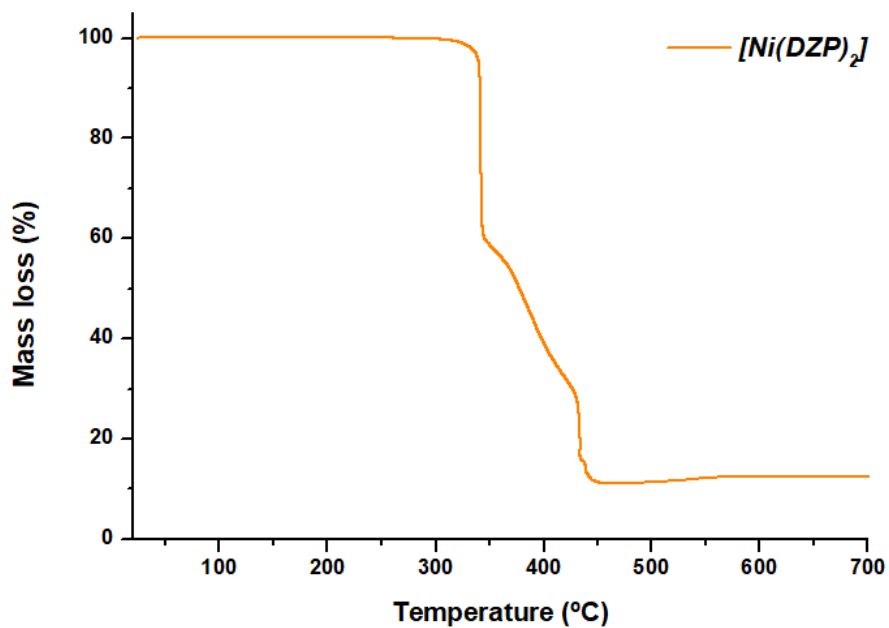
**Figure S10:** Crystal packing of [Cu(DZP)<sub>2</sub>] showing non-classical C-H...F intermolecular interactions.



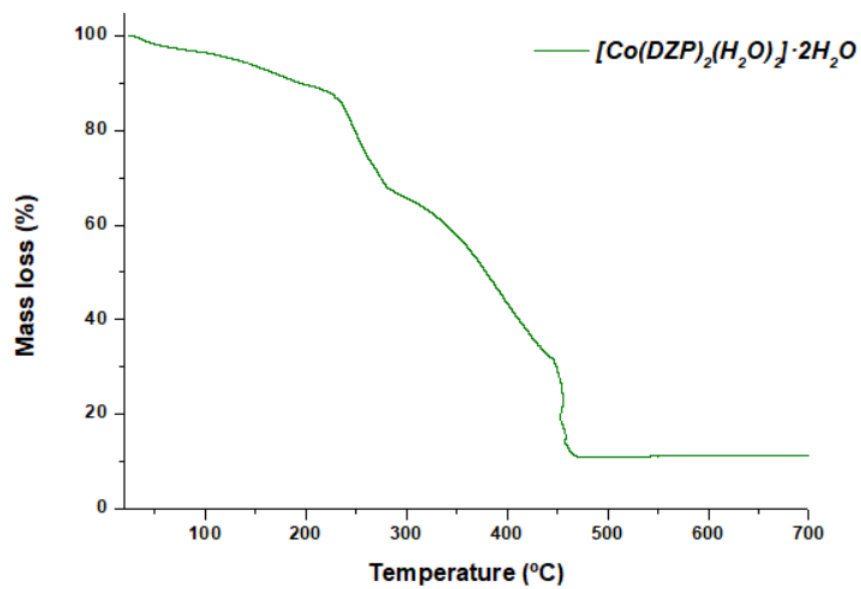
**Figure S11:** TGA Curve for the thermal decomposition of  $[\text{Cu}(\text{DZP})_2] \cdot 2\text{H}_2\text{O}$ .



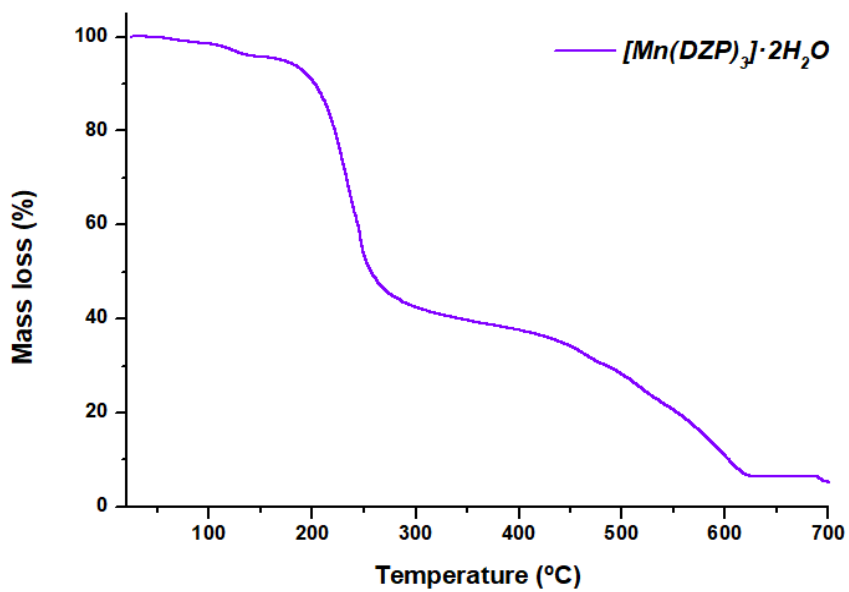
**Figure S12:** TGA curve for the thermal decomposition of  $[\text{Ni}(\text{DZP})_2]$ .



**Figure 13:** TGA curve for the thermal decomposition of  $[\text{Co}(\text{DZP})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ .



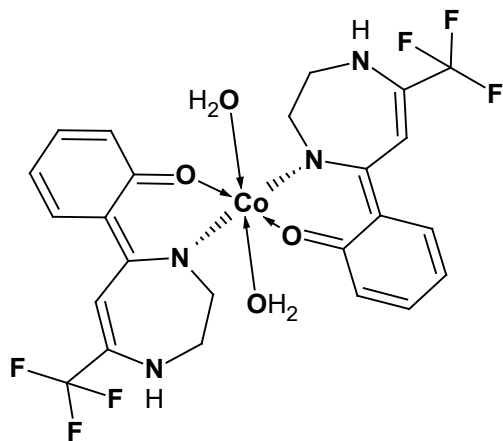
**Figure 14:** TGA curve for the thermal decomposition of  $[\text{Mn}(\text{DZP})_3] \cdot 2\text{H}_2\text{O}$ .



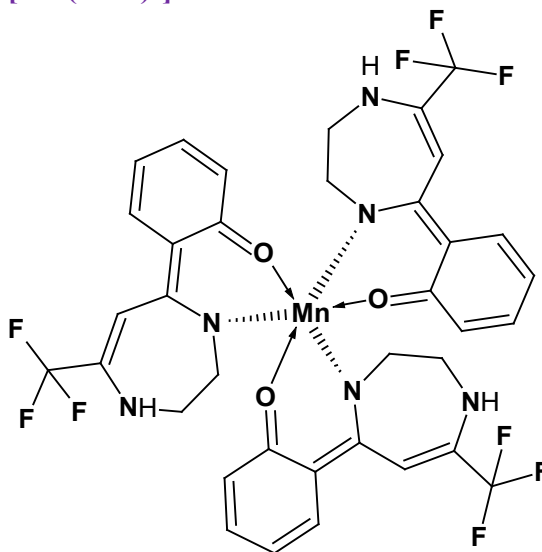


**Figure S15:** Proposed molecular structures of  $[\text{Co}(\text{DZP})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{Mn}(\text{DZP})_3] \cdot 2\text{H}_2\text{O}$  complexes.

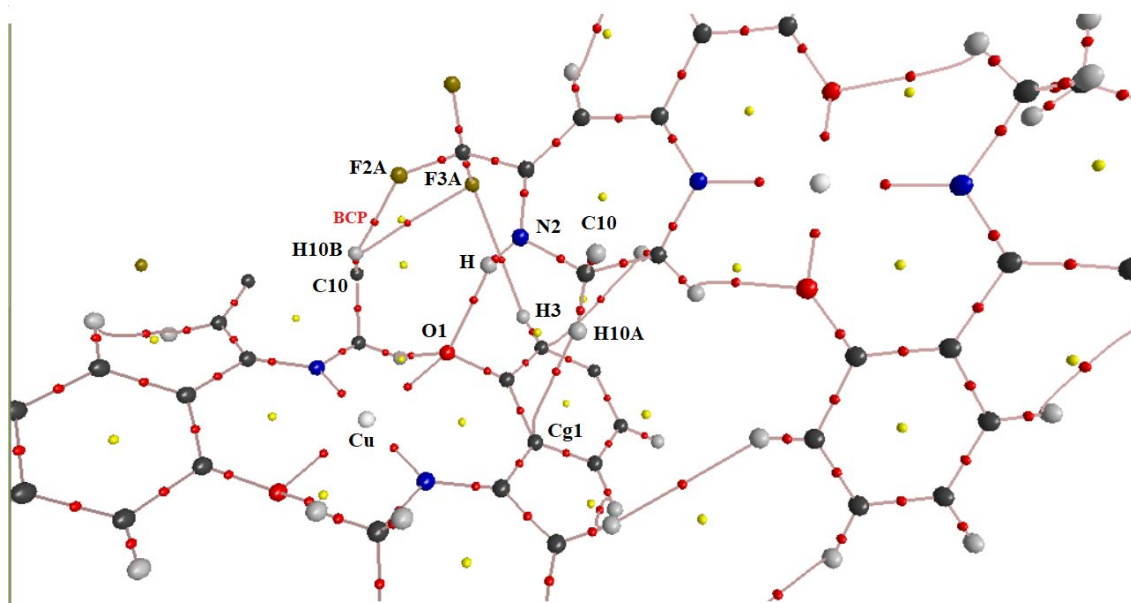
$[\text{Co}(\text{DZP})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$



$[\text{Mn}(\text{DZP})_3] \cdot 2\text{H}_2\text{O}$



**Figure S16:** Distribution of bond and ring (red and yellow spheres) critical points in a dimer of  $[\text{Cu}(\text{DZP})_2]$  complex.



**Table S1:** Main FTIR bands (in  $\text{cm}^{-1}$ ) and tentative assignment free ligand HDZP and its complexes  $[\text{Cu}(\text{DZP})_2] \cdot 2\text{H}_2\text{O}$  (Cu-DZP),  $[\text{Ni}(\text{DZP})_2]$  (Ni-DZP),  $[\text{Co}(\text{DZP})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (Co-DZP) and  $[\text{Mn}(\text{DZP})_3] \cdot 2\text{H}_2\text{O}$  (Mn-DZP).

<i>HDZP</i>	<i>Cu-DZP</i>	<i>Ni-DZP</i>	<i>Co-DZP</i>	<i>Mn-DZP</i>	<i>Assignments</i> <sup>a</sup>
3242	3229	3226	-	3221	$\nu$ N2-H
3054	3052	3051	3076	3080	$\nu$ C-H
2978	2971	2985	2978	2978	$\nu_a$ CH <sub>2</sub>
2921	2935	2936	-	2930	$\nu_a$ CH <sub>2</sub>
2866	2865	2870	-	2878	$\nu_s$ CH <sub>2</sub>
2768	-	-	-	-	$\nu$ N1-H
1635	1624	1624	1628	1628	$\nu$ C=O + $\nu$ C10-C11
1615	1596	1596	1594	1598	$\nu$ C=C (R1)
1540	1562	1565	1557	1558	$\nu$ C-N
1526	1539	1539	1537	1541	$\delta$ N2-H
1464	1469	1470	1469	1469	$\delta$ CH <sub>2</sub>
1442	1438	1439	1437	1448	$\delta$ CH <sub>2</sub>
1322	1312	1313	1313	1307	$\omega$ CH <sub>2</sub>
1302	1300	1301	1297	1295	$\omega$ CH <sub>2</sub>
1263	1291	1290	1254	1259	$\nu$ C-C (R1)
1243	1238	1236	-	1241	$\nu$ C10-C12
1211	1227	1208	1206	1227	$\tau\omega$ CH <sub>2</sub>
1189	1183	1183	1186	1188	$\nu_a$ CF <sub>3</sub>
1136	1132	1134	1136	1145	$\nu_a$ CF <sub>3</sub>
1036	1039	1040	1042	1044	$\nu_s$ CF <sub>3</sub>
1028	1031	1030	1033	1034	$\rho$ CH <sub>2</sub>
987	-	-	-	-	$\gamma$ N1-H
934	937	937	937	938	$\gamma$ N2-H
861	865	865	870	866	$\delta$ CCC (R2) + $\delta$ CCN (R2)
788	793	796	798	797	$\delta$ CCN (R2)
750	752	751	754	755	$\delta$ C=O
708	714	715	716	715	$\delta_s$ CF <sub>3</sub>
673	681	-	681	674	$\gamma$ NCC (R2)
563	564	-	579	565	$\delta_a$ CF <sub>3</sub>
536	552	552	552	552	$\delta$ CCO (R1)
-	590	597	594	591	$\nu$ M-N
-	487	451	489	487	$\nu$ M-O

<sup>a</sup>  $\nu$ : stretching,  $\delta$ : bending,  $\omega$ : wagging,  $\tau\omega$ : twisting,  $\gamma$ : out-of-plane bending modes; a: antisymmetric, s: symmetric.

**Table S2:** Electronic spectral data of [Cu(DZP)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O, [Ni(DZP)<sub>2</sub>], [Co(DZP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O and [Mn(DZP)<sub>3</sub>] $\cdot$ 2H<sub>2</sub>O complexes.

<i>Complex</i>	<i>UV-Vis bands (nm)</i>	<i>Assignment</i>
<i>[Cu(DZP)<sub>2</sub>]<math>\cdot</math>2H<sub>2</sub>O</i>	231	$\pi \rightarrow \pi^*$
	290	$\pi \rightarrow \pi^*$
	337	$n \rightarrow \pi^*$
	387	Charge transfer
	492	${}^2B_{1g} \rightarrow {}^2B_{2g}$
	674	${}^2B_{1g} \rightarrow {}^2A_{1g}$
<i>[Ni(DZP)<sub>2</sub>]</i>	234	$\pi \rightarrow \pi^*$
	268	$\pi \rightarrow \pi^*$
	334	$n \rightarrow \pi^*$
	389	Charge transfer
	563	${}^1A_{1g} \rightarrow {}^1B_{1g}$
<i>[Co(DZP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<math>\cdot</math>2H<sub>2</sub>O</i>	273	$\pi \rightarrow \pi^*$
	354	$n \rightarrow \pi^*$
	418	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	629	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
<i>[Mn(DZP)<sub>3</sub>]<math>\cdot</math>2H<sub>2</sub>O</i>	232	$\pi \rightarrow \pi^*$
	290	$\pi \rightarrow \pi^*$
	408	${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g} ({}^4G)$

**Table S3:** Hydrogen bonds for [Cu(DZP)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O [ $\text{\AA}$  and  $^\circ$ ].

D-H $\cdots$ A	d(D-H)	d(H $\cdots$ A)	d(D $\cdots$ A)	$\angle$ (DHA)
C(11)-H(11A) $\cdots$ O#1	0.97	2.47	2.984(3)	113
N(2)-H(2N) $\cdots$ O#2	0.86	2.17	2.871(3)	139

Symmetry transformations used to generate equivalent atoms: (#1) -x+1, -y+1, -z+2; (#2) -x+1, y-1/2, -z+3/2.