Supplementary Information for:

Benzene, an unexpected binding unit in anion-π recognition: The critical role of CH/π interactions.

Table S1. Variation of electron density ($\Delta\rho_{BCP}$ and $\Delta\rho_{CCP}$) and Laplacian ($\Delta\nabla^2\rho_{BCP}$ and $\Delta\nabla^2\rho_{CCP}$), in a.u., for the intermolecular bond critical points and cage critical points, respectively, in all three-component complexes with respect to the two-component analogues for the CH/π (Hπ) and anion-π (Aπ) interactions.

Compound	$\Delta\rho_{BCP}\times10^4$	$\Delta\nabla^2\rho_{BCP}\times10^4$	$\Delta\rho_{CCP}\times10^4$	$\Delta\nabla^2\rho_{CCP}\times10^4$
8a (Hπ)	3.89	10.02	3.23	11.69
(Aπ)	1.10	4.90	2.94	9.93
8b (Hπ)	3.95	10.10	3.20	11.56
(Aπ)	1.09	4.71	2.82	10.11
9a (Hπ)	3.90	7.64	1.72	7.36
(Aπ)	0.84	3.81	2.21	7.62
9b (Hπ)	3.82	7.51	1.71	7.36
(Aπ)	0.85	3.84	2.24	7.74
9c (Hπ)	3.78	6.97	1.79	7.75
(Aπ)	0.83	4.05	2.40	8.52
9d (Hπ)	3.71	6.67	1.74	7.51
(Aπ)	0.83	4.09	2.42	8.32
10a (Hπ)	1.34	1.95	0.67	2.18
(Aπ)	0.60	2.77	1.63	5.62
10b (Hπ)	1.38	0.66	0.62	2.10
(Aπ)	0.57	2.65	1.56	5.55
10c (Hπ)	0.68	0.68	0.45	1.12
(Aπ)	0.62	2.86	1.70	6.23
10d (Hπ)	1.54	1.54	0.64	2.15
(Aπ)	0.55	2.58	1.47	5.14
11a (Hπ)	3.96	11.24	3.19	13.39
(Aπ)	1.01	5.30	1.98	7.12
11b (Hπ)	4.11	11.83	3.30	14.04
(Aπ)	1.01	5.38	2.05	7.42

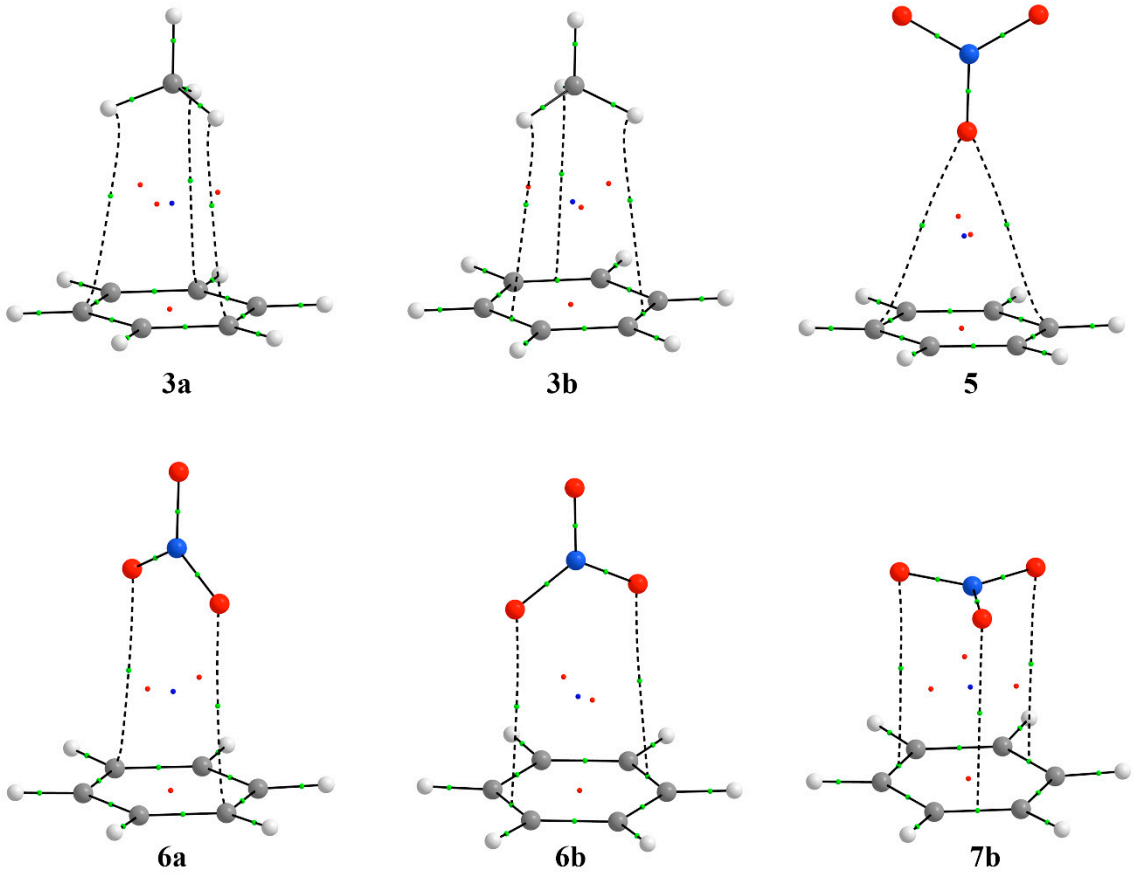

Figure S1. Molecular graphs of complexes **3a**-**b**, **5**-**6**, and **7b**. The BCPs, ring and cage critical points are represented by green, red, and blue dots, respectively. Only bond paths are depicted.

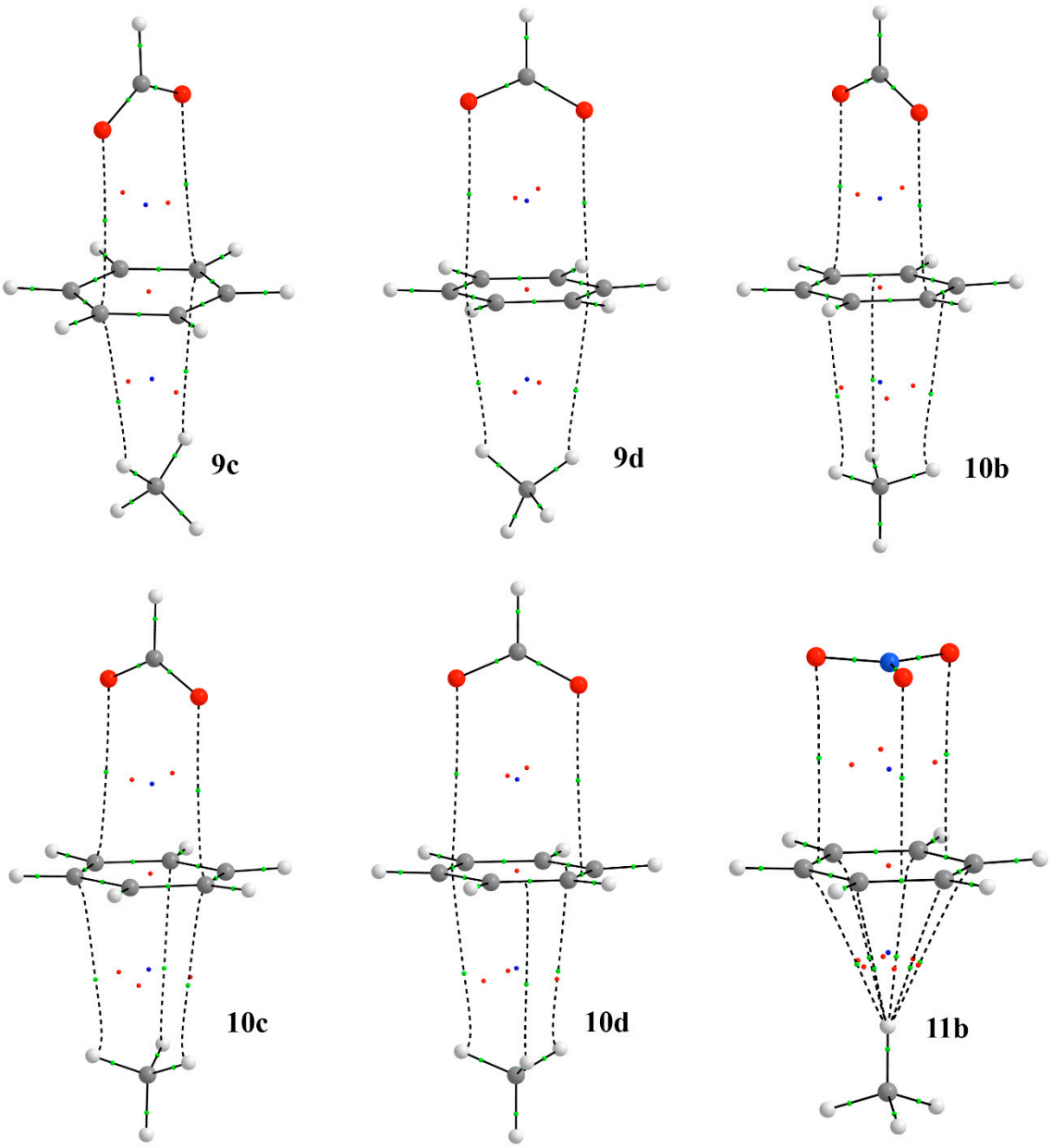

Figure S2. Molecular graphs of complexes **9c**-**d**, **10b**-**d**, and **11b**. The BCPs, ring and cage critical points are represented by green, red, and blue dots, respectively. Only bond paths are depicted.

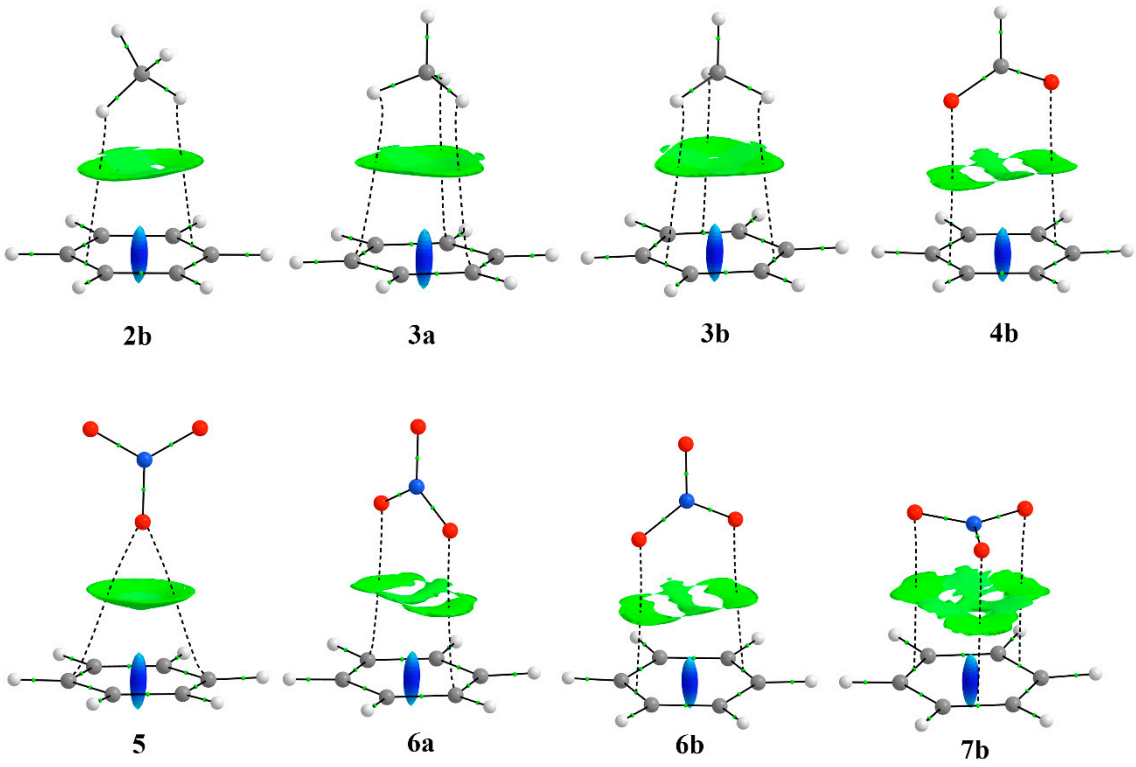

Figure S3. NCIPLOT gradient isosurfaces (isovalue = 0.5 au) for two-component complexes **2b**, **3a-b**, **4b**, **5**, **6a**-**b**, and **7b**. Green and blue indicate weak and strongly repulsive interactions, respectively.

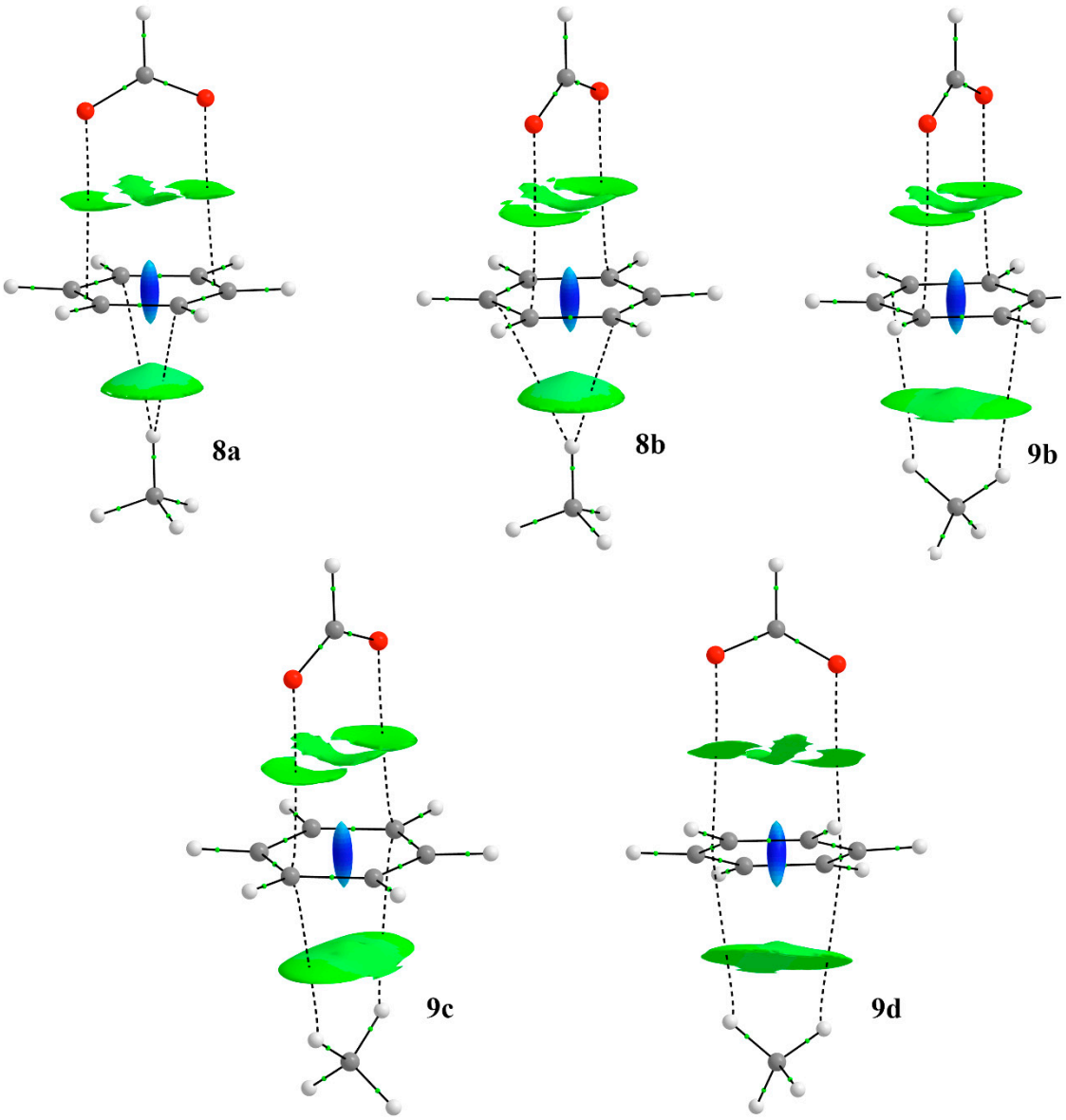

Figure S4. NCIPLOT gradient isosurfaces (isovalue = 0.5 au) for three-component complexes **8a**-**b**, and **9b**-**d**. Green and blue indicate weak and strongly repulsive interactions, respectively.

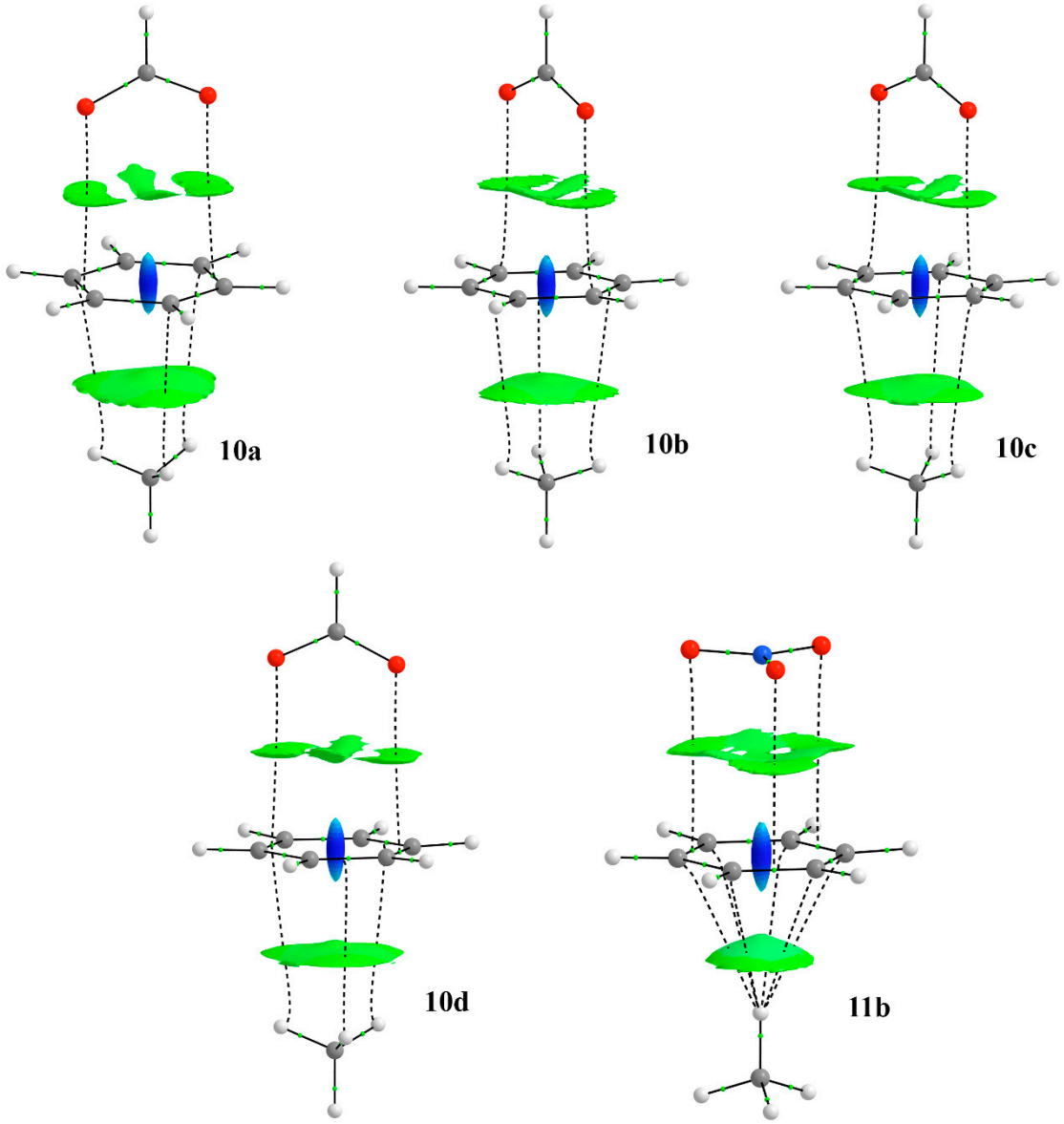

Figure S5. NCIPLOT gradient isosurfaces (isovalue = 0.5 au) for three-component complexes **10a-d**, and **11b**. Green and blue indicate weak and strongly repulsive interactions, respectively.

CARTESIAN COORDINATES

Complex 1

C 0.6967 -1.1049 1.2057
C 1.3928 -1.1057 0.0000
C 0.6967 -1.1049 -1.2057
C -0.6956 -1.1040 -1.2057
C -1.3917 -1.1032 0.0000
C -0.6956 -1.1040 1.2057
H 1.2374 -1.1042 2.1422
H 2.4742 -1.1056 0.0000

H 1.2374 -1.1042 -2.1422
H -1.2363 -1.1024 -2.1422
H -2.4731 -1.1011 0.0000
H -1.2363 -1.1024 2.1422
H -0.0011 1.5619 0.0000
C -0.0013 2.6482 0.0000
H 0.5106 3.0122 -0.8867
H -1.0253 3.0119 0.0000
H 0.5106 3.0122 0.8867

Complex 2a

C -0.6961 1.2057 1.0793
C -1.3921 0.0000 1.0807
C -0.6961 -1.2057 1.0793
C 0.6961 -1.2057 1.0793
C 1.3921 0.0000 1.0807
C 0.6961 1.2057 1.0793
H -1.2367 2.1423 1.0788
H -2.4736 0.0000 1.0823
H -1.2367 -2.1423 1.0788
H 1.2367 -2.1423 1.0788
H 2.4736 0.0000 1.0823
H 1.2367 2.1423 1.0788
H -0.8835 0.0000 -1.9615
C 0.0000 0.0000 -2.5933
H 0.0000 -0.8870 -3.2211
H 0.0000 0.8870 -3.2211
H 0.8835 0.0000 -1.9615

Complex 2b

C -0.6961 1.2057 1.0809
C -1.3922 0.0000 1.0795
C -0.6961 -1.2057 1.0809
C 0.6961 -1.2057 1.0809
C 1.3922 0.0000 1.0795
C 0.6961 1.2057 1.0809
H -1.2369 2.1422 1.0817
H -2.4736 0.0000 1.0785
H -1.2369 -2.1422 1.0817
H 1.2369 -2.1422 1.0817
H 2.4736 0.0000 1.0785
H 1.2369 2.1422 1.0817
H 0.0000 -0.8835 -1.9631
C 0.0000 0.0000 -2.5949
H 0.8870 0.0000 -3.2227
H -0.8870 0.0000 -3.2227
H 0.0000 0.8835 -1.9631

Complex 3a

C -0.6979 -1.0701 1.2056
C -1.3941 -1.0723 0.0000
C -0.6979 -1.0701 -1.2056
C 0.6942 -1.0656 -1.2057
C 1.3902 -1.0634 0.0000
C 0.6942 -1.0656 1.2057
H -1.2387 -1.0721 2.1422
H -2.4755 -1.0761 0.0000
H -1.2387 -1.0721 -2.1422
H 1.2349 -1.0640 -2.1422
H 2.4717 -1.0601 0.0000
H 1.2349 -1.0640 2.1422
H -0.5073 2.1999 -0.8854
C 0.0045 2.5659 0.0000
H 0.0064 3.6526 0.0000
H -0.5073 2.1999 0.8854
H 1.0262 2.1973 0.0000

Complex 3b

C 1.2053 -1.0672 -0.6961
C 1.2053 -1.0672 0.6961
C -0.0004 -1.0680 1.3922
C -1.2060 -1.0688 0.6961
C -1.2060 -1.0688 -0.6961
C -0.0004 -1.0680 -1.3922
H 2.1419 -1.0667 -1.2367
H 2.1419 -1.0667 1.2367
H -0.0005 -1.0682 2.4736
H -2.1425 -1.0696 1.2369
H -2.1425 -1.0696 -1.2369
H -0.0005 -1.0682 -2.4736
H 0.5119 2.1991 0.8854
C 0.0009 2.5662 0.0000
H 0.0015 3.6529 0.0000
H 0.5119 2.1991 -0.8854
H -1.0216 2.1999 0.0000

Complex 4a

C -0.6953 1.2036 -1.0057
C -1.3911 0.0000 -0.9996
C -0.6953 -1.2036 -1.0057
C 0.6953 -1.2036 -1.0057
C 1.3911 0.0000 -0.9996
C 0.6953 1.2036 -1.0057
H -1.2364 2.1395 -0.9647
H -2.4709 0.0000 -0.9454

H -1.2364 -2.1395 -0.9647
H 1.2364 -2.1395 -0.9647
H 2.4709 0.0000 -0.9454
H 1.2364 2.1395 -0.9647
O -1.1376 0.0000 2.3961
C 0.0000 0.0000 2.9274
O 1.1376 0.0000 2.3961
H 0.0000 0.0000 4.0522

Complex 4b

C -0.6951 1.2045 -1.0009
C -1.3897 0.0000 -1.0064
C -0.6951 -1.2045 -1.0009
C 0.6951 -1.2045 -1.0009
C 1.3897 0.0000 -1.0064
C 0.6951 1.2045 -1.0009
H -1.2344 2.1405 -0.9514
H -2.4711 0.0000 -0.9693
H -1.2344 -2.1405 -0.9514
H 1.2344 -2.1405 -0.9514
H 2.4711 0.0000 -0.9693
H 1.2344 2.1405 -0.9514
O 0.0000 1.1376 2.3932
C 0.0000 0.0000 2.9246
O 0.0000 -1.1376 2.3932
H 0.0000 0.0000 4.0494

Complex 5

C 0.0000 1.3910 1.1265
C 1.2042 0.6954 1.1273
C 1.2042 -0.6954 1.1273
C 0.0000 -1.3910 1.1265
C -1.2042 -0.6954 1.1273
C -1.2042 0.6954 1.1273
H 0.0000 2.4718 1.0909
H 2.1404 1.2361 1.0944
H 2.1404 -1.2361 1.0944
H 0.0000 -2.4718 1.0909
H -2.1404 -1.2361 1.0944
H -2.1404 1.2361 1.0944
O 0.0000 0.0000 -2.0726
N 0.0000 0.0000 -3.3300
O 0.0000 1.0896 -3.9594
O 0.0000 -1.0896 -3.9594

Complex 6a

C 0.0000 1.3911 1.0134
C 1.2039 0.6954 1.0168

C 1.2039 -0.6954 1.0168
C 0.0000 -1.3911 1.0134
C -1.2039 -0.6954 1.0168
C -1.2039 0.6954 1.0168
H 0.0000 2.4715 0.9688
H 2.1399 1.2364 0.9806
H 2.1399 -1.2364 0.9806
H 0.0000 -2.4715 0.9688
H -2.1399 -1.2364 0.9806
H -2.1399 1.2364 0.9806
O 0.0000 -1.0888 -2.3588
N 0.0000 0.0000 -2.9894
O 0.0000 1.0888 -2.3588
O 0.0000 0.0000 -4.2469

Complex 6b

C 0.0000 1.3900 1.0168
C 1.2046 0.6952 1.0139
C 1.2046 -0.6952 1.0139
C 0.0000 -1.3900 1.0168
C -1.2046 -0.6952 1.0139
C -1.2046 0.6952 1.0139
H 0.0000 2.4713 0.9829
H 2.1408 1.2350 0.9723
H 2.1408 -1.2350 0.9723
H 0.0000 -2.4713 0.9829
H -2.1408 -1.2350 0.9723
H -2.1408 1.2350 0.9723
O -1.0888 0.0000 -2.3563
N 0.0000 0.0000 -2.9869
O 1.0888 0.0000 -2.3563
O 0.0000 0.0000 -4.2445

Complex 7a

C -0.6955 0.8616 1.2046
C -1.3909 0.8629 0.0000
C -0.6955 0.8616 -1.2046
C 0.6955 0.8629 -1.2046
C 1.3909 0.8616 0.0000
C 0.6955 0.8629 1.2046
H -1.2355 0.8121 2.1400
H -2.4713 0.8150 0.0000
H -1.2355 0.8121 -2.1400
H 1.2356 0.8150 -2.1402
H 2.4711 0.8121 0.0000
H 1.2356 0.8150 2.1402
O 1.2581 -2.5135 0.0000
N 0.0000 -2.5143 0.0000

O -0.6291 -2.5135 1.0896
O -0.6291 -2.5135 -1.0896

Complex 7b

C -1.2048 0.8615 0.6951
C -1.2048 0.8615 -0.6951
C 0.0005 0.8614 -1.3910
C 1.2044 0.8614 -0.6959
C 1.2044 0.8614 0.6959
C 0.0005 0.8614 1.3910
H -2.1400 0.8129 1.2358
H -2.1400 0.8129 -1.2358
H -0.0002 0.8127 -2.4712
H 2.1402 0.8126 -1.2354
H 2.1402 0.8126 1.2354
H -0.0002 0.8127 2.4712
O 1.2581 -2.5101 0.0000
N -0.0000 -2.5119 0.0000
O -0.6291 -2.5115 1.0896
O -0.6291 -2.5115 -1.0896

Complex 8a

C -1.3917 0.1234 0.0000
C -0.6970 0.1291 1.2047
C 0.6932 0.1297 1.2046
C 1.3879 0.1239 0.0000
C 0.6932 0.1297 -1.2046
C -0.6970 0.1291 -1.2047
H -2.4731 0.1592 0.0000
H -1.2364 0.1769 2.1407
H 1.2326 0.1784 2.1406
H 2.4693 0.1599 0.0000
H 1.2326 0.1784 -2.1406
H -1.2364 0.1769 -2.1407
H -0.5134 -3.9495 0.8873
C -0.0006 -3.5862 0.0000
H 1.0232 -3.9524 0.0000
H -0.5134 -3.9495 -0.8873
H 0.0015 -2.4999 0.0000
O 0.0067 3.4887 1.1375
C 0.0064 4.0205 0.0000
O 0.0067 3.4887 -1.1375
H 0.0058 5.1451 0.0000

Complex 8b

C -0.1253 0.6948 1.2037
C -0.1319 1.3907 0.0000
C -0.1253 0.6948 -1.2037

C -0.1241 -0.6959 -1.2038
C -0.1300 -1.3916 0.0000
C -0.1241 -0.6959 1.2038
H -0.1656 1.2360 2.1395
H -0.1853 2.4705 0.0000
H -0.1656 1.2360 -2.1395
H -0.1630 -1.2371 -2.1396
H -0.1824 -2.4715 0.0000
H -0.1630 -1.2371 2.1396
H 3.9489 1.0279 0.0000
C 3.5873 0.0024 0.0000
H 3.9529 -0.5089 -0.8872
H 3.9529 -0.5089 0.8872
H 2.5010 -0.0004 0.0000
O -3.4924 1.1361 0.0000
C -4.0241 -0.0014 0.0000
O -3.4922 -1.1389 0.0000
H -5.1486 -0.0015 0.0000

Complex 9a

C -0.6951 1.2046 0.1095
C -1.3898 0.0000 0.1053
C -0.6951 -1.2046 0.1095
C 0.6951 -1.2046 0.1095
C 1.3898 0.0000 0.1053
C 0.6951 1.2046 0.1095
H -1.2343 2.1407 0.1591
H -2.4712 0.0000 0.1451
H -1.2343 -2.1407 0.1591
H 1.2343 -2.1407 0.1591
H 2.4712 0.0000 0.1451
H 1.2343 2.1407 0.1591
H -0.8790 0.0000 -2.9005
C 0.0000 0.0000 -3.5380
H 0.0000 -0.8881 -4.1659
H 0.0000 0.8881 -4.1659
H 0.8790 0.0000 -2.9005
O 0.0000 -1.1375 3.4768
C 0.0000 0.0000 4.0086
O 0.0000 1.1375 3.4768
H 0.0000 0.0000 5.1332

Complex 9b

C -0.6953 1.2037 0.1066
C -1.3911 0.0000 0.1111
C -0.6953 -1.2037 0.1066
C 0.6953 -1.2037 0.1066
C 1.3911 0.0000 0.1111

C 0.6953 1.2037 0.1066
H -1.2366 2.1395 0.1490
H -2.4710 0.0000 0.1646
H -1.2366 -2.1395 0.1490
H 1.2366 -2.1395 0.1490
H 2.4710 0.0000 0.1646
H 1.2366 2.1395 0.1490
H 0.0000 -0.8790 -2.9028
C 0.0000 0.0000 -3.5404
H 0.8880 0.0000 -4.1683
H -0.8880 0.0000 -4.1683
H 0.0000 0.8790 -2.9028
O -1.1376 0.0000 3.4802
C 0.0000 0.0000 4.0120
O 1.1376 0.0000 3.4802
H 0.0000 0.0000 5.1365

Complex 9c

C -0.6953 1.2037 0.1047
C -1.3911 0.0000 0.1123
C -0.6953 -1.2037 0.1047
C 0.6953 -1.2037 0.1047
C 1.3911 0.0000 0.1123
C 0.6953 1.2037 0.1047
H -1.2364 2.1396 0.1458
H -2.4709 0.0000 0.1692
H -1.2364 -2.1396 0.1458
H 1.2364 -2.1396 0.1458
H 2.4709 0.0000 0.1692
H 1.2364 2.1396 0.1458
H -0.8791 0.0000 -2.8996
C 0.0000 0.0000 -3.5371
H 0.0000 -0.8880 -4.1651
H 0.0000 0.8880 -4.1651
H 0.8791 0.0000 -2.8996
O -1.1376 0.0000 3.4784
C 0.0000 0.0000 4.0102
O 1.1376 0.0000 3.4784
H 0.0000 0.0000 5.1347

Complex 9d

C -0.6951 1.2046 0.1112
C -1.3898 0.0000 0.1039
C -0.6951 -1.2046 0.1112
C 0.6951 -1.2046 0.1112
C 1.3898 0.0000 0.1039
C 0.6951 1.2046 0.1112
H -1.2346 2.1405 0.1625

H -2.4712 0.0000 0.1404
H -1.2346 -2.1405 0.1625
H 1.2346 -2.1405 0.1625
H 2.4712 0.0000 0.1404
H 1.2346 2.1405 0.1625
H 0.0000 -0.8791 -2.9015
C 0.0000 0.0000 -3.5390
H 0.8880 0.0000 -4.1669
H -0.8880 0.0000 -4.1669
H 0.0000 0.8791 -2.9015
O 0.0000 1.1375 3.4761
C 0.0000 0.0000 4.0079
O 0.0000 -1.1375 3.4761
H 0.0000 0.0000 5.1325

Complex 10a

C -0.1039 0.6877 1.2046
C -0.0974 1.3823 0.0000
C -0.1039 0.6877 -1.2046
C -0.1061 -0.7025 -1.2045
C -0.1013 -1.3973 0.0000
C -0.1061 -0.7025 1.2045
H -0.1535 1.2271 2.1406
H -0.1337 2.4638 0.0000
H -0.1535 1.2271 -2.1406
H -0.1573 -1.2418 -2.1406
H -0.1409 -2.4786 0.0000
H -0.1573 -1.2418 2.1406
H 4.6182 -0.0067 0.0000
C 3.5303 0.0096 0.0000
H 3.1493 -0.4948 -0.8830
H 3.1493 -0.4948 0.8830
H 3.1725 1.0349 0.0000
O -3.4792 0.0041 1.1376
C -4.0109 0.0100 0.0000
O -3.4792 0.0041 -1.1376
H -5.1354 0.0226 0.0000

Complex 10b

C -1.2034 0.1006 0.6953
C 0.0003 0.1066 1.3910
C 1.2040 0.1004 0.6953
C 1.2040 0.1004 -0.6953
C 0.0003 0.1066 -1.3910
C -1.2034 0.1006 -0.6953
H -2.1393 0.1424 1.2364
H 0.0004 0.1614 2.4709
H 2.1398 0.1419 1.2366

H 2.1398 0.1419 -1.2366
H 0.0004 0.1614 -2.4709
H -2.1393 0.1424 -1.2364
H 0.0026 -4.6199 0.0000
C -0.0004 -3.5318 0.0000
H 1.0182 -3.1556 0.0000
H -0.5114 -3.1601 -0.8832
H -0.5114 -3.1601 0.8832
O -0.0002 3.4832 1.1376
C -0.0003 4.0149 0.0000
O -0.0002 3.4832 -1.1376
H -0.0008 5.1395 0.0000

Complex 10c

C -0.1005 0.6899 1.2037
C -0.1053 1.3856 0.0000
C -0.1005 0.6899 -1.2037
C -0.1037 -0.7007 -1.2037
C -0.1110 -1.3965 0.0000
C -0.1037 -0.7007 1.2037
H -0.1413 1.2312 2.1396
H -0.1577 2.4657 0.0000
H -0.1413 1.2312 -2.1396
H -0.1466 -1.2418 -2.1396
H -0.1683 -2.4763 0.0000
H -0.1466 -1.2418 2.1396
H 4.6237 -0.0016 0.0000
C 3.5357 0.0080 0.0000
H 3.1581 -0.4988 -0.8831
H 3.1581 -0.4988 0.8831
H 3.1717 1.0311 0.0000
O -3.4806 1.1424 0.0000
C -4.0149 0.0060 0.0000
O -3.4859 -1.1328 0.0000
H -5.1395 0.0086 0.0000

Complex 10d

C -1.2048 0.1048 0.6951
C -0.0001 0.0993 1.3898
C 1.2044 0.1050 0.6951
C 1.2044 0.1050 -0.6951
C -0.0001 0.0993 -1.3898
C -1.2048 0.1048 -0.6951
H -2.1407 0.1549 1.2346
H -0.0003 0.1371 2.4712
H 2.1405 0.1553 1.2344
H 2.1405 0.1553 -1.2344
H -0.0003 0.1371 -2.4712

H -2.1407 0.1549 -1.2346
H 0.0012 -4.6190 0.0000
C -0.0008 -3.5309 0.0000
H 0.5086 -3.1568 -0.8831
H -1.0212 -3.1595 0.0000
H 0.5086 -3.1568 0.8831
O -1.1363 3.4809 0.0000
C 0.0014 4.0123 0.0000
O 1.1388 3.4802 0.0000
H 0.0018 5.1369 0.0000

Complex 11a
C -0.6955 -0.2313 1.2047
C -1.3909 -0.2309 0.0000
C -0.6955 -0.2313 -1.2047
C 0.6956 -0.2308 -1.2046
C 1.3912 -0.2312 0.0000
C 0.6956 -0.2308 1.2046
H -1.2356 -0.2795 2.1402
H -2.4713 -0.2780 0.0000
H -1.2356 -0.2795 -2.1402
H 1.2358 -0.2777 -2.1403
H 2.4714 -0.2793 0.0000
H 1.2358 -0.2777 2.1403
O 1.2579 -3.5824 0.0000
N -0.0002 -3.5835 0.0000
O -0.6293 -3.5825 1.0896
O -0.6293 -3.5825 -1.0896
H -0.5123 3.8406 0.8872
C -0.0000 3.4766 0.0000
H 1.0244 3.8407 0.0000
H 0.0000 2.3903 0.0000
H -0.5123 3.8406 -0.8872

Complex 11b
C -1.2049 -0.2321 0.6951
C -1.2049 -0.2321 -0.6951
C 0.0005 -0.2320 -1.3911
C 1.2045 -0.2320 -0.6960
C 1.2045 -0.2320 0.6960
C 0.0005 -0.2320 1.3911
H -2.1402 -0.2796 1.2357
H -2.1402 -0.2796 -1.2357
H -0.0000 -0.2794 -2.4713
H 2.1403 -0.2793 -1.2356
H 2.1403 -0.2793 1.2356
H -0.0000 -0.2794 2.4713
O 1.2580 -3.5802 0.0000

N -0.0001 -3.5818 0.0000
O -0.6292 -3.5810 1.0896
O -0.6292 -3.5810 -1.0896
H -0.5122 3.8414 0.8872
C 0.0000 3.4773 0.0000
H 1.0245 3.8415 0.0000
H 0.0001 2.3911 0.0000
H -0.5122 3.8414 -0.8872