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Electronic Supplementary Information

A Ligand in the Metal Salt Sea: Extreme Metal-to-Ligand Ratios and the Thermodynamic Driving Force of the Halogen Bond

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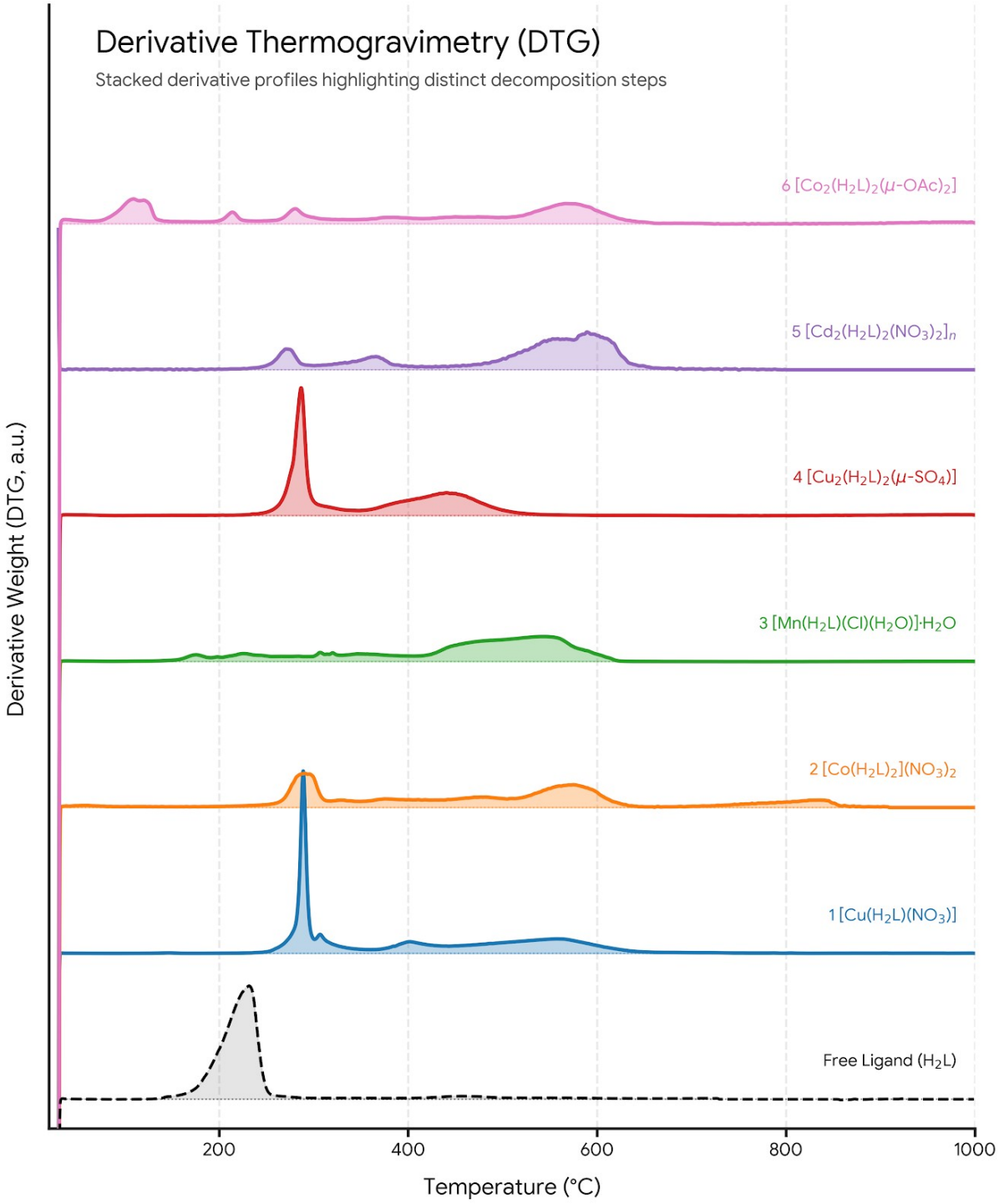
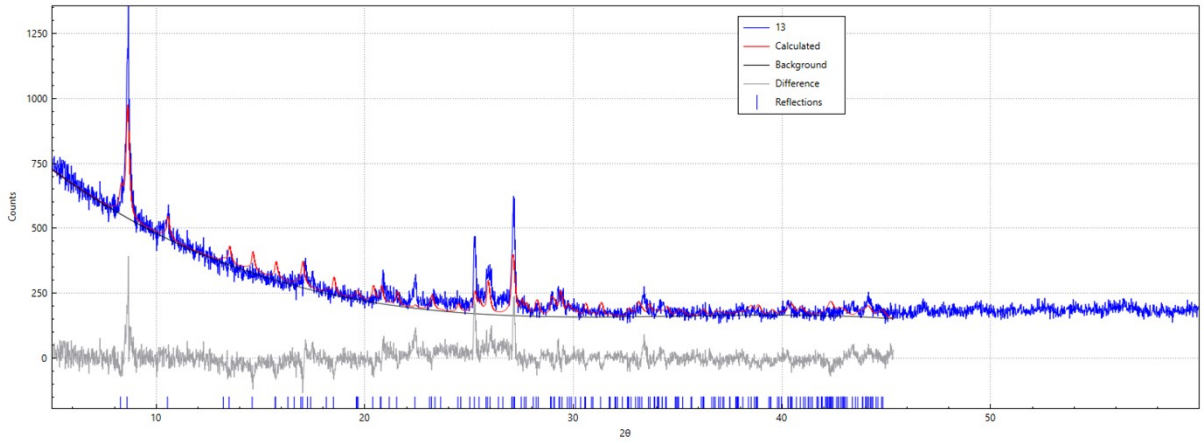


Figure S1. DTG curves of the free ligand and complexes **1–6**



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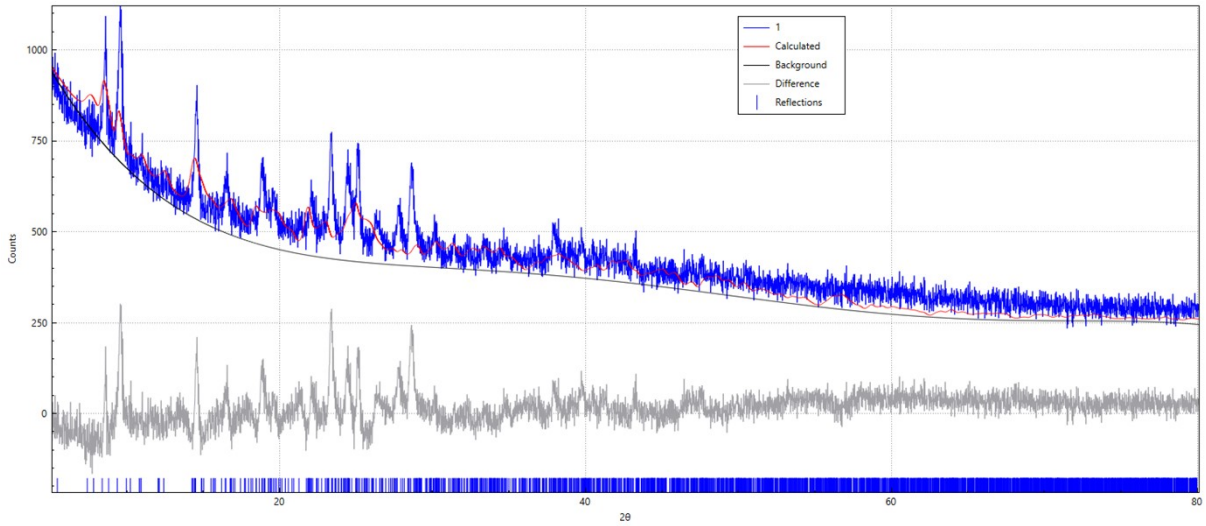

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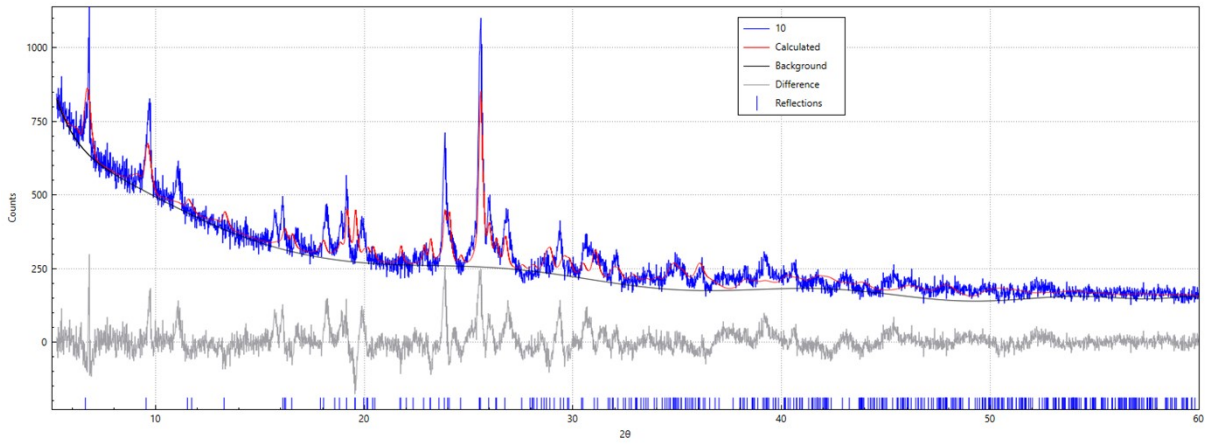

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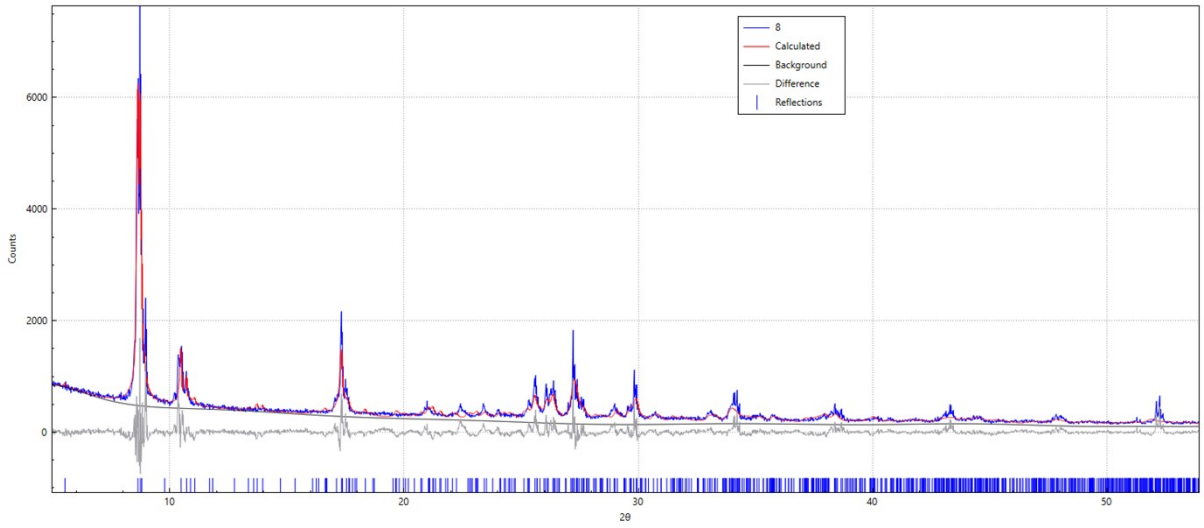

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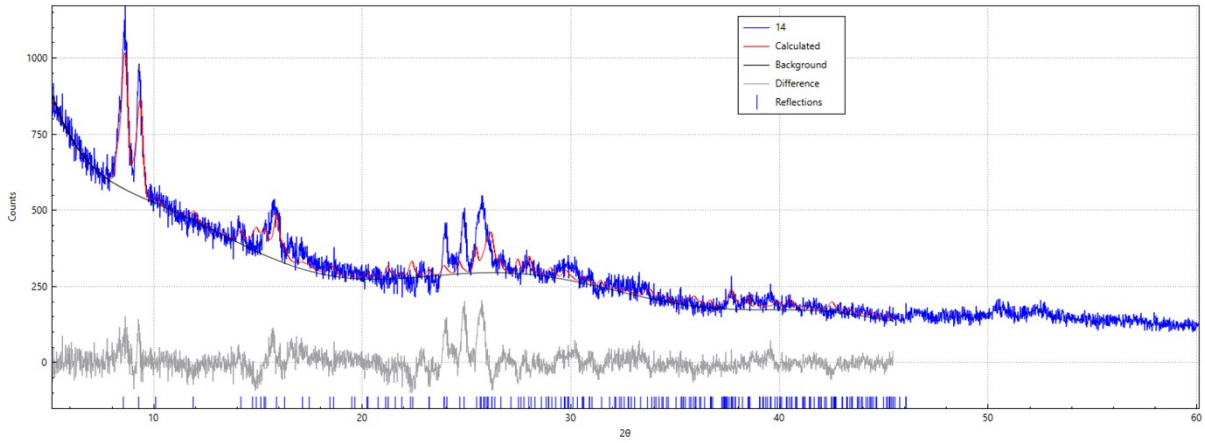

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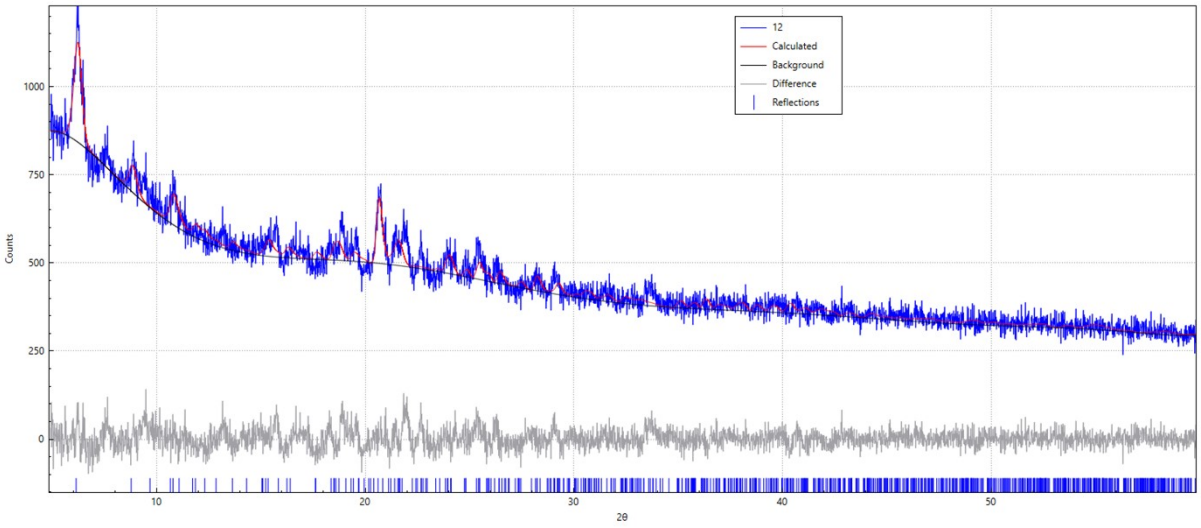


Figure S7. Rietveld refinement profiles for the PXRD data of the complex 6

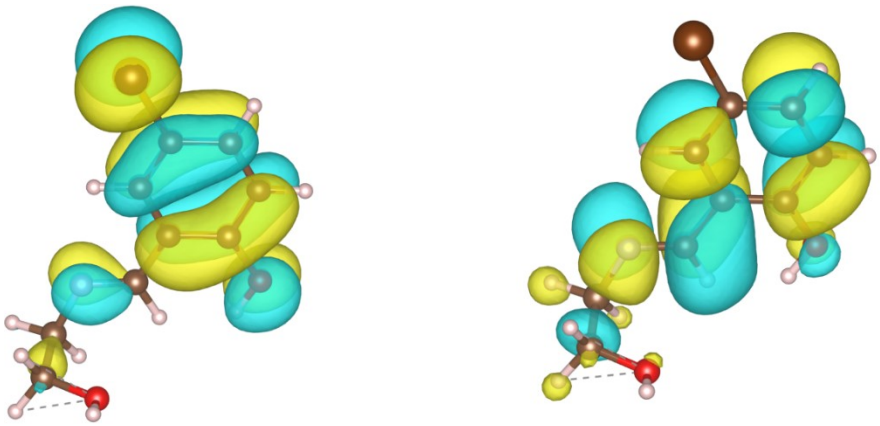
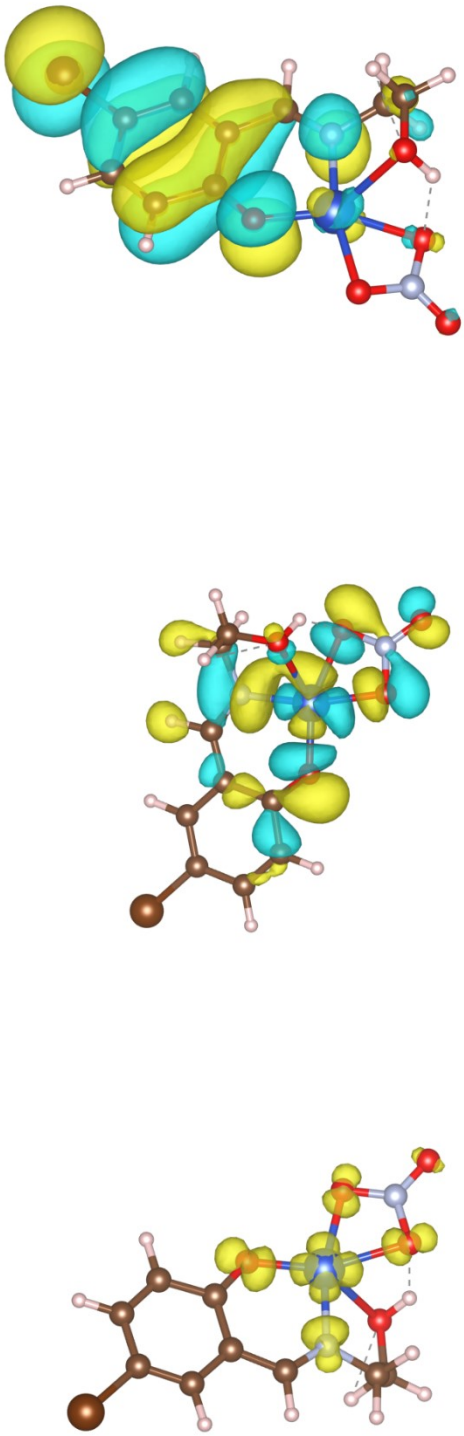


Figure S8. Frontier molecular orbitals (HOMO (left) and LUMO (right)) of the free ligand. The isodensity value is set to 0.02 a.u.



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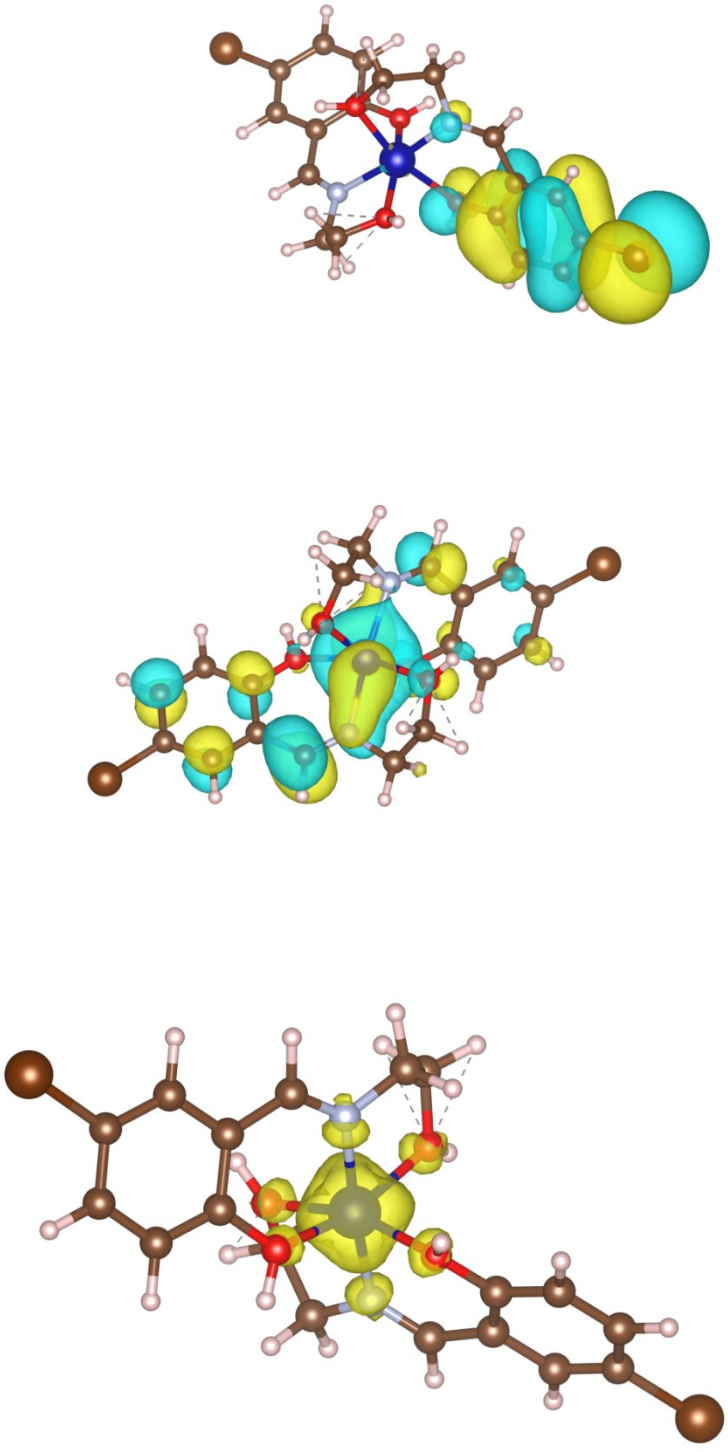
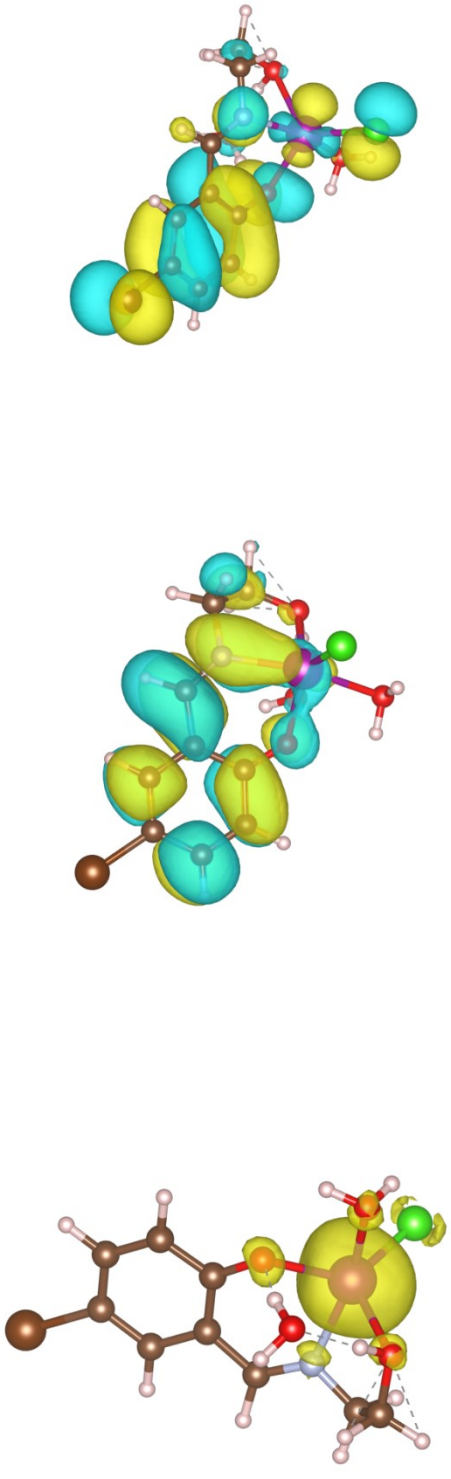


Figure S10. Frontier molecular orbitals (HOMO, LUMO) and spin density; from top to bottom, of the **2**. The isodensity value is set to 0.02 a.u.



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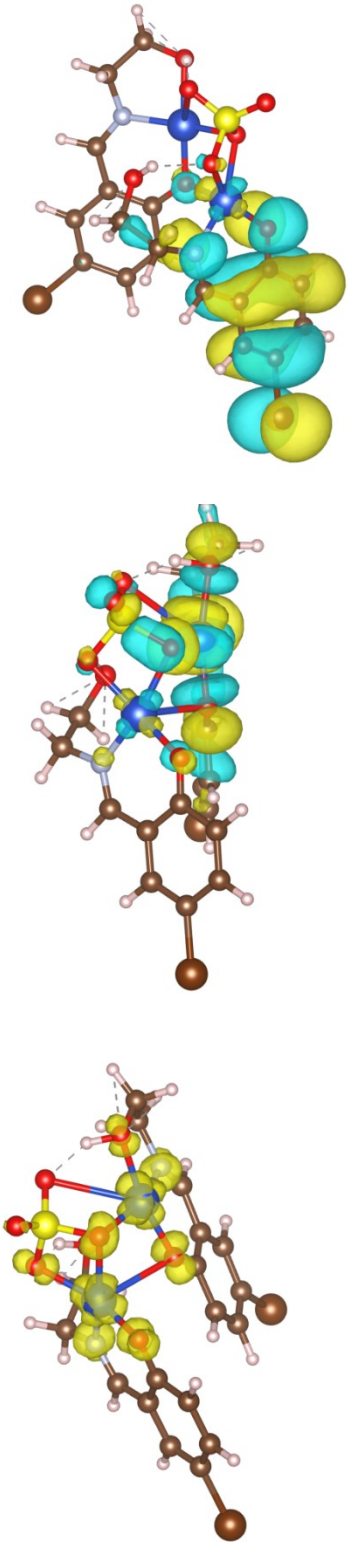

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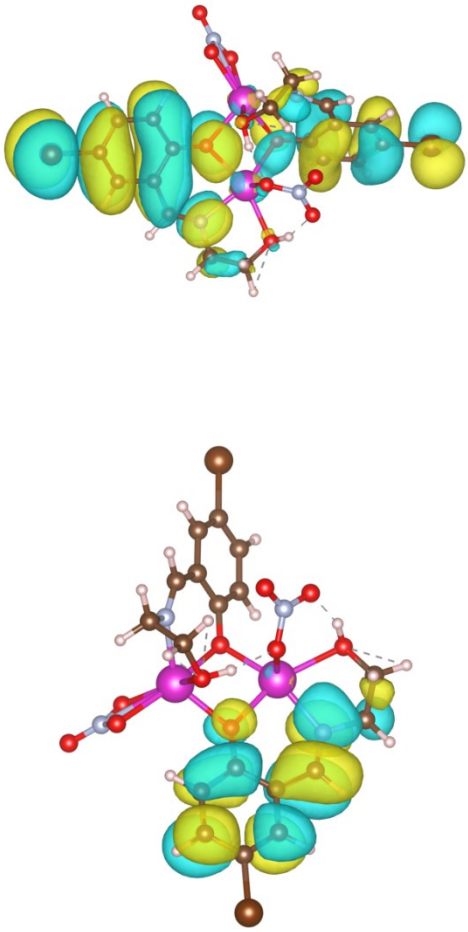
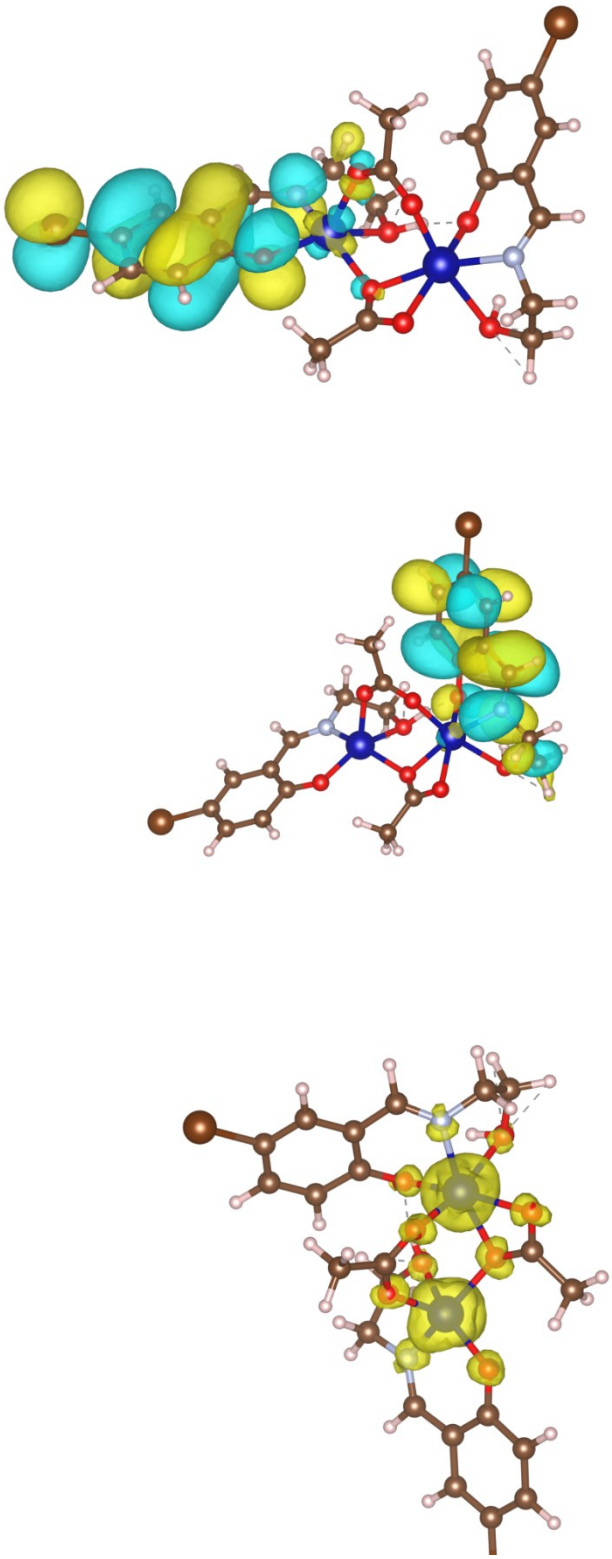


Figure S13. Frontier molecular orbitals (HOMO, LUMO ; from top to bottom) of the **5**. The isodensity value is set to 0.02 a.u



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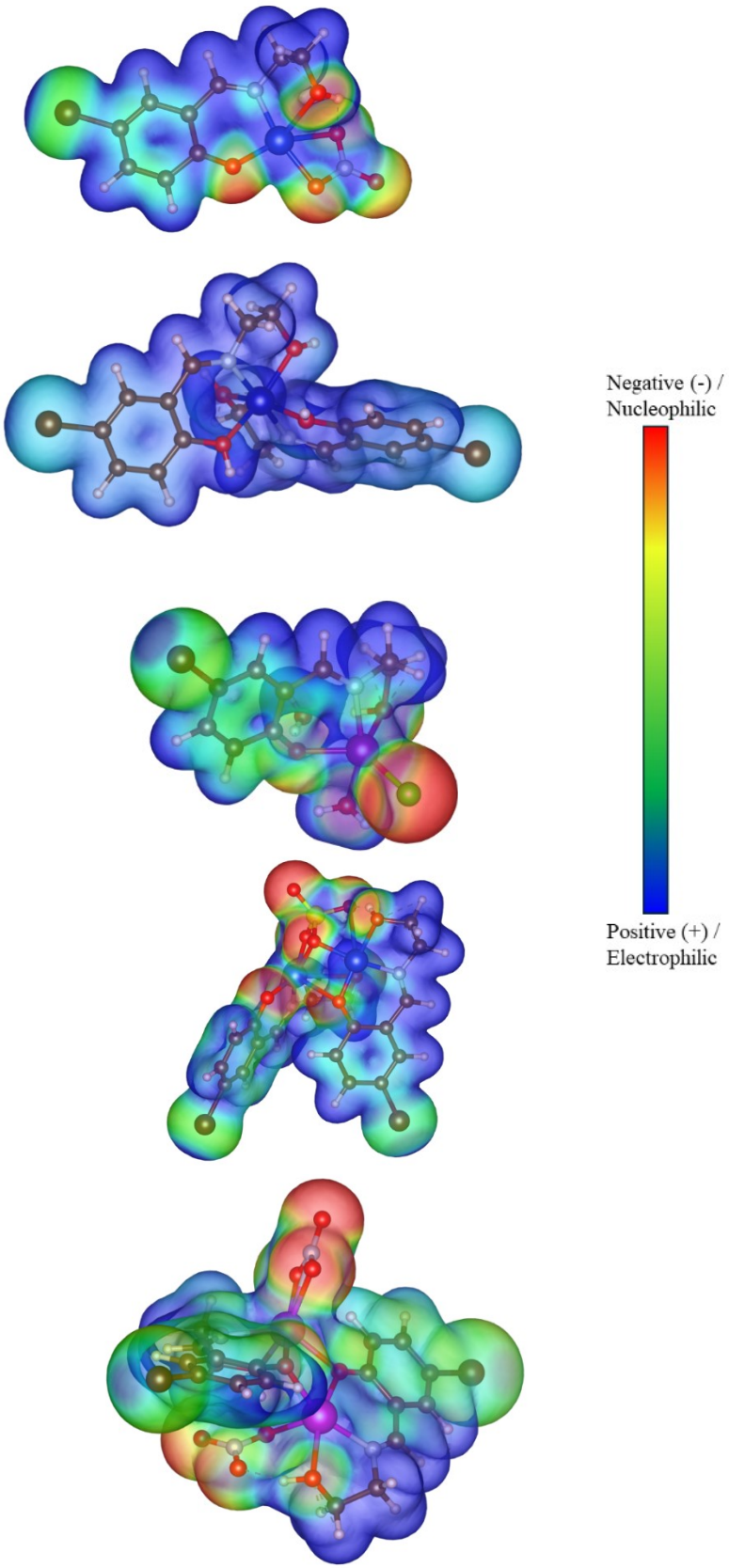
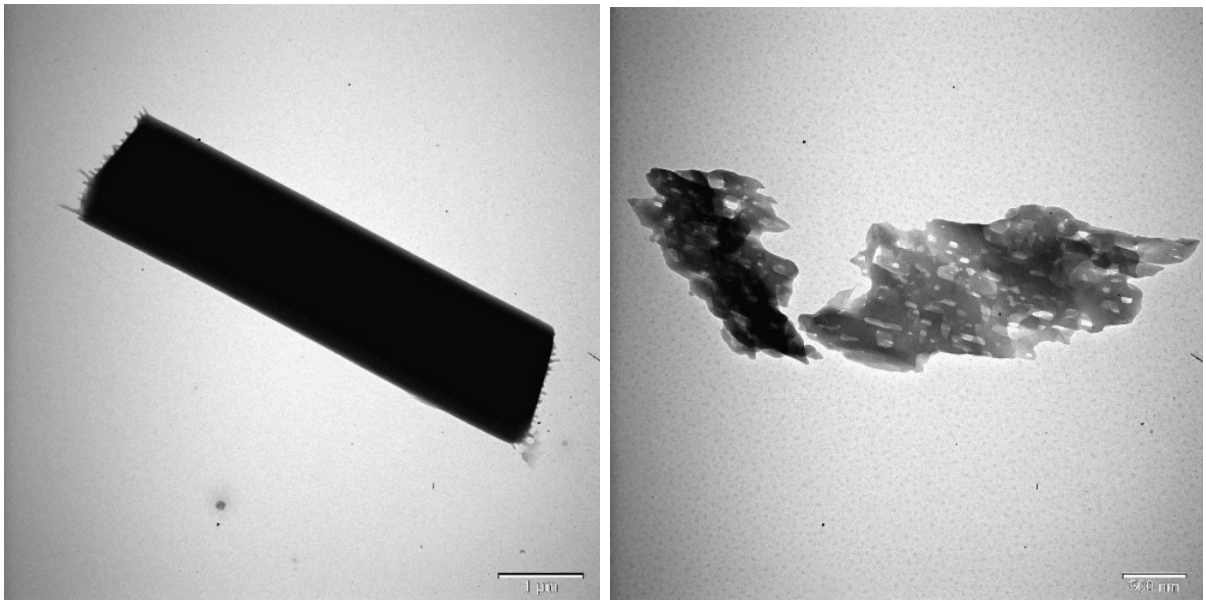
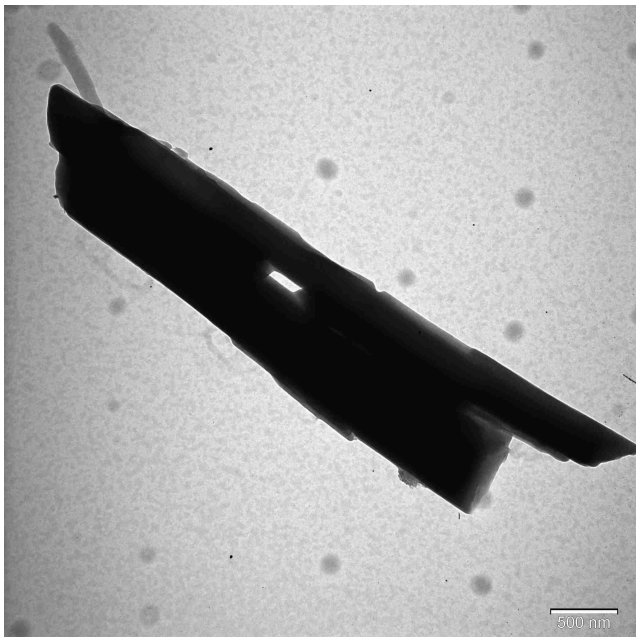


Figure S15. Computed electron density (or Molecular Electrostatic Potential) maps for complexes **1, 2, 3, 4**, and **5;** from top to bottom. The accompanying color scale illustrates the electrostatic potential trend, ranging from negative (nucleophilic) regions in red to positive (electrophilic) regions in blue, with the local surface potentials mapped in kcal/mol. *(Note: The corresponding maps for the free ligand and complex **6** are discussed and provided in the main text).*



a

b



c

Figure S16. Additional TEM images highlighting the morphological heterogeneity and polymorphism in selected coordination complexes (e.g., varying aggregate networks in complex 4 (a) and detailed internal voids in complex 3 (b) and 6 (c))

Table S1. Selected bond lengths (Å) and angles (°) for the complex **1**

Bond Lengths (Å)		**Bond Angles (°)**	
Cu1 – N1	1.945232	N1 – Cu1 – O1	74.89
Cu1 – O1	2.556177	N1 – Cu1 – O2	94.71
Cu1 – O2	1.877715	N1 – Cu1 – O4	164.69
Cu1 – O4	2.031633	N1 – Cu1 – O5	103.94
Cu1 – O5	2.170073	O1 – Cu1 – O2	129.16
		O1 – Cu1 – O4	99.15
		O1 – Cu1 – O5	70.34
		O2 – Cu1 – O4	99.84
		O2 – Cu1 – O5	156.67
		O4 – Cu1 – O5 *(bite)*	60.79

Table S2. Selected bond lengths (Å) and angles (°) for the complex **2**

Bond Lengths (Å)		**Bond Angles (°)**	
Co1 – N1	1.887563	N1 – Co1 – O1	91.05
Co1 – N2	1.889258	N1 – Co1 – O2	91.94
Co1 – O1	1.843560	N1 – Co1 – O3	92.40
Co1 – O2	1.860395	N1 – Co1 – O4	86.39
Co1 – O3	1.844025	N1 – Co1 – N2 *(trans)*	179.58
Co1 – O4	1.878827	N2 – Co1 – O1	89.22
		N2 – Co1 – O2	88.41
		N2 – Co1 – O4	93.35
		O2 – Co1 – O3 *(trans)*	175.60
		O2 – Co1 – O4	94.51
		O1 – Co1 – O2	83.46
		O1 – Co1 – O3	95.80
		O1 – Co1 – O4 *(trans)*	176.68
		O3 – Co1 – N2	87.25
		O1 – Co1 – O4	86.43

Table S3. Selected bond lengths (Å) and angles (°) for the complex **3**

Bond Lengths (Å)		**Bond Angles (°)**	
Mn1 – N1	2.1649	N1 – Mn1 – O1	73.84
Mn1 – Cl1	2.3003	N1 – Mn1 – O2	83.08
Mn1 – O1	2.2815	N1 – Mn1 – O3	152.39
Mn1 – O2	2.0938	O2 – Mn1 – O3	78.97
Mn1 – O3 *(coordinate water)*	2.2588	O1 – Mn1 – O2	110.83
Mn1 – O4 *(Lattice Water)*	4.5806	O1 – Mn1 – O3	93.14
Cl1 – H13 *(Lattice Water)*	3.0857	Cl1 – Mn1 – N1	120.9
		Cl1 – Mn1 – O2	126.96
		Cl1 – Mn1 – O3	86.71
		Cl1 – Mn1 – O1	120.81

Table S4. Selected bond lengths (Å) and angles (°) for the complex **4**

Bond Lengths (Å)		**Bond Angles (°)**	
Metal 1 (Cu1) Environment			
Cu1 – O1	1.846	O1 – Cu1 – O6 =	148.01
Cu1 – N1	1.957	N1 – Cu1 – O7 =	159.62
Cu1 – O6	1.981	O1 – Cu1 – N1 =	96.65
Cu1 – O7 *(sulfate/bridge)*	2.070	O6 – Cu1 – O7 =	70.91
Cu1 – O2 *(bridge)*	2.523	O1 – Cu1 – O2 =	86.93
Metal 2 (Cu2) Environment			
Cu2 – O2 *(bridge)*	1.842	O2 – Cu2 – O3 =	166.99
Cu2 – N2	1.945	N2 – Cu2 – O7 =	159.12
Cu2 – O7 *(sulfate/bridge)*	1.991	O2 – Cu2 – N2 =	94.58
Cu2 – O3	2.020	O3 – Cu2 – O7 =	94.56
Cu2 – O4	2.719	O4 – Cu2 – O7 =	59.13

Table S5. Selected bond lengths (Å) and angles (°) for the complex **5**

Bond Lengths (Å)		**Bond Angles (°)**	
Metal 1 (Cd1) Environment			
N1 – Cd1	2.268	O2 – Cd1 – O6	158.33
O1 – Cd1	2.485	O1 – Cd1 – O5	148.49
Cd1 – O2 *(bridge)*	2.332	N1 – Cd1 – O4	136.21
Cd1 – O4 *(bridge)*	2.255	N1 – Cd1 – O5	113.35
Cd1 – O5 *(nitrate)*	2.314	O2 – Cd1 – O4	77.67
Cd1 – O6 *(nitrate)*	2.322	O5 – Cd1 – O6 *(nitrate bite)*	55.86
Metal 2 (Cd2) Environment			
Cd2 – O2 *(bridge)* =	2.156	O2 – Cd2 – N2 =	157.50
Cd2 – N2 =	2.218	O3 – Cd2 – O4 =	158.32
Cd2 – O4 *(bridge)* =	2.235	O2 – Cd2 – O3 =	119.65
Cd2 – O9 *(nitrate)*	2.328	N2 – Cd2 – O9 =	108.67
Cd2 – O3 =	2.349	O2 – Cd2 – O4 =	81.85

Table S6. Selected bond lengths (Å) and angles (°) for the complex **6**

Bond Lengths (Å)		**Bond Angles (°)**	
Metal 1 (Co1) Environment			
Co1 – N1	2.064	N1 – Co1 – O6 =	166.87
Co1 – O7	2.017	O2 – Co1 – O5 =	159.89
Co1 – O2	2.107	N1 – Co1 – O2 =	82.48
Co1 – O6 *(bridge)*	2.131	O5 – Co1 – O6 = *(bite)*	61.26
Co1 – O5	2.141		
Metal 2 (Co2) Environment			
Co2 – O4 =	1.961	N2 – Co2 – O6 =	153.15
Co2 – O8 =	2.019	O3 – Co2 – O4 =	149.47
Co2 – N2 =	2.027	Co1 – O6 – Co2 = *(bridge angle)*	112.42
Co2 – O6 *(bridge)* =	2.072	N2 – Co2 – O3 =	78.18
Co2 – O3 =	2.171		

Table S7. Optimized Coordinates and absolute energy for Free Ligand (H_2L)

Absolute Energy: -3127.199277 Hartree

O	1.16133958047698	-0.98274860062046	2.40256248825989
C	1.65304798133162	-0.25143102700325	1.37370890772556
C	2.91361887764987	0.33682893136122	1.56576191002567
C	3.49199362483983	1.11669333907756	0.57137035094177
C	2.80537800472610	1.31997175376646	-0.63532007664162
Br	3.59831329513099	2.39757275785389	-1.99672277841118
C	1.56191068503111	0.74298729027003	-0.84433440998889
C	0.96865793669250	-0.05748946565083	0.15172681456240
C	-0.33711938391402	-0.68188032771790	-0.10371498539051
N	-1.01913114040248	-0.46299082551663	-1.15502359698105
C	-2.31975473121969	-1.08008506778193	-1.26069393049289
C	-3.39956481732001	-0.13155334369152	-0.74628197616158
O	-3.24105732151010	-0.00394179955645	0.65253736972740
H	0.25910416043170	-1.27101133253933	2.21248400768674
H	3.42240081890925	0.17004876952901	2.51704134368698
H	4.47146478631292	1.57140450684760	0.72857144482702
H	1.01124847800000	0.88249185308348	-1.77520228536946
H	-0.72313085288131	-1.38237954645849	0.66698890898562
H	-2.39333208863751	-2.02300548481115	-0.68015212261866
H	-2.52957338030990	-1.31306021665848	-2.31785126923604
H	-3.29194808319284	0.84147511410078	-1.26210687318699
H	-4.39372407173239	-0.54776868615478	-1.00724473008550
H	-3.67013835841262	0.80986940827117	0.94189648813532

Table S8. Optimized Coordinates and absolute energy for Complex **1**

Absolute Energy: -5046.886378 Hartree

Br	-8.32152201615177	-2.28065500840643	3.14595121738320
C	-7.25505520417251	-1.17275105264832	2.00257990702719
H	0.23889159901654	-0.60228288929091	-0.50118704278792
C	-5.88581441472552	-1.15489294031815	2.12631971226608
C	-7.87630534109075	-0.37146729256230	1.01710631253621
H	-5.40094064235656	-1.77889689676657	2.88103470514518
H	-8.96199426381624	-0.39194803759135	0.91893353553959
C	-5.08265355311508	-0.33802468669896	1.27418308956561
C	-7.11874838892497	0.42520202190446	0.17827438763050
C	-0.85646185594359	-0.45206573140465	-0.52588657384785
H	-0.83967133996480	1.29622968008129	-1.39012197343369
C	-5.69595177268264	0.47594335173612	0.26934367522230
C	-3.66071947730463	-0.41027698736617	1.41509407544435
H	-3.29155129108025	-1.16065874902814	2.13517323129842
H	-7.58913843763610	1.03929468848061	-0.59218032681654
Cu	-3.23539166682394	1.67650441228819	-0.52642518619168
N	-2.75783128706787	0.31096375076251	0.77402189217131
O	-1.24675129312180	0.44307155591569	-1.55501307428880
H	-1.32609230999327	-1.41830508146413	-0.75393538892838
O	-5.05770804189206	1.22514439528049	-0.56183123501958
H	-0.79387012151733	0.94679072570628	1.13736728601118
C	-1.33492364176796	0.02501995628671	0.85851556559993
H	-1.12150441542596	-0.74464970670880	1.62848914839162
N	-2.10990003881730	3.72195765511045	-1.47699950400815
O	-1.65572307900174	4.67269336690961	-2.01929764810279
O	-3.25940908217815	3.31219436256638	-1.73119670136725
O	-1.50586862244335	2.98655513722606	-0.56800308644011

Table S9. Optimized coordinates and absolute energy for Complex **2**

Absolute Energy: -7636.582672 Hartree

Br	4.46208637256572	0.30529916534864	0.39715607639925
O	-0.99215605796298	0.38414526453005	3.06822536068631
N	-2.04699732734653	0.52683042641958	0.44149021251543
C	0.25015660228811	0.38690477871643	2.45251766407166
C	1.40537013120767	0.37937139004122	3.22695524868536
C	2.66310145031652	0.35758941492243	2.62059613319370
C	2.76795866919625	0.33806421991843	1.22243314718491
C	1.60925842319079	0.33248152511113	0.44803249329621
C	0.32608386936246	0.36501011308555	1.03985598396556
C	-0.81085455096815	0.33058390287851	0.13250529741053
C	-3.08560102751511	0.41051930771407	-0.58318517248486
C	-4.09712139634338	1.53100436408936	-0.40124306643285
H	1.33348278831801	0.38779059565757	4.31858779880293
H	3.56363567781330	0.35253480532955	3.23754726267760
H	1.69174585521319	0.30016811411489	-0.64040139977410
H	-0.55508727684955	0.11382547635415	-0.91765908087217
H	-3.59817491652298	-0.55790907026368	-0.44786386487893
H	-2.67017481029883	0.42981404787496	-1.60464181184300
H	-3.65619971582791	2.51028559192808	-0.65603987956887
H	-4.97998240569554	1.36222567991692	-1.03589909948230
H	-3.31960565852328	4.55659034177633	2.65705962145740
C	-2.38567698518122	4.08987097995348	3.01424131299550
C	-4.44754968782694	1.81568229167509	4.70711193745213
H	-4.73214034161012	2.49357560935981	5.52871424516536
C	-6.53146660899696	0.67100964916063	5.26025133641492
C	-5.31769459140930	0.66386900846823	4.53554864052247
O	-1.90785769652142	3.14652473311686	2.03142970591246
Br	-9.05938753721180	-0.32829265373594	6.12975323473682
H	-1.63490993385607	4.87628377263582	3.18485317169319
C	-5.03737004835299	-0.45733730539219	3.71878627694492
C	-7.44359788372332	-0.37765229745627	5.16000105823360
O	-3.83073944381235	-0.52246838854114	3.04497267054474
H	-6.75826656794458	1.51984036479246	5.90880398315343
C	-5.94474005530156	-1.50787448102931	3.62481506285030

C	-7.14553602816536	-1.47322205937412	4.33708028873207
H	-5.71696065283067	-2.37456028984679	2.99693285732847
H	-7.84831905544976	-2.30473761947794	4.25680523633880
C	-2.62564331599388	3.30048606476134	4.29295604650383
H	-3.10841583425400	3.94287794558680	5.04828482785327
N	-3.41595747705714	2.10710516738047	3.99060741731370
H	-1.65223749910390	2.97634776418916	4.70027993583675
Co	-2.77211344612848	1.19462682548531	2.25272101924818
H	-3.73029981326972	-1.39302956886166	2.62863065726944
H	-0.91268848019592	0.15159244949107	4.00718302433337
H	-1.60303083919914	3.59695825610523	1.23036980050083
O	-4.46896876628292	1.51101847453725	0.99131705654768
H	-5.25055610593798	2.05639585155210	1.16193027056381

Table S10. Optimized coordinates and absolute energy for Complex **3**

Absolute Energy: -4890.279650 Hartree

C	-0.79472645557992	0.57501577809819	-3.63911677583564
C	0.46679414569042	0.93457146337147	-3.09418841377894
C	1.58533807975385	1.13499550803413	-3.88675215138181
C	1.49048214880727	1.00070730782065	-5.28391367933429
Br	3.02992392899830	1.29166760094703	-6.37141865465274
C	0.27914786779636	0.66615584733769	-5.86312951982734
C	-0.86886723111399	0.43263621283782	-5.07011991741974
C	-2.10555156806908	0.13242459981070	-5.76535833509474
N	-3.17510282664682	-0.31531796970178	-5.21082512311548
C	-4.44126313521868	-0.39147917370473	-5.90483040800413
C	-5.40238041902370	0.57915057637719	-5.19547034489444
O	-5.30323373748178	0.43654401531681	-3.78043772224111
H	0.52740550400039	1.04440441721368	-2.00930025163884
H	2.54138239758202	1.40204564566197	-3.43187696615126
H	0.20266138947193	0.57170924590651	-6.94896426361042
H	-2.10509703538089	0.32647854565603	-6.85521362960143
H	-4.82965119030557	-1.42130255018969	-5.81460412773132
H	-4.36725431923655	-0.14116412817478	-6.98021306879952
H	-5.14230291489436	1.61398346272518	-5.47768084851605
H	-6.44043113832306	0.38726135706985	-5.51327472074456
H	-4.92024103806818	1.28229949386799	-3.42387652735112
Mn	-3.49928926201521	-0.79602166259181	-3.12481792088274

O	-1.82372846122433	0.42788737472066	-2.84397739331938
Cl	-3.74851185616129	-2.97829787191457	-2.43934502067337
O	-3.74037909225903	-0.22460648323204	-0.95280120691729
O	-3.70839643547933	2.40458534158287	-3.01653313794967
H	-3.79997590601299	-1.16427794234130	-0.69128273216686
H	-2.81806149060273	0.03191944507855	-0.78444543541402
H	-2.92001613455444	1.83423341205153	-2.84394026549142
H	-3.40477135874831	3.05384796366415	-3.66475059295976

Table S11. Optimized coordinates and absolute energy for Complex **4**

Absolute Energy: -10232.389038 Hartree

Cu	-6.02066480543136	2.10304570813331	11.25172768907226
Br	-4.49382996631866	9.34434497769466	11.31829701255668
O	-6.66265656012180	3.75314969530382	10.56841341145121
N	-4.59759877015229	2.88790648457386	12.33868943413732
C	-6.16137266090103	4.92155741666449	10.76974158317865
C	-6.73431862362528	6.04178461587910	10.09159045258876
C	-6.24989416685554	7.32305162302232	10.25672196116745
C	-5.15147827174476	7.56550086733914	11.11232405169674
C	-4.56237406991510	6.51842377690605	11.78846146720474
C	-5.04073921296996	5.18942394951677	11.63685446179026
C	-4.35574905096374	4.15944682315372	12.36343796289999
C	-3.79321921977066	1.97042872119694	13.13214658350105
C	-2.98876686335871	0.99057609645072	12.27002907155324
H	-7.58053916974217	5.83948885170573	9.43273332601978
H	-6.71200037331038	8.15698414769402	9.72422818862791
H	-3.71300225565794	6.70337003058876	12.44999690548590
H	-3.52834008398042	4.50553510169383	13.00573767679029
H	-4.47167940465189	1.40195283147042	13.79043284331035
H	-3.09061250694018	2.53142065114475	13.77487426623807
H	-3.91325480114303	4.28772118625585	9.35307863854614
H	-5.34606460597036	-2.20313642169590	6.66392637095160
H	-1.54545902497435	5.02532654796735	9.29157137964552
C	-3.11700351328040	3.56898409036241	9.16273007054846
C	-1.79697969163220	3.97569219174951	9.12644421549741
H	-6.54351891112823	-1.89917318775699	9.28263397414107
Cu	-5.49799022312995	0.16584070197124	8.92495459071184
O	-4.75150773003469	1.90346995460608	9.05380582644608

C	-3.49182314021726	2.21146917630114	8.96044894877843
O	-6.34791430404547	-1.61776333604587	8.33778162209920
C	-5.35081864893049	-2.44517962550192	7.73779035785247
C	-0.77180970946070	3.03878203035024	8.87945617431144
N	-3.82939508409131	-0.70455153038689	8.42932875992804
Br	1.04597569858910	3.61226892508845	8.85510363296676
C	-2.43944100290966	1.27350646479078	8.68114396549211
H	-5.61554792963145	-3.50828653030310	7.85369128597369
C	-3.98723077141200	-2.15060115092407	8.35875609440755
C	-1.09099564512815	1.71470875549199	8.65360838643969
C	-2.67694024245125	-0.12681121063693	8.46052797657259
H	-3.17318878845078	-2.63119960399926	7.78720181771937
H	-0.29928757129258	0.98921562947154	8.45387657797535
H	-1.77911829042962	-0.75072599071809	8.31281775497830
H	-3.96137229132653	-2.54449336788628	9.39103999174272
S	-7.19345154775253	-0.34860038308190	11.30687483529883
O	-6.47531177852561	-1.59923327800454	10.88192665279582
O	-8.58406278467523	-0.50239283217571	11.68359059214010
O	-6.32639318644103	0.39168783635836	12.35398632533682
O	-7.03126661194273	0.69612724284332	10.08978356792057
O	-3.77646685666817	0.18340179817195	11.42811117845133
H	-2.37229813564442	0.37820579316552	12.95919398507193
H	-2.29796604606200	1.55330783735489	11.62085224750180
H	-4.55641079339350	-0.12995008331626	11.92566385248253

Table S12. Optimized coordinates and absolute energy for Complex **5**

Absolute Energy: -7148.821884 Hartree

C	-0.83922663884394	-0.59560304457574	-3.09589317047442
C	0.40944999872053	-1.10416955701396	-2.67106767098753
C	1.54722108633511	-1.02577564706804	-3.46103405619551
C	1.47492983298812	-0.41536578658611	-4.72223917551548
Br	3.03618163512376	-0.28970372992168	-5.80738384614955
C	0.27129239229603	0.10594160483392	-5.16791096192907
C	-0.90380009979113	0.02011296023652	-4.38560834430279
C	-2.08754582144543	0.65536059666726	-4.94734252143364
N	-3.29887054463239	0.53666012744849	-4.54399789903293
C	-4.36152854756164	1.35574382830684	-5.09614380524882
C	-4.81908137421884	2.36376848525433	-4.02304307699273
O	-4.92121335057520	1.74854645538226	-2.74103744050132
H	0.45582066040000	-1.57651930849801	-1.68652524305662
H	2.49513077089104	-1.43286311627304	-3.10436329435857
H	0.22283803909379	0.59766509380929	-6.14173124219390
H	-1.88810507684756	1.31365475994351	-5.81260803939275
H	-5.20000797408445	0.69127433800218	-5.36609571993876
H	-4.04343915917730	1.90288359734054	-6.00248698389004
H	-4.09106583441056	3.18553549408081	-3.97028543163884
H	-5.80368460131797	2.77133514482214	-4.30494435120090
H	-4.18275743345558	2.09123932505937	-2.19145092709659
Cd	-4.15881164242205	-0.61680509983855	-2.79121716187198
O	-1.88351779068522	-0.67978120118917	-2.28454726515611
Br	-8.75147665890279	-0.64939695433943	3.39451981322856
C	-7.29041952629101	-0.56117476339033	2.17423581927787
H	-1.23007098566281	2.83558304345199	1.54521019515342
C	-6.03502136310069	-0.19427832567470	2.61398228799352
C	-7.49255341865780	-0.86686422094253	0.81453576632019
H	-5.88165986130976	0.04892775174097	3.66768250599841
H	-8.48549076171040	-1.15313681578595	0.46241083722133
C	-4.92704164097590	-0.12379894558586	1.72535096466071
C	-6.43632391405944	-0.80367148650423	-0.07653102197414
C	-0.59664013515028	1.95913186398144	1.77099695433517
H	-0.10071312299570	2.00718428812970	-0.17341462888899

C	-5.12670852587193	-0.44097139607302	0.33486924458564
C	-3.68772037161588	0.30090453706530	2.33663338744335
H	-3.78292172151048	0.54065357848723	3.41134344418507
H	-6.60039912253658	-1.03550545985899	-1.13176643833799
Cd	-2.03365641396592	0.25881200323572	-0.35064514763345
N	-2.51672430445836	0.44291562205850	1.80659972950326
O	-0.16022460322701	1.34198219345176	0.56340104178199
H	0.27259982641321	2.29852231769989	2.36004139543539
O	-4.15819963666677	-0.40511296470184	-0.54530730157964
H	-1.72684841383859	1.40156446996260	3.53473096671029
C	-1.39562509703769	0.94131783700506	2.58652712467851
H	-0.72897161320587	0.09609992322134	2.83764728814204
N	-5.85711749059271	-2.61746416265988	-3.54085232515215
O	-4.62274627585092	-2.82836092930819	-3.28732606120834
O	-6.24931446785215	-1.39714205801549	-3.43357617861272
O	-6.61071625464555	-3.50221266360216	-3.85959821142148
N	-1.59996684118493	2.84439402810805	-2.07937777359592
O	-1.87419485659102	3.42558033752159	-3.11197982866049
O	-2.54740942229928	2.27104892879739	-1.40265342183177
O	-0.43604153102284	2.77613310230080	-1.63893279919812

Table S13. Optimized coordinates and absolute energy for Complex **6**

Absolute Energy: -9475.027876 Hartree

C	5.50721366903224	3.04780801909532	-2.25492795287054
C	6.32464001837817	3.72067063959831	-1.31062729189085
C	7.70925180396919	3.62118486130025	-1.33477584713738
C	8.34408206079184	2.84844620972944	-2.32217365544425
Br	10.24932576434474	2.73413812654018	-2.36312754667060
C	7.58529689633635	2.18075576367588	-3.27256327693355
C	6.17814653215074	2.24118076847376	-3.23903912640301
C	5.42179270420899	1.54332972792149	-4.26597208389840
N	4.20035645235242	1.18410974232579	-4.10856337246934
C	3.32241849861574	0.80846115998054	-5.18935091787066
C	2.31165159303886	1.97494211061282	-5.33463688906472
O	1.98596626794231	2.53700358998973	-4.06346257691337
H	5.83598302550680	4.32085900869425	-0.54035848332995
H	8.31015252940455	4.14882569202735	-0.59047999957902
H	8.07550448073991	1.58328729787070	-4.04409082115303

H	5.93339902257550	1.35330649003811	-5.22970185309051
H	2.78314205575163	-0.10788132671197	-4.89804727559413
H	3.85031207259633	0.63365555932926	-6.14403954798798
H	2.73818699216296	2.75459107134545	-5.98685116651886
H	1.37988167174605	1.61180807571603	-5.79164723678935
H	2.62874335996880	3.24156500200367	-3.86792921335195
Co	3.11815520665673	1.38314073458704	-2.36283918933782
O	4.20246348411635	3.18473333402249	-2.22187506209429
Br	-0.75234863928930	2.17693729582572	7.74206464641118
C	-0.11509418941842	1.91515562651149	5.95460285865875
H	2.30985281119071	5.79416682338579	0.70402296971098
C	0.79853154065682	2.78806406914817	5.40000416650388
C	-0.59098906900718	0.82272160370597	5.20041930333110
H	1.17021337268223	3.63437576994650	5.98352909711469
H	-1.31378503684856	0.13347935178987	5.64448649317825
C	1.27351203874866	2.61388711830732	4.07362042629928
C	-0.14149883667421	0.62280033879451	3.91082426442267
C	3.20253493671179	5.15167097808544	0.59542055024880
H	3.48972420598649	3.85945600259851	-0.97399892465049
C	0.79971523597189	1.49521333208739	3.28094942163251
C	2.20548483210653	3.60154161253643	3.58648173834858
H	2.48724419158111	4.39115272294814	4.30809787898984
H	-0.50253241027606	-0.22056087051712	3.32089267612936
Co	2.41115949445006	2.26106942895241	0.94369404756944
N	2.71460444320896	3.63532570291604	2.40234823137044
O	2.86218922890503	4.04274733705737	-0.21113034381222
H	3.99856431211721	5.75713313634163	0.12913395430984
O	1.16356235061960	1.24645919936792	2.06523985064868
H	3.70205919938256	5.50560900301167	2.69165888199852
C	3.64627513361505	4.66093449396842	1.97993517773039
H	4.64641627062890	4.19920444474488	1.90079939568507
H	-0.86593841593818	0.87062370178518	-0.31653624547217
C	-0.18024228646266	0.04755931949526	-0.56174459012857
H	0.17038653087481	-0.35109272245186	0.40358311331551
H	-0.68813923898271	-0.73156595833392	-1.14253500844035
C	1.01298780693128	0.57830908399231	-1.30101944940098
O	1.46452057213283	0.02404843595896	-2.32752589980216
O	1.62219965008287	1.62829337827586	-0.86474177748464

H	6.36017717620493	0.24131746372337	1.44585786519076
C	6.24424231846635	0.29011767295443	0.35468251593226
H	6.98451946037413	1.00424419045205	-0.04278433591581
H	6.43490387677298	-0.68750077136234	-0.10442539228070
C	4.87254803712542	0.80668691347170	-0.02079188649518
O	4.39702141251863	0.43104199139772	-1.12759983182903
O	4.31850152046086	1.62414112095999	0.76763454737526

S1. Extended Experimental and Computational Details

S1.1. Structure Determination from Powder Data (SDPD) and Rietveld Refinement

Due to the rapid precipitation nature of the highly supersaturated reaction environments, the products were obtained as microcrystalline powders rather than single crystals. Consequently, high-resolution Powder X-ray Diffraction (PXRD) was employed for structural elucidation. The PXRD patterns were collected on a Panalytical Empyrean diffractometer using Cu-K\α radiation (λ = 1.54056 Å). The crystal structures were solved by direct-space methodologies utilizing the simulated annealing approach implemented in the EXPO2014 software suite.[S1] The theoretically optimized molecular geometries (obtained via DFT calculations) were imported as rigid bodies during the initial structure solution phase. Following the successful location of the asymmetric units, rigorous Rietveld refinements were performed to minimize the discrepancy between the experimental and calculated diffraction profiles.[S2] The final refinement cycles included the optimization of unit cell parameters, profile variables, and background coefficients, yielding excellent agreement factors.

It should be noted that the final R_{wp} and GOF values obtained for the complexes (e.g., R_{wp} = 14.45% for complex 4) are completely consistent with the accepted literature standards for *ab initio* structure determination of complex coordination networks from laboratory powder data.

The slight elevation in these profile-fitting indicators is a natural consequence of the microcrystalline nature, peak overlap, and inherent morphological microstrain induced by the rapid kinetic precipitation methodology.

S1.2. Computational Details

To corroborate the experimental structural findings and to evaluate the energetic stabilities of the varying coordination topologies (e.g., the anisobidentate nitrate coordination and acetate-bridged polymeric chains), Density Functional Theory (DFT) calculations were performed using the ORCA 6.1.1 quantum chemistry program package.[S3] The geometry optimizations were conducted employing the B3LYP functional in conjunction with the def2-SVP basis set for all atoms.[S4-S6] To accurately describe the weak intermolecular interactions and packing effects, Grimme's dispersion correction with Becke-Johnson damping (D3BJ) was applied. The Resolution of Identity approximation combined with the Chain of Spheres exchange (RIJCOSX) algorithm was utilized to accelerate the energetic calculations without compromising accuracy.[S7-S9] The stationary points were verified as true minima by the absence of imaginary frequencies in the subsequent vibrational analyses.

Following the generation of the wavefunction (Molden format), advanced topological analyses of the electron density were carried out using the Multiwfn code (version 3.8).[S10] The Quantum Theory of Atoms in Molecules (QTAIM) framework, originally proposed by Bader, was employed to locate the bond critical points (BCPs) between the interacting atoms and to evaluate the local electron density properties, including the electron density (ρ(r)), its Laplacian ($\nabla^2\rho$), and the local potential energy density (V(r)).[S11] The interaction energy (E_{int}) of the non-covalent contact was estimated using the established Espinosa correlation (E_{int}) = 0.5 V(r)).[S12] Furthermore, to visually map and categorize the supramolecular contacts, the Non-Covalent Interaction (NCI) index was utilized.[S13] The NCI analysis was mapped by plotting the Reduced

Density Gradient (RDG) versus the electron density multiplied by the sign of the second eigenvalue of the Hessian matrix (sign(λ_2)ρ), allowing for the precise differentiation between strong attractive halogen bonds and weak van der Waals forces. Subsequently, the high-resolution 3D isosurface visualizations of these computed electronic and magnetic properties were rendered utilizing the VESTA (Visualization for Electronic and Structural Analysis, version 3) software.[S14] The isosurface thresholds were carefully optimized (e.g., 0.02 a.u. for FMOs and 0.002–0.005 a.u. for spin densities) to accurately map the spatial distribution, orbital mixing, and spin delocalization pathways across the supramolecular frameworks.

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