Electronic Supplementary Information (ESI)

Effects of the substituents of pyrazole/thiazine ligands on the magnetic properties of chloro-bridged Cu(II) complexes

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Table S1. Crystal data and structure refinement details for compounds [{CuCl(PzTz)}$_2$(μ-Cl)$_2$], [{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$], [$CuCl_2$(DMPzTz)] and [{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$]

	[{CuCl(PzTz)}$_2$(μ-Cl)$_2$]	[{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$]	[$CuCl_2$(DMPzTz)]	[{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$]
Crystal shape	Prism	Prism	Prism	Needle
Colour	Green	Green	Dark green	Green
Size (mm)	0.30 × 0.26 × 0.24	0.24 × 0.17 × 0.16	0.48 × 0.46 × 0.35	0.29 × 0.05 × 0.03
Chemical formula	$C_{14}H_{18}Cl_4Cu_2N_6S_2$	$C_{18}H_{26}Cl_4Cu_2N_6S_2$	$C_9H_{13}Cl_2CuN_3S$	$C_{38}H_{34}Cl_4Cu_2N_6S_2$
Formula weight	603.34	659.45	329.72	907.71
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	C2/c	C2/c	Pbca	$P2_1/n$
Unit cell dimensions				
a (Å)	17.2598(4)	17.3533(6)	7.5613(3)	6.340(5)
b (Å)	8.9759(7)	9.0977(3)	17.6501(7)	15.756(5)
c (Å)	14.2902(12)	17.7828(6)	18.5075(7)	19.015(5)
β (º)	106.600(1)	118.7020(10)		98.637(5)
Cell volume (Å^3)	2121.6(3)	2462.51(15)	2469.97(17)	1877.9(17)
Z	4	4	8	2
T (K)	298(2)	100(2)	100(2)	110(2)
D_{calc} (g cm^{-3})	1.889	1.779	1.773	1.605
μ (mm^{-1})	2.720	2.352	2.344	1.567
F (000)	1208	1336	1336	924

θ range	2.46 – 28.22	2.61 – 26.42	2.20 – 26.41	1.69 – 26.41
Index range	-22 ≤ h ≤ 22, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18	-21 ≤ h ≤ 18, 0 ≤ k ≤ 11, 0 ≤ l ≤ 22	0 ≤ h ≤ 9, 0 ≤ k ≤ 22, 0 ≤ l ≤ 23	-7 ≤ h ≤ 7, 0 ≤ k ≤ 19, 0 ≤ l ≤ 23
Independent reflections	2482	2532	2533	3829
Observed reflections [$F > 4{,}0\ \sigma(F)$]	2300	2228	2367	3100
No. of ref. parameters	127	147	147	235
R [$F > 4{,}0\ \sigma(F)$]	0.0396	0.0228	0.0204	0.0504
wR [$F > 4{,}0\ \sigma(F)$]	0.1001	0.0517	0.0535	0.138
Goodness-of-fit (GOF)	1.111	1.022	1.169	1.133
ρ_{max}; ρ_{min} (e Å^{-3})	1.422; -0.453	0.339; -0.415	0.281; -0.585	1.433; -0.839

Table S2. Comparison of bond lengths in complexes with the mean value calculated for similar compounds found in the Cambridge Structural Database

	[{CuCl(PzTz)}$_2$(μ-Cl)$_2$]	**[{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$]**	**[[{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$]**	**Mean value**	**[CuCl$_2$(DMPzTz)]**	**Mean value**
Cu-N(1)	2.050(3)	1.998(2)	2.022(3)	1.97(7) [b]	1.985(1)	1.97(7) [b]
Cu-N(3)	1.988(3)	2.029(2)	2.026(3)	1.942(13)[c]	1.993(2)	1.98(4) [e]
Cu-Cl(1)	2.292(1)	2.273(1)	2.282(1)	2.29(4) [d]	2.237(1)	2.24(2) [f]
Cu-Cl(1a)[a]	2.795(1)	2.580(1)	2.675(2)	2.70(15) [d]		
Cu-Cl(2)	2.227(1)	2.264(1)	2.244(1)	2.27(5) [d]	2.203(1)	2.24(2)
Cu···Cu(a)[a]	3.538(1)	3.460(1)	3.588(2)	3.55(15) [d]		

[a] Symmetry code: 0.5-x, 0.5-y, -z for [{CuCl(PzTz)}$_2$(μ-Cl)$_2$] and [{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$]; 1-x, 1-y, -z for [{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$]

[b] Calculated average value for 9 copper(II) complexes with this bond Cu-$N_{thiazine}$

[c] Calculated average value for 7 five-coordinated copper(II) complexes with this type of unions containing the chromophore group $CuCl_3N_2$

[d] Calculated mean value using the data of 192 dichlorine-bridged dimers of copper(II) with a Cl_3N_2 environment

[e] Calculated average value for 6 four-coordinated copper(II) complexes with this type of unions containing the chromophore group $CuCl_2N_2$

[f] Calculated average value for 105 *cis*-squared planar copper(II) complexes the chromophore group $CuCl_2N_2$

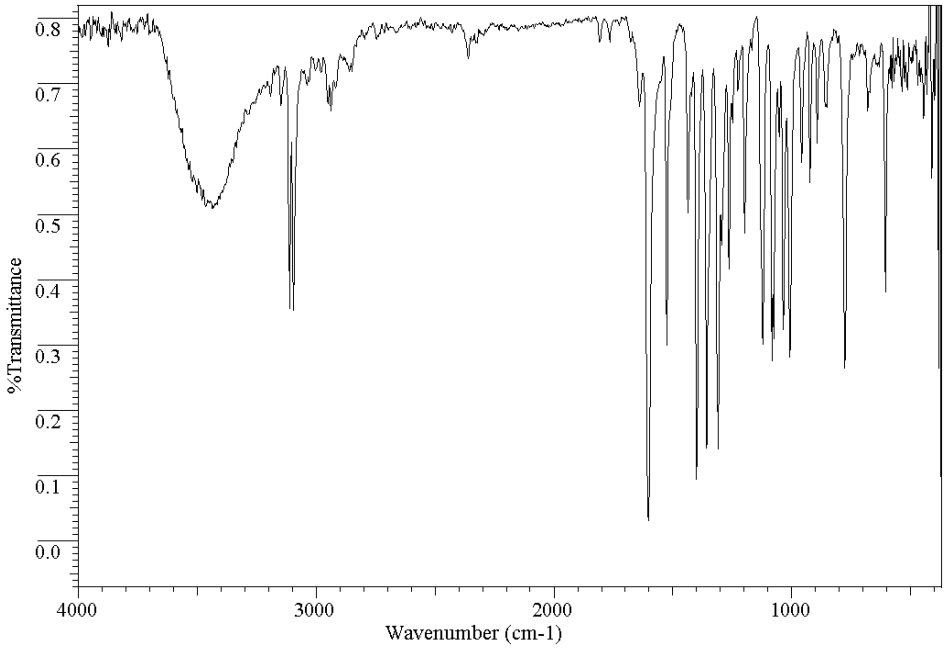

Figure S1. IR spectrum of $[\{CuCl(PzTz)\}_2(\mu\text{-}Cl)_2]$ in the 4000-370 cm^{-1} range

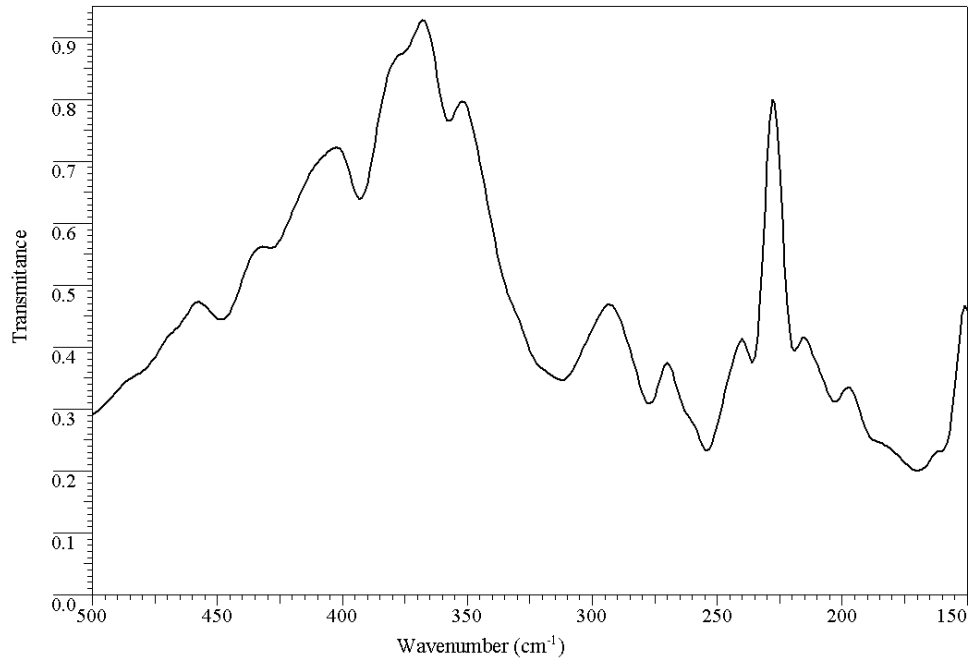

Figure S2. IR spectrum of $[\{CuCl(PzTz)\}_2(\mu\text{-}Cl)_2]$ in the 500-150 cm^{-1} range

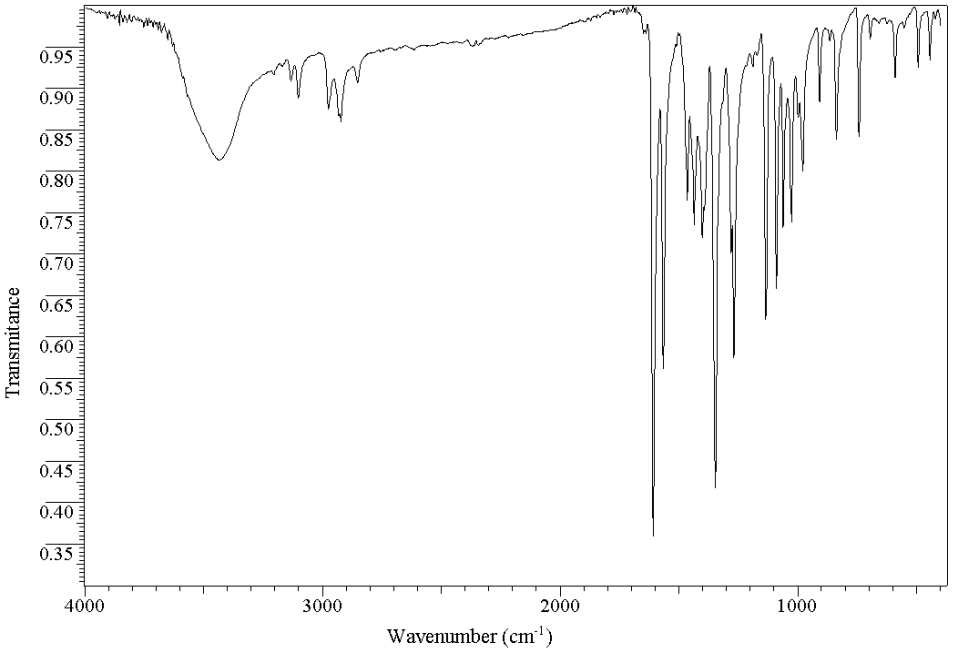

Figure S3. IR spectrum of [{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$] in the 4000-370 cm^{-1} range

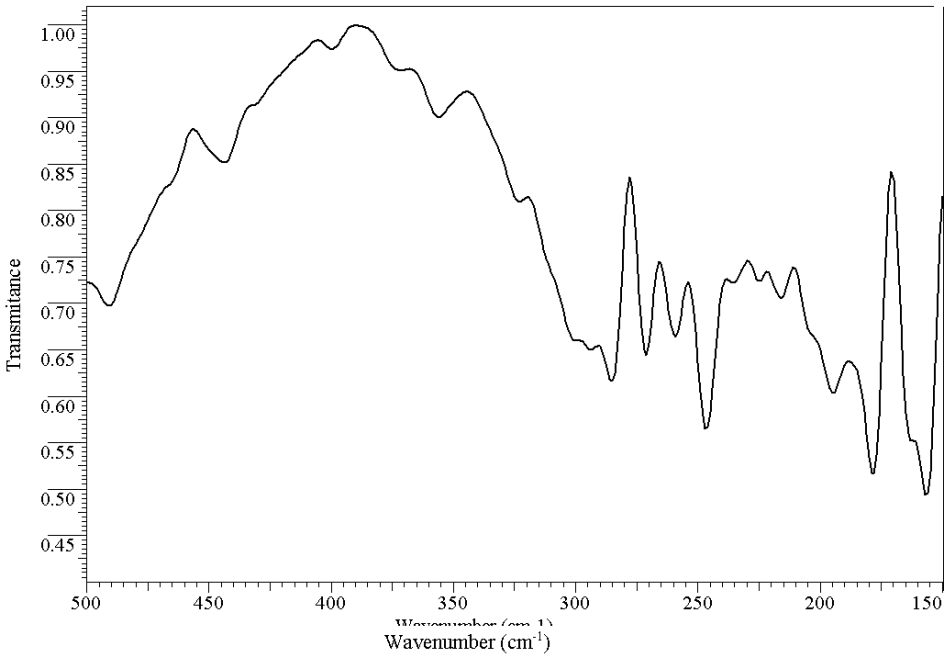

Figure S4. IR spectrum of [{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$] in the 500-150 cm^{-1} range

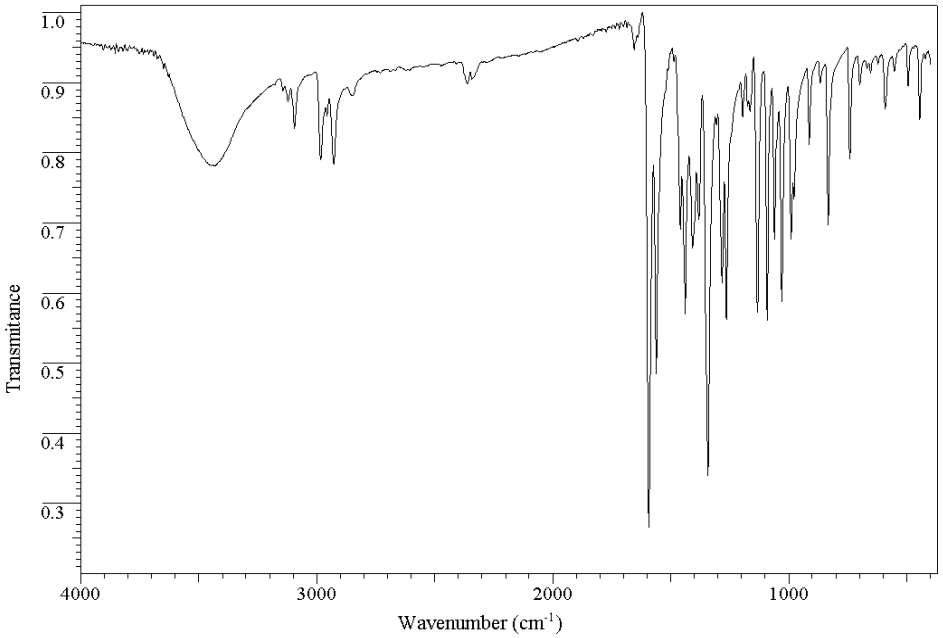

Figure S5. IR spectrum of [$CuCl_2$(DMPzTz)] in the 4000-370 cm^{-1} range

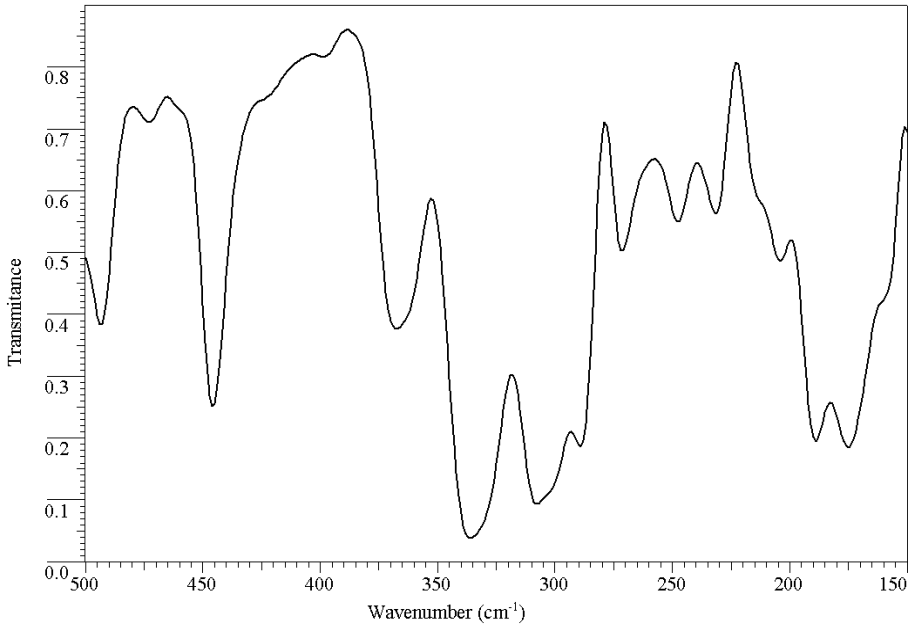

Figure S6. IR spectrum of [$CuCl_2$(DMPzTz)] in the 500-150 cm^{-1} range

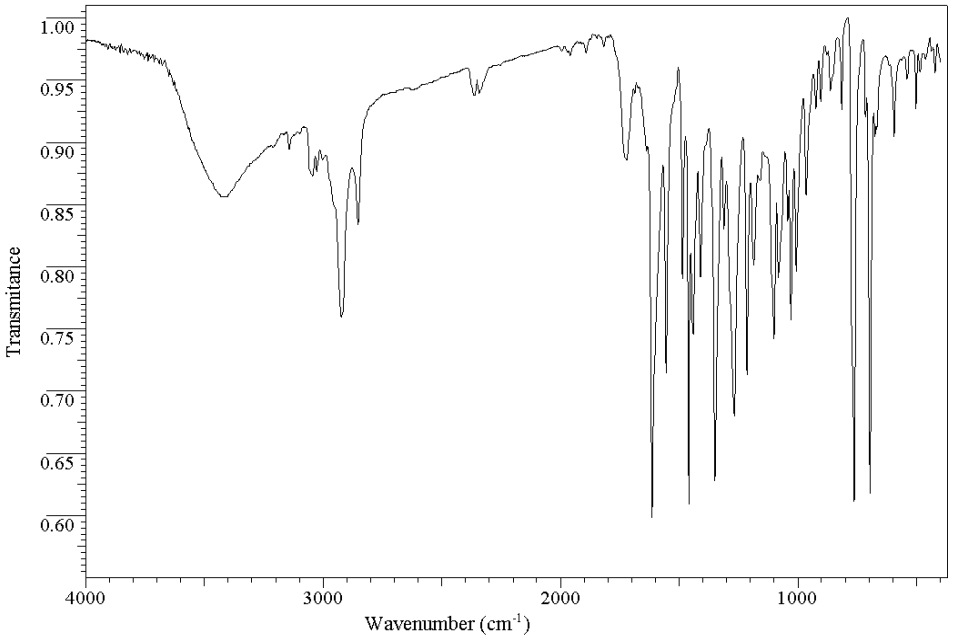

Figure S7. IR spectrum of [{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$] in the 4000-370 cm^{-1} range

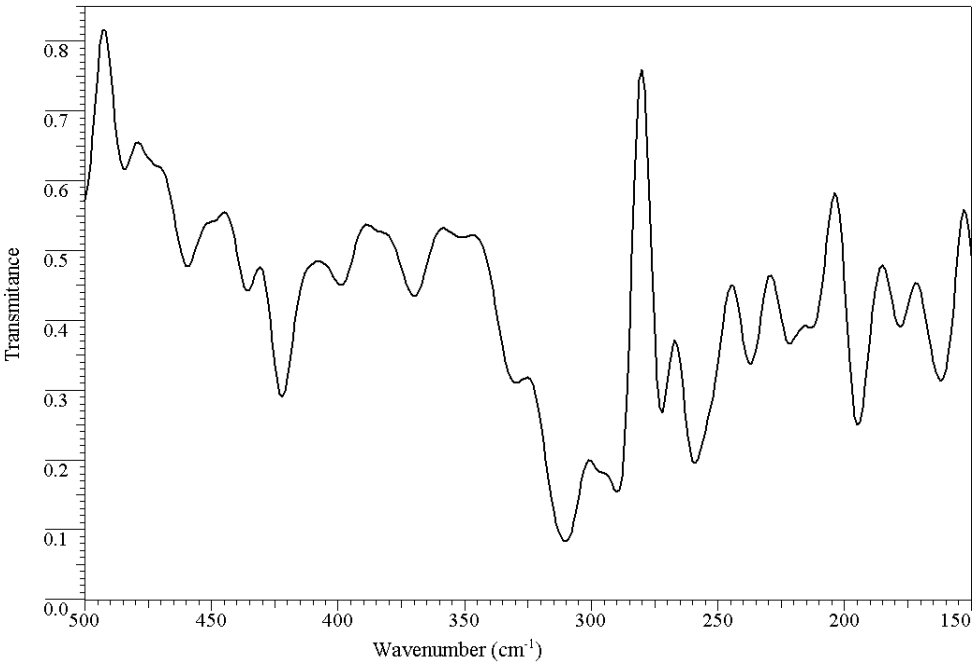

Figure S8. IR spectrum of [{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$] in the 500-150 cm^{-1} range

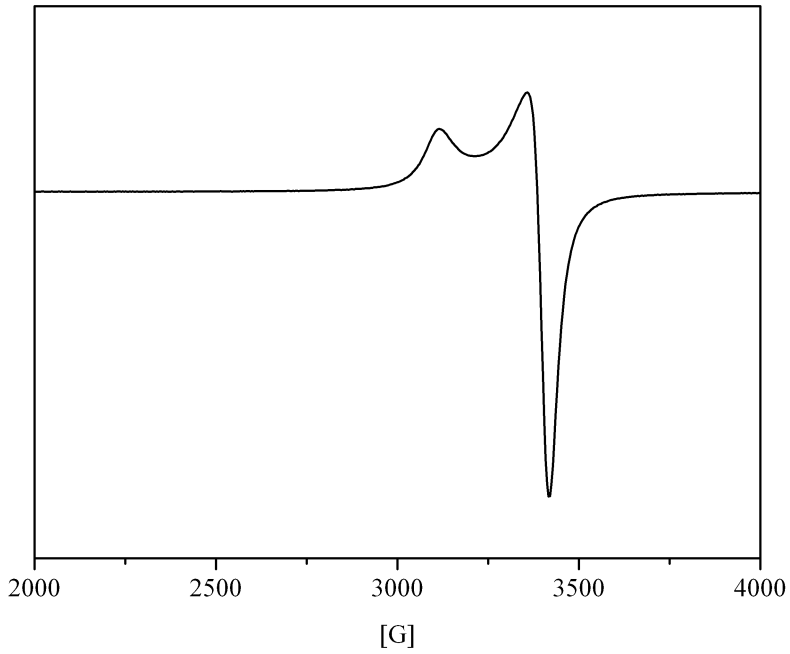

Figure S9. EPR spectrum of [{CuCl(PzTz)}$_2$(μ-Cl)$_2$] in the polycrystalline state at 298 K.

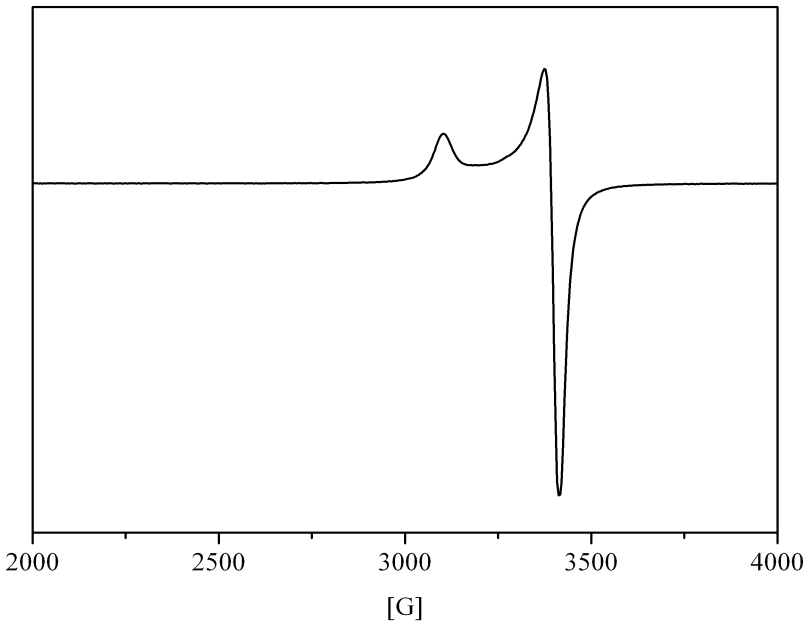

Figure S10. EPR spectrum of [{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$] in the polycrystalline state at 298 K.

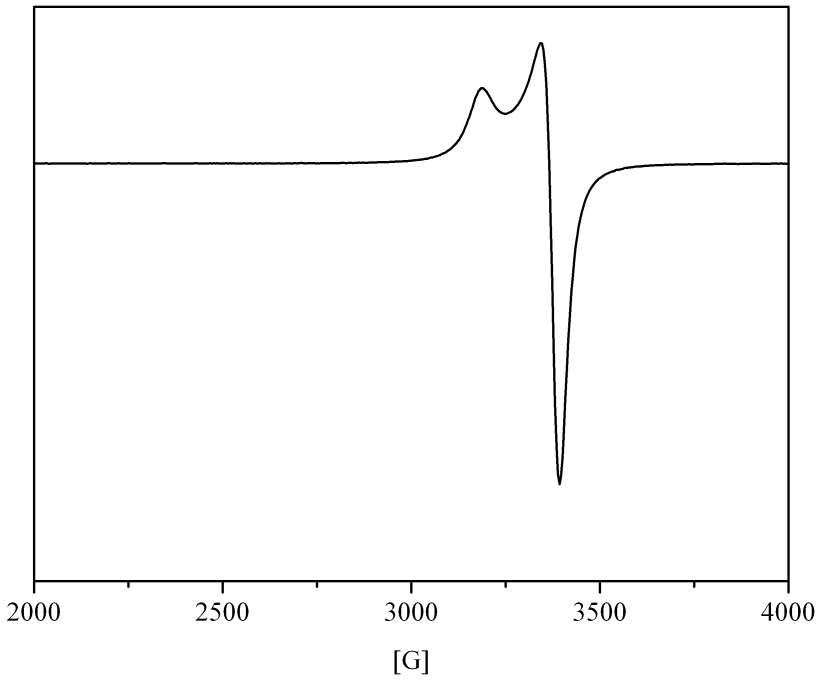

Figure S11. EPR spectrum of [$CuCl_2$(DMPzTz)] in the polycrystalline state at 298 K.

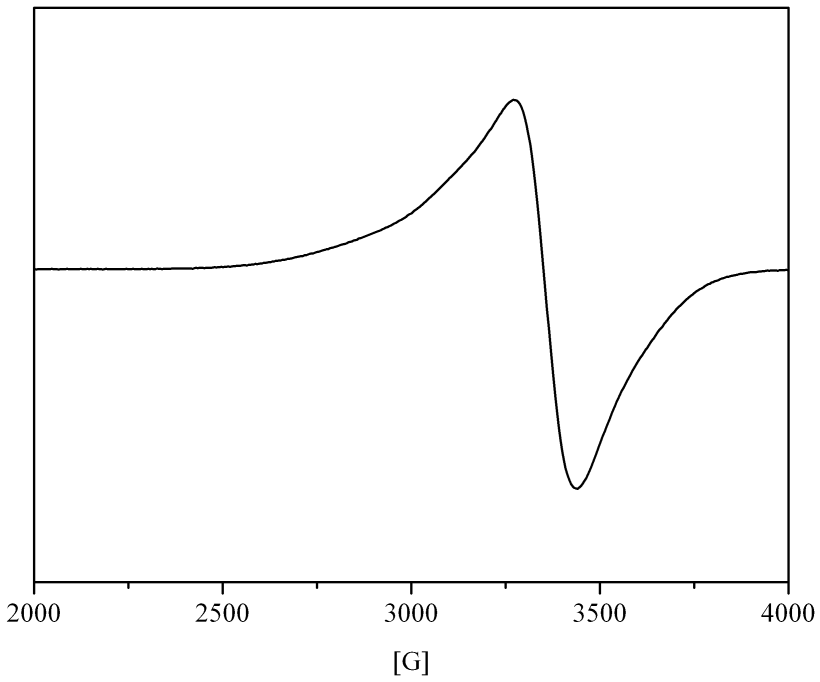

Figure S12. EPR spectrum of [{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$] in the polycrystalline state at 298 K.

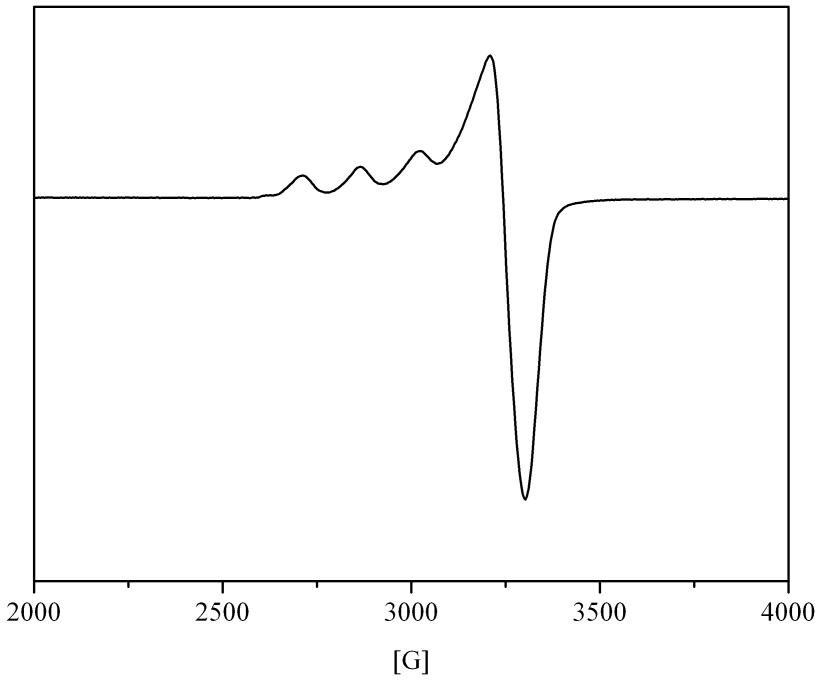

Figure S13. EPR spectrum of [{CuCl(PzTz)}$_2$(μ-Cl)$_2$] in MeOH solution at 77 K.

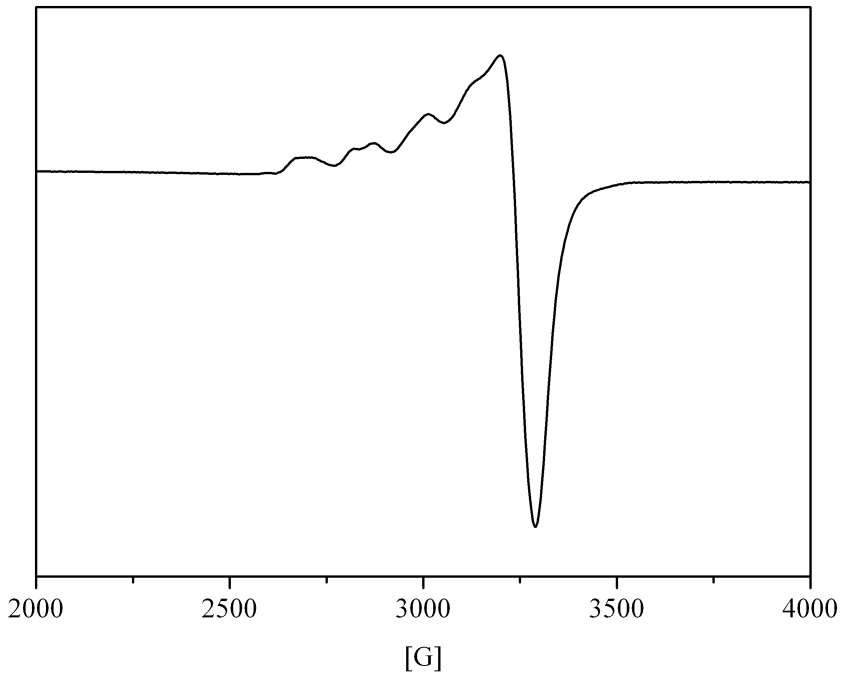

Figure S14. EPR spectrum of [{CuCl(DMPzTz)}$_2$(μ-Cl)$_2$] in MeOH solution at 77 K.

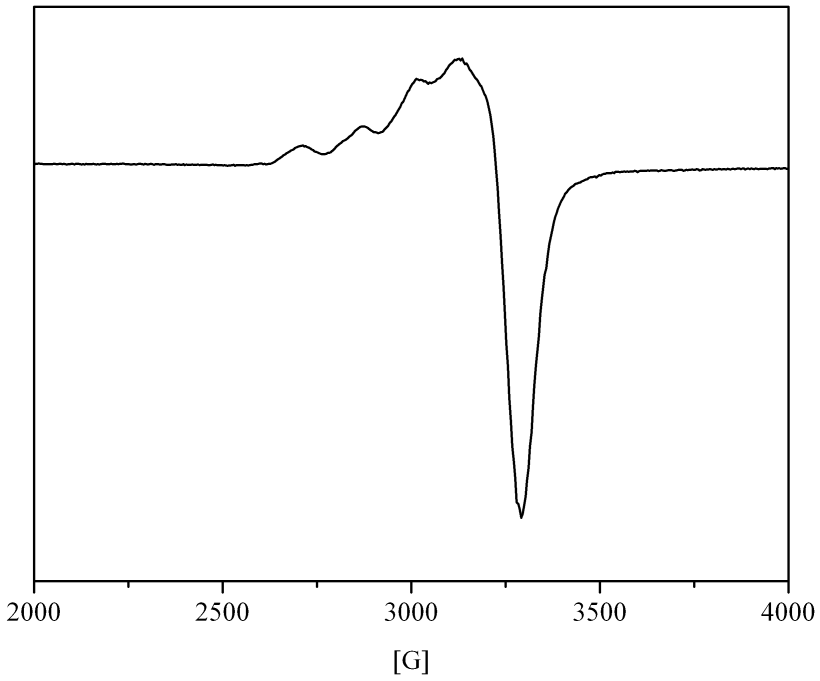

Figure S15. EPR spectrum of [$CuCl_2$(DMPzTz)] in MeOH solution at 77 K.

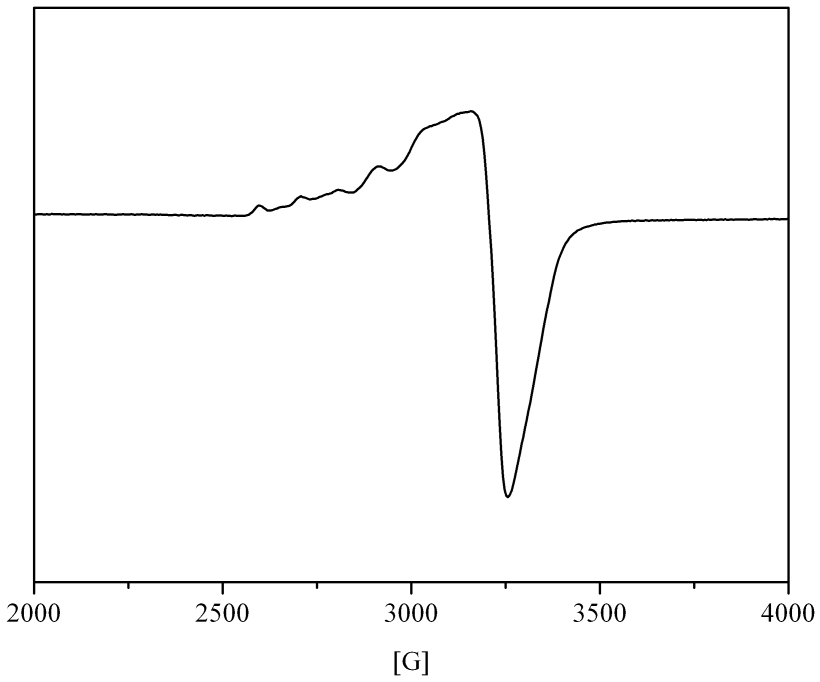

Figure S16. EPR spectrum of [{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$] in MeOH solution at 77 K.

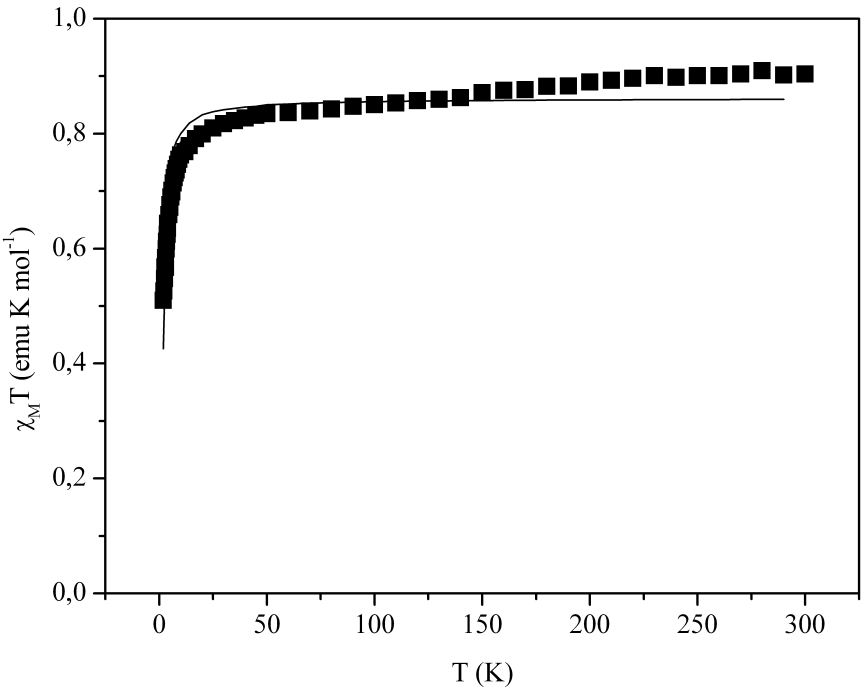

Figure S17**.** Experimental $\chi_M T$ *vs T* data for [{CuCl(PzTz)}$_2$(μ-Cl)$_2$]. Solid line represents the best fit of the data with the model described in the text.

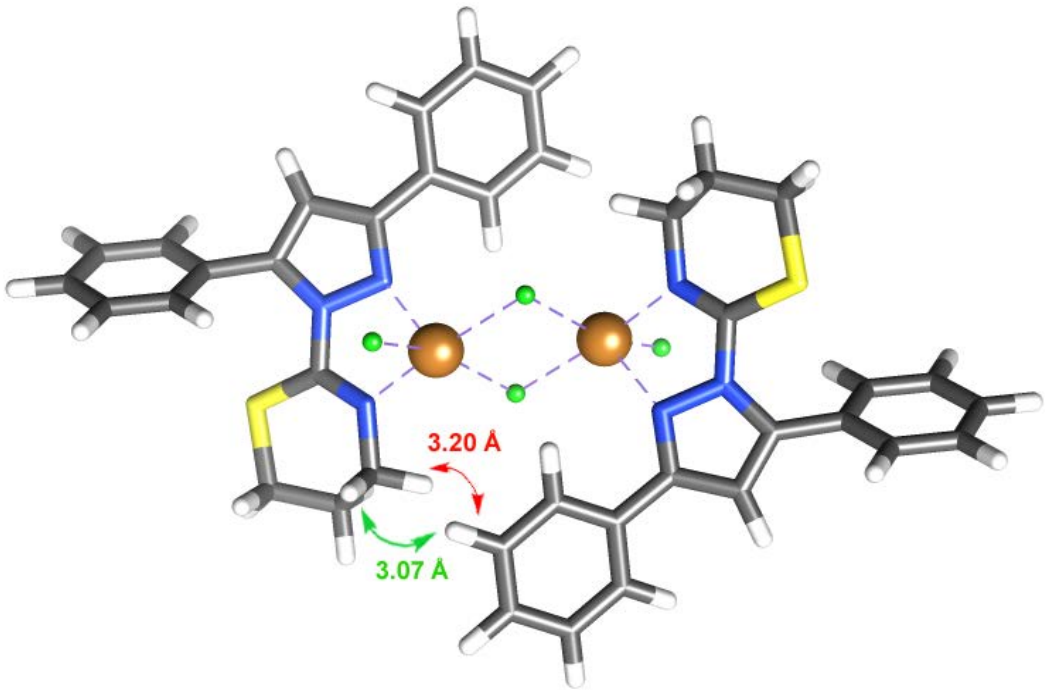

Figure S18**.** Structure of the *cis*-[{CuCl(DPhPzTz)}$_2$(μ-Cl)$_2$] complex optimized at the TPSSh/TZVP level highlighting the short H···H distances involving the phenyl and thiazine moieties.

Table S3. Coupling constant and magnetostructural correlation parameters for selected bis(μ-chloro) copper(II) dimers[a].

Compound	φ (deg)	R (Å)	φ/R (deg Å^{-1})	J (cm^{-1})	Reference
$[CuCl_2(2\text{-pic})_2]_2$	100.6	3.36	29.9	-3.7	2b
$[Cu(C_9H_{10}BrNO_2)Cl]_2\cdot H_2O$	84.66 84.25	2.685 2.669	31.51 (mean)	43.2	4c
$[\{CuCl(DPhPzTz)\}_2(\mu\text{-}Cl)_2]$	87.6	2.675	32.74	-1.01	This work
$[CuCl_2(C_{11}H_{16}N_2O_2)]_2$	92.65	2.827	32.8	-0.47	3a
$[CuCl(terpy)]_2^{2+}$	90.1	2.72	33.0	-3.0	2e
$[Cu(iyda)Cl]_2(ClO_4)_2$	88.81	2.657	33.42	0.58	2a
$[CuCl_2(Mebta)_2]_2$	88.1	2.629	33.5	3.4	3f
$[Cu(pfsa)Cl]_2$	95.27	2.846	33.6	0.15	2p
$[Cu(pmda)Cl]_2(ClO_4)_2$	88.2	2.581	34.17	1.12	2f
$[\{CuCl(DMPzTz)\}_2(\mu\text{-}Cl)_2]$	89.3	2.580	34.61	-0.32	This work
$[CuCl_2(Et_3en)]_2$	94.8	2.728	34.75	0.03	2c
$[\{CuCl(PzTz)\}_2(\mu\text{-}Cl)_2]$	98.6	2.795	35.28	0.48	This work
$[Cu(dpt)Cl]_2Cl_2$	91.4	2.545	35.91	42.94	2l
$[CuCl(Mebta)_3]_2^{2+}$	92.9	2.554	36.5	5.2	3f
$[CuCl(C_{13}H_{11}N_2O)]_2$	90.77	2.444	36.51	0.7	2j
$[CuCl_3]$ $(i\text{-}PrNH_3)_2$	95.5	2.315	41.34	19.46	4a

[a] Abbreviations: 2-pic, 2-methylpyridine; $C_9H_9BrNO_2$, 2-(E)-(2-hydroxyethylimino)methyl)-4-bromophenolate anion; $C_{11}H_{16}N_2O_2$, 5-[(pyridin-2-ylmethylene)-amino]-pentan-1-ol; terpy, 2,2':6',2''-terpyridine; iyda, 1-(imidazol-4-ylmethyl)-1,5-diazacyclooctane; Mebta, 1-methylbenzotriazole; pfsa, 3-[N-2-(pyridylethyl)formimidoyl]salicylic acid; pmda, 1-(2-pyridylmethyl)-1,5-diazacyclooctane; Et_3en, N,N,N-triethylenediamine; dpt, dipropylenetriamine; $C_{13}H_{11}N_2O$, 2-methyl-6-[(pyridine-2-ylmethylene)amino]phenolate anion; i-Pr, isopropyl.

Table S4. Comparison of experimental (X-ray) and calculated (TPSSh/TZVP) bond distances (Å) of the metal coordination environments in **[$CuCl_2L$]** systems.

[$CuCl_2L$]	**PzTz**	**DMPzTz**		**DPhPzTz**
	Calc.	**Exp.**	**Calc.**	**Calc.**
Cu-N(1)	1.997	1.9849(14)	2.003	2.005
Cu-N(3)	2.066	1.9926(15)	2.021	2.035
Cu-Cl(1)	2.272	2.2029(5)	2.266	2.262
Cu-Cl(2)	2.250	2.2371(4)	2.260	2.251

Table S5. Comparison of experimental (X-ray) and calculated (TPSSh/TZVP) bond distances (Å) of the metal coordination environments in *cis*-**[{CuClL}$_2$(μ-Cl$_2$)]** systems.

	PzTz		**DMPzTz**		**DPhPzTz**
	Exp.	**Calc.**	**Exp.**	**Calc.**	**Calc.**
Cu-N(1)	2.051(3)	2.067	1.998(4)	2.022	2.023
Cu-N(3)	1.988(3)	2.016	2.028(2)	2.053	2.295
Cu-Cl(1)	2.2920(8)	2.326	2.2727(7)	2.309	2.335
Cu-Cl(2)	2.2275(8)	2.280	2.2637(8)	2.312	2.306
Cu-Cl(1a)	2.795(-)	2.679	2.5799(8)	2.672	2.385

Table S6. Comparison of experimental (X-ray) and calculated (TPSSh/TZVP) bond distances (Å) of the metal coordination environments in *trans*-**[{CuClL}$_2$(μ-Cl$_2$)]** systems.

	PzTz	**DMPzTz**		**DPhPzTz**
	Calc.	**Calc.**	**Exp.**	**Calc.**
Cu-N(1)	2.096	2.072	2.022(3)	2.059
Cu-N(3)	2.002	2.011	2.026(3)	2.049
Cu-Cl(1)	2.298	2.319	2.2817(12)	2.332
Cu-Cl(2)	2.303	2.308	2.2444(12)	2.290
Cu-Cl(1a)	2.718	2.663	2.675 (2)	2.681

Table S7. Comparison of experimental and calculated exchange coupling constants [J, cm^{-1}] of the *cis* and *trans* isomers of **[{CuCl(PzTz)}$_2$(μ-Cl$_2$)].**

	***trans*-[{CuCl(PzTz)}$_2$(μ-Cl$_2$)]**	***cis*-[{CuCl(PzTz)}$_2$(μ-Cl$_2$)]**
BLYP	16.97	7.97
TPSS	14.55	6.99
TPSSh	9.49	4.21
B3LYP	8.09	3.25
TPSS0	5.13	1.83
BHLYP	2.55	0.76
CASSCF	0.50	0.30
CASSCF/NEVPT2	0.20	-0.1
Experimental	1.09[a]	-1.0 (-0.32)[b]

[a] Value determined for *trans*-[CuCl(DPhPzTz)](μ-Cl$_2$). [b] Value determined for *cis*-[CuCl(DMPzTz)](μ-Cl$_2$).

Table S8. Optimized Cartesian coordinates (Å) calculated for **[CuCl$_2$(PzTz)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.441823	0.340696	-0.050430
2	6	-1.308775	-2.056895	0.115529
3	1	-0.605457	-2.661704	0.684310
4	1	-1.346370	-2.477157	-0.893345
5	6	-2.685648	-2.074487	0.764444
6	1	-3.037539	-3.109094	0.785277
7	1	-2.621630	-1.724805	1.797640
8	6	-3.694131	-1.244607	-0.009283
9	1	-4.667494	-1.218976	0.478499
10	1	-3.813511	-1.592336	-1.034280
11	6	1.058729	2.742198	-0.086173
12	6	-0.021898	3.639905	-0.186566
13	1	0.022432	4.714246	-0.245972
14	6	-1.152035	2.858981	-0.193446
15	17	3.418996	0.296047	0.540832
16	17	1.883688	-2.476395	-0.600706
17	29	1.320998	-0.378480	-0.011739
18	7	-0.717517	-0.714819	0.016790
19	7	-0.736940	1.561649	-0.100979
20	7	0.620059	1.491462	-0.033592
21	16	-3.187039	0.528862	-0.075828
22	1	-2.197106	3.113811	-0.255800
23	1	2.119004	2.933251	-0.044760

E(UTPSSh) = -3395.8969876 Hartree
Zero-point correction = 0.162792
Thermal correction to Energy = 0.177715
Thermal correction to Enthalpy = 0.178659

Thermal correction to Gibbs Free Energy = 0.117503
Sum of electronic and zero-point Energies = -3395.734195
Sum of electronic and thermal Energies = -3395.719273
Sum of electronic and thermal Enthalpies = -3395.718329
Sum of electronic and thermal Free Energies = -3395.779485

Table S9. Optimized Cartesian coordinates (Å) calculated for **[$CuCl_2$(DMPzTz)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.422756	-0.093472	-0.003152
2	6	-0.944501	-2.472022	0.052538
3	1	-0.124207	-2.982751	0.553910
4	1	-0.982528	-2.858373	-0.969657
5	6	-2.256851	-2.726646	0.777251
6	1	-2.450631	-3.802192	0.764002
7	1	-2.182837	-2.413899	1.821485
8	6	-3.411289	-2.019496	0.095152
9	1	-4.352896	-2.155884	0.625729
10	1	-3.533358	-2.337486	-0.939303
11	6	0.807822	2.570011	-0.183153
12	6	-0.372985	3.340366	-0.236048
13	1	-0.439217	4.412466	-0.327107
14	6	-1.435784	2.475483	-0.154306
15	6	2.216115	3.046385	-0.267475
16	1	2.405392	3.795921	0.504570
17	1	2.385949	3.521217	-1.237436
18	1	2.912199	2.219836	-0.139001
19	6	-2.885221	2.819787	-0.174976
20	1	-2.967852	3.902125	-0.269542
21	1	-3.389677	2.515191	0.744222
22	1	-3.401967	2.358874	-1.019298
23	17	3.225992	-0.053240	1.200441
24	17	2.180844	-2.299354	-1.157239
25	29	1.379384	-0.511463	-0.030517
26	7	-0.568077	-1.053117	-0.021551
27	7	-0.884175	1.209189	-0.049044
28	7	0.492331	1.283582	-0.065684
29	16	-3.177787	-0.191779	0.097309

E(UTPSSh) = -3474.5648064 Hartree
Zero-point correction = 0.217664
Thermal correction to Energy = 0.236064
Thermal correction to Enthalpy = 0.237008
Thermal correction to Gibbs Free Energy = 0.168303
Sum of electronic and zero-point Energies = -3474.347142
Sum of electronic and thermal Energies = -3474.328742
Sum of electronic and thermal Enthalpies = -3474.327798
Sum of electronic and thermal Free Energies = -3474.396504

Table S10. Optimized Cartesian coordinates (Å) calculated for **[$CuCl_2$(DPhPzTz)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.289126	1.093922	0.206427
2	6	-0.772873	3.464463	0.244899
3	1	-0.104245	4.004780	-0.423204
4	1	-0.515138	3.768067	1.263450
5	6	-2.225024	3.789670	-0.065683
6	1	-2.378302	4.857578	0.110005
7	1	-2.445785	3.590971	-1.117134
8	6	-3.170373	3.008628	0.827091
9	1	-4.216424	3.212239	0.601319
10	1	-2.987619	3.199939	1.883886
11	6	0.901042	-1.609287	0.175997
12	6	-0.290199	-2.366418	0.121639
13	1	-0.381779	-3.439721	0.135108
14	6	-1.333236	-1.473907	0.047557
15	17	2.917515	0.801101	-1.874295
16	17	2.558308	3.298981	0.461710
17	29	1.485051	1.452198	-0.249132
18	7	-0.428411	2.042570	0.111001
19	7	-0.762237	-0.214884	0.067142
20	7	0.603795	-0.308184	0.128885
21	16	-3.013332	1.192775	0.544725
22	6	2.272907	-2.100754	0.317990
23	6	3.227775	-1.368323	1.036032
24	6	2.630802	-3.336767	-0.237192
25	6	4.520536	-1.857673	1.180392
26	1	2.951174	-0.425965	1.494427
27	6	3.926322	-3.820791	-0.092081
28	1	1.901273	-3.908492	-0.799440
29	6	4.873972	-3.082621	0.615420
30	1	5.251408	-1.286257	1.741035
31	1	4.196670	-4.773087	-0.533643
32	1	5.882844	-3.462448	0.730340
33	6	-2.768052	-1.777231	-0.095953
34	6	-3.434576	-2.467276	0.923107
35	6	-3.441469	-1.476178	-1.287362
36	6	-4.768593	-2.828604	0.761380
37	1	-2.910088	-2.707729	1.840542
38	6	-4.772573	-1.845272	-1.444160
39	1	-2.920543	-0.963420	-2.087796
40	6	-5.438920	-2.517347	-0.420057
41	1	-5.282470	-3.355585	1.557026
42	1	-5.287978	-1.613712	-2.369118
43	1	-6.477247	-2.802602	-0.545496

E(UTPSSh) = -3858.1794111 Hartree
Zero-point correction = 0.322660
Thermal correction to Energy = 0.347494
Thermal correction to Enthalpy = 0.348439
Thermal correction to Gibbs Free Energy = 0.263171
Sum of electronic and zero-point Energies = -3857.856751
Sum of electronic and thermal Energies = -3857.831917
Sum of electronic and thermal Enthalpies = -3857.830972
Sum of electronic and thermal Free Energies = -3857.916240

Table S11. Optimized Cartesian coordinates (Å) calculated for ***cis*-[{CuCl(PzTz)}$_2$(μ-Cl$_2$)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.146032	-0.294992	-0.071396
2	6	3.802876	2.090691	-0.068079
3	1	2.905833	2.630226	0.231143
4	1	4.122851	2.511796	-1.024853
5	6	4.891917	2.232907	0.985966
6	1	4.519021	1.910432	1.961039
7	1	5.152091	3.291764	1.063329
8	6	6.146436	1.457298	0.624191
9	1	6.913260	1.533732	1.393811
10	1	6.563597	1.770117	-0.331945
11	6	1.961169	-2.882312	-0.810127
12	1	0.963140	-3.156223	-1.111558
13	6	3.070979	-3.695064	-0.504619
14	1	3.120141	-4.770748	-0.521607
15	6	4.085520	-2.827789	-0.181164
16	1	5.108375	-2.999091	0.110982
17	17	-0.584672	-0.664456	-1.547956
18	17	1.146561	2.211926	-2.026488
19	29	1.474233	0.233072	-0.942071
20	7	3.385173	0.704969	-0.312877
21	7	3.577148	-1.565569	-0.295545
22	7	2.272343	-1.600044	-0.681447
23	16	5.799991	-0.351628	0.523452
24	6	-4.146036	0.295006	0.071397
25	6	-3.802906	-2.090681	0.068102
26	1	-2.905877	-2.630222	-0.231149
27	1	-4.122848	-2.511781	1.024890
28	6	-4.891986	-2.232900	-0.985904
29	1	-4.519120	-1.910447	-1.960996
30	1	-5.152176	-3.291755	-1.063240
31	6	-6.146483	-1.457269	-0.624099
32	1	-6.913335	-1.533709	-1.393689
33	1	-6.563612	-1.770066	0.332058
34	6	-1.961146	2.882300	0.810131
35	1	-0.963111	3.156200	1.111553
36	6	-3.070877	3.695072	0.504392
37	1	-3.119971	4.770761	0.521191
38	6	-4.085519	2.827800	0.181244
39	1	-5.108390	2.999114	-0.110838
40	17	0.584685	0.664409	1.547943
41	17	-1.146551	-2.211941	2.026452
42	29	-1.474227	-0.233070	0.942064
43	7	-3.385187	-0.704962	0.312872
44	7	-3.577139	1.565577	0.295547
45	7	-2.272329	1.600036	0.681432
46	16	-5.800015	0.351655	-0.523403

E(UTPSSh) = -6791.803126 Hartree
Zero-point correction = 0.326371
Thermal correction to Energy = 0.358208
Thermal correction to Enthalpy = 0.359152
Thermal correction to Gibbs Free Energy = 0.257253
Sum of electronic and zero-point Energies = -6791.476755
Sum of electronic and thermal Energies = -6791.444918
Sum of electronic and thermal Enthalpies = -6791.443974
Sum of electronic and thermal Free Energies = -6791.545873

Table S12. Optimized Cartesian coordinates (Å) calculated for ***trans*-[{CuCl(PzTz)}$_2$(μ-Cl$_2$)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.368926	0.030016	3.130844
2	6	2.093173	-1.939438	1.776852
3	1	3.029722	-2.160692	1.255713
4	1	1.278078	-2.162827	1.091172
5	6	1.960213	-2.776315	3.040484
6	1	2.041035	-3.829024	2.757017
7	1	0.973421	-2.629342	3.485554
8	6	3.043965	-2.470238	4.058119
9	1	4.043689	-2.633667	3.658193
10	1	2.924170	-3.045589	4.974985
11	6	1.800996	3.376204	2.419402
12	6	2.195408	3.564518	3.758513
13	1	2.267397	4.495036	4.295806
14	6	2.476973	2.309242	4.240486
15	17	-1.194611	0.663309	1.129361
16	17	1.562976	2.676129	-0.904607
17	29	1.450188	0.889952	0.545228
18	7	2.051163	-0.488195	2.004881
19	7	2.247621	1.433279	3.218580
20	7	1.834302	2.089300	2.102133
21	16	2.944053	-0.716333	4.617039
22	6	-2.368926	-0.030016	-3.130844
23	6	-2.093173	1.939438	-1.776852
24	1	-3.029722	2.160692	-1.255713
25	1	-1.278078	2.162827	-1.091172
26	6	-1.960213	2.776315	-3.040484
27	1	-2.041035	3.829024	-2.757017
28	1	-0.973421	2.629342	-3.485554
29	6	-3.043965	2.470238	-4.058119
30	1	-4.043689	2.633667	-3.658193
31	1	-2.924170	3.045589	-4.974985
32	6	-1.800996	-3.376204	-2.419402
33	6	-2.195408	-3.564518	-3.758513
34	1	-2.267397	-4.495036	-4.295806
35	6	-2.476973	-2.309242	-4.240486
36	17	1.194611	-0.663309	-1.129361
37	17	-1.562976	-2.676129	0.904607
38	29	-1.450188	-0.889952	-0.545228
39	7	-2.051163	0.488195	-2.004881
40	7	-2.247621	-1.433279	-3.218580
41	7	-1.834302	-2.089300	-2.102133
42	16	-2.944053	0.716333	-4.617039
43	1	1.506973	4.096664	1.673424
44	1	2.816879	1.972425	5.205863
45	1	-2.816879	-1.972425	-5.205863
46	1	-1.506973	-4.096664	-1.673424

E(UTPSSh) = -6791.801687 Hartree
Zero-point correction = 0.326341
Thermal correction to Energy = 0.358204
Thermal correction to Enthalpy = 0.359148
Thermal correction to Gibbs Free Energy = 0.257115
Sum of electronic and zero-point Energies = -6791.475346
Sum of electronic and thermal Energies = -6791.443483
Sum of electronic and thermal Enthalpies = -6791.442539
Sum of electronic and thermal Free Energies = -6791.544572

Table S13. Optimized Cartesian coordinates (Å) calculated for ***cis*-[{CuCl(DMPzTz)}$_2$(μ-Cl$_2$)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	17	-0.472824	0.975665	1.326368
2	17	1.117314	-1.677066	2.633809
3	6	6.207828	2.236870	-0.510100
4	1	6.832940	1.704640	0.209440
5	1	6.529400	3.277594	-0.543077
6	1	6.369780	1.797455	-1.496537
7	6	1.492592	3.645208	0.811373
8	1	1.127482	3.410312	1.811859
9	1	0.676386	3.454121	0.113624
10	1	1.761053	4.700603	0.766994
11	29	1.529081	-0.119575	0.975127
12	16	5.791956	-0.754054	-0.581903
13	7	3.240202	-1.031008	0.402192
14	7	3.971678	1.111873	0.095662
15	6	4.207966	-0.276782	0.031081
16	7	2.693675	1.489839	0.459153
17	6	3.282482	-2.497531	0.336085
18	1	2.261025	-2.818686	0.139545
19	1	3.550240	-2.865259	1.329628
20	6	4.228252	-3.044660	-0.721018
21	1	4.198427	-4.136290	-0.672066
22	1	3.899705	-2.746096	-1.719418
23	6	3.962018	3.306753	0.113303
24	1	4.257550	4.340719	0.037635
25	6	5.652452	-2.587246	-0.475658
26	1	6.341241	-2.939308	-1.242830
27	1	6.018517	-2.894613	0.503169
28	6	4.769200	2.221060	-0.119495
29	6	2.688176	2.821995	0.470201
30	17	0.472738	-0.977148	-1.325078
31	17	-1.115498	1.676812	-2.632412
32	6	-6.209534	-2.235678	0.507189
33	1	-6.833881	-1.702752	-0.212491
34	1	-6.531650	-3.276259	0.539405
35	1	-6.371948	-1.796703	1.493747
36	6	-1.493892	-3.645768	-0.810953
37	1	-1.128530	-3.411678	-1.811549
38	1	-0.677824	-3.454250	-0.113174
39	1	-1.762522	-4.701090	-0.765893
40	29	-1.528726	0.119044	-0.974254
41	16	-5.792060	0.755110	0.580803
42	7	-3.239714	1.031109	-0.402006
43	7	-3.972402	-1.111510	-0.096554
44	6	-4.208045	0.277243	-0.031646
45	7	-2.694305	-1.489975	-0.459209
46	6	-3.281307	2.497633	-0.335517
47	1	-2.259784	2.818236	-0.138400
48	1	-3.548402	2.865746	-1.329097
49	6	-4.227307	3.044945	0.721284
50	1	-4.196953	4.136573	0.672602
51	1	-3.899340	2.746001	1.719761
52	6	-3.963772	-3.306394	-0.114901
53	1	-4.259841	-4.340246	-0.039762
54	6	-5.651616	2.588275	0.475195
55	1	-6.340543	2.940427	1.242201
56	1	-6.017151	2.896121	-0.503680
57	6	-4.770622	-2.220392	0.117611
58	6	-2.689428	-2.822127	-0.470653

E(UTPSSh) = -6949.13326369 Hartree

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Zero-point correction = 0.436403
Thermal correction to Energy = 0.475096
Thermal correction to Enthalpy = 0.476040
Thermal correction to Gibbs Free Energy = 0.358218
Sum of electronic and zero-point Energies = -6948.696861
Sum of electronic and thermal Energies = -6948.658168
Sum of electronic and thermal Enthalpies = -6948.657223
Sum of electronic and thermal Free Energies = -6948.775046
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Table S14. Optimized Cartesian coordinates (Å) calculated for ***trans*-[{CuCl(DMPzTz)}$_2$(μ-Cl$_2$)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.602680	0.011731	3.123010
2	6	2.099062	-1.972896	1.833387
3	1	2.937093	-2.228145	1.178159
4	1	1.186597	-2.169769	1.273577
5	6	2.131710	-2.808583	3.102607
6	1	2.137683	-3.862872	2.813676
7	1	1.232458	-2.632276	3.697832
8	6	3.370666	-2.521824	3.927859
9	1	4.288116	-2.703460	3.369199
10	1	3.396220	-3.093479	4.854831
11	6	1.626187	3.294117	2.535006
12	6	2.229670	3.525720	3.789143
13	1	2.267320	4.461412	4.323318
14	6	2.759433	2.334621	4.220024
15	6	0.895101	4.272421	1.682264
16	6	3.500310	2.084021	5.489063
17	17	-1.149187	0.785424	1.028166
18	17	2.001486	2.430628	-0.953693
19	29	1.481055	0.817725	0.613610
20	7	2.132763	-0.520852	2.054723
21	7	2.471992	1.414551	3.225470
22	7	1.781355	2.018337	2.199121
23	16	3.386171	-0.771893	4.496819
24	6	-2.602680	-0.011731	-3.123010
25	6	-2.099062	1.972896	-1.833387
26	1	-2.937093	2.228145	-1.178159
27	1	-1.186597	2.169769	-1.273577
28	6	-2.131710	2.808583	-3.102607
29	1	-2.137683	3.862872	-2.813676
30	1	-1.232458	2.632276	-3.697832
31	6	-3.370666	2.521824	-3.927859
32	1	-4.288116	2.703460	-3.369199
33	1	-3.396220	3.093479	-4.854831
34	6	-1.626187	-3.294117	-2.535006
35	6	-2.229670	-3.525720	-3.789143
36	1	-2.267320	-4.461412	-4.323318
37	6	-2.759433	-2.334621	-4.220024
38	6	-0.895101	-4.272421	-1.682264
39	6	-3.500310	-2.084021	-5.489063
40	17	1.149187	-0.785424	-1.028166
41	17	-2.001486	-2.430628	0.953693
42	29	-1.481055	-0.817725	-0.613610
43	7	-2.132763	0.520852	-2.054723
44	7	-2.471992	-1.414551	-3.225470
45	7	-1.781355	-2.018337	-2.199121
46	16	-3.386171	0.771893	-4.496819
47	1	1.598741	4.864252	1.092042
48	1	0.223972	3.760570	0.995726

49	1	0.326035	4.953582	2.317735
50	1	3.615063	3.039992	5.999524
51	1	2.960353	1.404947	6.152266
52	1	4.493038	1.668247	5.306615
53	1	-2.960353	-1.404947	-6.152266
54	1	-3.615063	-3.039992	-5.999524
55	1	-4.493038	-1.668247	-5.306615
56	1	-0.223972	-3.760570	-0.995726
57	1	-1.598741	-4.864252	-1.092042
58	1	-0.326035	-4.953582	-2.317735

E(UTPSSh) = -6949.13329011 Hartree
Zero-point correction = 0.436309
Thermal correction to Energy = 0.475038
Thermal correction to Enthalpy = 0.475983
Thermal correction to Gibbs Free Energy = 0.358361
Sum of electronic and zero-point Energies = -6948.696982
Sum of electronic and thermal Energies = -6948.658252
Sum of electronic and thermal Enthalpies = -6948.657307
Sum of electronic and thermal Free Energies = -6948.774929

Table S15. Optimized Cartesian coordinates (Å) calculated for ***cis*-[{CuCl(DPhPzTz)}$_2$(μ-Cl$_2$)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	17	0.165575	-0.858487	1.331886
2	17	-2.511579	0.672399	2.617473
3	29	-1.613978	0.409461	0.509371
4	16	-5.567898	1.819362	-1.327517
5	7	-3.037563	1.617850	-0.268988
6	7	-4.282729	-0.306308	-0.331867
7	6	-4.165276	1.084564	-0.558725
8	7	-3.126291	-1.036175	-0.433425
9	6	-2.730243	3.034320	-0.503716
10	1	-1.660263	3.092055	-0.698427
11	1	-2.924319	3.565199	0.433328
12	6	-3.509741	3.661922	-1.650843
13	1	-3.226428	4.715647	-1.717044
14	1	-3.240981	3.184422	-2.595932
15	6	-4.894079	-2.405150	-0.103921
16	1	-5.479854	-3.296789	0.048139
17	6	-5.007068	3.572862	-1.424340
18	1	-5.574824	3.977925	-2.261413
19	1	-5.314626	4.075644	-0.508167
20	6	-5.379005	-1.118246	-0.106924
21	6	-3.497107	-2.311832	-0.313300
22	17	-0.165458	0.858263	-1.331991
23	17	2.512008	-0.672249	-2.617310
24	29	1.614258	-0.409610	-0.509324
25	16	5.567820	-1.818817	1.328715
26	7	3.037810	-1.617931	0.269244
27	7	4.282717	0.306393	0.332172
28	6	4.165363	-1.084436	0.559237
29	7	3.126262	1.036231	0.433697
30	6	2.730701	-3.034389	0.504132
31	1	1.660633	-3.092421	0.698266
32	1	2.925412	-3.565468	-0.432675
33	6	3.509772	-3.661548	1.651811
34	1	3.226569	-4.715291	1.718181
35	1	3.240515	-3.183805	2.596635
36	6	4.893931	2.405169	0.103348
37	1	5.479631	3.296779	-0.049183
38	6	5.007191	-3.572360	1.425950

39	1	5.574626	-3.977032	2.263431
40	1	5.315225	-4.075447	0.510103
41	6	5.378910	1.118281	0.106688
42	6	3.497007	2.311867	0.313039
43	6	-6.747952	-0.663843	0.189087
44	6	-6.997083	0.190830	1.271558
45	6	-7.822236	-1.165862	-0.554051
46	6	-8.301445	0.550700	1.589706
47	1	-6.170316	0.562822	1.866433
48	6	-9.126383	-0.800150	-0.232169
49	1	-7.632217	-1.830615	-1.388932
50	6	-9.368279	0.059515	0.837348
51	1	-8.486305	1.209686	2.430394
52	1	-9.952552	-1.187126	-0.817716
53	1	-10.384477	0.342674	1.087483
54	6	-2.536222	-3.412111	-0.454130
55	6	-1.387570	-3.259924	-1.242723
56	6	-2.782530	-4.646959	0.161248
57	6	-0.504972	-4.321438	-1.408578
58	1	-1.200071	-2.312164	-1.732876
59	6	-1.894426	-5.705114	-0.004253
60	1	-3.662795	-4.776288	0.780869
61	6	-0.754554	-5.546594	-0.790829
62	1	0.375932	-4.194226	-2.027777
63	1	-2.093042	-6.653789	0.481662
64	1	-0.066434	-6.373869	-0.924059
65	6	2.536055	3.412111	0.453667
66	6	2.782090	4.646774	-0.162184
67	6	1.387584	3.260061	1.242550
68	6	1.893871	5.704870	0.003106
69	1	3.662223	4.776006	-0.782011
70	6	0.504868	4.321506	1.408175
71	1	1.200298	2.312451	1.733072
72	6	0.754162	5.546479	0.789944
73	1	2.092277	6.653398	-0.483182
74	1	-0.375886	4.194404	2.027609
75	1	0.065943	6.373702	0.922990
76	6	6.747790	0.663776	-0.189419
77	6	7.822268	1.166427	0.553022
78	6	6.996659	-0.191684	-1.271326
79	6	9.126342	0.800586	0.231004
80	1	7.632451	1.831778	1.387472
81	6	8.300952	-0.551682	-1.589614
82	1	6.169741	-0.564187	-1.865676
83	6	9.367978	-0.059849	-0.837956
84	1	9.952662	1.188057	0.816010
85	1	8.485603	-1.211278	-2.429870
86	1	10.384123	-0.343106	-1.088197

E(UTPSSh) = -7716.36155215 Hartree
Zero-point correction = 0.645903
Thermal correction to Energy = 0.697546
Thermal correction to Enthalpy = 0.698490
Thermal correction to Gibbs Free Energy = 0.547790
Sum of electronic and zero-point Energies = -7715.715649
Sum of electronic and thermal Energies = -7715.664006
Sum of electronic and thermal Enthalpies = -7715.663062
Sum of electronic and thermal Free Energies = -7715.813762

Table S16. Optimized Cartesian coordinates (Å) calculated for ***trans*-[{CuCl(DPhPzTz)}$_2$(μ-Cl$_2$)]** (TPSSh/TZVP; PCM = methanol; 0 Imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.438148	0.132404	3.195424
2	6	1.832332	-1.785643	1.853231
3	1	2.689581	-2.095853	1.248484
4	1	0.941932	-1.906639	1.238711
5	6	1.720633	-2.632258	3.111048
6	1	1.656758	-3.680676	2.808130
7	1	0.803685	-2.387412	3.652565
8	6	2.924995	-2.458208	4.014546
9	1	3.855902	-2.723010	3.514405
10	1	2.839793	-3.031091	4.937479
11	6	1.371725	3.427531	2.908970
12	6	2.227385	3.625146	4.016273
13	1	2.374463	4.537102	4.570671
14	6	2.857077	2.428711	4.260963
15	6	0.458227	4.415772	2.329313
16	6	-0.756595	4.030093	1.748724
17	1	-1.014319	2.979188	1.689623
18	6	-1.630494	4.991330	1.254067
19	1	-2.571242	4.683106	0.811540
20	6	-1.305293	6.345348	1.330598
21	1	-1.989730	7.092267	0.944155
22	6	-0.097919	6.735796	1.907750
23	1	0.163410	7.786256	1.967041
24	6	0.777029	5.778535	2.409806
25	1	1.718429	6.089397	2.848410
26	6	3.908818	2.155873	5.255472
27	6	3.647674	2.370408	6.613568
28	1	2.652239	2.660983	6.928925
29	6	4.658668	2.195694	7.554125
30	1	4.447432	2.355104	8.605269
31	6	5.936286	1.818777	7.145489
32	1	6.723159	1.684779	7.879101
33	6	6.204410	1.620256	5.791201
34	1	7.200607	1.339678	5.468966
35	6	5.198358	1.789189	4.847277
36	1	5.411135	1.645754	3.794142
37	17	-1.293522	0.398934	1.049172
38	17	1.646234	2.871336	-0.596104
39	29	1.288219	1.065055	0.765401
40	7	1.967480	-0.344825	2.103330
41	7	2.365614	1.542174	3.322967
42	7	1.469649	2.163083	2.485456
43	16	3.071505	-0.717129	4.602627
44	6	-2.438148	-0.132404	-3.195424
45	6	-1.832332	1.785643	-1.853231
46	1	-2.689581	2.095853	-1.248484
47	1	-0.941932	1.906639	-1.238711
48	6	-1.720633	2.632258	-3.111048
49	1	-1.656758	3.680676	-2.808130
50	1	-0.803685	2.387412	-3.652565
51	6	-2.924995	2.458208	-4.014546
52	1	-3.855902	2.723010	-3.514405
53	1	-2.839793	3.031091	-4.937479
54	6	-1.371725	-3.427531	-2.908970
55	6	-2.227385	-3.625146	-4.016273
56	1	-2.374463	-4.537102	-4.570671
57	6	-2.857077	-2.428711	-4.260963
58	6	-0.458227	-4.415772	-2.329313
59	6	0.756595	-4.030093	-1.748724
60	1	1.014319	-2.979188	-1.689623

61	6	1.630494	-4.991330	-1.254067
62	1	2.571242	-4.683106	-0.811540
63	6	1.305293	-6.345348	-1.330598
64	1	1.989730	-7.092267	-0.944155
65	6	0.097919	-6.735796	-1.907750
66	1	-0.163410	-7.786256	-1.967041
67	6	-0.777029	-5.778535	-2.409806
68	1	-1.718429	-6.089397	-2.848410
69	6	-3.908818	-2.155873	-5.255472
70	6	-3.647674	-2.370408	-6.613568
71	1	-2.652239	-2.660983	-6.928925
72	6	-4.658668	-2.195694	-7.554125
73	1	-4.447432	-2.355104	-8.605269
74	6	-5.936286	-1.818777	-7.145489
75	1	-6.723159	-1.684779	-7.879101
76	6	-6.204410	-1.620256	-5.791201
77	1	-7.200607	-1.339678	-5.468966
78	6	-5.198358	-1.789189	-4.847277
79	1	-5.411135	-1.645754	-3.794142
80	17	1.293522	-0.398934	-1.049172
81	17	-1.646234	-2.871336	0.596104
82	29	-1.288219	-1.065055	-0.765401
83	7	-1.967480	0.344825	-2.103330
84	7	-2.365614	-1.542174	-3.322967
85	7	-1.469649	-2.163083	-2.485456
86	16	-3.071505	0.717129	-4.602627

E(UTPSSh) = -7716.36280222 Hartree
Zero-point correction = 0.646234
Thermal correction to Energy = 0.697687
Thermal correction to Enthalpy = 0.698631
Thermal correction to Gibbs Free Energy = 0.551203
Sum of electronic and zero-point Energies = -7715.716569
Sum of electronic and thermal Energies = -7715.665115
Sum of electronic and thermal Enthalpies = -7715.664171
Sum of electronic and thermal Free Energies = -7715.811599