Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Table S1. Cartesian atomic coordinates (Å) of the equilibrium structures. Nuclear charges are indicated in the first column.

2, B3LYP

35	-1.019544	1.376459	1.757821
30	-1.134624	0.467172	-0.433747
7	-2.901317	-0.693685	-0.469177
7	-5.366620	-0.511688	-0.434009
6	-4.057430	-0.584608	-0.451577
6	-6.048738	-0.272556	0.846721
1	-5.426940	-0.638945	1.661647
1	-6.995449	-0.815752	0.846653
1	-6.239943	0.794883	0.994104
6	-6.075910	-0.152979	-1.671340
1	-7.022652	-0.695216	-1.702699
1	-5.471847	-0.439207	-2.530491
1	-6.269713	0.923336	-1.712435
35	-1.070786	1.582527	-2.530507
7	0.398871	-0.984752	-0.522954
7	2.856612	-1.248060	-0.569915
6	1.555692	-1.084815	-0.543923
6	3.577247	-1.019154	-1.831287
1	2.903693	-1.191035	-2.668998
1	4.410284	-1.721799	-1.891749
1	3.958815	0.005277	-1.882843
6	3.612629	-1.138078	0.686698
1	4.446403	-1.841822	0.657081
1	2.962762	-1.389521	1.523014
1	3.996462	-0.122442	0.824094

2, M06-2X

35	-2.546671	1.361146	1.176578
30	-1.153330	0.271317	-0.441410
7	-2.596672	-0.953368	-1.466524
7	-4.911646	-0.571450	-0.696444
6	-3.682621	-0.766410	-1.094051
6	-5.304165	-1.142760	0.599689
1	-4.798642	-2.096343	0.739602
1	-6.382182	-1.303473	0.583941
1	-5.028682	-0.458568	1.406291
6	-5.544693	0.703988	-1.062385
1	-6.623335	0.549932	-1.093067
1	-5.195726	1.008688	-2.047190
1	-5.286974	1.470547	-0.326859
35	0.422113	1.274609	-1.943911
7	0.047566	-1.288208	0.430763
7	2.400489	-1.230424	-0.316540
6	1.152747	-1.252345	0.069845
6	2.699876	-1.716230	-1.671102
1	2.038876	-2.547568	-1.908595
1	3.733902	-2.060908	-1.684056
1	2.553365	-0.911121	-2.395613
6	3.240899	-0.130882	0.179482

1	4.276466	-0.471090	0.182198
1	2.941171	0.120323	1.195126
1	3.125829	0.744141	-0.465587

8, B3LYP

35	0.848326	0.071256	-3.103771
35	-0.517196	-2.972873	-0.381788
30	0.023054	-0.759485	-1.041836
7	-1.717561	0.296636	-0.460392
7	-4.028935	0.656099	0.355186
7	1.426599	0.020164	0.363229
7	3.849883	0.354846	0.758628
6	-2.794580	0.478148	-0.079332
6	-4.963821	-0.443334	0.272130
6	-4.489802	-1.755771	0.275567
1	-3.427861	-1.966559	0.346269
6	-5.398326	-2.805471	0.165810
1	-5.025663	-3.822716	0.159809
6	-6.765454	-2.554134	0.070184
1	-7.466858	-3.376099	-0.008842
6	-7.224772	-1.238301	0.069824
1	-8.285120	-1.030740	-0.015143
6	-6.328833	-0.176395	0.161764
1	-6.687102	0.844761	0.143926
6	-4.373254	1.942047	0.920544
6	-4.112656	3.103962	0.197373
1	-3.672299	3.039265	-0.790783
6	-4.420472	4.342073	0.758437
1	-4.214018	5.247027	0.199476
6	-5.000893	4.414836	2.022613
1	-5.245964	5.378515	2.453096
6	-5.263463	3.244376	2.734942
1	-5.706775	3.296099	3.722447
6	-4.943490	2.003640	2.191867
1	-5.132266	1.091477	2.744298
6	2.561826	0.164843	0.551923
6	4.559029	-0.563208	1.621005
6	3.977791	-0.971655	2.819910
1	3.005961	-0.590060	3.110028
6	4.651520	-1.881268	3.631840
1	4.195861	-2.205337	4.559896
6	5.903596	-2.364119	3.258400
1	6.427029	-3.067933	3.894390
6	6.477981	-1.943447	2.059298
1	7.446349	-2.324201	1.756630
6	5.806946	-1.048752	1.230992
1	6.241922	-0.734696	0.290638
6	4.509205	1.434492	0.054828
6	5.488272	2.179485	0.712612
1	5.754965	1.945886	1.735750
6	6.115487	3.222814	0.037866
1	6.878376	3.801969	0.545026
6	5.756002	3.531988	-1.273756
1	6.243789	4.348826	-1.792435

6	4.766658	2.788350	-1.913107
1	4.478701	3.019792	-2.931603
6	4.142642	1.728542	-1.257769
1	3.377085	1.149223	-1.764363

8, M06-2X, asymmetric

35	-1.092507	0.949868	2.864095
35	0.366360	-2.667424	0.924803
30	-0.080146	-0.337575	1.145962
7	1.770269	0.478974	0.532028
7	4.079503	0.469841	-0.346344
7	-1.297636	0.137936	-0.554830
7	-3.736508	0.224493	-0.949743
6	2.846326	0.493968	0.121820
6	4.786359	-0.785466	-0.333769
6	4.062594	-1.973882	-0.322676
1	2.976861	-1.970257	-0.324104
6	4.748844	-3.181291	-0.278580
1	4.181619	-4.103796	-0.256714
6	6.139009	-3.204435	-0.263533
1	6.668408	-4.148653	-0.235225
6	6.847157	-2.006992	-0.274056
1	7.930070	-2.014215	-0.248576
6	6.177668	-0.789537	-0.299550
1	6.728030	0.142816	-0.286690
6	4.637116	1.691910	-0.861495
6	4.473816	2.870633	-0.144347
1	3.946585	2.858446	0.803098
6	4.987301	4.055763	-0.660264
1	4.856700	4.978225	-0.108126
6	5.673301	4.054357	-1.869096
1	6.078860	4.977851	-2.263785
6	5.835641	2.864265	-2.573718
1	6.363018	2.859785	-3.519800
6	5.310114	1.677795	-2.079196
1	5.416980	0.747387	-2.624032
6	-2.439142	0.172097	-0.734180
6	-4.428270	-0.975765	-1.335108
6	-3.738379	-1.969945	-2.022072
1	-2.691442	-1.836286	-2.269979
6	-4.399975	-3.141694	-2.366945
1	-3.859688	-3.919622	-2.892229
6	-5.741092	-3.315176	-2.043789
1	-6.253919	-4.228763	-2.317146
6	-6.417659	-2.312647	-1.357238
1	-7.458636	-2.444497	-1.088347
6	-5.766507	-1.140570	-0.991894
1	-6.287466	-0.369354	-0.438840
6	-4.412171	1.465451	-0.656979
6	-5.350781	1.952729	-1.560803
1	-5.569207	1.396548	-2.464851
6	-5.996625	3.149216	-1.279679
1	-6.731693	3.535611	-1.975326
6	-5.689816	3.856653	-0.119519

1	-6.192331	4.792650	0.091641
6	-4.737561	3.362506	0.764496
1	-4.492838	3.907737	1.667747
6	-4.097175	2.154117	0.507558
1	-3.360349	1.757036	1.200913

8, M06-2X, C_2 symmetry

35	0.604057	-2.083990	1.900798
35	-0.604006	2.083538	1.901092
30	-0.000012	-0.000171	0.922436
7	1.601385	0.332916	-0.435629
7	4.041838	0.095098	-0.745918
6	2.743499	0.235391	-0.571839
6	4.882838	1.259085	-0.683524
6	4.408107	2.471574	-1.171270
1	3.417215	2.532049	-1.607237
6	5.211980	3.601675	-1.080994
1	4.840103	4.548459	-1.453131
6	6.483853	3.517518	-0.526112
1	7.109363	4.399327	-0.464356
6	6.947450	2.296233	-0.046117
1	7.932858	2.224066	0.397972
6	6.148614	1.161819	-0.113899
1	6.497055	0.212655	0.274426
6	4.555619	-1.243620	-0.900565
6	5.597073	-1.473073	-1.794265
1	6.021386	-0.650152	-2.357142
6	6.076841	-2.767290	-1.948297
1	6.888593	-2.954639	-2.640675
6	5.509279	-3.818783	-1.233148
1	5.884310	-4.826493	-1.363251
6	4.459753	-3.572665	-0.355427
1	4.007958	-4.383180	0.203328
6	3.981348	-2.279370	-0.173761
1	3.164950	-2.086703	0.516911
7	-1.601436	-0.333013	-0.435654
7	-4.041845	-0.094970	-0.746126
6	-2.743532	-0.235388	-0.571941
6	-4.882930	-1.258915	-0.684156
6	-4.408232	-2.471299	-1.172194
1	-3.417296	-2.531721	-1.608070
6	-5.212197	-3.601370	-1.082323
1	-4.840340	-4.548078	-1.454674
6	-6.484127	-3.517277	-0.527563
1	-7.109706	-4.399059	-0.466124
6	-6.947694	-2.296092	-0.047284
1	-7.933149	-2.223977	0.396709
6	-6.148764	-1.161717	-0.114652
1	-6.497187	-0.212638	0.273897
6	-4.555534	1.243832	-0.900376
6	-5.596881	1.473651	-1.794106
1	-6.021175	0.650948	-2.357316
6	-6.076566	2.767948	-1.947734
1	-6.888243	2.955578	-2.640125

6	-5.509032	3.819160	-1.232150
1	-5.884001	4.826933	-1.361942
6	-4.459618	3.572681	-0.354398
1	-4.007848	4.382973	0.204701
6	-3.981297	2.279298	-0.173140
1	-3.164981	2.086353	0.517550

1, B3LYP

17	-1.011505	1.285230	1.610446
30	-1.136292	0.435486	-0.446796
7	-2.912728	-0.712398	-0.457817
7	-5.375985	-0.504791	-0.399727
6	-4.067060	-0.590742	-0.429574
6	-6.040777	-0.243418	0.885676
1	-5.419282	-0.618096	1.697054
1	-6.998440	-0.766875	0.897611
1	-6.208708	0.828625	1.028744
6	-6.091383	-0.140980	-1.631980
1	-7.049528	-0.663431	-1.648043
1	-5.503441	-0.447350	-2.495363
1	-6.263298	0.938844	-1.680556
17	-1.092984	1.449870	-2.431517
7	0.405301	-1.009402	-0.536762
7	2.865655	-1.248314	-0.596923
6	1.562687	-1.097350	-0.564081
6	3.575356	-1.014158	-1.863423
1	2.901492	-1.206255	-2.696481
1	4.422032	-1.700393	-1.922664
1	3.936233	0.017309	-1.925075
6	3.627008	-1.116073	0.654229
1	4.474588	-1.803011	0.622806
1	2.987694	-1.376565	1.495893
1	3.991325	-0.092222	0.784503

1, M06-2X

17	-2.545685	1.463363	0.845829
30	-1.139806	0.330219	-0.498722
7	-2.543752	-0.983118	-1.485073
7	-4.842692	-0.569963	-0.680582
6	-3.622562	-0.782035	-1.099575
6	-5.165811	-1.002674	0.687067
1	-4.645870	-1.934190	0.902755
1	-6.241641	-1.169281	0.741660
1	-4.857750	-0.234978	1.401591
6	-5.498718	0.665104	-1.135490
1	-6.576608	0.514095	-1.077810
1	-5.217926	0.862642	-2.168260
1	-5.193410	1.501855	-0.501663
17	0.454346	1.113446	-1.882042
7	-0.014401	-1.189987	0.545404
7	2.318310	-1.263736	-0.264531
6	1.081640	-1.217904	0.157072
6	2.546806	-1.805832	-1.612149
1	1.855447	-2.626876	-1.792418
1	3.569759	-2.179819	-1.655109

1	2.390933	-1.022522	-2.358418
6	3.203106	-0.162113	0.143242
1	4.230950	-0.521852	0.097423
1	2.968859	0.128299	1.165619
1	3.064439	0.691396	-0.525642

7, B3LYP

17	0.966138	-1.336047	-2.936758
17	-0.773401	-2.932470	0.362449
30	-0.013793	-1.292733	-0.940416
7	-1.681323	0.025602	-0.940112
7	-3.927559	0.563398	-0.042406
7	1.376779	-0.123022	0.183651
7	3.814296	0.277555	0.380982
6	-2.725820	0.289929	-0.515432
6	-4.929320	-0.482418	-0.085430
6	-4.563777	-1.797309	0.198246
1	-3.540226	-2.045483	0.460455
6	-5.529692	-2.798979	0.120718
1	-5.244303	-3.822575	0.331677
6	-6.845223	-2.488509	-0.215834
1	-7.592723	-3.271256	-0.267828
6	-7.196639	-1.167338	-0.492878
1	-8.215622	-0.920108	-0.766947
6	-6.239186	-0.158646	-0.439450
1	-6.503693	0.865436	-0.671925
6	-4.167870	1.855942	0.550581
6	-3.615651	2.996129	-0.032278
1	-3.026748	2.911846	-0.938193
6	-3.824893	4.238980	0.560758
1	-3.391624	5.123358	0.108724
6	-4.595497	4.347188	1.716206
1	-4.762730	5.316394	2.170628
6	-5.149368	3.201301	2.286121
1	-5.743252	3.275502	3.189601
6	-4.933093	1.951401	1.713230
1	-5.349015	1.059222	2.163697
6	2.518795	0.053022	0.285632
6	4.551518	-0.319675	1.469384
6	3.974982	-0.389586	2.736815
1	2.984488	0.015748	2.907204
6	4.677393	-0.994404	3.776292
1	4.224549	-1.054971	4.758773
6	5.953102	-1.509589	3.558214
1	6.498754	-1.974867	4.370319
6	6.521772	-1.429118	2.287709
1	7.508959	-1.837702	2.106266
6	5.823342	-0.842672	1.236213
1	6.256622	-0.796873	0.245274
6	4.448300	1.057318	-0.662781
6	5.397456	2.018287	-0.314255
1	5.661058	2.171041	0.724971
6	5.998454	2.773585	-1.316908
1	6.738203	3.519690	-1.051037

6	5.640617	2.584335	-2.651870
1	6.107058	3.179279	-3.428246
6	4.680230	1.631229	-2.983147
1	4.393662	1.477983	-4.016693
6	4.083390	0.853230	-1.992495
1	3.338566	0.108595	-2.255951

7, M06-2X, C_2 symmetry

17	-0.633520	1.943537	2.042631
17	0.633763	-1.944107	2.042185
30	0.000067	-0.000202	1.139070
7	-1.602822	-0.358629	-0.213118
7	-4.041008	-0.051399	-0.479113
6	-2.744087	-0.230284	-0.329358
6	-4.910710	-1.194455	-0.438645
6	-4.471945	-2.404711	-0.964321
1	-3.487455	-2.477755	-1.412775
6	-5.303299	-3.516366	-0.897262
1	-4.958702	-4.461457	-1.298791
6	-6.567376	-3.415853	-0.327339
1	-7.214398	-4.283083	-0.283355
6	-6.994928	-2.197178	0.190930
1	-7.973975	-2.112629	0.646837
6	-6.168150	-1.081728	0.146697
1	-6.488827	-0.135542	0.564863
6	-4.519826	1.305019	-0.588291
6	-5.570270	1.587491	-1.455928
1	-6.027574	0.792338	-2.032732
6	-6.016406	2.898098	-1.566280
1	-6.835658	3.126732	-2.237101
6	-5.406639	3.913478	-0.833811
1	-5.755396	4.934343	-0.929835
6	-4.348632	3.614417	0.016793
1	-3.864095	4.396804	0.588033
6	-3.902919	2.304143	0.155066
1	-3.077700	2.072089	0.822989
7	1.602775	0.358469	-0.213261
7	4.040936	0.051453	-0.479715
6	2.744023	0.230204	-0.329744
6	4.910519	1.194609	-0.439406
6	4.471667	2.404717	-0.965341
1	3.487204	2.477567	-1.413884
6	5.302903	3.516473	-0.898425
1	4.958244	4.461454	-1.300158
6	6.566946	3.416192	-0.328390
1	7.213875	4.283498	-0.284517
6	6.994588	2.197658	0.190142
1	7.973608	2.113297	0.646139
6	6.167924	1.082119	0.146056
1	6.488658	0.136039	0.564421
6	4.519892	-1.304906	-0.588993
6	5.570397	-1.587203	-1.456613
1	6.027656	-0.791963	-2.033332
6	6.016658	-2.897760	-1.567063

1	6.835956	-3.126254	-2.237878
6	5.406960	-3.913265	-0.834713
1	5.755818	-4.934088	-0.930813
6	4.348881	-3.614378	0.015865
1	3.864389	-4.396860	0.587013
6	3.903042	-2.304159	0.154239
1	3.077771	-2.072249	0.822149

Table S2. Crystallographic data for **1**, **2**, **3**, **8** and **9**.

Compound	**1**	**2**	**3**	**8**	**9**
Formula	$C_6H_{12}Cl_2N_4Zn$	$C_6H_{12}Br_2N_4Zn$	$C_6H_{12}I_2N_4Zn$	$C_{26}H_{20}Br_2N_4Zn$	$C_{26}H_{20}N_4ZnI_2$
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
a (Å)	14.6053(6)	14.8739(10)	13.8920(3)	9.6653(9)	9.93005(20)
b (Å)	5.98157(17)	6.1147(3)	13.3250(4)	18.1538(16)	18.0924(4)
c (Å)	15.2271(6)	15.5444(9)	7.5335(2)	14.5506(13)	14.7012(3)
α (°)	90	90	90	90	90.00
β (°)	118.214(5)	117.993(8)	90	92.564(8)	93.9238(18)
γ (°)	90	90	90	90	90.00
V (Å^3)	1172.23(7)	1248.35(12)	1394.53(6)	2550.5(4)	2634.99(9)
Molecular weight	276.47	365.39	459.37	613.65	707.63
Space group	*P*2/*c*	*P*2/*c*	*Pnma*	$P2_1/c$	$P2_1/c$
μ (mm^{-1})	6.828	8.336	6.160	4.117	3.296
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Z	4	4	4	4	4
D_{calc} (g/cm^3)	1.567	1.944	2.188	1.598	1.784
Crystal size (mm^3)	0.20×0.09×0.02	0.23×0.18×0.15	0.37×0.25×0.19	0.31×0.24×0.19	0.18x0.16x0.08
Radiation	Cu*K*α	Mo*K*α	Mo*K*α	Mo*K*α	Mo*K*α
Total reflections	4799	10011	11091	13595	13063
Unique reflections	2118	2857	1655	5860	5869
Angle range 2θ (°)	6.86–139.96	5.94–55.00	5.86–55.00	5.44–55.00	5.3 - 55°
Reflections with $\|F_o\| \geq 4\sigma_F$	1961	2503	1554	4519	5025
R_{int}	0.0221	0.0361	0.0213	0.0358	0.0274
R_σ	0.0221	0.0345	0.0133	0.0564	0.0410
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0256	0.0490	0.0143	0.0333	0.0281
wR_2 ($\|F_o\| \geq 4\sigma_F$)	0.0668	0.1055	0.0309	0.0551	0.0503
R_1 (all data)	0.0278	0.0570	0.0168	0.0528	0.0366
wR_2 (all data)	0.0682	0.1081	0.0317	0.0605	0.0535
S	1.098	1.331	1.112	0.980	1.062
ρ_{min}, ρ_{max}, e/Å^3	–0.371, 0.286	–0.652, 1.286	–0.334, 0.533	–0.475, 0.519	0.60,-0.64
CCDC №	1002740	1002739	1002738	1002743	1007640

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

Table S3. Crystallographic data for **10** and **11**.

Compound	**10**	**11**
Formula	$C_{52}H_{44}N_8O_2Zn$, Cl_6Zn_2	$C_{52}H_{44}N_8O_2Zn$, Br_6Zn_2
Crystal System	Monoclinic	Monoclinic
a (Å)	9.9007(3)	9.9094(4)
b (Å)	25.2926(8)	25.7218(12)
c (Å)	10.9442(3)	14.0861(7)
α (°)	90	90
β (°)	96.116(3)	128.053(3)
γ (°)	90	90
V (Å^3)	2724.99(13)	2827.2(2)
Molecular weight	1221.82	1488.52
Space group	$P2_1/n$	$P2_1/c$
μ (mm^{-1})	1.651	5.548
Temperature (K)	100(2)	100(2)
Z	2	2
D_{calc} (g/cm^3)	1.489	1.696
Crystal size (mm^3)	0.35×0.28×0.19	0.28×0.17×0.07
Radiation	Mo$K\alpha$	Mo$K\alpha$
Total reflections	16137	9183
Unique reflections	6107	4844
Angle range 2θ (°)	5.24–54.98	5.20–50.00
Reflections with $\|F_o\| \geq 4\sigma_F$	4976	2503
R_{int}	0.0235	0.0400
R_σ	0.0315	0.0684
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0323	0.0544
wR_2 ($\|F_o\| \geq 4\sigma_F$)	0.0655	0.1034
R_1 (all data)	0.0443	0.0724
wR_2 (all data)	0.0706	0.1120
S	1.073	1.128
ρ_{min}, ρ_{max}, e/Å^3	–0.351, 0.360	–1.093, 1.277
CCDC №	1002745	1002744

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

Table S4. Crystallographic data for **12a, 12b** and **13**.

Compound	**12a**	**12b**	**13**
Formula	$C_9H_{22}N_6O_2Zn$, $2(CF_3SO_3)$	$C_8H_{12}F_6N_4O_6S_2Zn$	$C_{18}H_{34}N_6O_2Zn$, $2(CF_3SO_3)$
Crystal System	Monoclinic	Triclinic	Orthorhombic
a (Å)	14.7059(7)	9.3213(6)	7.5157(2)
b (Å)	9.2052(4)	9.5366(7)	17.6633(6)
c (Å)	18.8942(9)	11.0391(10)	23.4601(9)
α (°)	90	98.656(7)	90
β (°)	103.429(5)	113.153(7)	90
γ (°)	90	92.342(6)	90
V (Å^3)	2487.8(2)	886.56(13)	3114.37(19)
Molecular weight	609.84	503.71	730.02
Space group	$P2_1/c$	P-1	$Pccn$
μ (mm^{-1})	3.809	1.716	3.148
Temperature (K)	100(2)	100(2)	100(2)
Z	4	2	4
D_{calc} (g/cm^3)	1.628	1.887	1.557
Crystal size (mm^3)	0.24×0.15×0.12	0.31×0.26×0.18	0.29×0.16×0.07
Radiation	Cu$K\alpha$	Mo$K\alpha$	Cu$K\alpha$
Total reflections	13153	8380	19816
Unique reflections	4668	3941	3097
Angle range 2θ (°)	6.18–139.90	5.39–55.00	7.54–145.00
Reflections with $\|F_o\| \geq 4\sigma_F$	3502	3152	2488
R_{int}	0.0364	0.0348	0.0579
R_σ	0.0375	0.0558	0.0276
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0426	0.0381	0.0428
wR_2 ($\|F_o\| \geq 4\sigma_F$)	0.1044	0.0825	0.1067
R_1 (all data)	0.0634	0.0547	0.0551
wR_2 (all data)	0.1209	0.0907	0.1196
S	1.048	1.072	1.051
ρ_{min}, ρ_{max}, e/Å^3	–0.335, 0.753	–0.625, 0.719	–0.667, 0.654
CCDC №	967882	1006350	1002742

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

Table S5. Crystallographic data for **14**, **15**, **17** and **18**.

Compound	**14**	**15**	**17**	**18**
Formula	$C_6H_{16}O_2Cl_2ZnN_4$	$C_6H_{16}N_4ZnBr_2O_2$	$C_{12}H_{24}N_4O_2Cl_2Zn$	$C_{12}H_{24}Br_2N_4O_2Zn$
Crystal System	Orthorhombic	Monoclinic	Triclinic	Monoclinic
a (Å)	13.2455(7)	7.5270(5)	9.6999(11)	10.6266(2)
b (Å)	10.3779(9)	12.6536(9)	9.9427(11)	17.3401(5)
c (Å)	18.5884(11)	14.1711(8)	10.1598(7)	9.7944(2)
α (°)	90	90.00	88.738(7)	90
β (°)	90	89.364(6)	88.449(7)	93.340(2)
γ (°)	90	90.00	61.132(11)	90
V (Å^3)	2555.2(3)	1349.62(15)	857.73(15)	1801.71(7)
Molecular weight	312.50	401.42	392.62	481.54
Space group	*Pbca*	*P2$_1$/n*	*P*-1	*P*2$_1$/*c*
μ (mm^{-1})	6.456	9.407	4.935	5.807
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Z	8	4	2	4
D_{calc} (g/cm^3)	1.625	1.976	1.520	1.775
Crystal size (mm^3)	0.18×0.16×0.10	0.16 × 0.12 × 0.08	0.20×0.14×0.10	0.36×0.28×0.21
Radiation	Cu*K*α	Cu*K*α	Cu*K*α	Mo*K*α
Total reflections	8196	7946	8757	10704
Unique reflections	2447	257]	3206	4014
Angle range 2θ (°)	9.52 - 144.98	9.38 - 145°	8.7 - 143°	5.98–54.99
Reflections with $\|F_o\| \geq 4\sigma_F$	2447	2228	2453	3291
R_{int}	0.0448	0.0376	0.0789	0.0341
R_σ	0.0366	0.0371	0.0850	0.0477
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0391	0.0327	0.0592	0.0320
wR_2 ($\|F_o\| \geq 4\sigma_F$)	0.0967	0.0762	0.1402	0.0561
R_1 (all data)	0.0527	0.0430	0.0813	0.0456
wR_2 (all data)	0.1096	0.0815	0.1601	0.0609
S	1.058	1.052	1.053	1.048
ρ_{min}, ρ_{max}, *e*/Å^3	–0.608, 0.523	0.67,-0.60	–0.66, 0.87	–0.482, 0.486
CCDC №	1004423	1007855	1004425	1002741

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where *n* is the number of reflections and *p* is the number of refinement parameters.

Table S6. Selected bond lengths [Å] and angles [°] for zinc complexes **14**, **15**, **17** and **18** and literature analogs.

Parameter	**14**	**15**	**17**	**18**	**$[ZnCl_2\{OC(NH_2)_2\}_2]$**[1]	**Dimethylurea unsym.**[2]
Zn(1)–O(1)	1.968(2)	1.959(6)	1.962(4)	1.951(2)	1.987(3)	
Zn(1)–O(1A)	2.000(2)	2000(6)	1.995(4)	1.994(2)	1.947(3)	
Zn(1)–X(1)	2.2261(9)	2.378(1)	2.211(2)	2.3837(5)	2.238(3)	
Zn(1)–X(1A)	2.2494(8)	2.352(1)	2.249(1)	2.3349(5)	2.217(2)	
O(1A)–C(1A)	1.278(4)	1.27(1)	1.268(6)	1.270(4)	1.272(4)	
O(1)–C(1)	1.275(4)	1.26(1)	1.274(6)	1.270(4)	1.254(3)	1.250(2)
C(1A)–N(2A)	1.339(4)	1.34(1)	1.343(7)	1.345(4)	1.328(4)	
C(1)–N(1)	1.346(4)	1.35(1)	1.353(7)	1.338(4)	1.323(4)	1.349(2)
C(1)–N(2)	1.338(4)	1.35(1)	1.335(7)	1.330(4)	1.332(3)	1.350(3)
X(1)–Zn(1)–O(1)	110.57(7)	109.6(2)	111.3(1)	111.65(6)	110.19(5)	
X(1)–Zn(1)–O(1A)	110.64(7)	109.6(2)	111.6(1)	115.97(6)	110.71(5)	
X(1)–Zn(1)–X(1A)	115.30(3)	116.78(5)	117.29(5)	114.78(2)	118.55(3)	
O(1A)–Zn(1)–O(1)	101.55(9)	101.2(3)	101.8(2)	100.97(8)	99.23(7)	
Zn(1)–O(1)–C(1)	129.8(2)	130.3(6)	134.7(3)	126.3(2)	125.2(2)	
Zn(1)–O(1A)–C(1A)	129.8(2)	128.9(6)	129.1(3)	132.1(2)	131.5(2)	
N(1A)–C(1A)–N(2A)	119.9(3)	120.1(8)	119.5(5)	120.3(3)	118.9(2)	
N(2)–C(1)–N(1)	119.1(3)	119.0(8)	120.1(5)	119.8(3)	118.5(2)	117.9(2)

1. N. G. Furmanova, V. F. Resnyanskii, K. S. Sulaimankulov, D. K. Sulaimankulova, and S. Z. Zhorobekova, *Kristallografiya*, 1998, **43**, 269–271. CA 1998:237666

2. H. M. K. K. Pathirana, T. J. Weiss, J. H. Reibenspies, R. A. Zingaro, and E. A. Meyers, *Zeitschrift fuer Krist.*, 1994, **209**, 696.

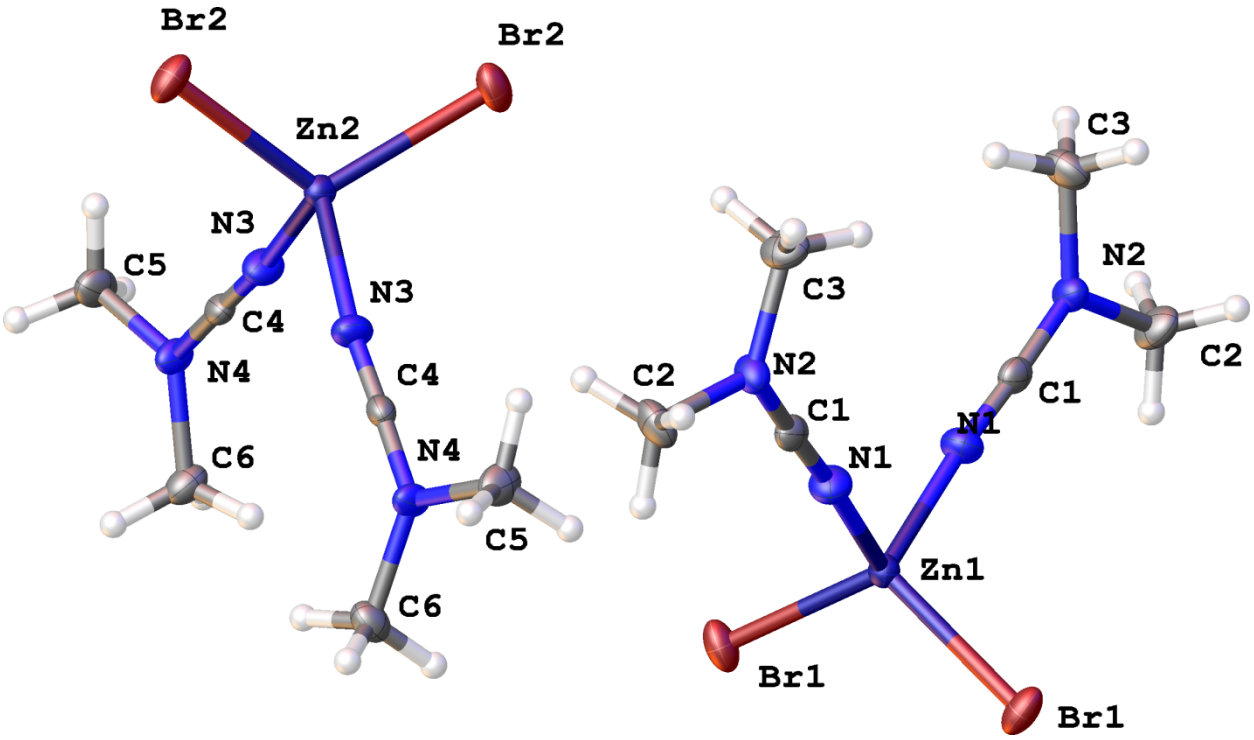

Figure S1. View of **2** with the atomic numbering scheme; two nonequivalent molecules were displayed. Thermal ellipsoids are given at the 50% probability level.

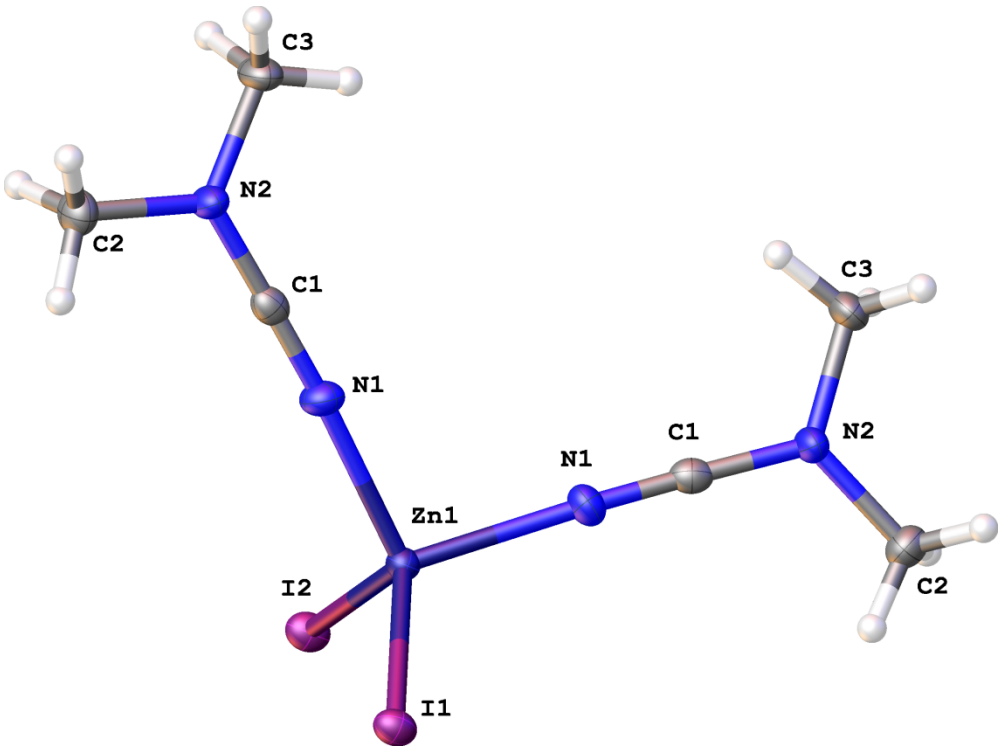

Figure S2. View of **3** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.

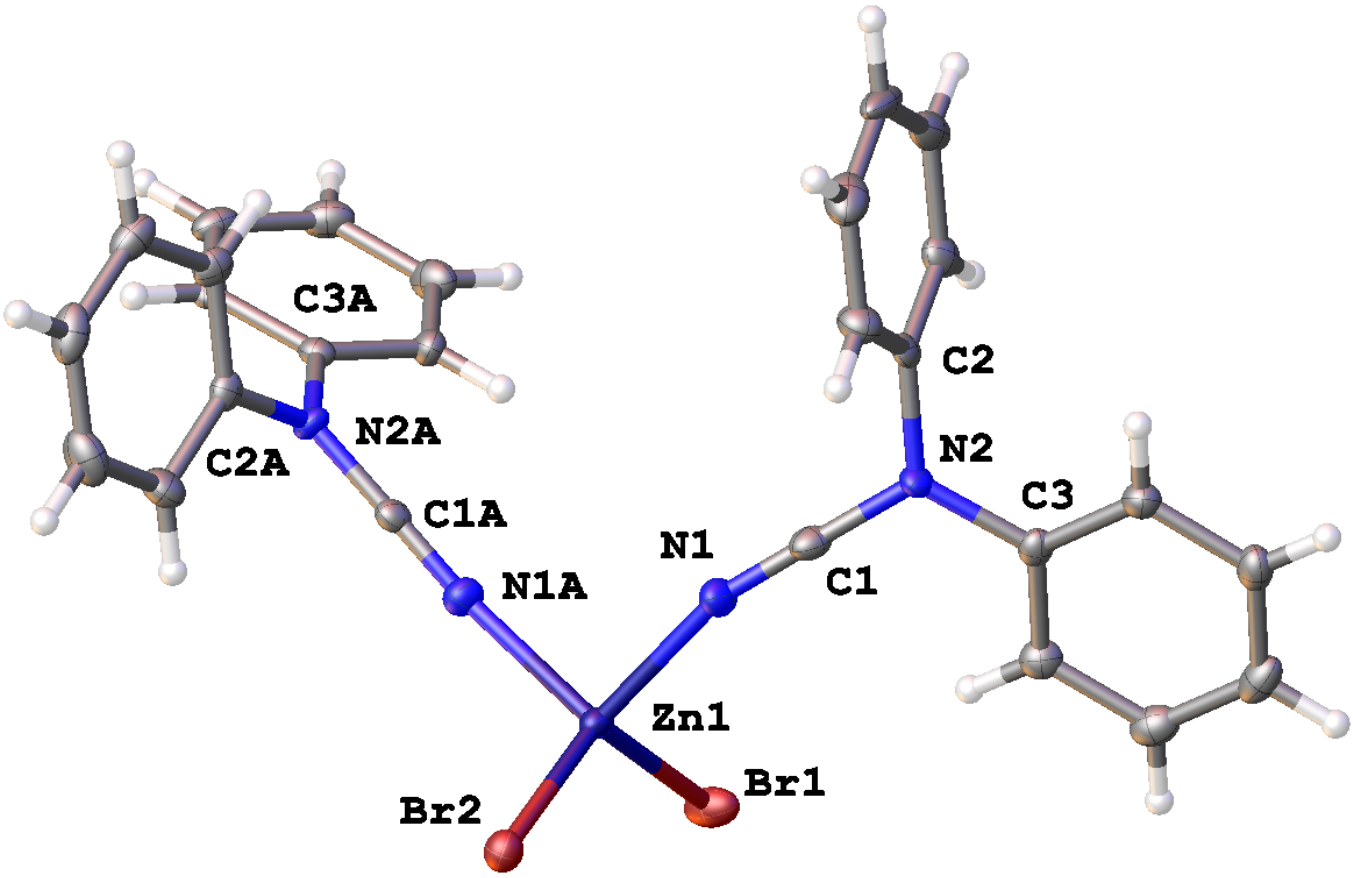

Figure S3. View of **8** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.

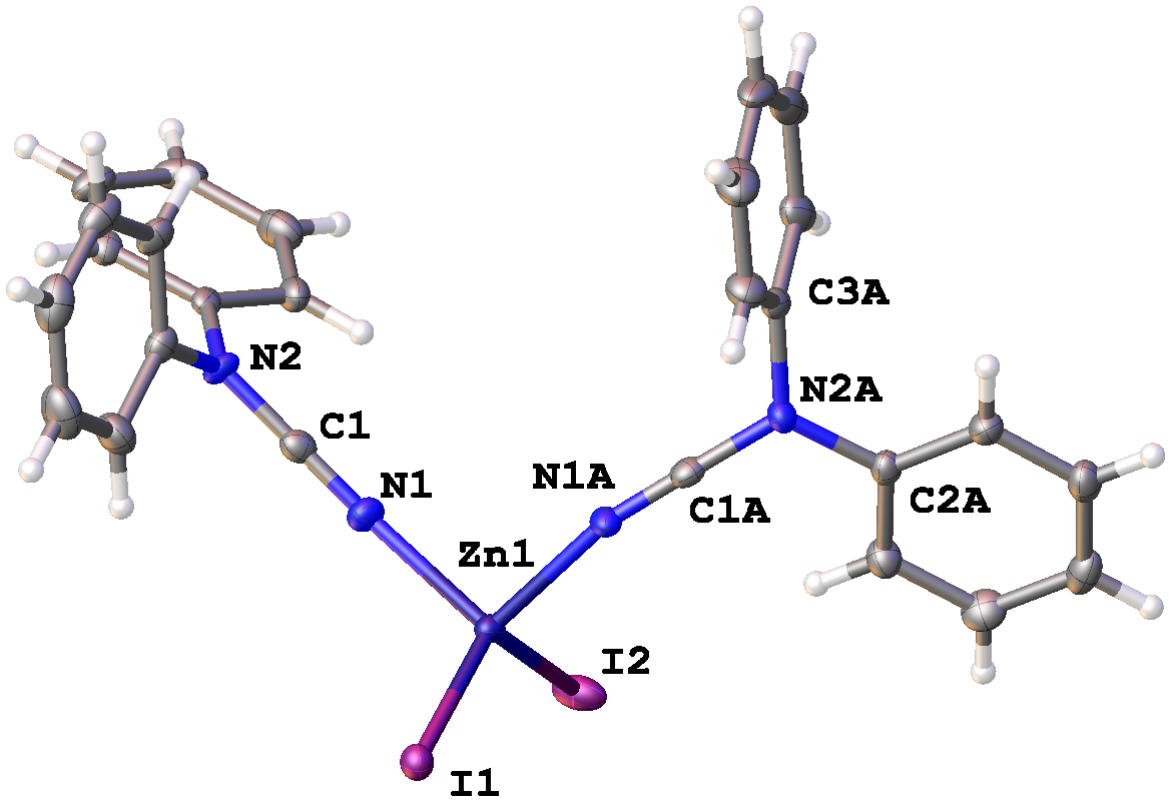

Figure S4. View of **9** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.

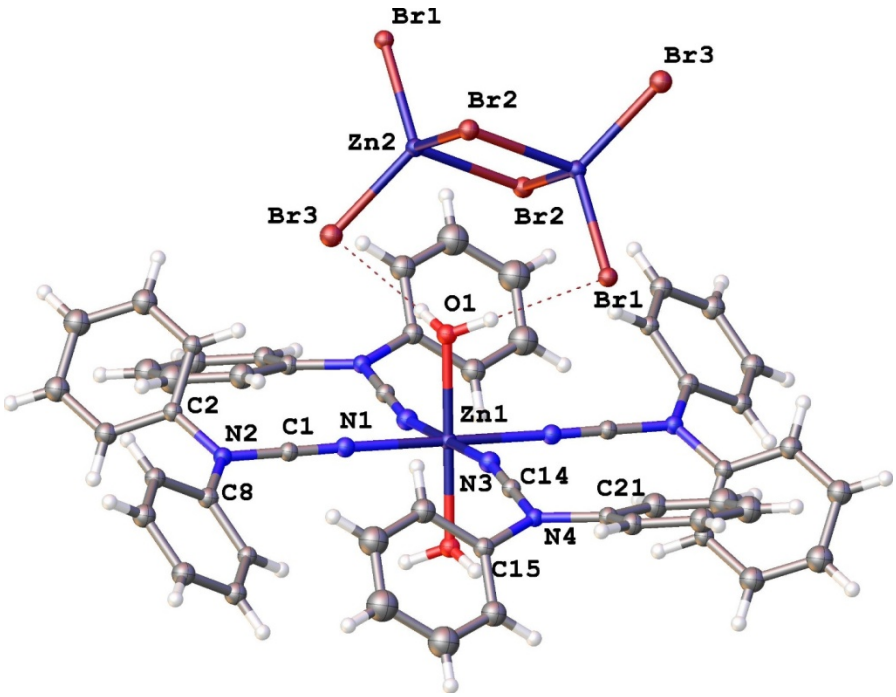

Figure S5. View of $[Zn(NCNPh_2)_4(H_2O)_2][Zn_2(\mu\text{-}Br)_2Br_4]$ (**11**). Selected bond distances (Å) and angles (°): Zn(1)–N(1) 2.142(6), Zn(1)–N(3) 2.097(6), N(1)–C(1) 1.14(1), N(3)–C(14) 1.157(9), N(4)–C(14) 1.329(9), N(2)–C(1) 1.33(1), Zn(1)–N(1)–C(1) 175.5(6), C(1)–N(2)–C(2) 119.1(7), C(1)–N(2)–C(8) 116.9(6), C(2)–N(2)–C(8) 122.8(6), Zn(1)–N(3)–C(14) 165.2(6), N(1)–Zn(1)–N(3) 89.0(2), N(3)–Zn(1)–N(1) 91.0(2), N(3)–Zn(1)–N(3) 180.0(2).

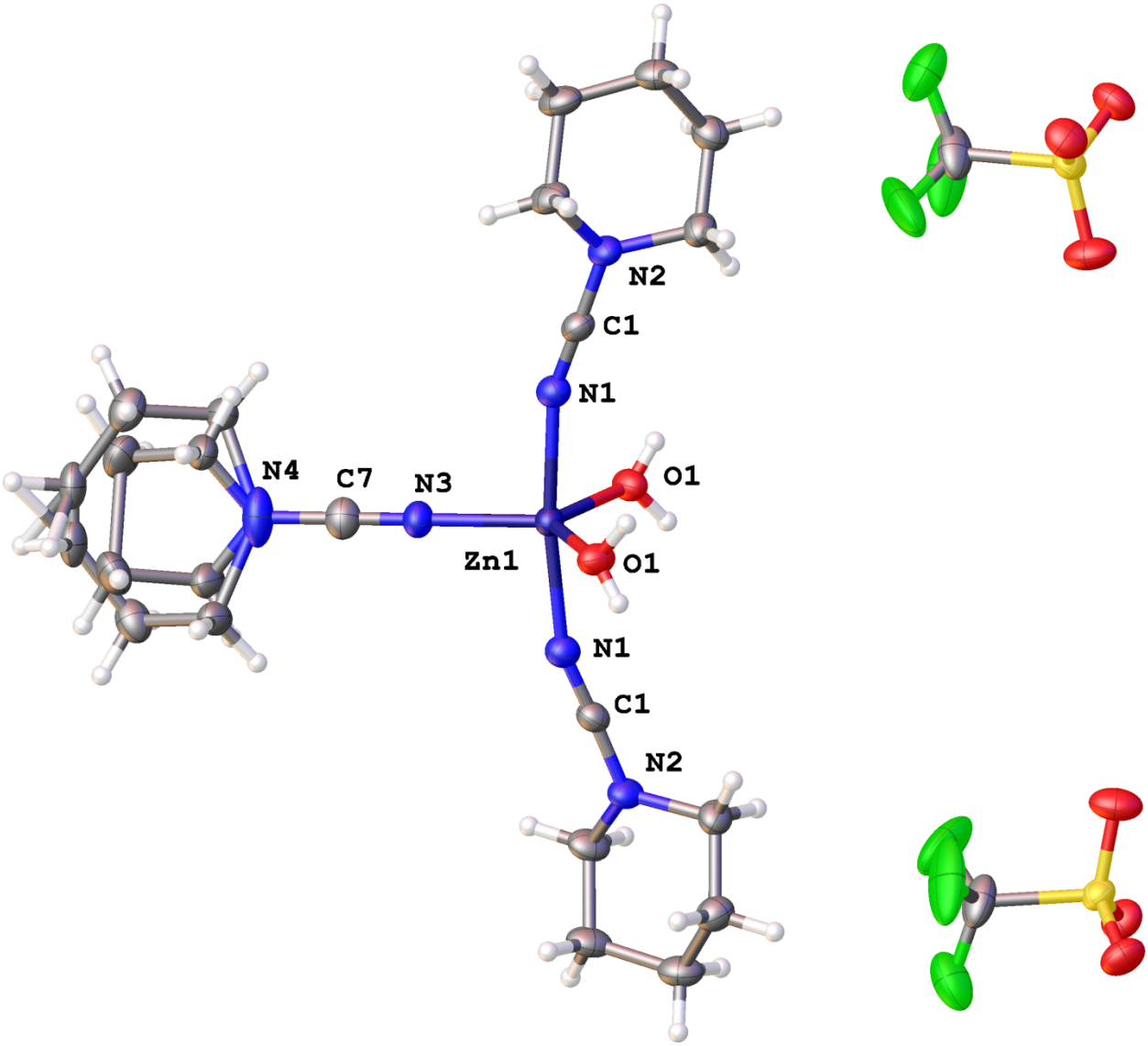

Figure S6. View of **13** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.

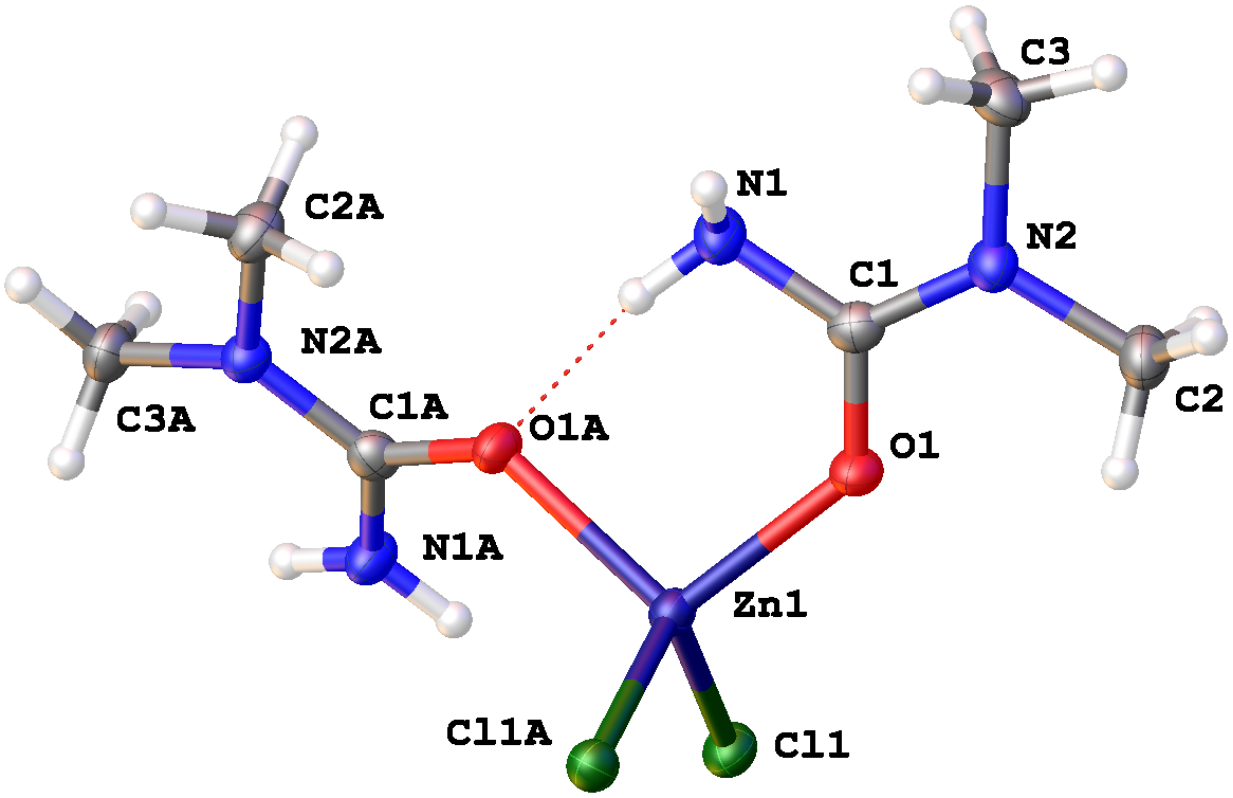

Figure S7. View of **14** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.

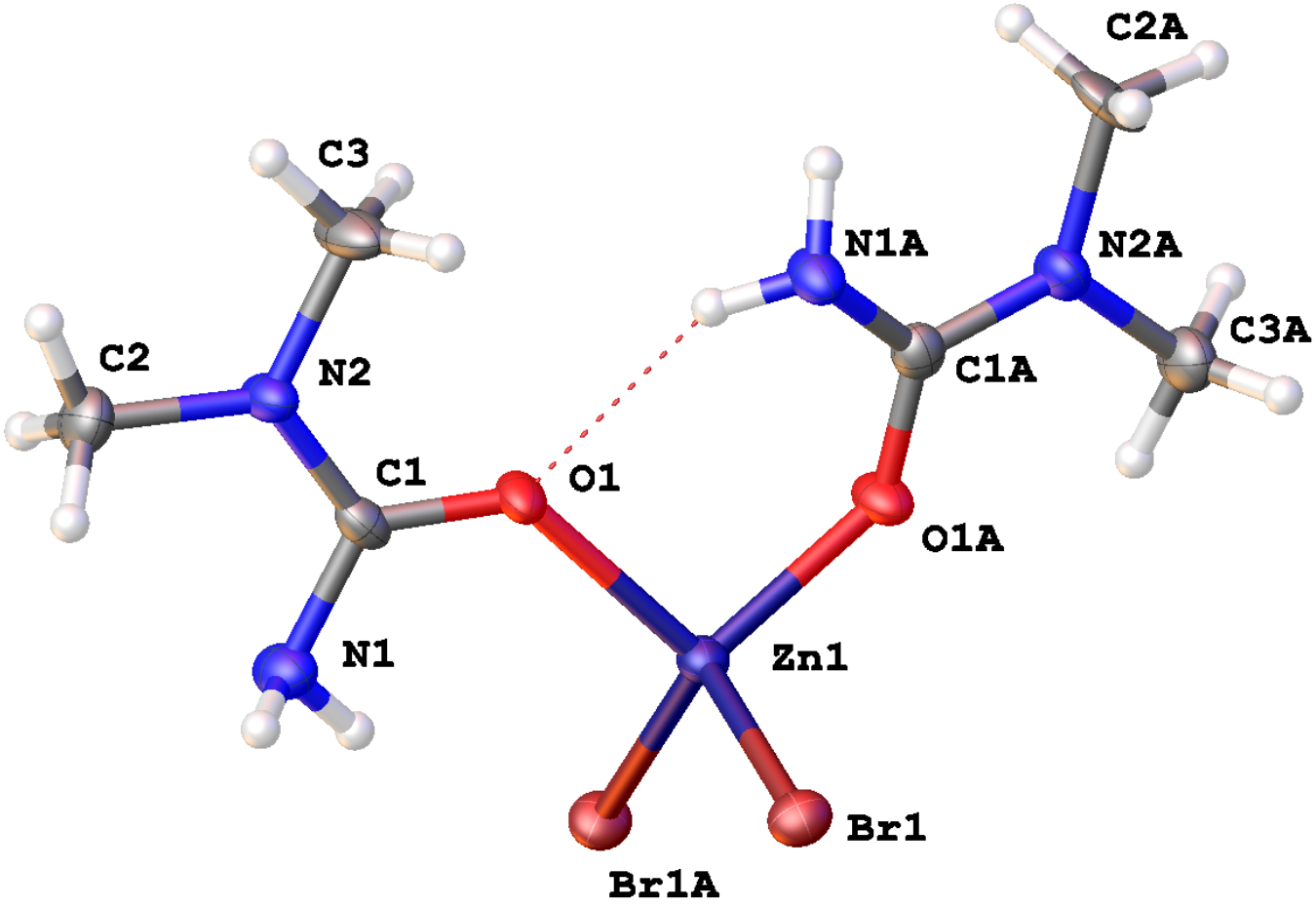

Figure S8. View of **15** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.

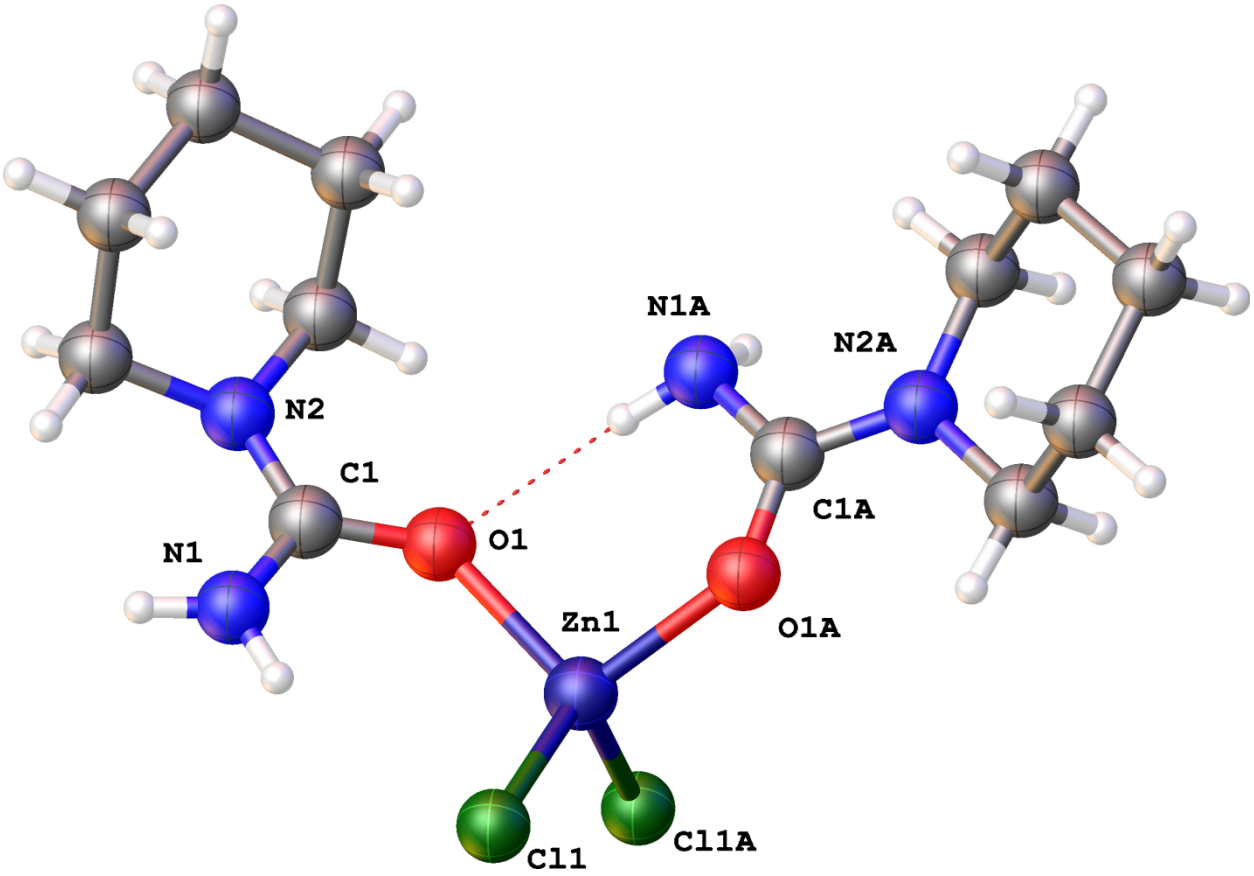

Figure S9. View of **17** with the atomic numbering scheme; Thermal ellipsoids are given at the 50% probability level.