Supplementary Materials

Stereochemical Geometries and Photoluminescence in Pseudo-Halido-Zinc(II) Complexes. Structural Comparison between the Corresponding Cadmium(II) Analogs

Franz A. Mautner [1,*], Roland C. Fischer [2], Ana Torvisco [2], Nahed M. H. Salem [3], Amber R. Dugas [4], Shelby F. Aaron [4], Sushant P. Sahu [4], Febee R. Louka [4] and Salah S. Massoud [3,4,*]

[1] Institut für Physikalische and Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria
[2] Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9/V, A-8010 Graz, Austria;
roland.fischer@tugraz.at (R.C.F.); ana.torviscogomez@tugraz.at (A.T.)
[3] Department of Chemistry, Faculty of Science, Alexandria University, Moharam Bey, Alexandria 21511, Egypt; nahed_s@yahoo.com
[4] Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 43700, Lafayette, LA 70504, USA;
amber.dugas2@louisiana.edu (A.R.D.); shelby.aaron1@louisiana.edu (S.F.A.);
sushant.sahu@louisiana.edu (S.P.S.); febee.louka@louisiana.edu (F.R.L.)
* Correspondence: mautner@tugraz.at (F.A.M.); ssmassoud@louisiana.edu (S.S.M.);
Tel.: +43-316-4873-8234 (F.A.M.); +1-337-482-5672 (S.S.M.);
Fax: +43-316-4873-8225 (F.A.M.); +1-337-482-5676 (S.S.M.)

Contents

Preparation of Nitrate Complexes

[Zn(NTB)(N_3)]NO_3 (**3a**)

Sodium azide (0.065 g, 1.0 mmol) dissolved in H_2O (5 mL) was added to a mixture containing tris(2-benzimidazolyl)amine monohydrate, NTP (0.213 g, 0.50 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.150 g, 0.5 mmol) dissolved in MeOH (15 mL). The resulting solution was heated for 10 min on a steam-bath, filtered through celite, and then allowed to crystallize at room temperature. After one day, the compound which separated was collected by filtration and recrystallized from CH_3CN to afford colorless tiny, long needles (yield: 0.225 g, 78%). Characterization: Anal. Calcd. ($C_{24}H_{21}N_{11}O_3Zn$, MM = 576.89 g/mol): C, 49.97; H, 3.67; N, 26.71%. Found: C, 49.74; H, 3,59; N, 26.27 IR bands (ATR, cm^{-1}): 3173 (vw) ν(N-H); 3106 (vw), 3047 (vw), 2974 (vw), 2900 (vw), 2844 (vw) ν(C-H); 2063 (vs), 2029 (m) ν(N_3^-); 1625 (m), 1596, 1540 (m), 1474 (m), 1454 (s), 1389 (m), 1343 (m) ν(C=C and C=N); 1277 (s), 1041 (s), 966 (s), 915 (m), 750 (vs). UV (MeOH) λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$): ~243 (1.27×10^4, b), 263 (1.50×10^4), 271 (1.50×10^4), 278 (1.26×10^4), 286 (sh). Molar conductivity, Λ_M (MeOH) = 141 $\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$.

[Zn(TPA)(NCS)]$NO_3{\cdot}½H_2O$ (**4c**)

Ammonium thiocyanate (0.076 g, 1.0 mmol) was added to a mixture containing tris(2-aminomethylpyridine)amine, TPA (0.146 g, 0.50 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.150 g, 0.5 mmol) dissolved in MeOH (15 mL). The resulting clear solution was heated for 10 min on a steam-bath, filtered and then allowed to crystallize at room temperature. After 3 days, the compound which separated was collected by filtration and recrystallized from EtOH to afford colorless single crystals ox X-ray quality (yield: 0.185 g, 76%). Characterization: Anal. Calcd: $C_{19}H_{19}N_6O_{3.5}SZn$ (484.85 g/mol): C, 47.07; H, 3.95; N, 17.33%. Found: C, 46.89, H, 3.95; N, 17.53%. IR bands (ATR, cm^{-1}): ~3500 (vw, b) ν(O-H); 3056 (vw), 2905 (vw) ν(C-H); 2064 (vs) (C≡N, NCS^-); 1603 (s), 1574 (m), 1480 (m), 1437 (s)

ν(C=C and C=N); 1573 (m), 1480 (m), 1437 (s); 1288 (m), 1152 (m), 1050 (m), 1019 (m), 908 (m), 827 (m), 756 (vs). UV (MeOH) λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$): ~264, 270 , 291 , 297, 304, 309 , 317. Molar conductivity, Λ_M (MeOH) = 151 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

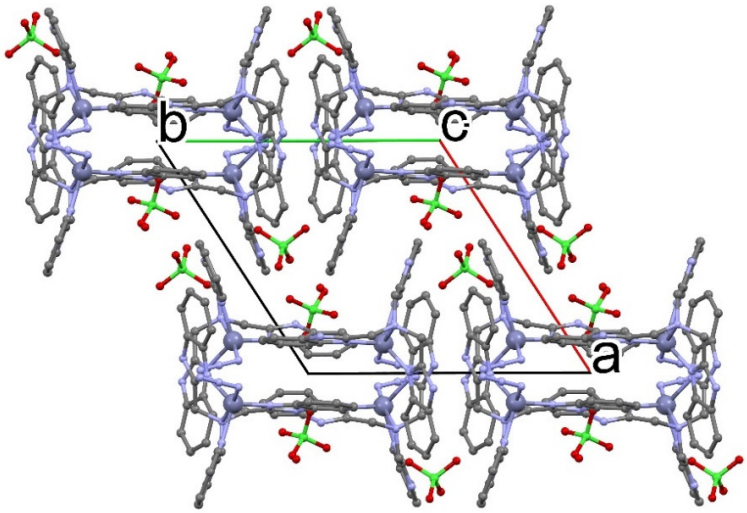

Figure S1. Packing plot of **3**.

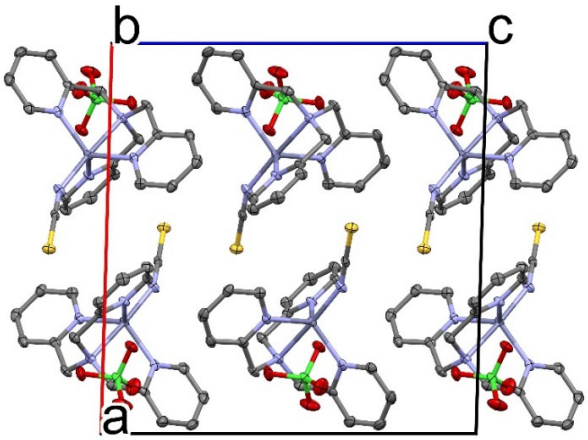

Figure S2. Packing plot of **4**.

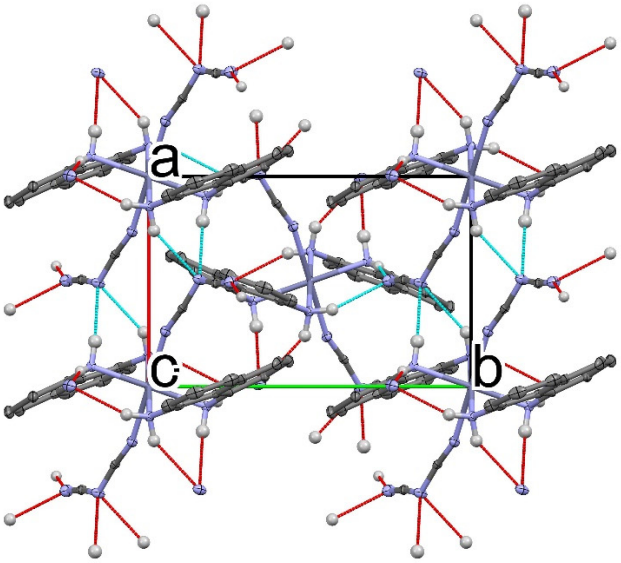

Figure S3. Packing plot of **5**. Broken lines indicate hydrogen bonds.

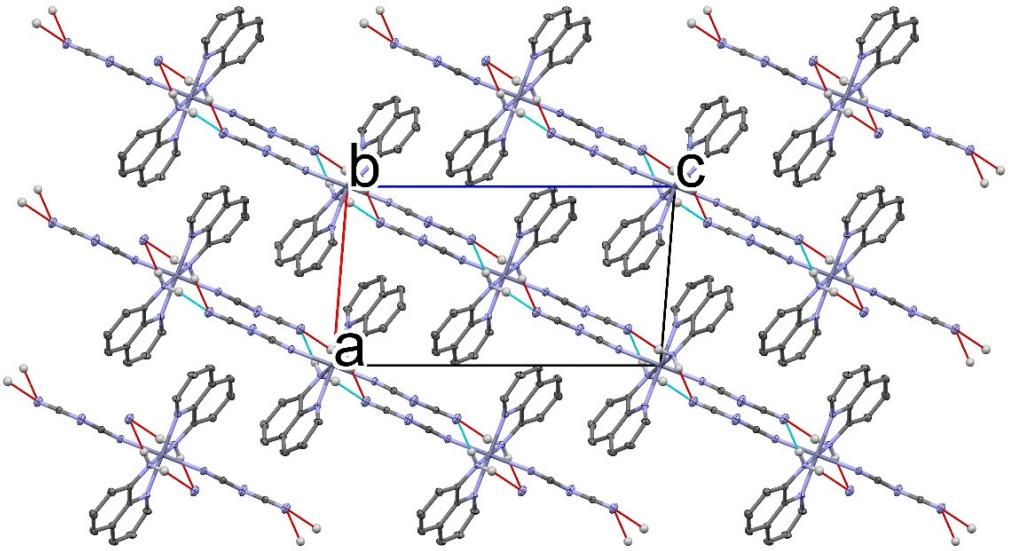

Figure S4. Packing plot of **6a**. Broken lines indicate hydrogen bonds.

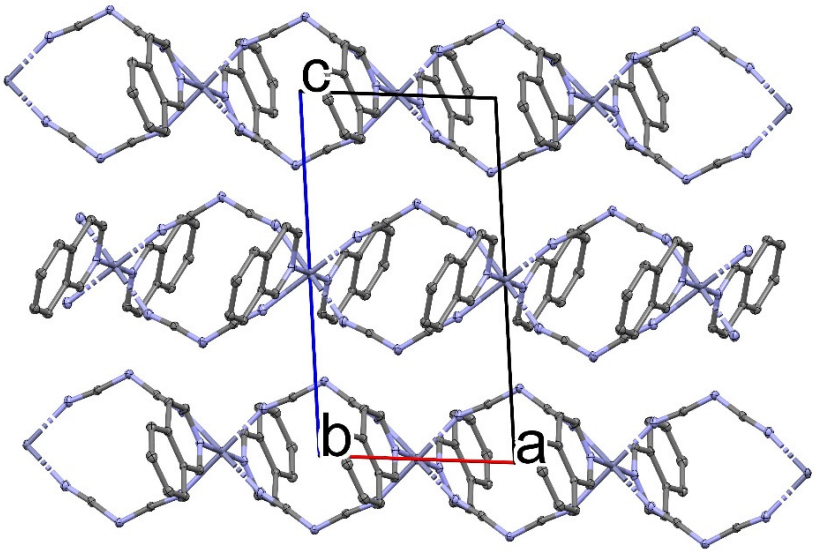

Figure S5. Packing plot of **7**.

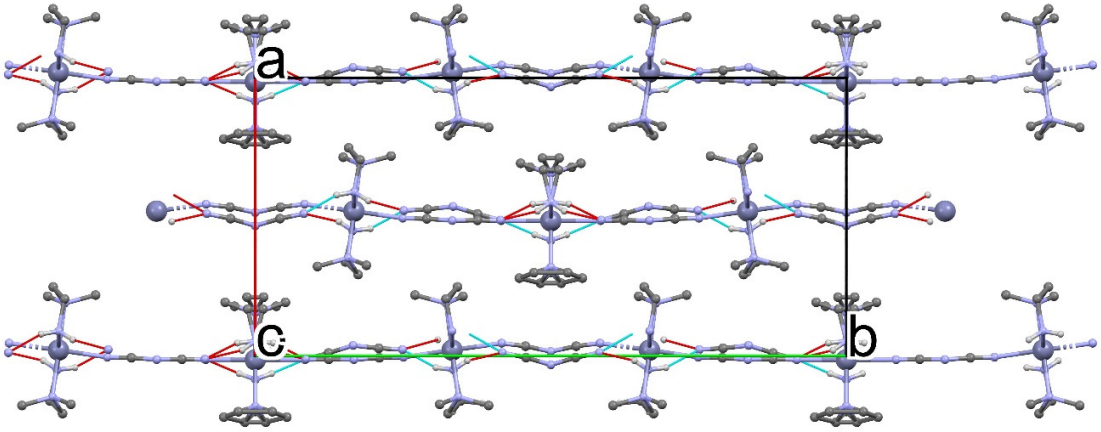

Figure S6. Packing plot of **8**.

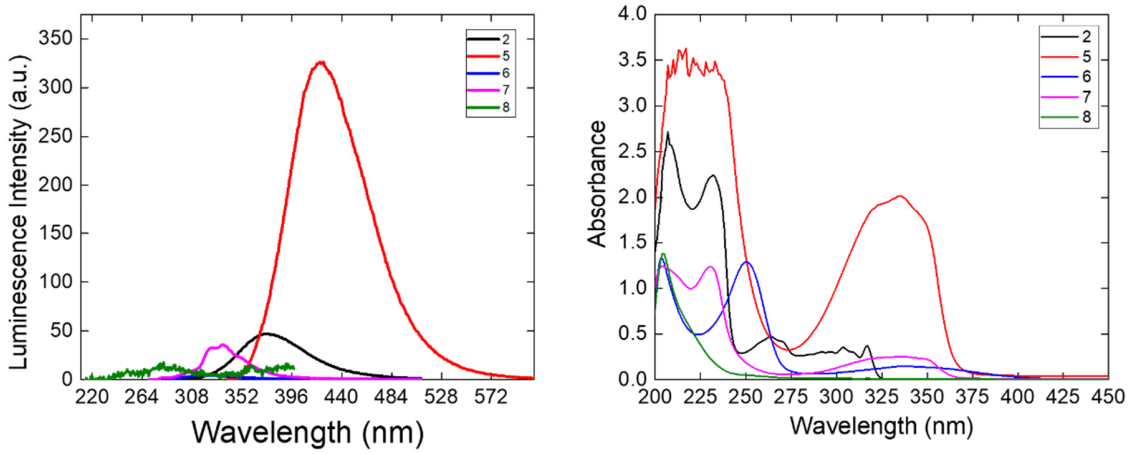

Figure S7. Left: Fluorescence and Right: UV-Vis. absorption spectra of the dicyanamido Zn(II) complexes **2**, **5**, **6**, **7** and **8** in methanol.

Table S1. Selected bond distances (Å) and bond angles (°) of **3**, **4**, **5**, **6a**, **7** and **8**.

Compound **3**			
Zn1-N1	2.020(5)	Zn2-N11	2.019(5)
Zn1-N4	2.491(5)	Zn2-N14	2.489(5)
Zn1-N5	2.043(5)	Zn2-N15	2.034(5)
Zn1-N7	2.013(5)	Zn2-N17	2.002(5)
Zn1-N9	2.013(5)	Zn2-N19	2.038(5)
N1-N2	1.193(8)	N11-N12	1.206(8)
N2-N3	1.158(8)	N12-N13	1.171(8)
N1-Zn1-N4	174.4(2)	N11-Zn2-N14	173.0(2)
N9-Zn1-N5	122.3(2)	N19-Zn2-N15	123.3(2)
N7-Zn1-N5	112.0(2)	N17-Zn2-N15	110.3(2)
N7-Zn1-N9	106.1(2)	N17-Zn2-N19	108.5(2)
Zn1-N1-N2	119.9(4)	Zn2-N11-N12	120.7(4)
N1-N2-N3	178.5(6)	N11-N12-N13	177.6(7)
Compound **4**			
Zn1-N1	2.006(3)	Zn1-N2	2.261(3)
Zn1-N3	2.079(3)	Zn1-N4	2.058(3)
Zn1-N5	2.044(3)	N1-C19	1.175(4)
S1-C19	1.627(4)		
N1-Zn1-N2	175.26(12)	N3-Zn1-N4	115.27(11)
N3-Zn1-N5	107.47(11)	N4-Zn1-N5	124.32(11)
N1-Zn1-N3	98.53(11)	Zn1-N1-C19	154.3(3)
N1-C19-S1	178.8(3)		
Compound **5**			
Zn1-N1	2.1620(14)	Zn1-N2	2.1199(15)
Zn1-N3	2.2179(14)	N3-C11	1.158(2)
N4-C11	1.310(2)	N4-C12	1.321(2)
N5-C12	1.155(2)		
N1-Zn1-N2	80.25(6)	N1-Zn1-N3	92.75(5)
Zn1-N1-C1	117.41(11)	Zn1-N2-C7	114.89(11)
Zn1-N3-C11	161.72(14)	C11-N4-C12	121.66(16)
N3-C11-N4	173.05(18)	N5-C12-N4	172.85(19)
Compound **6a**			
Zn1-N1	2.1227(11)	Zn1-N2	2.1586(11)
Zn1-N3	2.2051(11)	N3-C10	1.1648(18)
N4-C11	1.3042(17)	N4-C10	1.3107(18)
N5-C11	1.1591(17)		

N1-Zn1-N2	78.94(4)	Zn1-N1-C6	109.08(8)
Zn1-N2-C1	127.56(9)	Zn1-N3-C10	147.31(10)
C10-N4-C11	122.26(12)	N3-C10-N4	173.71(14)
N5-C11-N4	171.69(14)		
Compound **7**			
Zn1-N1	2.1369(17)	Zn2-N5	2.1593(17)
Zn1-N2	2.1675(17	Zn2-N6	2.1438(1)
Zn1-N4	2.1721(17)	Zn2-N8	2.1735(17)
N2-C10	1.159(2)	N3-C10	1.307(2)
N3-C11	1.313(2)	N4-C11	1.154(2)
N1‘-Zn1-N2	90.22(6)	N1-Zn1-N4“	90.47(6)
N2‘-Zn1-N4“	90.27(7)	N6*-Zn2-N5	90.31(6)
N6*-Zn2-N8^{+}	90.59(7)	N5*-Zn2-N8^{+}	90.24(6)
Zn1-N2-C10	168.49(16)	C10-N3-C11	119.51(17)
Zn1^{-}-N4-C11	148.80(15)	C20-N5-C12	117.85(16)
Zn2-N5-C20	121.19(13)	Zn2-N5-C12	120.92(12)
Zn2-N6-C21	166.26(15)	C21-N7-C22	119.09(17)
Zn2^{-}-N8-C22	154.04(15)	N2-C10-N3	174.7(2)
N4-C1-N3	174.6(2)		
Compound **8**			
Zn1-N1	2.278(3)	Zn2-N5	2.263(3)
Zn1-N3	2.246(3)	Zn2-N5‘	2.263(3)
Zn1-N11	2.255(3)	Zn2-N15	2.067(5)
Zn1-N12	2.063(4)	Zn2-N16	2.258(4)
Zn1-N13	2.262(3)	Zn2-N17	2.107(5)
Zn1-N14	2.111(4)	Zn2-N18	2.239(4)
C1-N1	1.162(4)	C1-N2	1.302(4)
C2-N3	1.152(4)	C3-N4	1.296(4)
C3-N5	1.144(4)	C2-N4	1.298(4)
C4-N6	1.170(5)	C4-N7	1.296(4)
C6-N10	1.149(4)	C6-N9	1.313(4)
C5-N8	1.146(5)	C5-N9	1.312(4)
N12-Zn1-N14	178.55(11)	N15-Zn2-N17	179.25(19)
N11-Zn1-N13	179.34(17)	N18-Zn2-N16	178.92(19)
N3-Zn1-N1	179.22(16)	N5-Zn2-N5‘	177.66(18)
Zn1-N1-C1	158.5(3)	Zn1-N3-C2	163.6(3)
N1-C1-N2	172.2(4)	N4-C3-N5	171.0(4)
Zn2-N5-C3	162.4(3)	N3-C2-N4	170.5(4)

C1-N2-C1“	124.8(5)	C2-N4-C3	125.7(4)
N6-C4-N7	172.3(5)	N9-C6-N10	172.4(4)
N8-C5-N9	172.8(4)	C4-N7-C4“	120.9(5)

Symmetry codes for **7**: (′) -x,-y,1-z; (“) -x-1,-y,1-z; (*) 1-x,1-y,-z; ($^{+}$) -x,1-y,-z; ($^{-}$) -1+x,y,z.
Symmetry codes for **8**: (′) x,1-y,z; (“) x,2-y,z.

Table S2. Possible hydrogen bonds.

D-H…A	Symmetry code	D…A (Å)	D-H…A (°)
Compound **3**			
O9-H9C..O3		2.805(13)	162
N6-H6..N3	[2-x,1-y,1-z]	3.097(9)	145
N8-H8..O6A	[1-x,1-y,1-z]	2.808(10)	171
N10-H10..O9		2.709(10)	167
N16-H16..O8A	[1-x,1-y,1-z]	2.861(16)	164
N18-H18..O8A	[x,1+y,-1+z]	2.986(14)	152
N20-H20A..N13	[-x,1-y,z]	3.002(10)	152
Compound **5**			
N1-H1A..N5	[3/2-x,1/2+y,1/2-z]	3.147(2)	157
N1-H1B..N4	[-1+x,y,z]	3.217(2)	149
N2-H2A..N4	[-1+x,y,z]	3.080(2)	158
N2-H2B..N5	[-1/2+x,1/2-y,1/2+z]	3.058(2)	163
Compound **6a**			
N1-H1A..N5	[1/2+x,3/2-y,1/2+z]	3.0136(17)	179
N1-H1B..N5	[1/2-x,1/2-y,1/2-z]	3.0204(16)	168
Compound **8**			
N12-H12A..N10	[x,1-y,z]	3.058(5)	166
N12-H12B..N6	[x,y,-1+z]	3.105(5)	159
N14_H14A..N10	[x,1-y,1+z]	3.087(5)	158
N14-H14B-N6		2.990(5).	163
N15-H15A..N8		3.070(5)	163
N15-H15B..N8	[x,1-y,z]	3.070(5)	156
N17-H17D..N8	[x,y,1+z]	3.076(5)	171
N17..H17E..N8	[x,1-y,1+z]	3.076(5)	171

Table S3. Ring···ring interactions in **7.**

```
 6-Membered Ring ( 1)   (N1, C1, C2, C7, C8, C9)
 6-Membered Ring ( 2)   (C2, C3, C4, C5, C6, C7)
10-Membered Ring ( 3)   (N1, C1, C2, C3, C4, C5, C6, C7, C8, C9, C10)
 6-Membered Ring ( 4)   (N5, C12, C13, C14, C19, C20)
 6-Membered Ring ( 5)   (C14, C15, C16, C17, C18, C19)
10-Membered Ring ( 6)   (N5, C12, C13, C14, C15, C16, C17, C18, C19, C20)

================================================================================
Short Ring-Interactions with Cg-Cg Distances < 6 Ang., Alpha < 20 Deg., Beta < 60 Deg.
================================================================================
- Cg(I)    = Plane number I (= ring number in () above)
- Alpha    = Dihedral Angle between Planes I and J (Deg)
- Beta     = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma    = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg    = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpend. Projection of Cg(J) on Ring I (Ang).

Cg(I) Cg(J) [ARU(J)]   Cg-Cg    Alpha  Beta Gamma    CgI_Perp    CgJ_Perp  Slippage

Cg1 -> Cg1 [2566]    4.505(2)  0.00(8)  39.6  39.6   3.4737(7)   3.4737(7)   2.869
Cg1 -> Cg1 [2666]    5.031(2)  0.00(8)  44.5  44.5   3.5879(7)   3.5878(7)   3.527
Cg1 -> Cg2 [2566]  3.7498(19)  0.65(9)  21.6  22.0   3.4768(7)   3.4858(9)   1.382
Cg1 -> Cg2 [2666]  3.7763(19)  0.65(9)  18.8  19.4   3.5619(7)   3.5757(9)   1.214
Cg1 -> Cg3 [2566]  3.9637(19)  0.35(7)  28.6  28.6   3.4817(7)   3.4806(6)   1.896
Cg1 -> Cg3 [2666]    4.277(2)  0.35(7)  33.2  33.5   3.5678(7)   3.5809(6)   2.339
Cg1 -> Cg4 [1555]    5.925(3) 36.70(9)  53.7  89.8   0.0209(7)   3.5056(8)
Cg2 -> Cg2 [2566]    4.438(2) 0.00(10)  38.6  38.6   3.4672(9)   3.4672(9)   2.770
Cg2 -> Cg2 [2666]    3.883(2) 0.00(10)  23.1  23.1   3.5716(9)   3.5716(9)   1.523
Cg2 -> Cg3 [2566]  3.9255(19)  0.30(8)  27.8  27.5   3.4822(9)   3.4728(6)   1.830
Cg2 -> Cg3 [2666]  3.6296(18)  0.30(8)  10.7  10.6   3.5673(9)   3.5659(6)   0.677
Cg3 -> Cg3 [2566]  3.7538(18)  0.00(6)  21.9  21.9   3.4828(6)   3.4828(6)   1.401
Cg3 -> Cg3 [2666]  3.7737(18)  0.00(6)  19.1  19.1   3.5667(6)   3.5667(6)   1.233
Cg4 -> Cg2 [2666]    5.869(3) 37.26(9)  53.7  89.9   0.0071(8)   3.4719(9)
Cg4 -> Cg4 [2555]    4.587(2)  0.02(9)  40.1  40.1   3.5107(8)   3.5107(8)   2.952
Cg4 -> Cg4 [2655]    4.968(2)  0.02(9)  45.5  45.5   3.4828(8)   3.4828(8)   3.543
Cg4 -> Cg5 [2555]  3.7582(19)  1.01(9)  20.8  21.8   3.4892(8)   3.5125(9)   1.336
Cg4 -> Cg5 [2655]  3.7455(19   1.01(9)  21.7  22.5   3.4611(8)   3.4809(9)   1.383
Cg4 -> Cg6 [2555]  4.0133(19)  0.52(8)  28.9  29.3   3.5011(8)   3.5119(6)   1.942
Cg4 -> Cg6 [2655]    4.226(2)  0.52(8)  34.5  34.8   3.4705(8)   3.4816(6)   2.396
Cg5 -> Cg4 [2555]  3.7581(19)  1.01(9)  21.8  20.8   3.5125(9)   3.4891(8)   1.396
Cg5 -> Cg4 [2655]  3.7456(19)  1.01(9)  22.5  21.7   3.4809(9)   3.4611(8)   1.432
Cg5 -> Cg5 [2555]    4.372(2) 0.00(10)  37.1  37.1   3.4865(9)   3.4865(9)   2.638
Cg5 -> Cg5 [2655]    3.909(2) 0.00(10)  27.6  27.6   3.4638(9)   3.4638(9)   1.811
Cg5 -> Cg6 [2555]  3.8911(19)  0.49(8)  26.3  25.9   3.5008(9)   3.4881(6)   1.725
Cg5 -> Cg6 [2655]  3.6270(18)  0.49(8)  17.3  16.9   3.4708(9)   3.4622(6)   1.081
Cg6 -> Cg6 [2555]  3.7614(18)  0.02(6)  21.4  21.4   3.5013(6)   3.5012(6)   1.375
Cg6 -> Cg6 [2655]  3.7434(18)  0.02(6)  22.0  22.0   3.4704(6)   3.4704(6)   1.403
```

[2566] = -X,1-Y,1-Z
[2666] = 1-X,1-Y,1-Z
[1555] = X,Y,Z
[2555] = -X,-Y,-Z
[2655] = 1-X,-Y,-Z

Cg(I) refer to Ring Centre-of-Gravity numbers given in () in the Ring-Analysis above

Cg(I)	x	y	z
Cg1	0.15000(9)	0.34427(8)	0.46940(6)
Cg2	0.31703(11)	0.59243(8)	0.54045(6)
Cg3	0.23369(8)	0.46825(6)	0.50512(4)
Cg4	0.31077(10)	0.15613(7)	0.03752(6)
Cg5	0.22093(11)	-0.09376(8)	-0.03165(6)
Cg6	0.26610(8)	0.03132(6)	0.00271(4)