Supplementary Material for

An Exceptional 5:4 Enantiomeric Structure

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1. Information about attempts to grow crystals (1 pg)
2. Full atom-numbering scheme for the cations (1 pg)
3. Ellipsoid plots for
   (a) the cations and for the anions and solvent molecules located in the cation layer (1 pg)
   (b) the anions and solvent molecules located between the cation layers (1 pg)
4. Lists of
   (a) Ru-N and P-F bond lengths (2 pp)
   (b) N-Ru-N bond angles (2 pp)
5. Projection showing the cation layer and the two adjacent anion/solvent layers.. The anions that are embedded in the layer have been circled. The anions in the two anion/solvent layers line up well although they are not related by translation. (1 pg)
6. List of anomalous racemates (ordered structures having an enantiomeric ratio other than 1:1 (3 pp)
7. Drawings of structures with "striped" layers (refcodes KEXLUV, DACGIY, KITQIN, LAXJUQ, and TARNEG; 5 pp) and structures with molecules in very different orientations (refcodes ETCABZ10 and NIMRIK08; 2 pp)

Information about attempts to grow crystals.

Attempt #1 7/17/12
with the PF6 counter-ions

mg	dissolved in (mL)	crystallized in (mL)	
2.9	CH_2Cl_2 (0.5 mL)	THF (3 mL)	
5	CH_2Cl_2 (0.5 mL)	Ether (3 mL)	
5.1	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)	gave too-small crystals
3.2	Acetone (0.5 mL)	THF (3 mL)	
4.2	Acetone (0.5 mL)	Ether (3 mL)	
3.6	Acetone (0.5 mL)	Hexanes (3mL)	

Attempt #2 8/6/12
with the PF6 counter-ions

mg	dissolved in (mL)	crystallized in (mL)
3.1	Acetonitrile (0.5 mL)	THF (3 mL)
4.2	Acetonitrile (0.5 mL)	Ether (3 mL)
4.1	Acetonitrile (0.5 mL)	Hexanes (3mL)
4.3	Methanol (0.5 mL)	THF (3 mL)
4.5	Methanol (0.5 mL)	Ether (3 mL)
3.9	Methanol (0.5 mL)	Hexanes (3mL)

Attempt #3 11/1/12
with the PF6 counter-ions

mg	dissolved in (mL)	crystallized in (mL)
1.5	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)
3.1	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)
5.1	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)
1.4	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)
2.9	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)
4.5	CH_2Cl_2 (0.5 mL)	Hexanes (3mL)

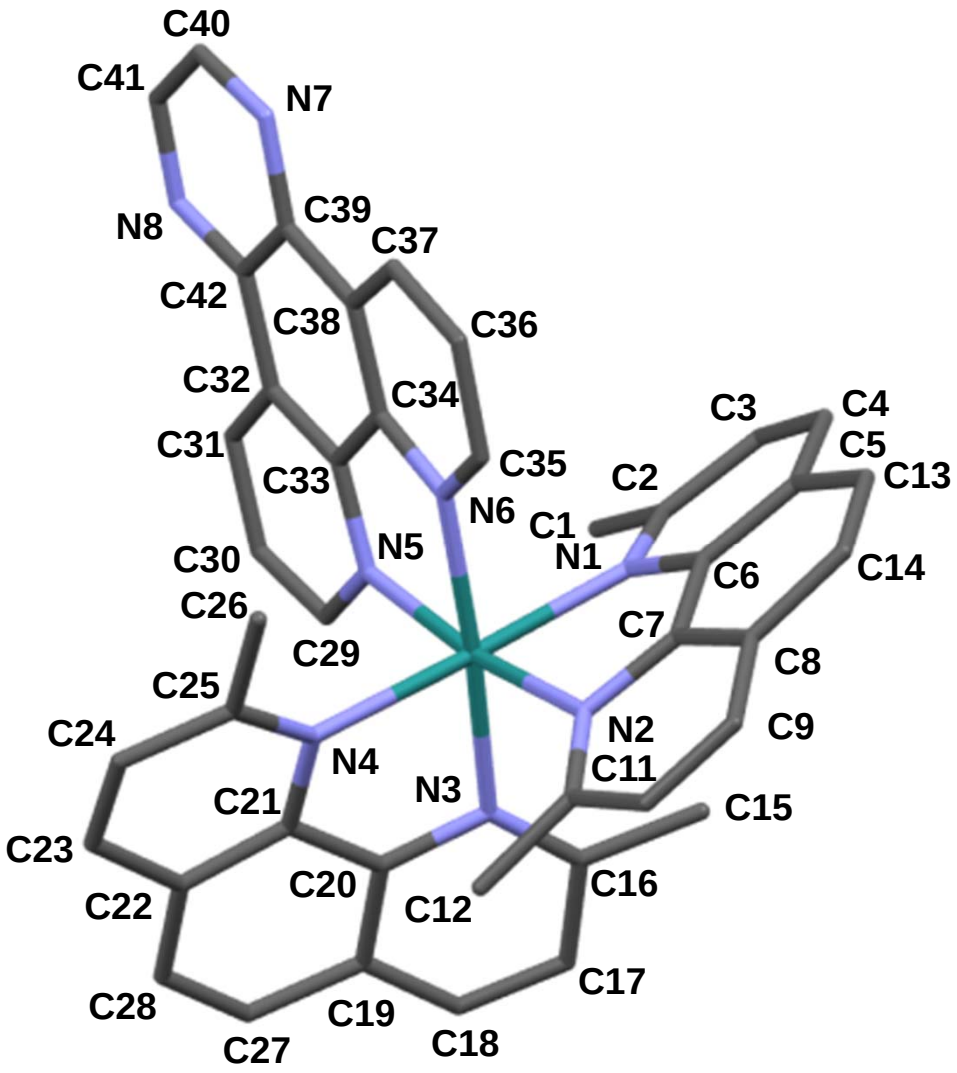
Attempt #4 1/10/13
with the NO2 counter-ions

mg	dissolved in (mL)	crystallized in (mL)
4.8	Methanol (0.5 mL)	Hexanes (3mL)
2.9	Methanol (0.5 mL)	Ether (3 mL)
2.2	Methanol (0.5 mL)	THF (3 mL)
4	Acetone (0.5 mL)	Hexanes (3mL)
2.9	Acetone (0.5 mL)	Ether (3 mL)
2.3	Acetone (0.5 mL)	THF (3 mL)

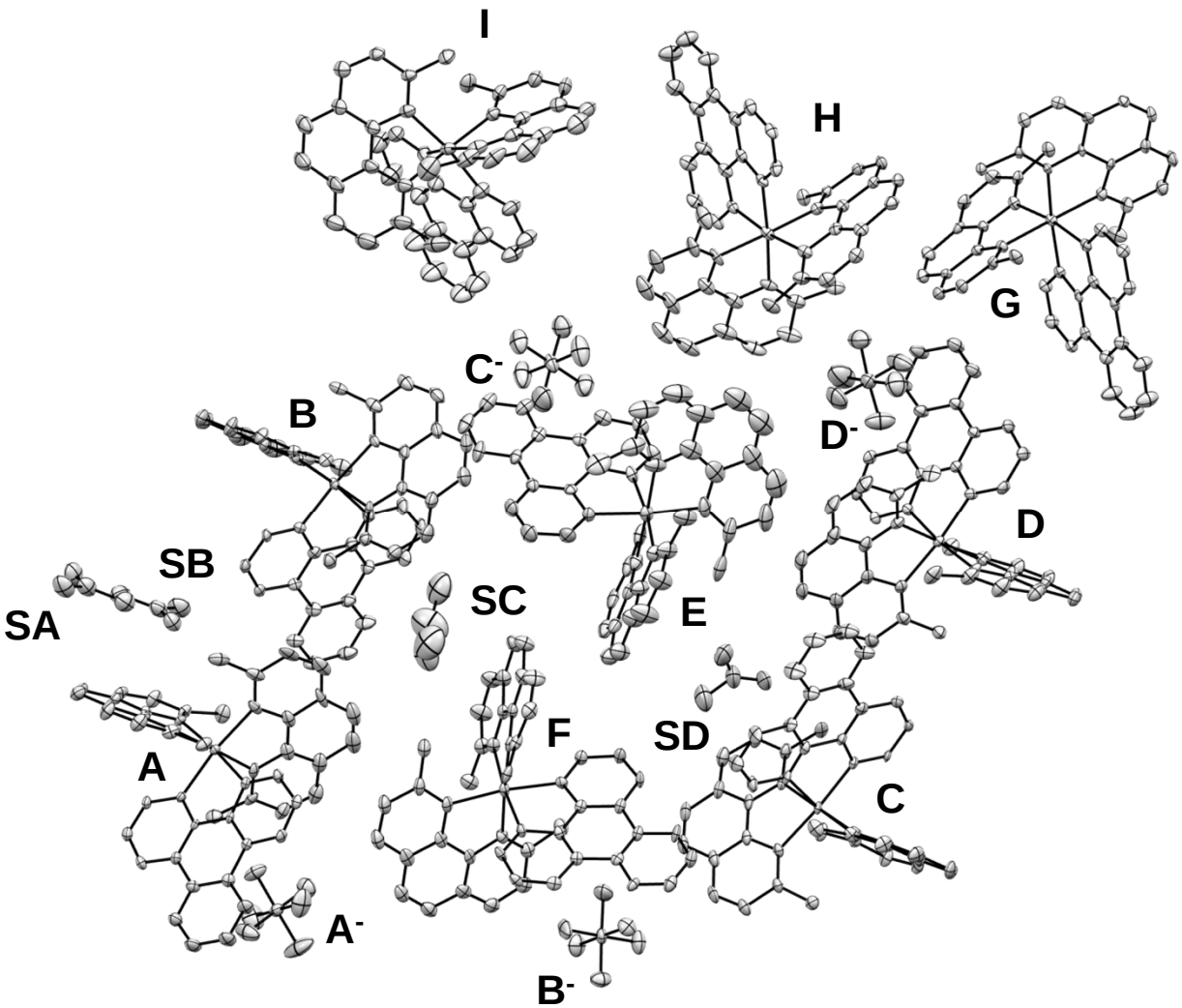
Attempt #5 7/22/14
with the PF6 counter-ions

mg	dissolved in (mL)	crystallized in (mL)	
3.3	Acetone (1.5 mL)	THF (3 mL)	
2.6	**Acetone (1.5 mL)**	**Ether (3 mL)**	**x14409sq**
1.9	Acetone (1.5 mL)	Hexanes (3mL)	
2.3	CH_2Cl_2 (1.5 mL)	THF (3 mL)	
3	CH_2Cl_2 (1.5 mL)	Ether (3 mL)	
3.1	CH_2Cl_2 (1.5 mL)	Hexanes (3mL)	

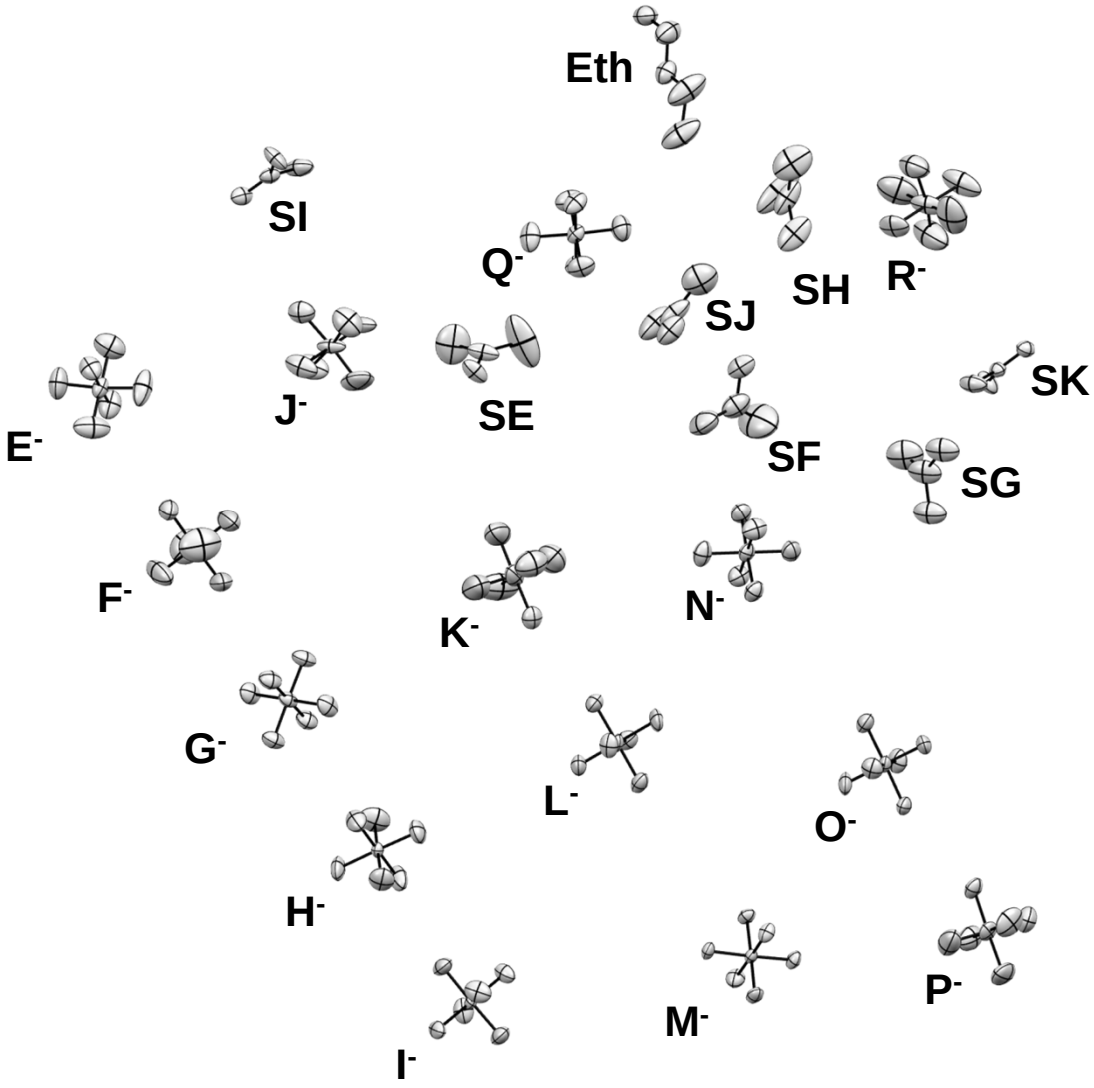
Full numbering scheme for the cations. The full atom number includes the letter that identifies the cation; *eg*, C13B for atom C13 in the second cation.



Drawing showing the displacement ellipsoids for the atoms in the cation layer. Labels for anions have a superscript minus; labels for acetone solvent molecules begin with an S.



Drawing showing the displacement ellipsoids for the atoms of the anions and solvent molecules that lie between the cation layers. Labels for anions have a superscript minus; labels for acetone solvent molecules begin with an S. The label for the diethyl ether molecule is Eth.



Ru-N and P-F bond lengths.

Atom 1	Atom 2	Distance (Å)	esd (Å)	Atom 1	Atom 2	Distance (Å)	esd (Å)
Ru1A	N1A	2.105	0.008	Ru1A	N2A	2.091	0.008
Ru1B	N1B	2.106	0.008	Ru1B	N2B	2.100	0.008
Ru1C	N1C	2.131	0.008	Ru1C	N2C	2.094	0.008
Ru1D	N1D	2.123	0.008	Ru1D	N2D	2.113	0.008
Ru1E	N1E	2.090	0.009	Ru1E	N2E	2.106	0.009
Ru1F	N1F	2.120	0.008	Ru1F	N2F	2.119	0.008
Ru1G	N1G	2.112	0.007	Ru1G	N2G	2.104	0.008
Ru1H	N1H	2.080	0.008	Ru1H	N2H	2.097	0.008
Ru1I	N1I	2.089	0.008	Ru1I	N2I	2.084	0.010
Ru1A	N3A	2.122	0.007	Ru1A	N4A	2.119	0.008
Ru1B	N3B	2.116	0.008	Ru1B	N4B	2.111	0.008
Ru1C	N3C	2.110	0.008	Ru1C	N4C	2.137	0.008
Ru1D	N3D	2.105	0.008	Ru1D	N4D	2.124	0.008
Ru1E	N3E	2.071	0.009	Ru1E	N4E	2.132	0.009
Ru1F	N3F	2.136	0.008	Ru1F	N4F	2.098	0.008
Ru1G	N3G	2.115	0.007	Ru1G	N4G	2.111	0.008
Ru1H	N3H	2.104	0.008	Ru1H	N4H	2.118	0.008
Ru1I	N3I	2.097	0.008	Ru1I	N4I	2.109	0.010
Ru1A	N5A	2.083	0.007	Ru1A	N6A	2.093	0.007
Ru1B	N5B	2.097	0.008	Ru1B	N6B	2.071	0.007
Ru1C	N5C	2.082	0.007	Ru1C	N6C	2.092	0.007
Ru1D	N5D	2.082	0.008	Ru1D	N6D	2.077	0.008
Ru1E	N5E	2.092	0.008	Ru1E	N6E	2.073	0.008
Ru1F	N5F	2.061	0.008	Ru1F	N6F	2.070	0.008
Ru1G	N5G	2.083	0.008	Ru1G	N6G	2.074	0.007
Ru1H	N5H	2.090	0.008	Ru1H	N6H	2.108	0.008
Ru1I	N5I	2.041	0.010	Ru1I	N6I	2.079	0.009

Atom 1	Atom 2	Distance (Å)	esd (Å)	Atom 1	Atom 2	Distance (Å)	esd (Å)
P1A	F1A	1.583	0.007	P1A	F2A	1.575	0.008
P1B	F1B	1.594	0.007	P1B	F2B	1.612	0.007
P1C	F1C	1.592	0.008	P1C	F2C	1.609	0.008
P1D	F1D	1.605	0.009	P1D	F2D	1.558	0.009
P1E	F1E	1.580	0.008	P1E	F2E	1.593	0.008
P1F	F1F	1.611	0.009	P1F	F2F	1.554	0.010
P1G	F1G	1.625	0.009	P1G	F2G	1.583	0.008
P1H	F1H	1.576	0.007	P1H	F2H	1.585	0.007
P1I	F1I	1.599	0.007	P1I	F2I	1.596	0.007
P1J	F1J	1.587	0.009	P1J	F2J	1.564	0.009
P1K	F1K	1.606	0.009	P1K	F2K	1.570	0.012
P1L	F1L	1.590	0.007	P1L	F2L	1.607	0.007
P1M	F1M	1.614	0.006	P1M	F2M	1.586	0.006
P1N	F1N	1.593	0.008	P1N	F2N	1.600	0.008

Atom 1	Atom 2	Distance (Å)	esd (Å)	Atom 1	Atom 2	Distance (Å)	esd (Å)
P1O	F1O	1.608	0.008	P1O	F2O	1.569	0.008
P1P	F1P	1.576	0.010	P1P	F2P	1.541	0.011
P1Q	F1Q	1.607	0.007	P1Q	F2Q	1.584	0.008
P1R	F1R	1.551	0.009	P1R	F2R	1.584	0.011
P1A	F3A	1.599	0.008	P1A	F4A	1.572	0.008
P1B	F3B	1.596	0.007	P1B	F4B	1.587	0.007
P1C	F3C	1.583	0.009	P1C	F4C	1.571	0.008
P1D	F3D	1.551	0.008	P1D	F4D	1.588	0.009
P1E	F3E	1.536	0.010	P1E	F4E	1.604	0.011
P1F	F3F	1.502	0.012	P1F	F4F	1.536	0.014
P1G	F3G	1.592	0.007	P1G	F4G	1.608	0.008
P1H	F3H	1.551	0.008	P1H	F4H	1.588	0.008
P1I	F3I	1.556	0.007	P1I	F4I	1.579	0.007
P1J	F3J	1.595	0.010	P1J	F4J	1.508	0.011
P1K	F3K	1.540	0.014	P1K	F4K	1.534	0.013
P1L	F3L	1.597	0.007	P1L	F4L	1.597	0.007
P1M	F3M	1.610	0.006	P1M	F4M	1.579	0.007
P1N	F3N	1.586	0.008	P1N	F4N	1.583	0.008
P1O	F3O	1.606	0.007	P1O	F4O	1.585	0.007
P1P	F3P	1.574	0.008	P1P	F4P	1.587	0.010
P1Q	F3Q	1.597	0.009	P1Q	F4Q	1.565	0.008
P1R	F3R	1.536	0.012	P1R	F4R	1.473	0.013
P1A	F5A	1.572	0.007	P1A	F6A	1.582	0.008
P1B	F5B	1.565	0.007	P1B	F6B	1.598	0.007
P1C	F5C	1.594	0.009	P1C	F6C	1.582	0.010
P1D	F5D	1.600	0.010	P1D	F6D	1.567	0.011
P1E	F5E	1.541	0.009	P1E	F6E	1.542	0.009
P1F	F5F	1.541	0.010	P1F	F6F	1.510	0.011
P1G	F5G	1.603	0.008	P1G	F6G	1.572	0.008
P1H	F5H	1.544	0.009	P1H	F6H	1.568	0.008
P1I	F5I	1.591	0.007	P1I	F6I	1.576	0.007
P1J	F5J	1.639	0.011	P1J	F6J	1.597	0.011
P1K	F5K	1.558	0.013	P1K	F6K	1.576	0.015
P1L	F5L	1.598	0.007	P1L	F6L	1.600	0.007
P1M	F5M	1.607	0.006	P1M	F6M	1.585	0.006
P1N	F5N	1.587	0.008	P1N	F6N	1.590	0.008
P1O	F5O	1.604	0.007	P1O	F6O	1.579	0.007
P1P	F5P	1.582	0.010	P1P	F6P	1.587	0.010
P1Q	F5Q	1.604	0.009	P1Q	F6Q	1.589	0.009
P1R	F5R	1.472	0.016	P1R	F6R	1.613	0.017

N-Ru-N angles.

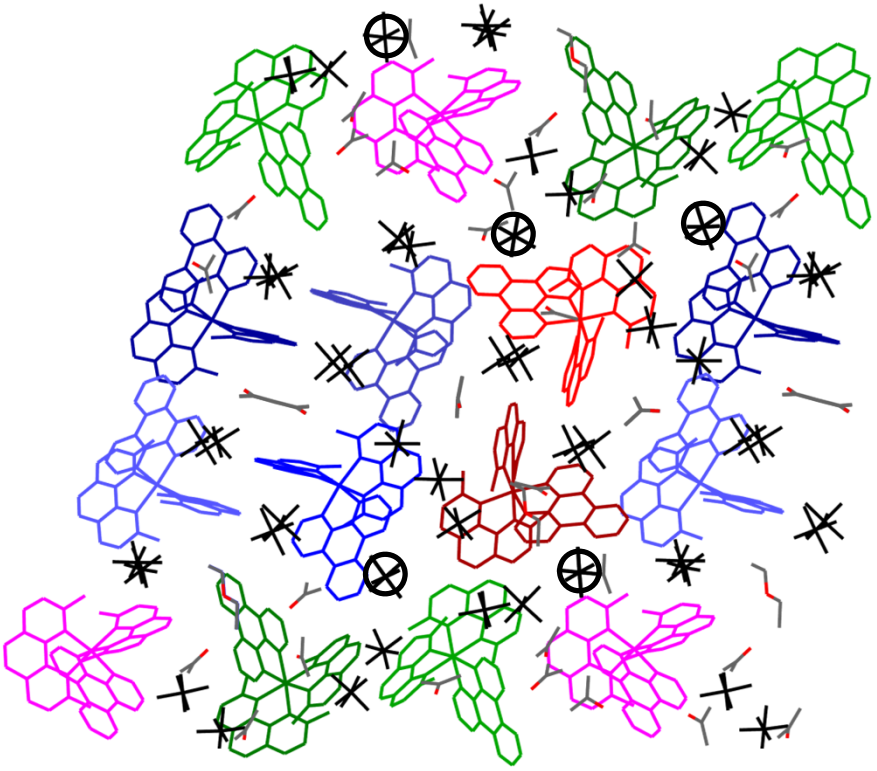
Atom 1	Atom 2	Atom 3	Angle (°)	esd (°)
Angle N5-Ru-N6				
N5A	Ru1A	N6A	79.1	0.3
N6B	Ru1B	N5B	79.6	0.3
N5C	Ru1C	N6C	78.6	0.3
N6D	Ru1D	N5D	79.3	0.3
N6E	Ru1E	N5E	79.4	0.3
N5F	Ru1F	N6F	79.6	0.3
N6G	Ru1G	N5G	78.8	0.3
N5H	Ru1H	N6H	79.1	0.3
N5I	Ru1I	N6I	79.7	0.4
Angle N1-Ru-N2				
N2A	Ru1A	N1A	80.3	0.3
N2B	Ru1B	N1B	79.3	0.3
N2C	Ru1C	N1C	80.2	0.3
N2D	Ru1D	N1D	80.3	0.3
N1E	Ru1E	N2E	81.3	0.4
N2F	Ru1F	N1F	79.7	0.3
N2G	Ru1G	N1G	79.2	0.3
N2H	Ru1H	N1H	79.3	0.3
N2I	Ru1I	N1I	79.5	0.4
Angle N3-Ru-N4				
N4A	Ru1A	N3A	80.2	0.3
N4B	Ru1B	N3B	79.2	0.3
N3C	Ru1C	N4C	79.4	0.3
N3D	Ru1D	N4D	78.7	0.3
N3E	Ru1E	N4E	79.5	0.4
N4F	Ru1F	N3F	79.9	0.3
N4G	Ru1G	N3G	79.4	0.3
N3H	Ru1H	N4H	79.5	0.3
N3I	Ru1I	N4I	79.0	0.3
Angle N1-Ru-N4				
N1A	Ru1A	N4A	177.4	0.3
N1B	Ru1B	N4B	179.1	0.3
N1C	Ru1C	N4C	179.1	0.3
N1D	Ru1D	N4D	177.9	0.3
N1E	Ru1E	N4E	177.9	0.4
N4F	Ru1F	N1F	177.4	0.3
N4G	Ru1G	N1G	178.8	0.3
N4H	Ru1H	N1H	178.4	0.2
N1I	Ru1I	N4I	177.0	0.4

Atom 1	Atom 2	Atom 3	Angle (°)	esd (°)
Angle N2-Ru-N5				
N5A	Ru1A	N2A	170.8	0.3
N5B	Ru1B	N2B	172.2	0.3
N5C	Ru1C	N2C	173.5	0.3
N5D	Ru1D	N2D	171.9	0.3
N5E	Ru1E	N2E	173.4	0.4
N5F	Ru1F	N2F	172.1	0.3
N5G	Ru1G	N2G	170.9	0.3
N5H	Ru1H	N2H	171.6	0.3
N5I	Ru1I	N2I	173.6	0.4
Angle N3-Ru-N6				
N6A	Ru1A	N3A	174.4	0.3
N6B	Ru1B	N3B	174.2	0.3
N6C	Ru1C	N3C	172.1	0.3
N6D	Ru1D	N3D	173.4	0.3
N3E	Ru1E	N6E	172.6	0.4
N6F	Ru1F	N3F	173.6	0.3
N6G	Ru1G	N3G	173.6	0.3
N6H	Ru1H	N3H	174.2	0.3
N6I	Ru1I	N3I	170.5	0.4
Angle N2-Ru-N6				
N2A	Ru1A	N6A	91.7	0.3
N6B	Ru1B	N2B	93.0	0.3
N6C	Ru1C	N2C	94.9	0.3
N6D	Ru1D	N2D	92.5	0.3
N6E	Ru1E	N2E	94.1	0.4
N6F	Ru1F	N2F	93.0	0.3
N6G	Ru1G	N2G	92.9	0.3
N6H	Ru1H	N2H	93.0	0.3
N6I	Ru1I	N2I	93.9	0.4
Angle N3-Ru-N5				
N5A	Ru1A	N3A	95.3	0.3
N5B	Ru1B	N3B	94.6	0.3
N5C	Ru1C	N3C	94.4	0.3
N5D	Ru1D	N3D	94.0	0.3
N3E	Ru1E	N5E	93.3	0.4
N5F	Ru1F	N3F	94.2	0.3
N5G	Ru1G	N3G	94.8	0.3
N5H	Ru1H	N3H	95.2	0.3
N5I	Ru1I	N3I	93.0	0.3

Atom 1	Atom 2	Atom 3	Angle (°)	esd (°)
Angle N1-Ru-N6				
N6A	Ru1A	N1A	82.4	0.3
N6B	Ru1B	N1B	80.4	0.3
N6C	Ru1C	N1C	83.9	0.3
N6D	Ru1D	N1D	81.8	0.3
N6E	Ru1E	N1E	80.7	0.3
N6F	Ru1F	N1F	81.8	0.3
N6G	Ru1G	N1G	80.8	0.3
N6H	Ru1H	N1H	80.1	0.3
N6I	Ru1I	N1I	83.6	0.4
Angle N4-Ru-N5				
N5A	Ru1A	N4A	80.7	0.3
N5B	Ru1B	N4B	81.9	0.3
N5C	Ru1C	N4C	80.0	0.3
N5D	Ru1D	N4D	80.8	0.3
N5E	Ru1E	N4E	81.3	0.3
N5F	Ru1F	N4F	80.9	0.3
N5G	Ru1G	N4G	83.2	0.3
N5H	Ru1H	N4H	82.6	0.3
N5I	Ru1I	N4I	79.6	0.4
Angle N1-Ru-N5				
N5A	Ru1A	N1A	97.4	0.3
N5B	Ru1B	N1B	97.1	0.3
N5C	Ru1C	N1C	99.2	0.3
N5D	Ru1D	N1D	98.5	0.3
N1E	Ru1E	N5E	96.6	0.4
N5F	Ru1F	N1F	96.6	0.3
N5G	Ru1G	N1G	95.6	0.3
N5H	Ru1H	N1H	96.4	0.3
N5I	Ru1I	N1I	98.8	0.3
Angle N4-Ru-N6				
N6A	Ru1A	N4A	99.0	0.3
N6B	Ru1B	N4B	99.4	0.3
N6C	Ru1C	N4C	95.5	0.3
N6D	Ru1D	N4D	99.9	0.3
N6E	Ru1E	N4E	98.8	0.3
N6F	Ru1F	N4F	97.3	0.3
N6G	Ru1G	N4G	98.8	0.3
N6H	Ru1H	N4H	98.6	0.3
N6I	Ru1I	N4I	93.6	0.4

Atom 1	Atom 2	Atom 3	Angle (°)	esd (°)
Angle N2-Ru-N3				
N2A	Ru1A	N3A	93.9	0.3
N2B	Ru1B	N3B	92.9	0.3
N2C	Ru1C	N3C	92.0	0.3
N3D	Ru1D	N2D	94.1	0.3
N3E	Ru1E	N2E	93.3	0.4
N2F	Ru1F	N3F	93.3	0.3
N2G	Ru1G	N3G	93.5	0.3
N2H	Ru1H	N3H	92.8	0.3
N2I	Ru1I	N3I	93.4	0.4
Angle N1-Ru-N3				
N1A	Ru1A	N3A	98.3	0.3
N1B	Ru1B	N3B	100.9	0.3
N3C	Ru1C	N1C	101.1	0.3
N3D	Ru1D	N1D	99.4	0.3
N3E	Ru1E	N1E	100.8	0.4
N1F	Ru1F	N3F	100.8	0.3
N1G	Ru1G	N3G	100.9	0.3
N1H	Ru1H	N3H	101.7	0.3
N3I	Ru1I	N1I	103.6	0.3
Angle N2-Ru-N4				
N2A	Ru1A	N4A	101.8	0.3
N2B	Ru1B	N4B	101.6	0.3
N2C	Ru1C	N4C	100.6	0.3
N2D	Ru1D	N4D	100.7	0.3
N2E	Ru1E	N4E	100.8	0.4
N4F	Ru1F	N2F	102.8	0.3
N2G	Ru1G	N4G	102.0	0.3
N2H	Ru1H	N4H	101.6	0.3
N2I	Ru1I	N4I	101.8	0.4

Projection showing the cation layer and the two adjacent anion/solvent layers.. The anions that are embedded in the layer have been circled. The anions in the two anion/solvent layers line up well although they are not related by translation.



A List of anomalous racemates (ie, of enantiomers that crystallize in a ratio other than 1:1)

Structures containing resolvable enantiomers only (all but the last are organic structures)

REFCODE	Space Group	Z'	Ratio of Enantiomers	Enantiomers Resolvable?	Comments	Reference
AWUVUJ	P2(1)2(1)2(1)	3	2:1	Yes		in Fábián & Brock (2010)
MECZUP	P2(1)	3	2:1	Yes		in Fábián & Brock (2010)
MONVUG	P2(1)	3	2:1	Yes		in Fábián & Brock (2010)
MUSKAM	I4(1)	1.5=3(1/2)	2:1	Yes	All three molecules lie on twofold axes	in Fábián & Brock (2010)
NILYIR	P2(1)	3	2:1	Yes		in Fábián & Brock (2010)
QAQPED	P2(1)2(1)2(1)	3	2:1	Yes		in Fábián & Brock (2010)
SOQQOE	P1	4	3:1	Yes		in Fábián & Brock (2010)
VEFMEZ	P2(1)	3	2:1	Yes	Ellipsoids for molecule 3 suggest D/L disorder. Crystal grown from a racemic solution	in Fábián & Brock (2010)

WISAZ	P1	6	5:1	Yes	The one different enantiomer is disordered with a diastereomer	in Fábián & Brock (2010)
XURHIB	I4(1)	1.5=3(1/2)	2:1	Yes	All three molecules lie on twofold axes	in Fábián & Brock (2010)
YOBNEI	C2	1.5=1+1/2	2:1	Yes	One of the two enantiomers present lies on a twofold axis	in Fábián & Brock (2010)
TIQHOR	P2(1)	2	3:1	Yes	Salt pf [Co(en)2(ox)]+ with a dianion so that Z'=2 gives four cations. The en in one cation of the set of three has a different conformation.	in Bernal & Watkins (2015)

Structures containing enantiomeric conformers (all are organometallic structures)

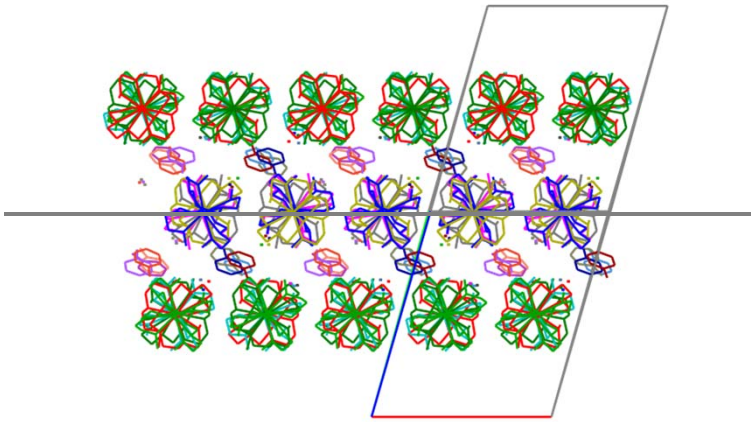
REFCODE	Space Group	Z'	Ratio of Enantiomers	Enantiomers Resolvable?	Comments	Reference
CIZSUZ01	P2(1)	4	3:1	No		in Bernal & Watkins (2015)
EVOXIX	P1	8	3:1	No	Two 3:1 sets of enantiomeric conformers; the two sets have quite different conformations	in Bernal & Watkins (2015)
REYDEG	P2(1)	6	3:1	No	The enantiomeric conformers are very similar	in Bernal & Watkins (2015)
TPNOIR	P3	1=3(1/3)	2:1	No	All three molecules lie on threefold axes	Albano et al. (1971)
TTPCUC	P3	1=3(1/3)	2:1	No	All three molecules lie on threefold axes	Gill et al. (1976)

Structures containing near enantiomers

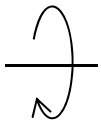
REFCODE	Space Group	Z'	Ratio of Enantiomers	Enantiomers Resolvable?	Comments	Reference
ABADUD	P2(1)	3	2:1	(Yes)	D:L pair of organic molecules plus one molecule related by replacement of -CMe2- by -CHMe-	in Fábián & Brock (2010)
QIJWEL	P2(1)2(1)2(1)	3	2:1	(Yes)	Complex cations (Z'=3) of Co3+, tren, and a deprotonated amino acid. One cation includes L-isoleucine; the other two include D-allo-isoleucine	Cai et al. (2001)

Projection along [0 1 -1]

KEXLUV
(*P*-1, *Z*'=8)

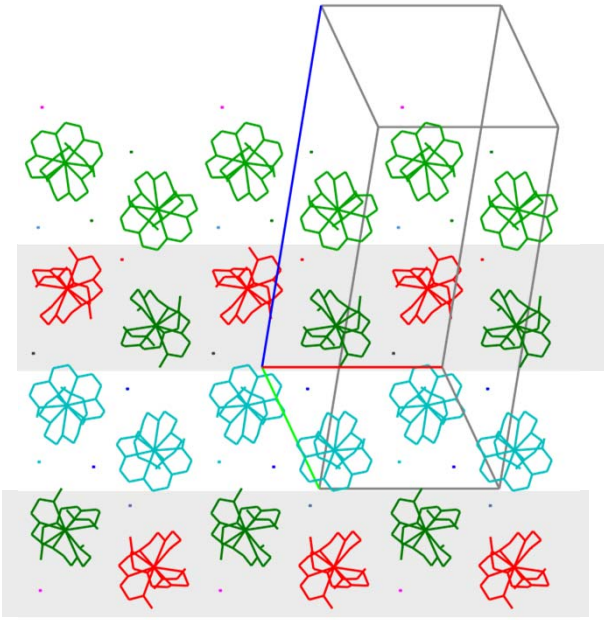


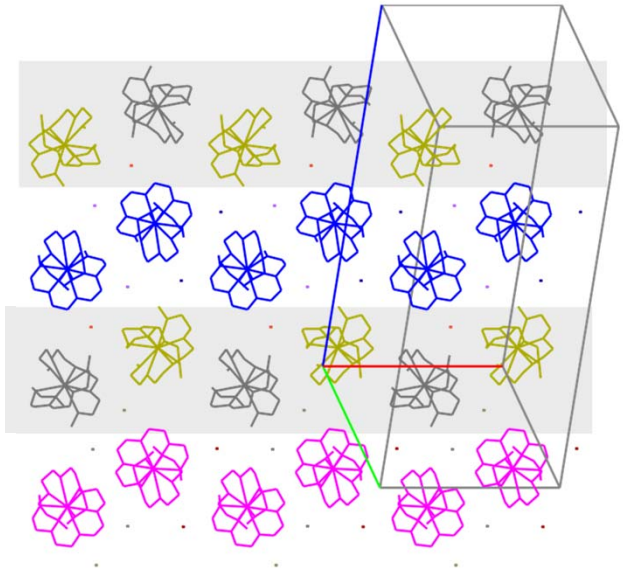
(0 1 1)



90°

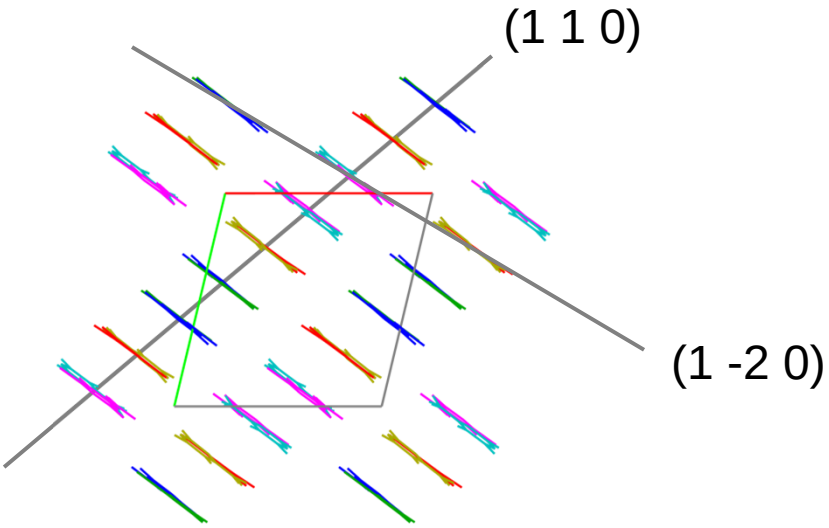
Layers (0 1 1)



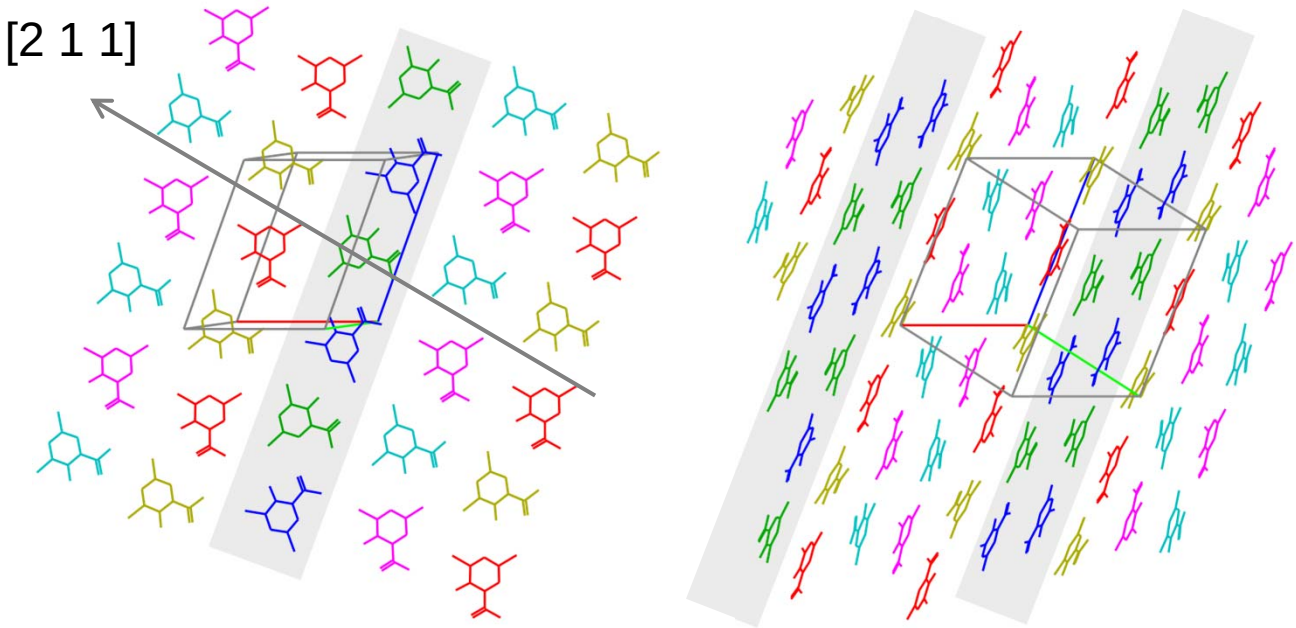


Projection along **c**

DACGIY
(*P*-1, *Z*'=6)

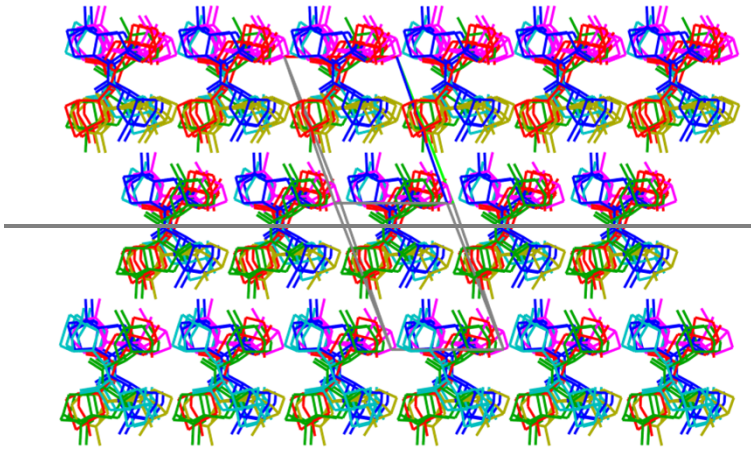


Layers (1 -2 0) and (1 1 0)

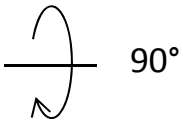


Projection along [0 1 -1]

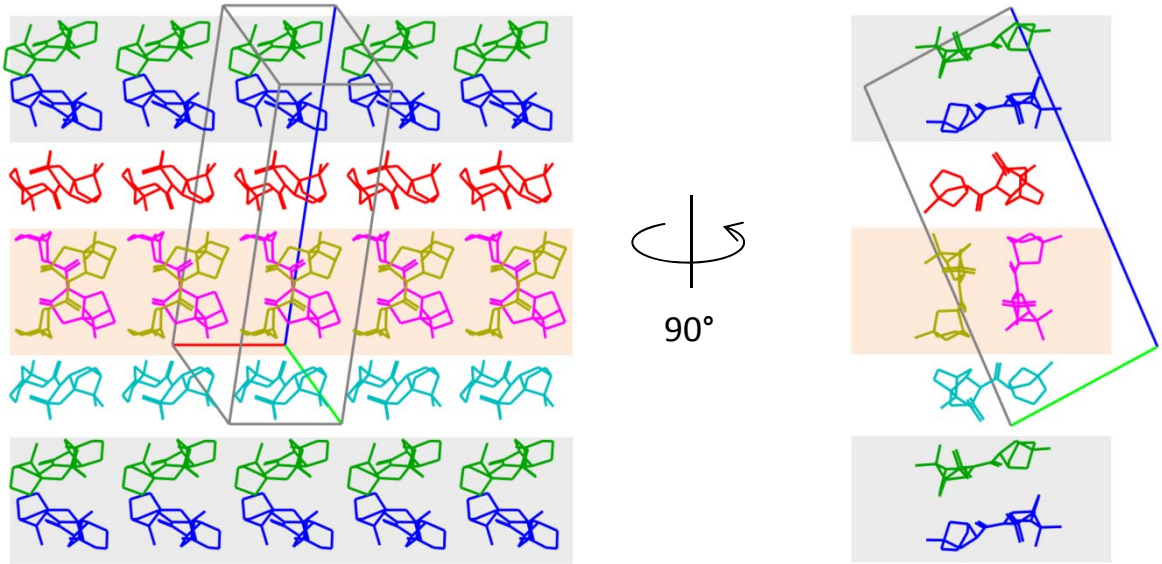
KITQIN
(*P*1, *Z*'=6)



(0 1 1)

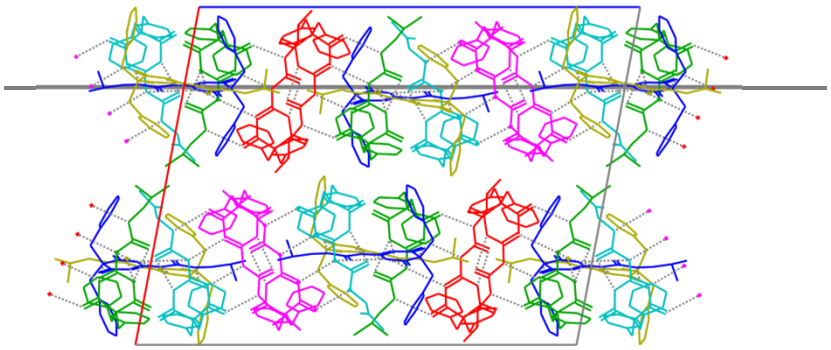


Layer (0 1 1)

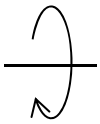


Projection along **b**

LAXJUQ
($P2_1/n$, Z'=6)

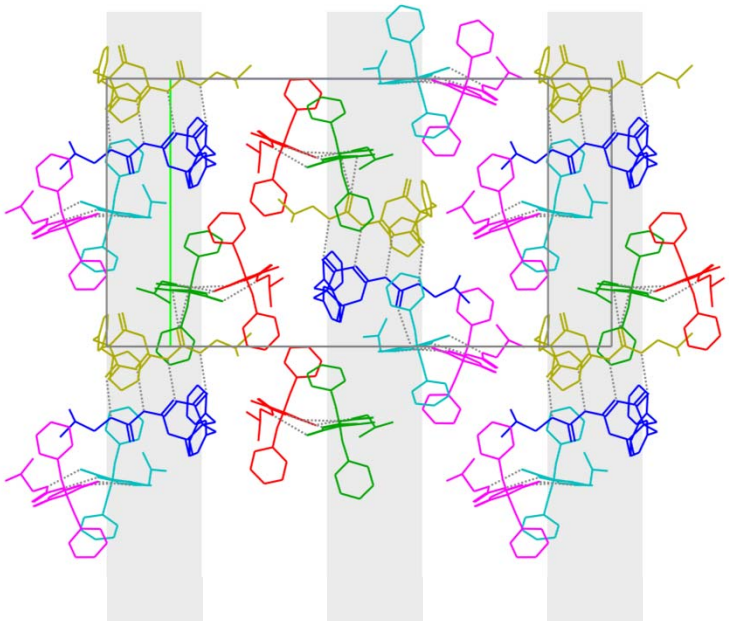


(1 0 0)



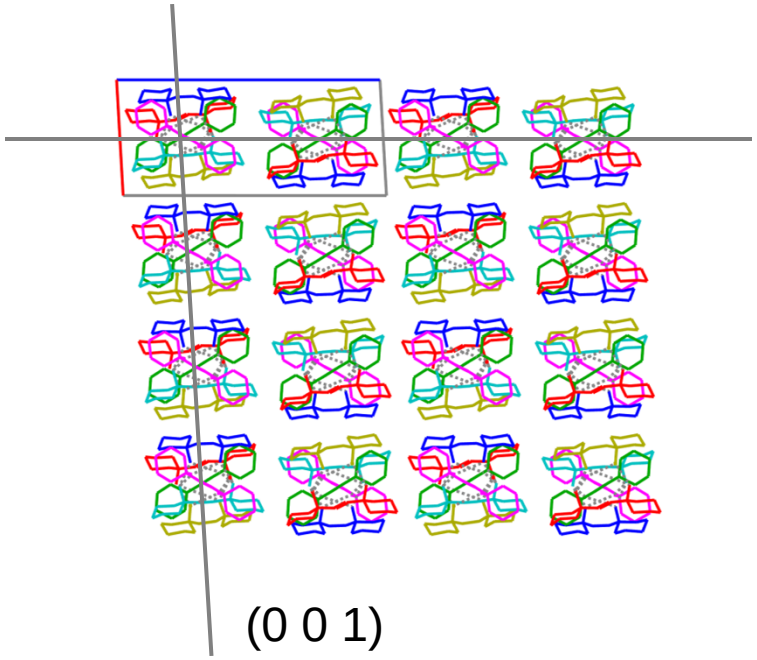
90°

Layer (1 0 0)

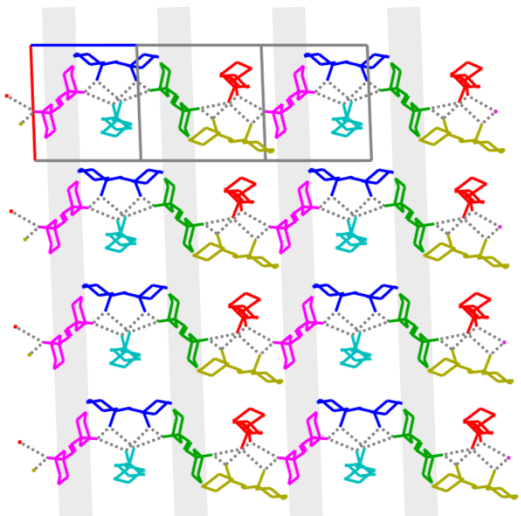


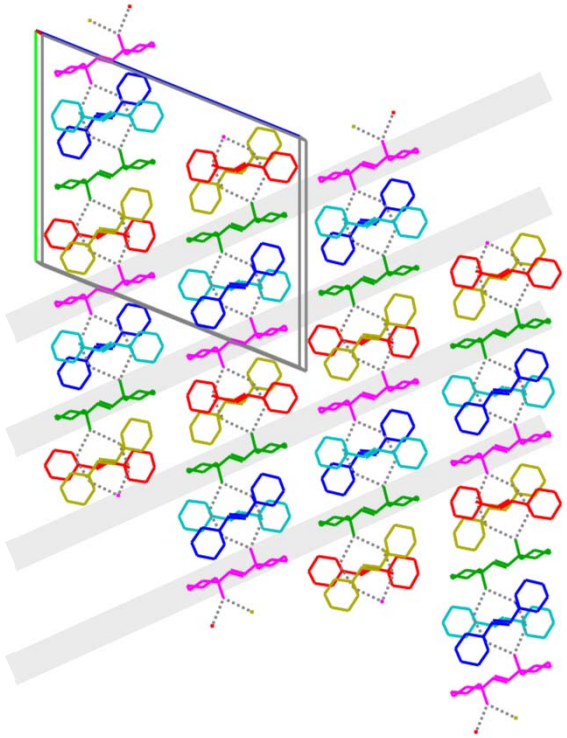
Projection along **b**

TARNEG
(*P*-1, *Z*'=6)



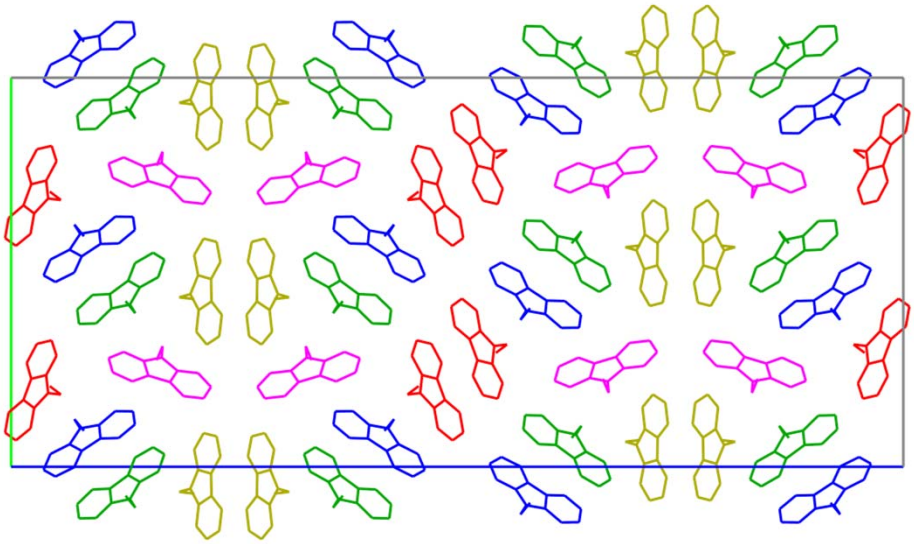
Layers (1 0 0) and (0 0 1)

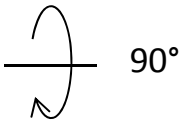


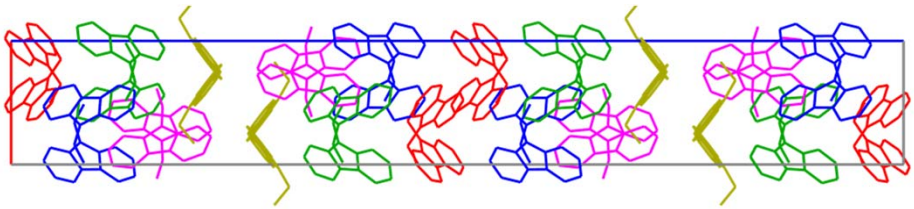


Projection along **a**

ETCABZ10
(*Pbca*, *Z*'=5)







Projection along **b**

NIMRIK08
(*C*2/*c*, *Z*'=6)