

Heteroleptic Zn(II) pentaiodobenzoate complexes: structures and features of halogen...halogen non-covalent interactions in solid state

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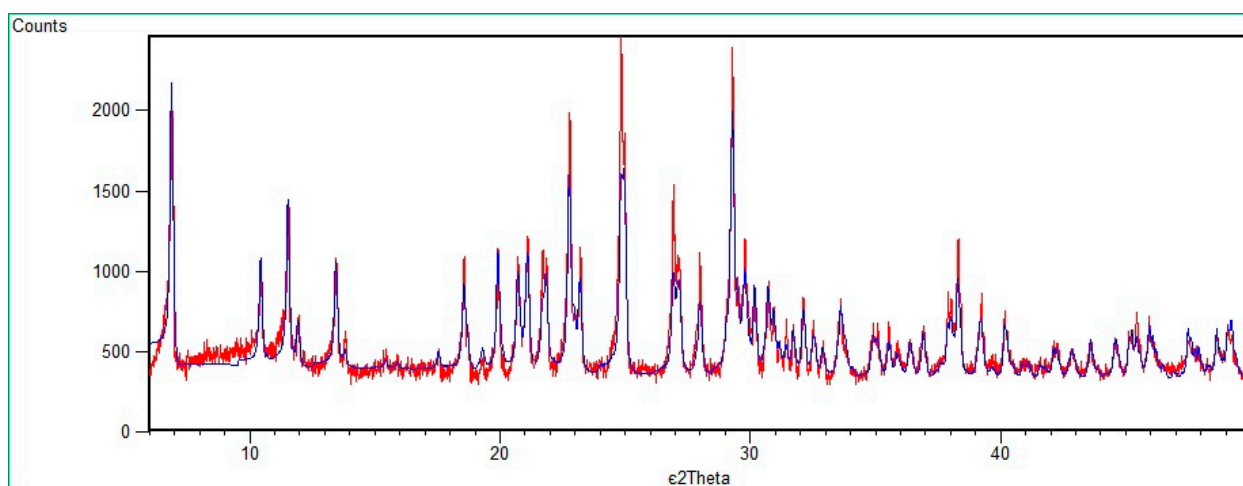


Figure S1. Comparison of experimental (red) and calculated (blue) PXRD patterns for **1**

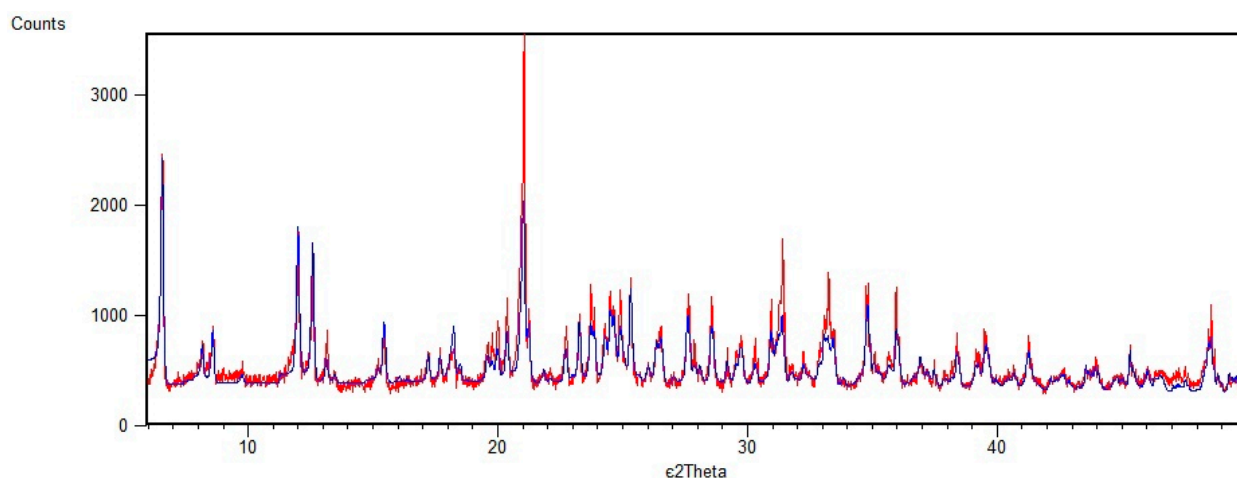


Figure S2. Comparison of experimental (red) and calculated (blue) PXRD patterns for **2**

Computational details

The DFT calculations based on the experimental X-ray geometries of **1** and **2** have been carried out using the dispersion-corrected hybrid functional ω B97XD [Phys. Chem. Chem. Phys. 2008, 10, 6615.] with the help of Gaussian-09 [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A.; J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,

K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J., D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [Mol. Phys. 2010, 108, 1965. || J. Chem. Phys. 2009, 130, 064108. || Chem. Phys. Lett. 2013, 582, 158. || J. Mol. Struct. - Theochem 2010, 961, 107.] for all atoms. The topological analysis of the electron density distribution has been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Cartesian atomic coordinates for model supramolecular associates are presented in **Table S1**.

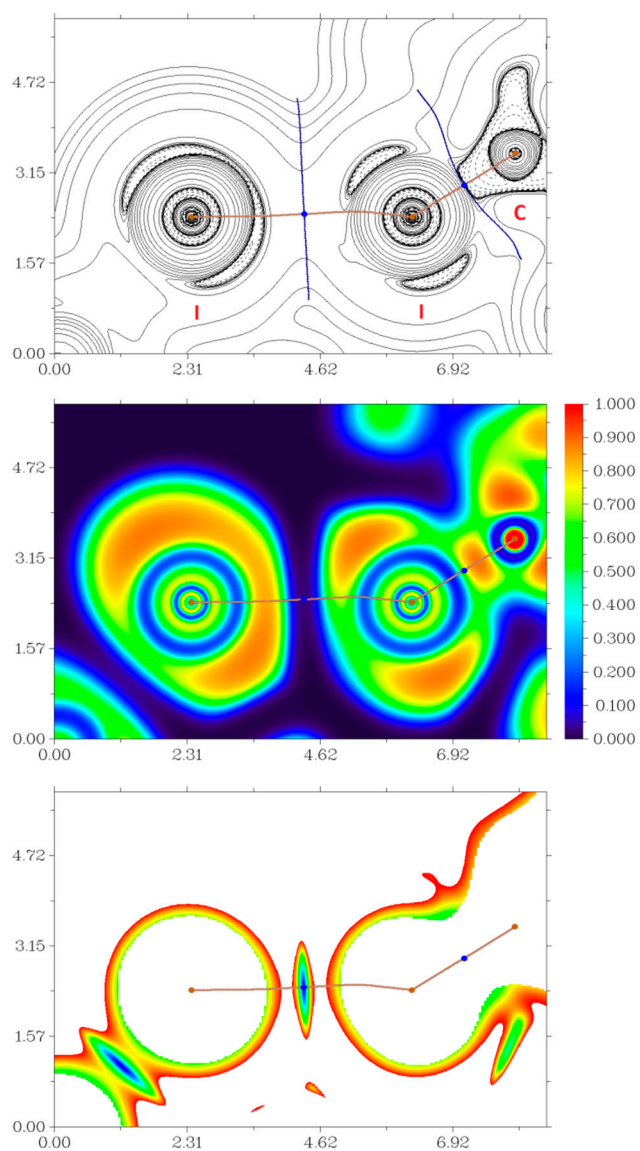


Figure S3. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for intermolecular interactions I...I in **1**. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

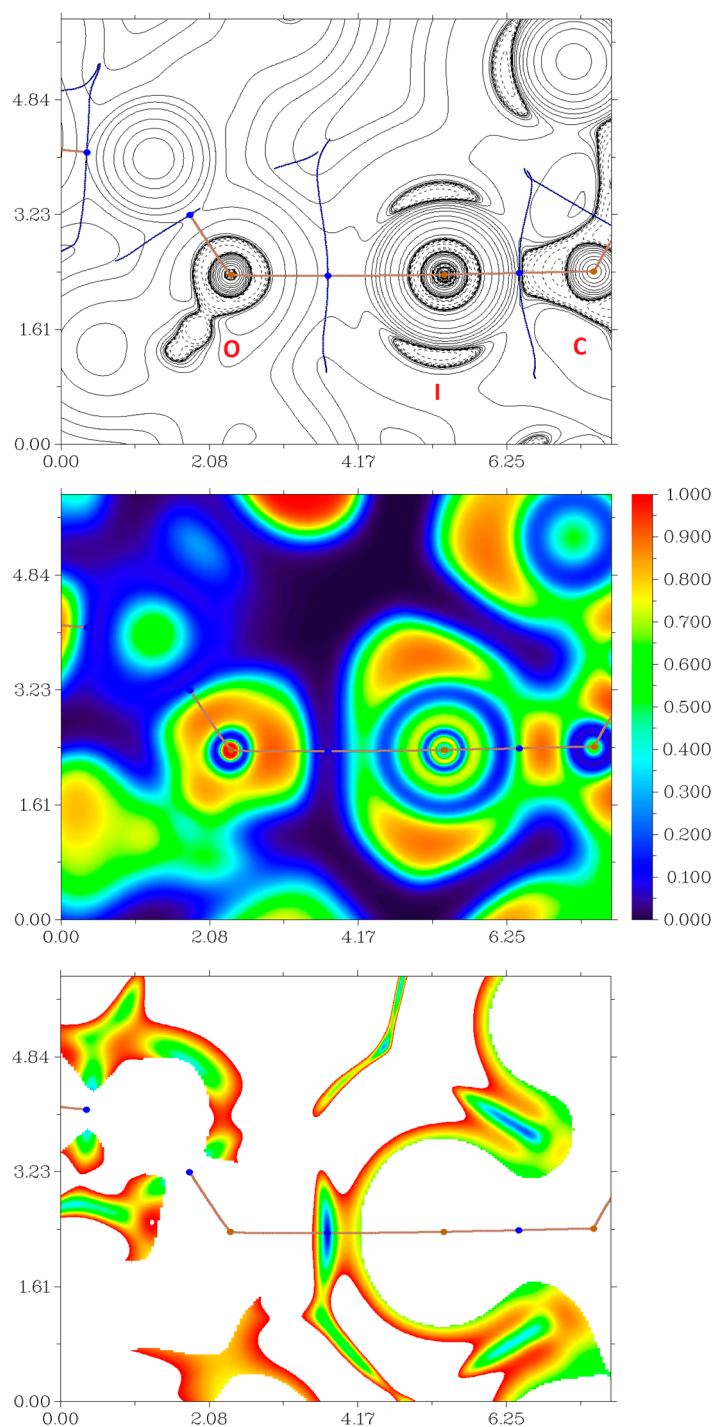


Figure S4. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for intermolecular interactions $\text{I}\cdots\text{O}$ in **2**. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

Table S1. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1			
I	17.481604	1.428625	8.442763
N	13.184513	1.022502	6.003012
C	15.194854	3.621403	8.034730
O	14.157045	3.042842	8.500044
Zn	12.749500	2.569100	7.236018
I	20.145230	2.739174	10.358690
C	16.189315	4.086924	9.095892
O	15.463614	3.826931	6.850713
I	19.477156	5.533225	12.418818
C	17.308721	3.305918	9.372316
I	16.630448	7.490982	11.791796
C	18.316952	3.763218	10.227695
C	18.107860	4.957335	10.941791
I	14.507911	6.583884	9.039378
C	12.513889	-0.220943	4.060364
C	11.538807	-0.389476	2.933168
H	10.719780	-0.810808	3.269484
H	11.938632	-0.954678	2.239036
H	11.321556	0.489157	2.555388
C	16.049071	5.325230	9.711704
C	16.960915	5.746563	10.693009
C	13.619526	-1.051276	4.238504
H	13.784759	-1.755209	3.621157
C	14.481392	-0.860135	5.307345
C	15.673725	-1.757264	5.517734
H	15.375897	-2.619454	5.875550
H	16.288761	-1.335932	6.153510
H	16.130667	-1.898051	4.663891
C	14.222322	0.187030	6.176545
H	14.799620	0.319596	6.919819
C	12.343556	0.811836	4.972564
H	11.602045	1.394507	4.866602
I	8.017396	3.709575	8.442763
N	12.314487	4.115698	6.003012
C	10.304146	1.516797	8.034730
O	11.341955	2.095358	8.500044
I	5.353770	2.399026	10.358690
C	9.309685	1.051276	9.095892
O	10.035386	1.311269	6.850713
I	6.021844	-0.395025	12.418818
C	8.190279	1.832282	9.372316

I	8.868552	-2.352782	11.791796
C	7.182048	1.374982	10.227695
C	7.391140	0.180865	10.941791
I	10.991089	-1.445684	9.039378
C	12.985111	5.359143	4.060364
C	13.960193	5.527676	2.933168
H	14.779220	5.949008	3.269484
H	13.560368	6.092878	2.239036
H	14.177444	4.649043	2.555388
C	9.449929	-0.187030	9.711704
C	8.538085	-0.608363	10.693009
C	11.879474	6.189476	4.238504
H	11.714241	6.893409	3.621157
C	11.017608	5.998335	5.307345
C	9.825275	6.895464	5.517734
H	10.123103	7.757654	5.875550
H	9.210239	6.474132	6.153510
H	9.368333	7.036251	4.663891
C	11.276678	4.951170	6.176545
H	10.699380	4.818604	6.919819
C	13.155444	4.326364	4.972564
H	13.896955	3.743693	4.866602
I	-4.732104	9.135925	4.603538
N	-0.435013	8.729802	2.163787
C	-2.445354	11.328703	4.195505
O	-1.407545	10.750142	4.660819
Zn	0.000000	10.276400	3.396793
I	-7.395730	10.446474	6.519465
C	-3.439815	11.794224	5.256667
O	-2.714114	11.534231	3.011488
I	-6.727656	13.240525	8.579593
C	-4.559221	11.013218	5.533091
I	-3.880948	15.198282	7.952571
C	-5.567452	11.470518	6.388470
C	-5.358360	12.664635	7.102566
I	-1.758411	14.291184	5.200153
C	0.235611	7.486357	0.221139
C	1.210693	7.317824	-0.906057
H	2.029720	6.896492	-0.569741
H	0.810868	6.752622	-1.600189
H	1.427944	8.196457	-1.283837
C	-3.299571	13.032530	5.872479
C	-4.211415	13.453863	6.853784
C	-0.870026	6.656024	0.399279
H	-1.035259	5.952091	-0.218068

C	-1.731892	6.847165	1.468120
C	-2.924225	5.950036	1.678509
H	-2.626397	5.087846	2.036325
H	-3.539261	6.371368	2.314285
H	-3.381167	5.809249	0.824666
C	-1.472822	7.894330	2.337320
H	-2.050120	8.026896	3.080594
C	0.405944	8.519136	1.133339
H	1.147455	9.101807	1.027377
I	4.732104	11.416875	4.603538
N	0.435013	11.822998	2.163787
C	2.445354	9.224097	4.195505
O	1.407545	9.802658	4.660819
I	7.395730	10.106326	6.519465
C	3.439815	8.758576	5.256667
O	2.714114	9.018569	3.011488
I	6.727656	7.312275	8.579593
C	4.559221	9.539582	5.533091
I	3.880948	5.354518	7.952571
C	5.567452	9.082282	6.388470
C	5.358360	7.888165	7.102566
I	1.758411	6.261616	5.200153
C	-0.235611	13.066443	0.221139
C	-1.210693	13.234976	-0.906057
H	-2.029720	13.656308	-0.569741
H	-0.810868	13.800178	-1.600189
H	-1.427944	12.356343	-1.283837
C	3.299571	7.520270	5.872479
C	4.211415	7.098937	6.853784
C	0.870026	13.896776	0.399279
H	1.035259	14.600709	-0.218068
C	1.731892	13.705635	1.468120
C	2.924225	14.602764	1.678509
H	2.626397	15.464954	2.036325
H	3.539261	14.181432	2.314285
H	3.381167	14.743551	0.824666
C	1.472822	12.658470	2.337320
H	2.050120	12.525904	3.080594
C	-0.405944	12.033664	1.133339
H	-1.147455	11.450993	1.027377
I	-4.732104	3.997725	12.281988
N	-0.435013	3.591602	9.842237
C	-2.445354	6.190503	11.873955
O	-1.407545	5.611942	12.339269
Zn	0.000000	5.138200	11.075243

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C	-3.439815	6.656024	12.935117
O	-2.714114	6.396031	10.689938
I	-6.727656	8.102325	16.258043
C	-4.559221	5.875018	13.211541
I	-3.880948	10.060082	15.631021
C	-5.567452	6.332318	14.066920
C	-5.358360	7.526435	14.781016
I	-1.758411	9.152984	12.878603
C	0.235611	2.348157	7.899589
C	1.210693	2.179624	6.772393
H	2.029720	1.758292	7.108709
H	0.810868	1.614422	6.078261
H	1.427944	3.058257	6.394613
C	-3.299571	7.894330	13.550929
C	-4.211415	8.315663	14.532234
C	-0.870026	1.517824	8.077729
H	-1.035259	0.813891	7.460382
C	-1.731892	1.708965	9.146570
C	-2.924225	0.811836	9.356959
H	-2.626397	-0.050354	9.714775
H	-3.539261	1.233168	9.992735
H	-3.381167	0.671049	8.503116
C	-1.472822	2.756130	10.015770
H	-2.050120	2.888696	10.759044
C	0.405944	3.380936	8.811789
H	1.147455	3.963607	8.705827
I	4.732104	6.278675	12.281988
N	0.435013	6.684798	9.842237
C	2.445354	4.085897	11.873955
O	1.407545	4.664458	12.339269
I	7.395730	4.968126	14.197915
C	3.439815	3.620376	12.935117
O	2.714114	3.880369	10.689938
I	6.727656	2.174075	16.258043
C	4.559221	4.401382	13.211541
I	3.880948	0.216318	15.631021
C	5.567452	3.944082	14.066920
C	5.358360	2.749965	14.781016
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C	-0.235611	7.928243	7.899589
C	-1.210693	8.096776	6.772393
H	-2.029720	8.518108	7.108709
H	-0.810868	8.661978	6.078261
H	-1.427944	7.218143	6.394613

C	3.299571	2.382070	13.550929
C	4.211415	1.960737	14.532234
C	0.870026	8.758576	8.077729
H	1.035259	9.462509	7.460382
C	1.731892	8.567435	9.146570
C	2.924225	9.464564	9.356959
H	2.626397	10.326754	9.714775
H	3.539261	9.043232	9.992735
H	3.381167	9.605351	8.503116
C	1.472822	7.520270	10.015770
H	2.050120	7.387704	10.759044
C	-0.405944	6.895464	8.811789
H	-1.147455	6.312793	8.705827
2			
I	3.22640400	4.83870000	6.07441000
N	0.23290500	3.88671800	8.97946900
O	3.94470300	1.91891700	8.18176500
C	4.95593700	3.70364400	5.70467000
I	4.61819400	4.70192200	2.84415200
O	4.96150700	3.76211300	8.93144100
N	2.58237800	2.02914500	12.32725000
C	5.55473000	3.69214200	4.44197400
I	7.62003200	2.89792900	2.32737500
N	4.35327400	7.68046100	10.78255400
O	2.13992900	4.11963300	10.14476700
C	6.73045000	2.93588600	4.23805400
I	8.95521200	0.95409100	4.98853400
N	7.72086800	3.07391000	12.72194400
O	3.15266700	1.73105100	11.22795900
C	7.28667700	2.20455000	5.30031800
I	7.44437500	1.19687900	8.20349900
O	1.81601500	1.22304600	12.85180900
C	6.66509300	2.24001500	6.54772000
Zn	4.06461800	3.57395900	10.72915900
O	2.84340600	3.13525400	12.83463600
C	5.48600100	2.96751600	6.75110300
C	4.73058200	2.86112300	8.07578000
O	4.29866700	5.49124700	11.38304600
O	5.77731200	2.91575700	11.60762600
C	-0.48953800	3.43047200	7.80800100
C	-0.59418100	4.48194600	10.02965900
C	1.48054400	3.65763600	9.22471000
H	1.93237100	3.07007600	8.63173200
C	4.25070600	6.38361000	10.52738500
H	4.13124100	6.12098100	9.62181800

C	4.51178900	8.20476000	12.11984200
H	4.57402300	7.46192300	12.75575100
H	3.73913000	8.76452400	12.34522800
H	5.32908600	8.74247900	12.16545600
C	4.33110000	8.66292300	9.70499600
H	4.24470800	8.20284300	8.84638500
H	5.16315600	9.17955500	9.71841200
H	3.56881100	9.26773600	9.83110500
C	8.12761500	1.72625900	12.36669300
H	7.46176900	1.33135700	11.76566500
H	8.19921100	1.18183100	13.17700800
H	8.99676500	1.75501400	11.91592200
C	8.56990400	3.79374300	13.64387800
H	8.28506100	4.73019800	13.68680900
H	9.49954000	3.74869400	13.33531400
H	8.50175800	3.38925600	14.53468800
C	6.55325900	3.56370300	12.29156400
H	6.31851000	4.45319100	12.52768300
I	1.51498300	9.63120000	7.34139900
N	4.50848200	8.67921800	4.43634000
O	0.79668400	6.71141700	5.23404400
C	-0.21455100	8.49614400	7.71113900
I	0.12319300	9.49442200	10.57165800
O	-0.22012000	8.55461300	4.48436800
N	2.15900900	6.82164500	1.08855900
C	-0.81334300	8.48464200	8.97383500
I	-2.87864500	7.69042900	11.08843500
N	0.38811300	12.47296100	2.63325500
O	2.60145800	8.91213300	3.27104300
C	-1.98906300	7.72838600	9.17775500
I	-4.21382500	5.74659100	8.42727500
N	-2.97948100	7.86641000	0.69386600
O	1.58872000	6.52355100	2.18785000
C	-2.54529100	6.99705000	8.11549100
I	-2.70298800	5.98937900	5.21231000
O	2.92537200	6.01554600	0.56400100
C	-1.92370600	7.03251500	6.86808900
Zn	0.67676900	8.36645900	2.68665000
O	1.89798100	7.92775400	0.58117300
C	-0.74461400	7.76001600	6.66470600
C	0.01080500	7.65362300	5.34002900
O	0.44271900	10.28374700	2.03276300
O	-1.03592500	7.70825700	1.80818300
C	5.23092500	8.22297100	5.60780800
C	5.33556800	9.27444600	3.38615000

C	3.26084300	8.45013600	4.19109900
H	2.80901600	7.86257600	4.78407800
C	0.49068100	11.17611000	2.88842400
H	0.61014600	10.91348100	3.79399100
C	0.22959800	12.99726000	1.29596700
H	0.16736400	12.25442300	0.66005800
H	1.00225700	13.55702400	1.07058200
H	-0.58769900	13.53497900	1.25035300
C	0.41028700	13.45542300	3.71081300
H	0.49667900	12.99534300	4.56942500
H	-0.42176900	13.97205500	3.69739700
H	1.17257600	14.06023700	3.58470400
C	-3.38622800	6.51875900	1.04911600
H	-2.72038200	6.12385700	1.65014500
H	-3.45782400	5.97433000	0.23880100
H	-4.25537800	6.54751400	1.49988700
C	-3.82851700	8.58624300	-0.22806900
H	-3.54367400	9.52269800	-0.27099900
H	-4.75815300	8.54119400	0.08049500
H	-3.76037100	8.18175600	-1.11887800
C	-1.81187200	8.35620300	1.12424500
H	-1.57712300	9.24569100	0.88812700
I	9.84921700	-0.04620000	-7.34139900
N	6.85571800	0.90578200	-4.43634000
O	10.56751600	2.87358300	-5.23404400
C	11.57875100	1.08885600	-7.71113900
I	11.24100700	0.09057800	-10.57165800
O	11.58432000	1.03038700	-4.48436800
N	9.20519100	2.76335600	-1.08855900
C	12.17754300	1.10035800	-8.97383500
I	14.24284500	1.89457100	-11.08843500
N	10.97608700	-2.88796100	-2.63325500
O	8.76274200	0.67286700	-3.27104300
C	13.35326300	1.85661400	-9.17775500
I	15.57802500	3.83840900	-8.42727500
N	14.34368100	1.71859100	-0.69386600
O	9.77548000	3.06144900	-2.18785000
C	13.90949100	2.58795000	-8.11549100
I	14.06718800	3.59562100	-5.21231000
O	8.43882800	3.56945400	-0.56400100
C	13.28790600	2.55248500	-6.86808900
Zn	10.68743100	1.21854100	-2.68665000
O	9.46621900	1.65724700	-0.58117300
C	12.10881400	1.82498400	-6.66470600
C	11.35339500	1.93137700	-5.34002900

O	10.92148100	-0.69874600	-2.03276300
O	12.40012500	1.87674300	-1.80818300
C	6.13327500	1.36202800	-5.60780800
C	6.02863200	0.31055400	-3.38615000
C	8.10335700	1.13486400	-4.19109900
H	8.55518400	1.72242500	-4.78407800
C	10.87351900	-1.59111000	-2.88842400
H	10.75405400	-1.32848100	-3.79399100
C	11.13460200	-3.41226000	-1.29596700
H	11.19683600	-2.66942300	-0.66005800
H	10.36194300	-3.97202400	-1.07058200
H	11.95189900	-3.94997900	-1.25035300
C	10.95391300	-3.87042300	-3.71081300
H	10.86752100	-3.41034300	-4.56942500
H	11.78596900	-4.38705500	-3.69739700
H	10.19162400	-4.47523700	-3.58470400
C	14.75042800	3.06624100	-1.04911600
H	14.08458200	3.46114300	-1.65014500
H	14.82202400	3.61067000	-0.23880100
H	15.61957800	3.03748700	-1.49988700
C	15.19271700	0.99875700	0.22806900
H	14.90787400	0.06230300	0.27099900
H	16.12235300	1.04380700	-0.08049500
H	15.12457100	1.40324400	1.11887800
C	13.17607200	1.22879700	-1.12424500
H	12.94132300	0.33930900	-0.88812700
I	12.87918300	0.04620000	7.34139900
N	15.87268200	-0.90578200	4.43634000
O	12.16088400	-2.87358300	5.23404400
C	11.14964900	-1.08885600	7.71113900
I	11.48739300	-0.09057800	10.57165800
O	11.14408000	-1.03038700	4.48436800
N	13.52320900	-2.76335600	1.08855900
C	10.55085700	-1.10035800	8.97383500
I	8.48555500	-1.89457100	11.08843500
N	11.75231300	2.88796100	2.63325500
O	13.96565800	-0.67286700	3.27104300
C	9.37513700	-1.85661400	9.17775500
I	7.15037500	-3.83840900	8.42727500
N	8.38471900	-1.71859100	0.69386600
O	12.95292000	-3.06144900	2.18785000
C	8.81890900	-2.58795000	8.11549100
I	8.66121200	-3.59562100	5.21231000
O	14.28957200	-3.56945400	0.56400100
C	9.44049400	-2.55248500	6.86808900

Zn	12.04096900	-1.21854100	2.68665000
O	13.26218100	-1.65724700	0.58117300
C	10.61958600	-1.82498400	6.66470600
C	11.37500500	-1.93137700	5.34002900
O	11.80691900	0.69874600	2.03276300
O	10.32827500	-1.87674300	1.80818300
C	16.59512500	-1.36202800	5.60780800
C	16.69976800	-0.31055400	3.38615000
C	14.62504300	-1.13486400	4.19109900
H	14.17321600	-1.72242500	4.78407800
C	11.85488100	1.59111000	2.88842400
H	11.97434600	1.32848100	3.79399100
C	11.59379800	3.41226000	1.29596700
H	11.53156400	2.66942300	0.66005800
H	12.36645700	3.97202400	1.07058200
H	10.77650100	3.94997900	1.25035300
C	11.77448700	3.87042300	3.71081300
H	11.86087900	3.41034300	4.56942500
H	10.94243100	4.38705500	3.69739700
H	12.53677600	4.47523700	3.58470400
C	7.97797200	-3.06624100	1.04911600
H	8.64381800	-3.46114300	1.65014500
H	7.90637600	-3.61067000	0.23880100
H	7.10882200	-3.03748700	1.49988700
C	7.53568300	-0.99875700	-0.22806900
H	7.82052600	-0.06230300	-0.27099900
H	6.60604700	-1.04380700	0.08049500
H	7.60382900	-1.40324400	-1.11887800
C	9.55232800	-1.22879700	1.12424500
H	9.78707700	-0.33930900	0.88812700
H	6.25787396	8.73721871	3.31105966
H	4.81645024	9.22419508	2.45186332
H	5.53716210	10.29716717	3.62760649
H	6.16611969	8.73873043	5.67340601
H	4.65114560	8.42278310	6.48463807
H	5.40863265	7.17071444	5.52985845
H	-0.07506324	5.30933526	10.46651568
H	-1.51648696	4.82235889	9.60731934
H	-0.79577510	3.74938681	10.78306251
H	0.09024131	2.69025623	7.29727938
H	-1.42473267	3.00620304	8.10851185
H	-0.66724568	4.25827236	7.15373306
H	17.62207396	-0.84778129	3.31105966
H	16.18065024	-0.36080492	2.45186332
H	16.90136210	0.71216717	3.62760649

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H	17.53031967	-0.84626848	5.67340552
H	16.01534569	-1.16221528	6.48463799
H	16.77283268	-2.41428461	5.52985921
H	6.71305431	1.16221528	-6.48463799
H	5.19808033	0.84626848	-5.67340552
H	5.95556732	2.41428461	-5.52985921
H	6.54774976	0.36080492	-2.45186332
H	5.10632604	0.84778129	-3.31105966
H	5.82703790	-0.71216717	-3.62760649