Supporting Information

Self-assembly of ordered water tetramers in an encapsulated $[Br(H_2O)_{12}]^-$ complex

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Synthesis

$[H_6L(BrH_2O)_{12}]Br_5$: The ligand L was synthesized according to previously published methods and isolated as the free base.[1] The bromide complex was prepared by mixing of the neutral ligand L (20 mg, 32 μmol) with 48% aqueous HBr (0.1 mL) in methanol (2 mL). The yellowish precipitate formed immediately was re-dissolved in a water/methanol mixture (1:1, v/v; 1 mL), and X-ray quality crystals were grown from this solution by slow evaporation after five days. Yield: 28 mg, 78%. ESI-MS: *m*/*z* 617.3 $[HL]^+$, 697.3 and 699.2 $[H_2LBr]^+$. ^{1}H NMR (500 MHz, D_2O, TSP): δ 7.275 (s, 6H, Ar*H*), 4.457 (s, 12H, ArCH_2), 3.388 (t, $^3J_{HH}$ = 5.5 Hz, 12H, NCH_2CH_2), 2.813 (t, $^3J_{HH}$ = 5.5 Hz, 12H, NCH_2CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 136.77 (*C*Ar), 134.54 (H*C*Ar), 53.10 (NCH_2CH_2), 48.92 (ArCH_2), 47.46 (NCH_2CH_2). Elemental analysis (%) calcd for $C_{30}H_{78}Br_6N_8O_{12}S_3$: C 27.33, H 5.96; N 8.50; found: C 27.12, H 5.87; N 8.55.

Crystallography: X-ray diffraction data for a single crystal of $[H_6L(Br(H_2O)_{12})]Br_5$ were collected using a Bruker APEX CCD area detector.[2] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[3] The positions of hydrogens bonded to carbon atoms were initially determined by geometry and refined by a riding model. Hydrogens bonded to nitrogen and oxygen atoms were located on a difference map, and their positions were refined independently. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms.

1. M. A. Saeed, F. R. Fronczek and M. A. Hossain, *Chem. Commun.*, 2009, 6409–6411.
2. *(a)* Data Collection: SMART Software Reference Manual, 1998. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711–5373, USA; *(b)* Data Reduction: SAINT Software Reference Manual, 1998. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711–5373, USA.
3. G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112–122.

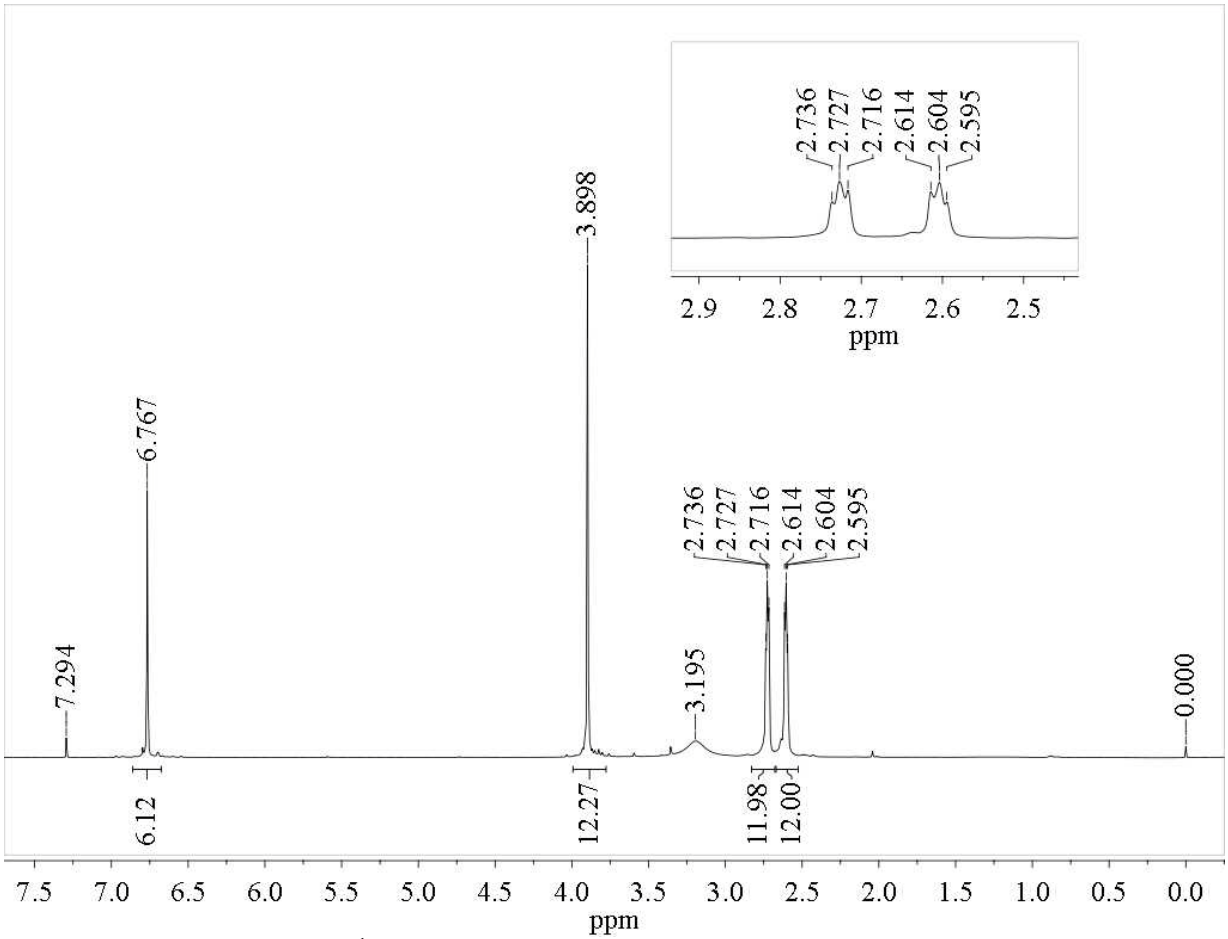

Figure S1. ^{1}H NMR spectra of L in $CDCl_3$ (500 MHz, 298K).

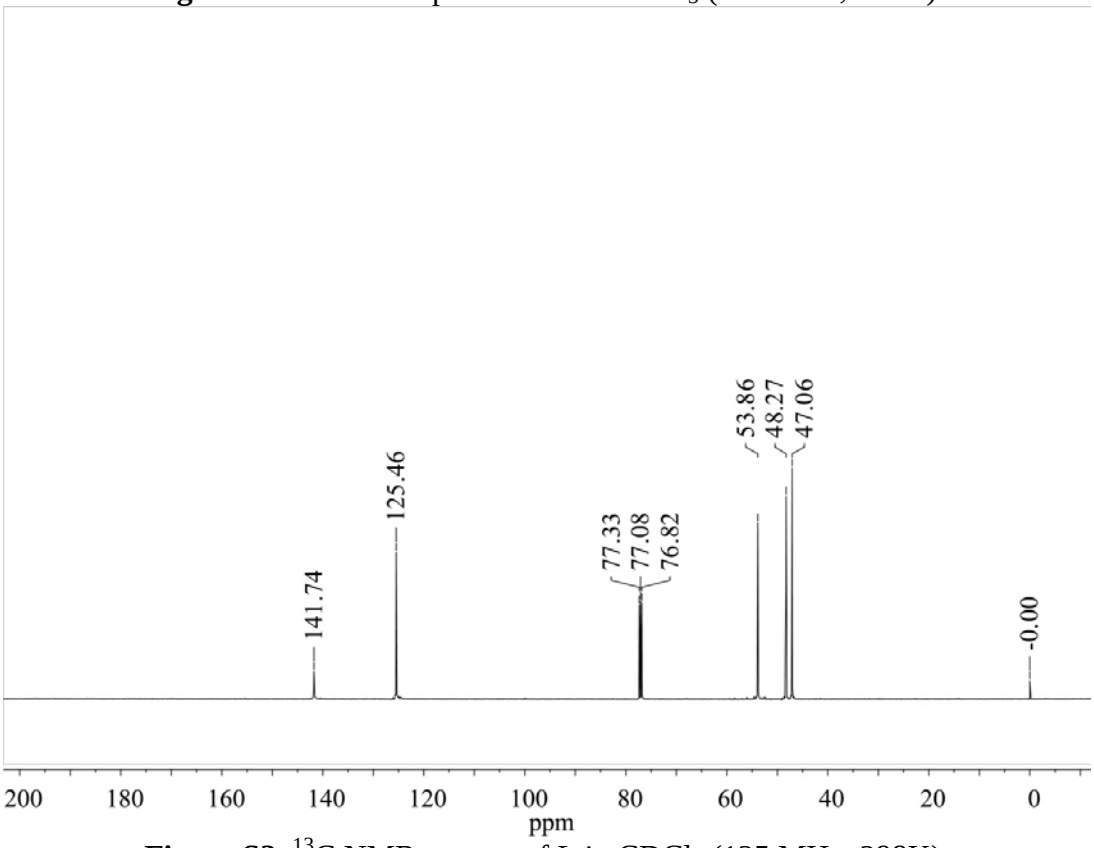

Figure S2. ^{13}C NMR spectra of L in $CDCl_3$ (125 MHz, 298K).

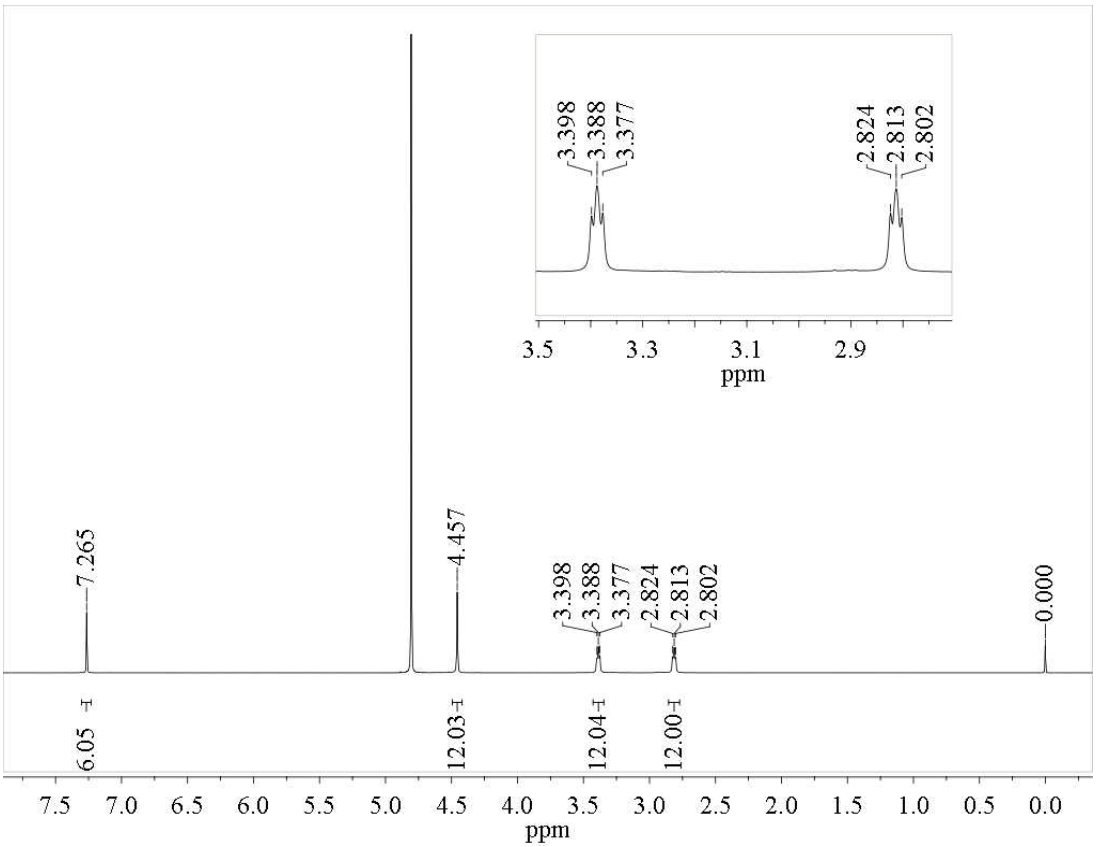

Figure S3. ^{1}H NMR spectra of $[H_6\mathbf{L}(Br)(6H_2O)]Br_5\cdot 6H_2O$, **5** in D_2O (500 MHz, 298K).

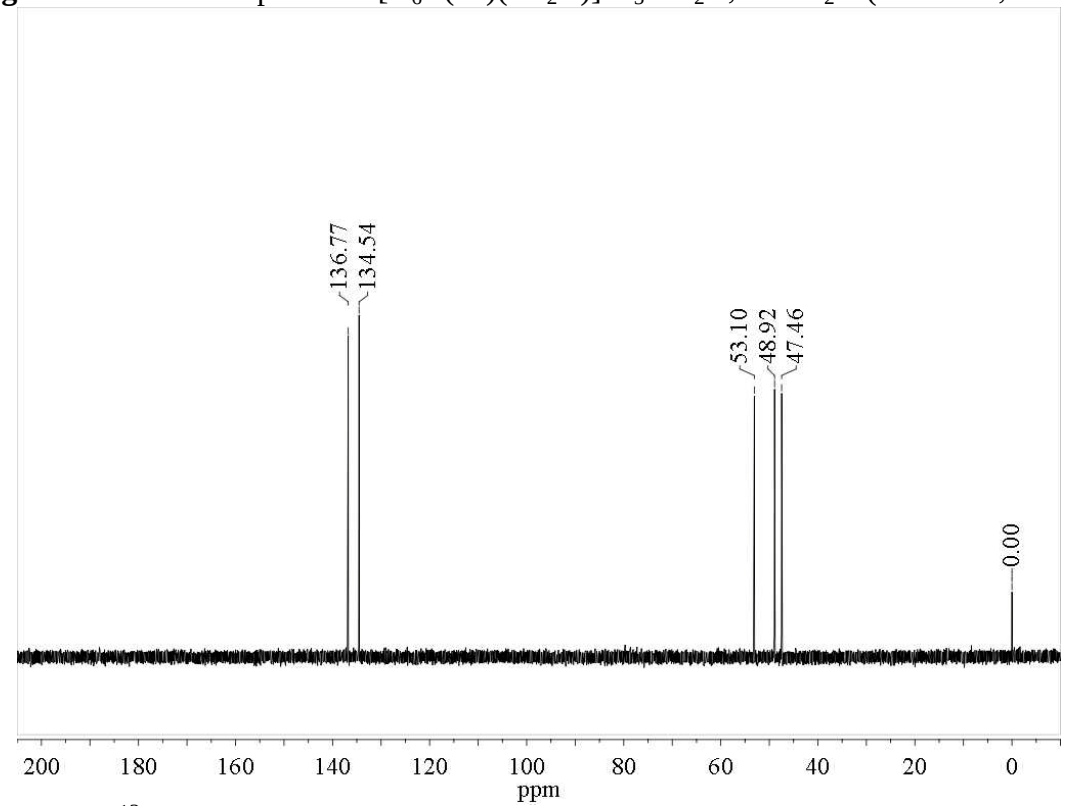

Figure S4. ^{13}C NMR spectra of $[H_6L(Br)(6H_2O)]Br_5\cdot 6H_2O$, **5** in D_2O (125 MHz, 298K).

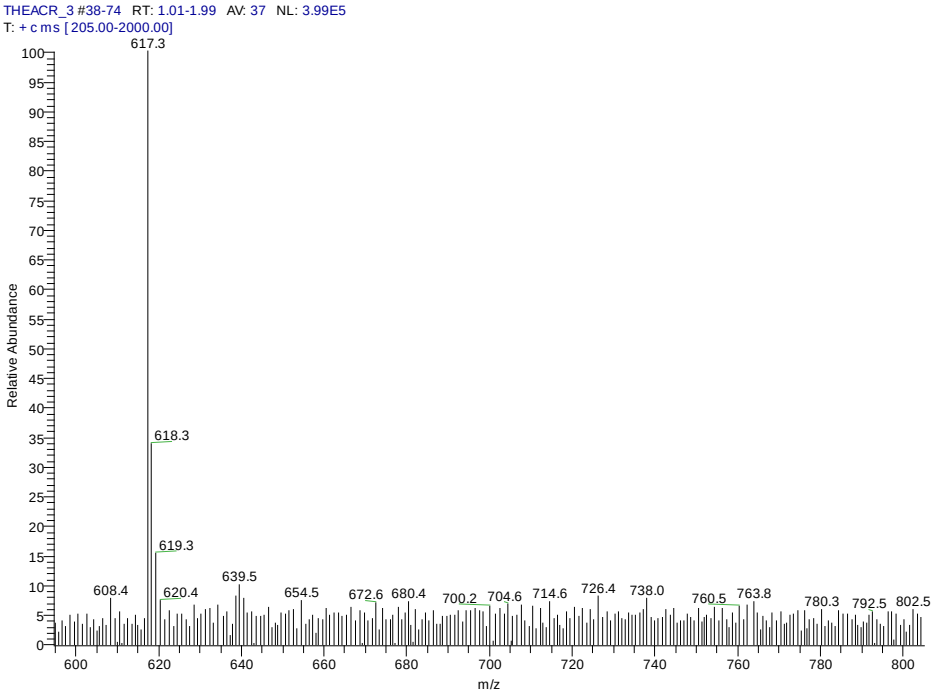

Figure S5. ESI-MS(positive mode) spectra of L in 50:50 water methanol mixture.

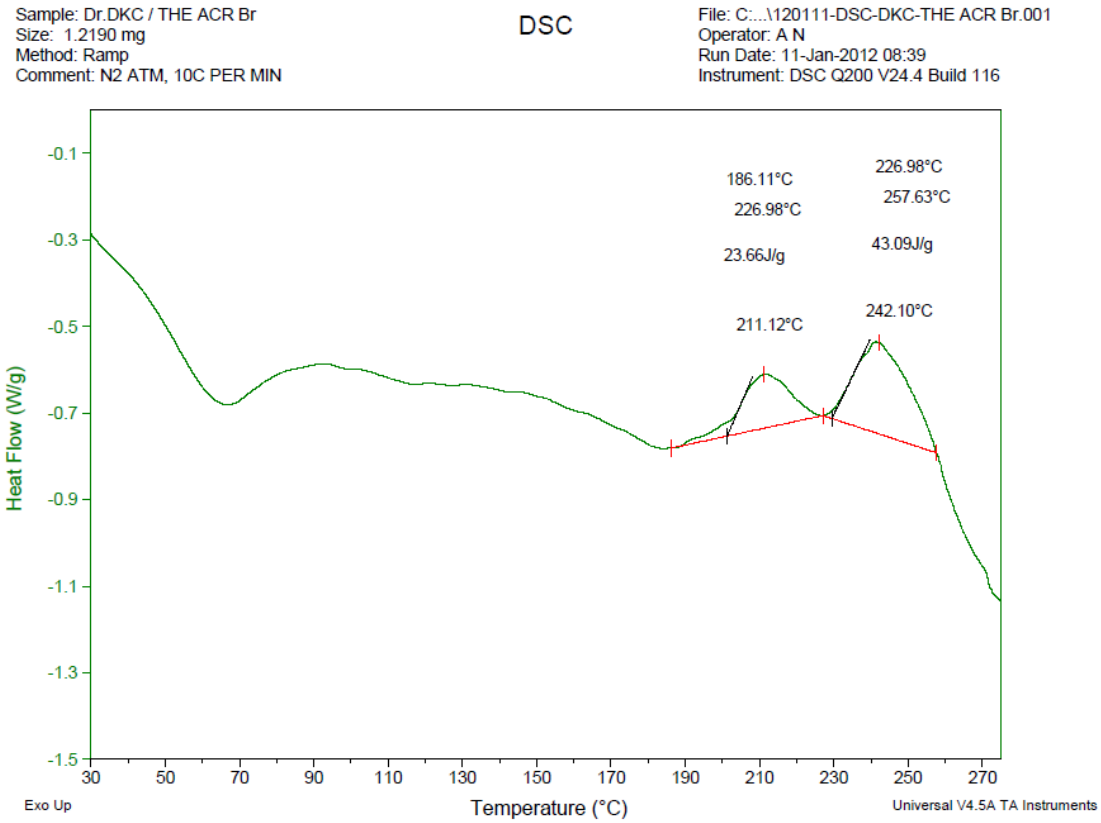

Figure S6. DSC curve of $[H_6L(Br)(6H_2O)]Br_5 \cdot 6H_2O$.

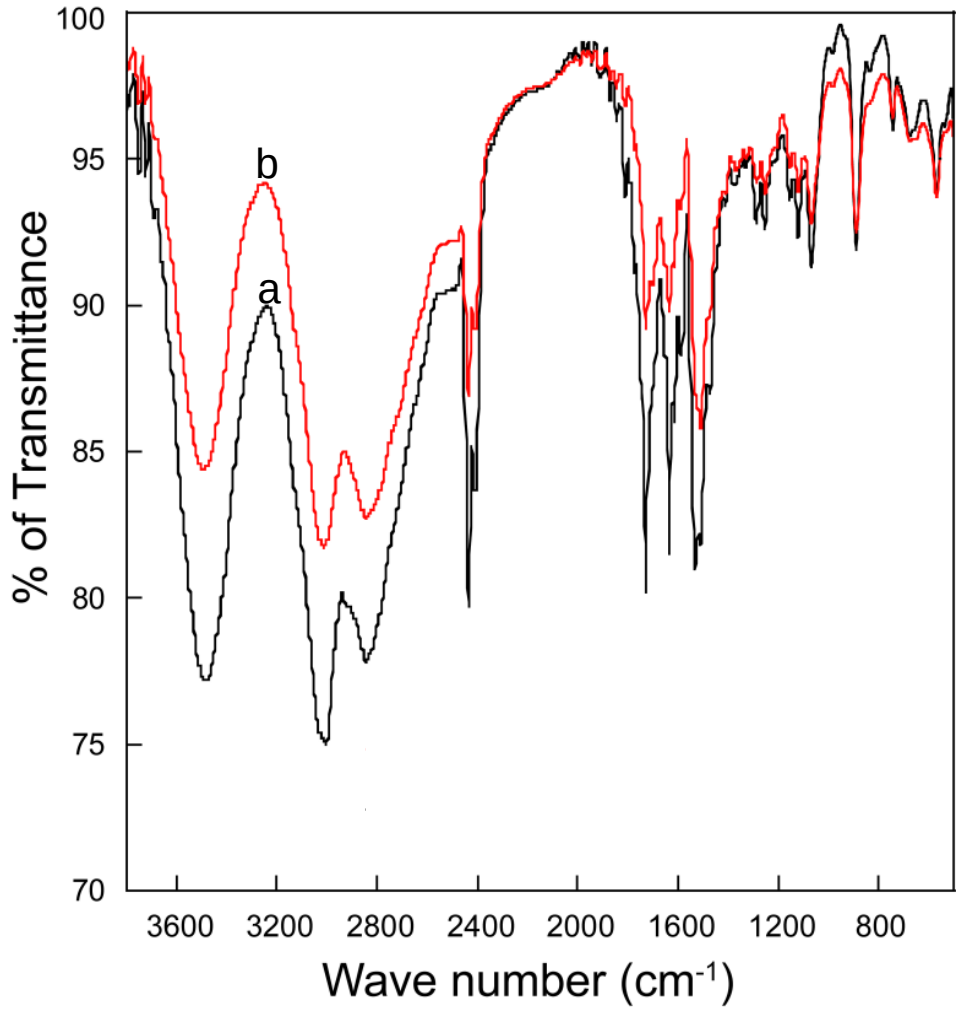

Figure S7. FTIR spectra of $[H_6L(Br)(6H_2O)]Br_5 \cdot 6H_2O$ (a) before and (b) after heating (130 °C for 12 hrs) showing an almost identical O–H vibration of water at 3480 cm^{-1}.

DFT Calculations

Table 1. Cartesian coordinates (Å)for the bromine-ligand complex:

S	0.046588	3.650839	0.441368
N	-4.849073	0.077978	0.010401
C	-5.344292	0.985285	1.064506
H	-5.167617	0.518041	2.037776
H	-6.432044	1.140353	0.983130
C	-4.684076	2.354484	1.085169
H	-5.080251	2.925534	1.928876
H	-4.856659	2.940988	0.180124
N	-3.202547	2.247510	1.260275
H	-2.969145	1.587136	2.028731
H	-2.787952	1.849276	0.404097
C	-2.560468	3.583049	1.518442
H	-2.811378	4.217575	0.665529
H	-3.039187	4.002006	2.407206

C	-1.084888	3.483025	1.737728
C	-0.446396	3.397943	2.945358
H	-0.970856	3.363473	3.894473
C	0.969910	3.463205	2.825817
H	1.647449	3.459769	3.673164
C	1.388976	3.603783	1.530425
C	2.808773	3.722049	1.064707
H	3.396094	4.265460	1.809341
H	2.887762	4.241342	0.106409
N	3.424617	2.357807	0.896319
H	3.095509	1.739378	1.661233
H	3.006770	1.947456	0.030907
C	4.915227	2.347709	0.797628
H	5.314281	2.959006	1.611281
H	5.190763	2.835929	-0.139608
C	5.470749	0.934707	0.942849
H	6.569522	1.007952	0.899491
H	5.220352	0.589521	1.950864
N	4.957415	-0.057074	-0.024124
S	-0.039507	-2.267706	2.977311
C	-5.396739	-1.270509	0.259394
H	-5.225117	-1.885877	-0.628515
H	-6.486416	-1.241287	0.417651
C	-4.770800	-1.990658	1.443626
H	-5.182545	-3.001363	1.504415
H	-4.950134	-1.504147	2.404768
N	-3.290236	-2.104698	1.276432
H	-3.055317	-2.416207	0.312455
H	-2.862469	-1.173553	1.390479
C	-2.657399	-3.034621	2.273047
H	-2.895775	-2.643668	3.264702
H	-3.147123	-4.005563	2.162949
C	-1.184131	-3.175292	2.056980
C	-0.561267	-4.077893	1.237502
H	-1.095626	-4.793581	0.621628
C	0.854967	-4.042530	1.357989
H	1.518084	-4.708304	0.816013
C	1.289338	-3.115086	2.266353
C	2.715911	-2.846052	2.641766
H	3.264990	-3.788563	2.712413
H	2.800947	-2.317302	3.594154
N	3.380447	-2.002781	1.586303
H	3.055966	-2.313857	0.651064
H	2.988753	-1.039453	1.689846
C	4.871613	-1.963103	1.648594
H	5.237013	-2.985975	1.771145
H	5.155787	-1.407868	2.544938
C	5.455959	-1.393700	0.359693
H	6.553182	-1.401651	0.461211
H	5.211464	-2.094054	-0.445093

S	0.001590	-1.438694	-3.386952
C	-5.338689	0.555691	-1.297655
H	-5.118680	1.623666	-1.383855
H	-6.432079	0.450784	-1.381367
C	-4.716095	-0.140302	-2.498342
H	-5.113706	0.307438	-3.412738
H	-4.920441	-1.212292	-2.541246
N	-3.229570	0.022248	-2.517334
H	-2.968451	1.013058	-2.342594
H	-2.818689	-0.522944	-1.744401
C	-2.613895	-0.453175	-3.804958
H	-2.875393	-1.508846	-3.903947
H	-3.100703	0.095855	-4.614874
C	-1.136426	-0.224759	-3.855984
C	-0.505197	0.871962	-4.378316
H	-1.035944	1.718518	-4.801141
C	0.910114	0.733878	-4.402861
H	1.581906	1.473943	-4.824836
C	1.337077	-0.466360	-3.903193
C	2.761524	-0.927746	-3.824564
H	3.326074	-0.510895	-4.662633
H	2.855101	-2.015988	-3.855168
N	3.403989	-0.449238	-2.550980
H	3.088601	0.520622	-2.358414
H	2.985611	-1.014830	-1.778711
C	4.893994	-0.548141	-2.514977
H	5.285925	-0.150530	-3.454676
H	5.158723	-1.606806	-2.476174
C	5.472028	0.275178	-1.367991
H	6.569086	0.181414	-1.415609
H	5.239420	1.324755	-1.573235
O	-1.280852	-0.289639	5.523577
H	-1.522292	0.354033	6.206899
H	-1.446747	-1.149984	5.936902
O	2.062665	0.331335	2.246420
H	1.799599	0.222304	3.201275
H	1.245268	0.351146	1.718334
O	-2.220657	2.465131	-1.484780
H	-1.369551	2.019203	-1.337076
H	-2.007570	3.330241	-1.894326
O	1.483167	-0.243515	4.753282
H	0.577219	-0.240012	5.113530
H	2.078994	-0.090236	5.497828
O	-2.299150	-2.476322	-1.353049
H	-1.423115	-2.196799	-1.037570
H	-2.159177	-3.291268	-1.880639
O	-1.540380	-4.715310	-2.905384
H	-1.891442	-5.594468	-2.697215
H	-1.594888	-4.655070	-3.870534
O	-1.240788	4.932893	-2.518445

H	-1.508168	5.206682	-3.408960
H	-1.364968	5.726597	-1.977072
O	2.021630	-2.125335	-0.856023
H	1.681690	-2.957282	-1.287911
H	1.237525	-1.650010	-0.527490
O	2.075261	1.720996	-1.427538
H	1.809437	2.589827	-1.836738
H	1.259530	1.251033	-1.179335
O	1.505201	4.150957	-2.267410
H	0.604463	4.493956	-2.413432
H	2.102992	4.702972	-2.787579
O	1.141104	-4.318546	-2.023578
H	0.251131	-4.508825	-2.370684
H	1.717285	-5.030720	-2.327894
O	-2.243977	0.113202	2.866626
H	-1.384232	0.185957	2.418617
H	-2.045063	0.017322	3.821731
Br	-0.575874	-0.002675	0.009002

Table 2. Cartesian coordinates in Angstroms for the ligand complex:

S	-0.001574	3.494825	-0.765761
N	4.662728	0.002039	0.003440
C	5.229195	1.033017	-0.919558
H	5.145695	0.674495	-1.950737
H	6.310031	1.145107	-0.739424
C	4.637706	2.443850	-0.844368
H	5.332530	3.149304	-1.308824
H	4.458683	2.785520	0.177335
N	3.320607	2.598171	-1.576743
H	3.455101	2.401873	-2.576851
H	2.655078	1.900329	-1.231028
C	2.690567	3.994334	-1.454038
H	2.828333	4.298832	-0.413178
H	3.282639	4.661207	-2.086045
C	1.250249	4.017254	-1.863076
C	0.715838	4.579563	-2.988737
H	1.308629	5.033069	-3.777842
C	-0.713044	4.578965	-2.990943
H	-1.304000	5.031470	-3.782014
C	-1.250340	4.015718	-1.867212
C	-2.691888	3.990882	-1.462942
H	-3.283190	4.655225	-2.098400
H	-2.833695	4.297313	-0.423172
N	-3.318439	2.593077	-1.584662
H	-3.447898	2.393207	-2.584730
H	-2.653079	1.897674	-1.233755
C	-4.638403	2.438538	-0.857482
H	-5.331901	3.141548	-1.327617

H	-4.464966	2.783318	0.164129
C	-5.226886	1.026598	-0.931438
H	-6.308471	1.137393	-0.755274
H	-5.139360	0.666665	-1.961771
N	-4.661807	-0.001880	-0.004430
S	0.004802	-2.412252	-2.648505
C	5.230645	-1.313448	-0.424702
H	5.143977	-2.026385	0.401724
H	6.312168	-1.215095	-0.608420
C	4.641946	-1.955259	-1.684899
H	5.337691	-2.709837	-2.062497
H	4.462336	-1.242412	-2.492499
N	3.325475	-2.668021	-1.453974
H	3.460656	-3.436487	-0.784928
H	2.659293	-2.020562	-1.022310
C	2.696284	-3.258545	-2.725413
H	2.834675	-2.508989	-3.509032
H	3.288007	-4.139515	-2.987025
C	1.255769	-3.623300	-2.540941
C	0.721074	-4.879053	-2.460617
H	1.314306	-5.788825	-2.452411
C	-0.707485	-4.880274	-2.461191
H	-1.299326	-5.790962	-2.453890
C	-1.244132	-3.625443	-2.541667
C	-2.685042	-3.263044	-2.727119
H	-3.275614	-4.145517	-2.986334
H	-2.824012	-2.515894	-3.512974
N	-3.315243	-2.669608	-1.457519
H	-3.448112	-3.435888	-0.785517
H	-2.650952	-2.018570	-1.028324
C	-4.633437	-1.961011	-1.691047
H	-5.326519	-2.718030	-2.068633
H	-4.454491	-1.248666	-2.499268
C	-5.225895	-1.319065	-0.432680
H	-6.307077	-1.222833	-0.619444
H	-5.140054	-2.031302	0.394453
S	-0.006707	-1.094375	3.415919
C	5.225157	0.289615	1.358756
H	5.133281	1.361498	1.563343
H	6.307462	0.085459	1.368533
C	4.634926	-0.483916	2.541944
H	5.326561	-0.430279	3.387403
H	4.460749	-1.540609	2.327243
N	3.314085	0.067928	3.036444
H	3.443147	1.034472	3.361578
H	2.650804	0.110049	2.256832
C	2.684718	-0.734024	4.186420
H	2.823539	-1.788616	3.933937
H	3.276020	-0.515989	5.079532
C	1.244124	-0.391059	4.407894

C	0.708748	0.314086	5.449676
H	1.300842	0.780397	6.231810
C	-0.720446	0.315147	5.449629
H	-1.311969	0.781626	6.232093
C	-1.256609	-0.389002	4.407659
C	-2.697548	-0.729954	4.186006
H	-3.289410	-0.508192	5.077811
H	-2.838045	-1.785022	3.936444
N	-3.323773	0.069840	3.032922
H	-3.453926	1.037031	3.355728
H	-2.658041	0.110595	2.255341
C	-4.643003	-0.483569	2.535580
H	-5.337534	-0.427964	3.378551
H	-4.468311	-1.540751	2.323874
C	-5.229517	0.286835	1.348787
H	-6.311472	0.080821	1.355570
H	-5.140200	1.359104	1.552443

Thermochemical data for bromide-ligand complex

Enthalpy of formation: 10484.34 kcal/mol

Table 3: Vibrational frequencies (1/cm):

20.2773	25.5199	31.6858
37.2995	40.9977	42.8056
46.4357	47.2526	50.0028
53.4802	55.3111	56.8825
60.2636	61.7088	63.8989
64.4527	67.5608	70.3914
72.2443	78.1631	79.4809
80.8867	85.0936	88.9068
92.6375	94.7536	98.0409
100.2421	102.4276	107.9375
109.6870	110.2759	116.0300
120.5571	133.0319	136.7556
141.3607	144.2353	148.0777
161.3484	165.1718	169.8100
172.0099	174.3720	181.4433
182.5388	183.8930	186.4365
191.8505	194.2051	197.9843
198.8693	203.5828	204.5654
210.8820	222.5433	224.5989
229.3047	236.7406	238.2512
246.7047	247.1362	250.5069
258.3260	260.2019	262.6378
270.2528	272.0487	273.7604
278.2855	279.9396	281.6048

293.0931	295.2794	296.9282
299.5429	300.2132	303.9833
304.7892	315.8693	322.2130
328.8173	330.3687	334.8321
335.6734	339.2869	347.9515
349.9555	358.6814	360.7469
365.1283	366.3604	373.5519
375.2564	381.8470	382.9897
391.7329	395.1774	397.0682
433.7492	436.3253	442.1518
475.3630	480.1323	483.8160
493.1365	503.7437	505.2749
509.3702	515.3550	530.3010
534.7652	565.2918	569.5358
570.9558	583.2512	592.5901
593.8052	601.1109	602.1730
604.1058	610.9636	615.4352
621.4693	623.7195	624.0440
629.2805	632.3268	637.7475
639.1703	670.2942	679.0321
712.5528	717.8408	720.6501
723.1249	726.2494	727.9547
729.8852	733.6042	738.3013
753.3062	759.8866	760.2967
762.3383	762.7816	769.8439
775.3021	791.1642	799.9623
802.4856	808.8795	833.0419
834.0448	834.9904	841.2967
846.1530	851.9963	853.2883
857.8716	861.0442	867.2768
868.8611	873.2157	884.7264
902.2627	910.8274	915.7355
922.8824	924.0400	925.3674
925.8621	927.0314	928.5944
933.4159	935.2227	937.9767
964.7743	970.7228	997.7221
999.0676	1005.2568	1007.0428
1018.2684	1024.5773	1027.9326
1031.4192	1038.1053	1040.2993
1064.4326	1072.0588	1072.2905
1079.5563	1081.0516	1083.2174
1086.2994	1086.7436	1093.5479
1097.7529	1103.0379	1112.0635
1112.3080	1116.4582	1117.0502
1129.4577	1131.5547	1163.0873
1163.8216	1164.3013	1166.0050
1181.9309	1188.2191	1215.8397
1216.6859	1223.6216	1225.0461
1230.9902	1239.0501	1248.4382
1248.6704	1260.5659	1261.2537

1276.1910	1280.9712	1281.8555
1311.7496	1312.4014	1316.2209
1318.4768	1331.6474	1340.0565
1347.9277	1349.2949	1350.8665
1358.3167	1359.9285	1360.8307
1364.9221	1365.2508	1366.2428
1367.7524	1368.5235	1368.9133
1405.9825	1406.0841	1407.0082
1412.2833	1414.3173	1417.4668
1419.8045	1428.0667	1430.0306
1433.0301	1434.6127	1439.6215
1443.7054	1446.1471	1447.6228
1448.7746	1449.9415	1454.8075
1456.2917	1458.4311	1460.1275
1482.0775	1484.4366	1489.4576
1492.1200	1494.1137	1495.3634
1495.8070	1498.2782	1499.2811
1499.6013	1500.5911	1503.2050
1505.0468	1507.0557	1511.3095
1514.0733	1515.9200	1516.8827
1517.3649	1518.8375	1522.7023
1523.0281	1525.4476	1533.0412
1554.8631	1557.7842	1557.9719
1629.0066	1633.8121	1635.2821
1643.3556	1645.2102	1645.7549
1658.3270	1661.5754	1662.1441
1664.0990	1665.8126	1668.5238
1675.2466	1677.9534	1687.8649
1695.0788	1698.7903	1706.7670
1712.9579	1716.2409	1724.8529
3041.3515	3044.3428	3046.8363
3047.6711	3051.9858	3053.8521
3070.2094	3080.8776	3091.9061
3115.7543	3117.4553	3118.2129
3119.3806	3119.7377	3120.2658
3121.8079	3122.5970	3122.7666
3122.7894	3123.9246	3124.5087
3127.6656	3130.8354	3134.1794
3136.4142	3137.3501	3139.8731
3176.0796	3176.7927	3180.1027
3180.5026	3181.4680	3181.6787
3182.1370	3182.8155	3182.9415
3183.5831	3184.1219	3185.4180
3203.6291	3213.2487	3214.4582
3221.1798	3224.6239	3225.7399
3226.5461	3227.4102	3229.1353
3238.3847	3238.9463	3246.1047
3281.7604	3289.7899	3298.0370
3394.4904	3400.5307	3406.4128
3582.9594	3598.8081	3602.8405

3687.6658	3699.6620	3700.2295
3732.6625	3746.5843	3762.6617
3790.8824	3792.6421	3801.9266
3812.3468	3815.0236	3817.7852
3896.2908	3896.8469	3900.2741
3903.6908	3909.6644	3913.5351

Thermochemical data for the ligand

Enthalpy of formation: 7202.79 kcal/mol

Table 4. Vibrational frequencies (1/cm):

25.1733	26.6212	29.5494
32.1095	35.3840	35.7707
48.5726	49.6864	50.9698
58.6149	61.9725	64.3567
67.3644	68.3313	70.6217
91.3386	93.1073	106.9904
110.3031	113.2992	123.7446
123.9128	133.6819	134.5862
170.4435	177.3328	179.3210
197.4549	213.1322	214.3592
214.5214	217.5679	222.6555
249.2479	254.7931	257.9233
262.8464	275.3720	276.2798
282.6753	286.1036	314.5746
333.0259	333.3777	337.1286
342.4010	346.2042	349.5301
354.8802	368.1211	370.4461
434.5552	434.9221	437.9554
474.9548	484.6634	485.5852
518.0888	536.6135	537.6631
546.5109	560.2255	561.1633
576.2776	578.5015	579.6222
613.4346	614.2002	616.6692
678.9824	680.2448	681.2789
694.3806	696.3694	697.0241
722.9075	723.3810	753.6458
754.2523	755.8327	781.9316
782.7296	782.8155	783.5110
820.5359	821.7074	845.2710
845.5983	847.6358	848.2335
872.1672	877.5162	882.4314
886.6915	889.2408	889.2855
891.6767	900.6003	908.9392
918.9617	919.5740	921.5268
928.2320	929.9697	930.6955

936.8567	937.2213	975.2260
977.4721	981.6065	982.4768
982.6874	986.5957	988.9104
1035.4202	1035.6986	1039.4545
1039.6191	1043.2062	1051.7989
1065.2591	1068.9279	1071.1052
1073.5192	1081.4472	1082.3391
1091.4950	1092.6747	1096.3649
1097.0609	1098.8986	1138.0839
1138.2437	1140.1856	1140.3640
1162.5362	1164.7193	1188.8163
1189.1413	1189.5381	1189.9504
1207.9041	1214.3427	1215.7709
1217.7359	1222.3087	1223.9092
1266.9488	1268.1859	1276.2583
1292.1730	1293.5463	1295.4101
1296.4922	1307.1016	1307.6274
1332.1226	1333.5916	1337.5846
1340.3416	1342.5706	1346.4001
1358.5170	1360.7669	1363.6112
1366.8823	1369.5230	1372.0238
1388.0167	1389.6011	1390.3887
1390.5033	1391.7576	1392.4436
1395.2680	1396.8461	1400.5576
1403.3376	1404.4845	1410.7717
1411.8785	1412.9641	1413.1749
1415.9887	1418.2492	1419.2964
1424.7885	1433.5035	1433.5432
1453.5169	1454.0234	1455.9858
1456.1128	1456.7214	1456.8819
1480.7598	1481.1691	1484.0437
1484.1645	1487.7135	1487.9036
1494.4494	1494.5489	1495.7809
1495.8585	1497.7221	1497.9710
1502.2048	1502.4262	1506.3116
1506.4645	1507.8637	1508.0079
1558.5134	1560.5421	1561.2070
1642.7216	1644.2899	1644.9563
1651.2983	1652.1457	1656.3428
1657.0473	1657.1409	1657.9745
3050.5443	3050.8363	3053.2776
3053.6461	3054.7323	3054.7994
3116.7205	3116.7721	3117.5301
3117.5993	3121.2753	3121.3379
3122.1697	3122.3408	3122.4707
3122.5783	3124.1202	3124.4471
3125.2158	3125.2975	3131.2470
3131.2718	3131.6973	3131.7158
3180.5452	3180.6076	3183.5584
3183.5850	3184.4309	3184.5553

3187.0186	3187.3468	3187.6471
3187.8760	3188.3888	3188.6706
3233.3169	3234.1758	3240.3494
3241.8529	3242.7009	3248.8284
3412.4234	3412.6964	3415.7054
3416.0095	3417.6563	3418.3541
3488.5298	3488.9313	3501.6246
3502.3362	3502.9539	3503.9228