ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Octahedral Werner Complexes with Substituted Ethylenediamine Ligands: A Stereochemical Primer for a Historic Series of Compounds now Emerging as a Modern Family of Catalysts

Andreas Ehnbom, Subrata K. Ghosh, Kyle G. Lewis, and John A. Gladysz*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012, USA

E-mail: gladysz@mail.chem.tamu.edu

Stereoisomers of $[Co(pn)_3]^{3+}$ trications comprised of all combinations of (*R*)-pn and (*S*)-pn ligands. A brief introduction to Figures s1 and s2 is provided to aid the reader. The major objective is to couple each three dimensional structure to a unique and unambiguous stereochemical descriptor.

First, each trication is viewed along the formal C_3 axis (see text). Second, for each cobalt configuration (Λ, Δ), the triangles **X** and **XI** are defined, the apices of which "point" to the three chelate ligands. The first stereochemical designation in each sequence of three (λ vs. δ; *R* vs. *S*; *ob* vs. *lel*) is given for the apex labeled "1", followed by "2" and "3". For consistency, if there is one unlike λ/δ configuration (e.g., λδδ or δλλ), it is assigned to apex 1. Note that there are some fixed relationships between metal configurations, chelate conformations, and perspectives (*ob*, *lel*), as summarized by the box in Figure s1.

In any case, 24 structures, corresponding to those summarized in Table 1, result. The unique stereochemical descriptors are highlighted in the boxes underneath each structure.

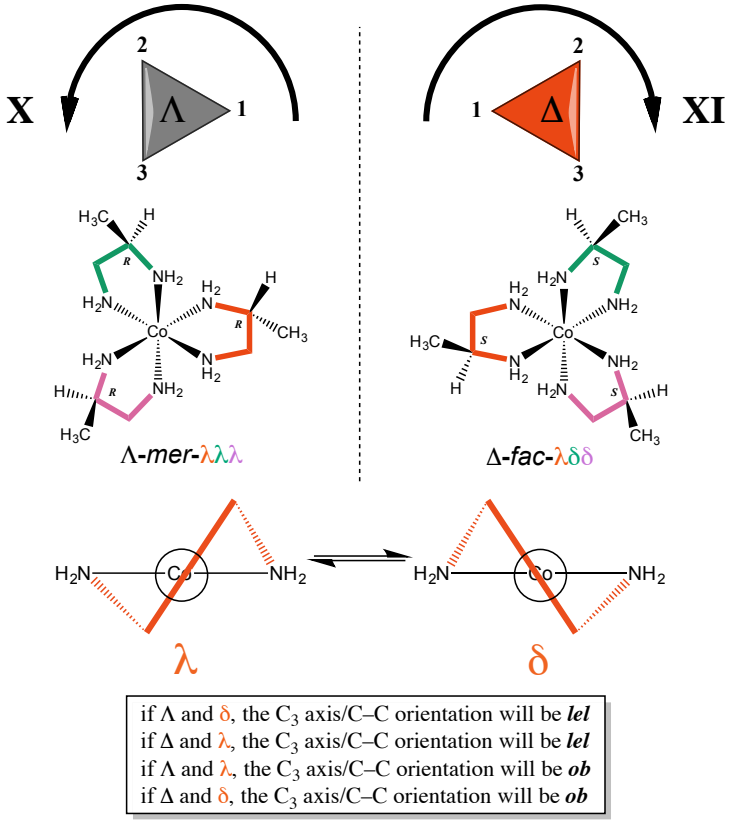
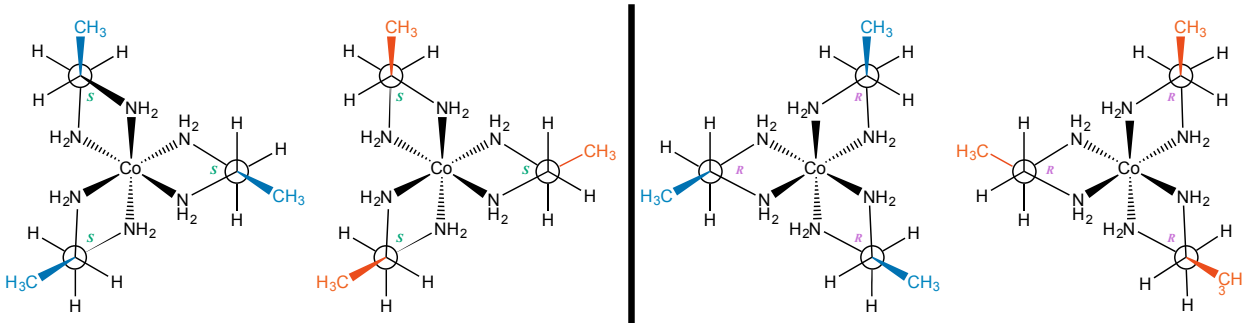
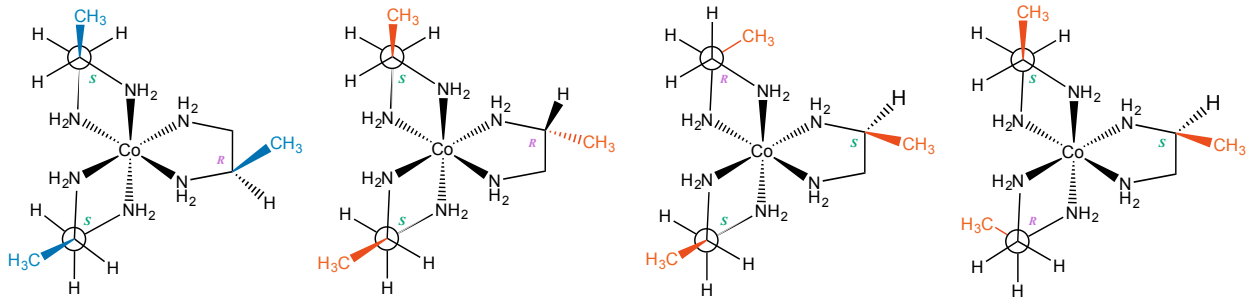


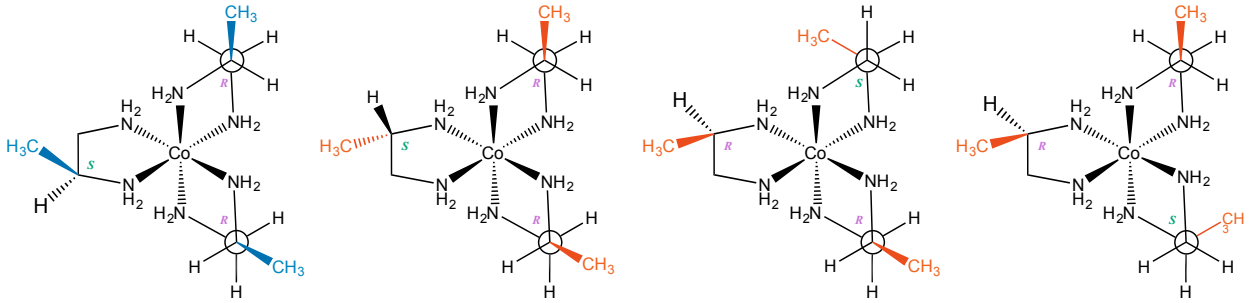
Figure s1. Conventions used in designating chelate stereochemistry (*R* vs. *S*; λ vs. δ; *ob* vs. *lel*) in the structural representations in Figure s2, and some "short cuts" involving these relationships.



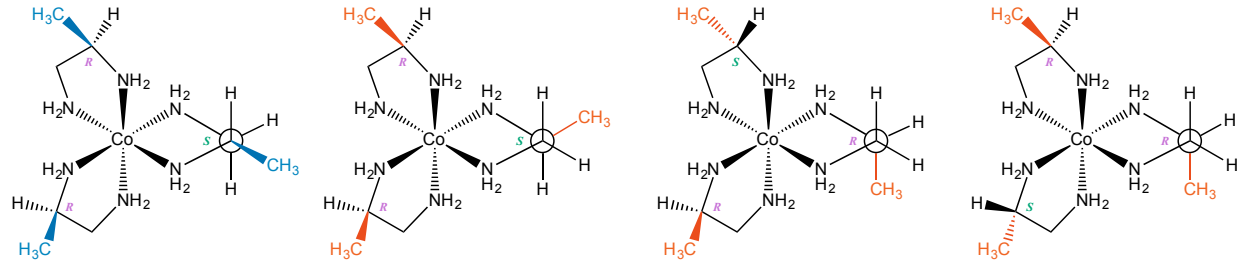
Λ-*fac*-δδδ *SSS* | Λ *lel*$_3$ | Λ-*mer*-δδδ *SSS* | Δ-*fac*-λλλ *RRR* | Δ *lel*$_3$ (Figure 7) | Δ-*mer*-λλλ *RRR*



Λ-*fac*-λδδ *RSS* | Λ-*mer*-λδδ *RSS* | Λ *ob/lel/lel* | Λ-*mer*-λδδ *SRS* | Λ-*mer*-λδδ *SSR*



Δ-*fac*-δλλ *SRR* | Δ-*mer*-δλλ *SRR* | Δ *ob/lel/lel* | Δ-*mer*-δλλ *RSR* | Δ-*mer*-δλλ *RRS*



Λ-*fac*-δλλ *SRR* | Λ-*mer*-δλλ *SRR* | Λ *lel/ob/ob* | Λ-*mer*-δλλ *RSR* | Λ-*mer*-δλλ *RRS*

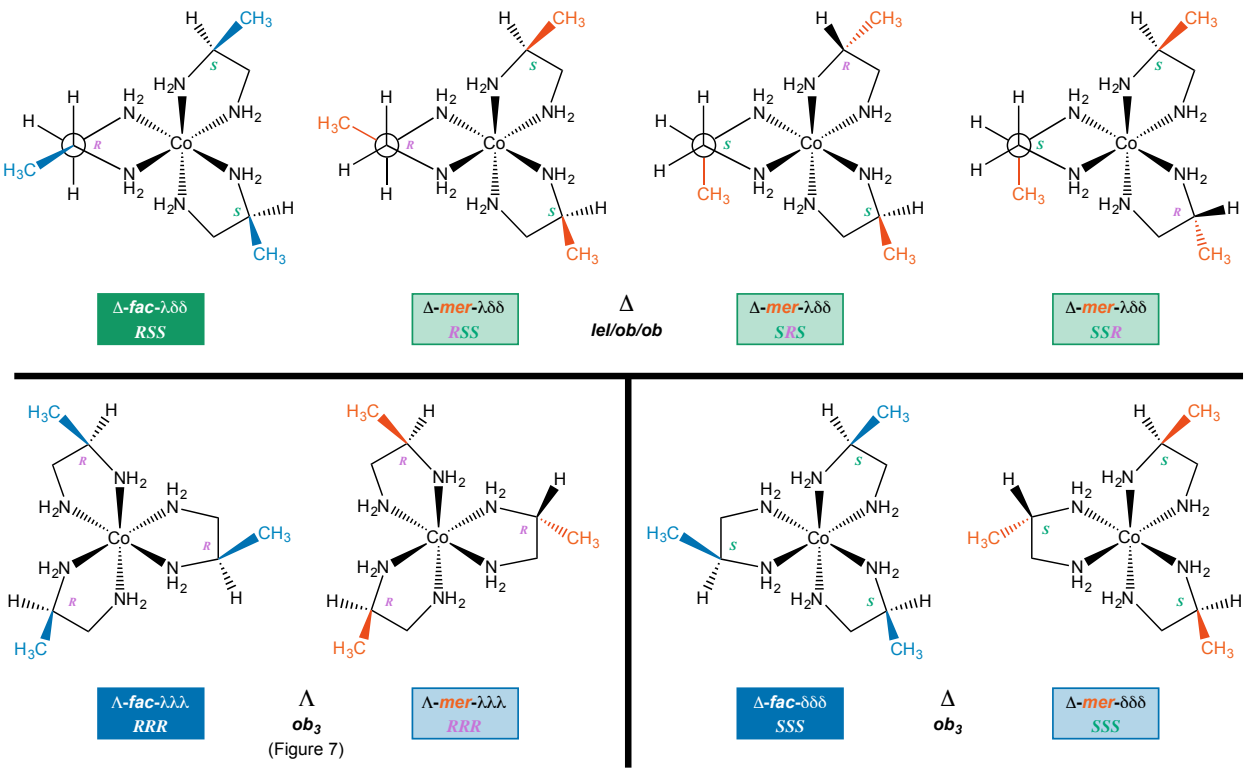


Figure s2. The 24 stereoisomers of the $[Co(pn)_3]^{3+}$ trication summarized in Table 1, allowing all combinations of *R* (purple labels) and *S* (turquoise labels) pn ligands. The methyl groups are depicted in blue for *fac* isomers, and in vermillion for *mer* isomers.

Stereoisomers of $[Co(cis\text{-chxn})_3]^{3+}$ trications (i.e., comprised only of *R*,*S*-chxn or *meso* ligands). In order to couple each three dimensional structure to a unique and unambiguous stereochemical descriptor, the conventions outlined in Figure s1 and the preceding text are adopted. One then views the formal C_3 axis from in front of the plane of the paper to order the two *RS* stereocenters of each chelate. As illustrated in Figure s3, one obtains the reverse order if the axis is viewed from behind the plane of the paper.

The first stereochemical designation in each sequence of three (λ vs. δ; *RS* vs. *SR*; *ob* vs. *lel*) is given for the apex labeled "1", followed by "2" and "3". Some 24 structures, summarized in Table s1, result. Each is assigned a number (1 through 24). The unique stereochemical descriptors are highlighted in the boxes beside each structure. The boxes are color coded according to the *ob*/*lel* pattern.

For each cobalt configuration (Λ/Δ), the stereoisomers exhibit two lel_3, four lel_2ob, four

lelob$_2$, and two *ob*$_3$ orientations. One from each group is *fac* isomer, and the others are *mer*. A representative pair of enantiomers is as follows: Λ-*mer*-λδδ-*SR*/*SR*/*RS* and Δ-*mer*-δλλ-*RS*/*RS*/*SR* (structures 6 and 18); both feature *lel*$_2$*ob* orientations.

Structures that are related by a single cyclohexane "ring flip" are summarized in Table s2. These link to give the four separate families of stereoisomers noted in Figure s4 (two for each cobalt Λ/Δ configuration). The "ring flip" relationships are also coded by the circled letters close to each of the three apices/cyclohexane rings of each structure (i.e., F, F', F" for structure 6). The structure that results from a "ring flip" of the nearby cyclohexane is labeled on the left side of the colored boxes with the letter of the apex/cyclohexane ring that "flipped".

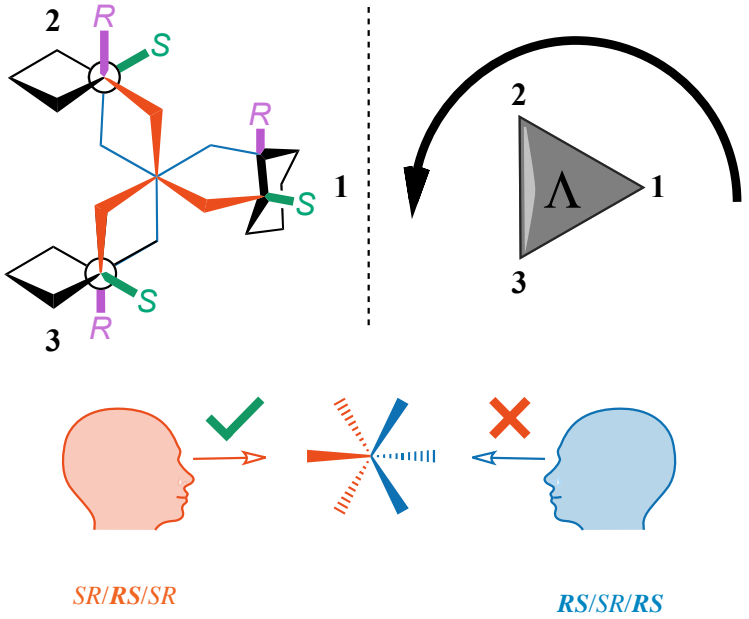
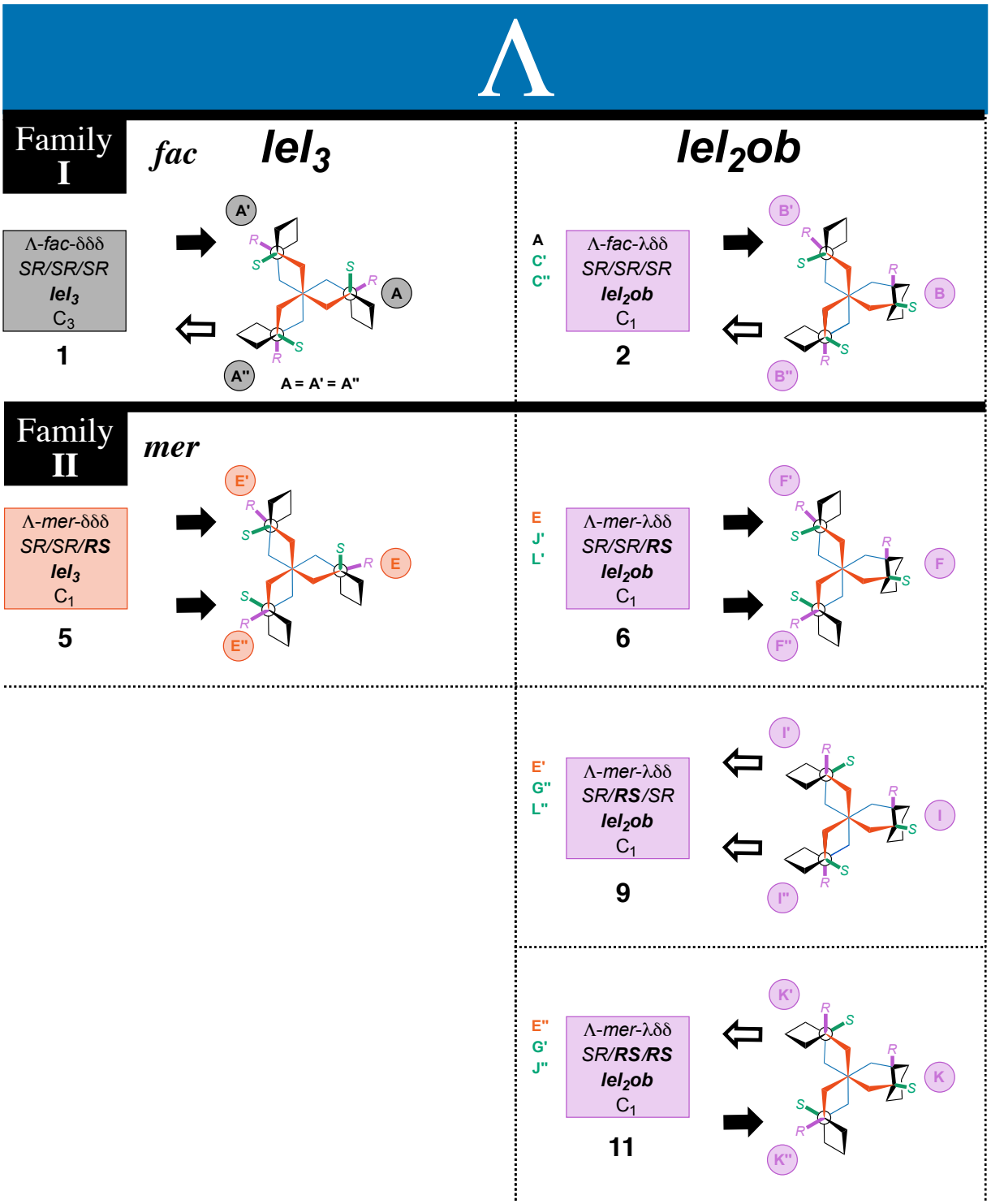


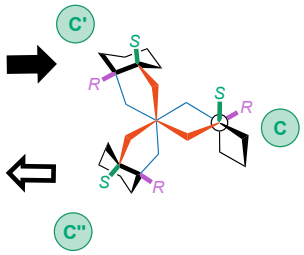
Figure s3. Conventions used in designating chelate stereochemistry in the structural representations in Figure s4. The procedure is analogous to that in Figure s1 except it is important to consistently view the C_3 axes from in front of the plane of the paper to "order" the *SR*/*RS* configurations of the chelate ring stereocenters.

Figure s4. The 24 stereoisomers of the $[Co(cis\text{-chxn})_3]^{3+}$ trication (*cis*-chxn = *R*,*S*-chxn) summarized in Table s1. In each vertical series, the λ/δ configuration of the chelate at apex 1 (Figure s3) is kept constant while the configurations in the remaining chelates are varied, as denoted by the arrows ⇐/⇒ (for λδδ and δλλ systems apex 1 is also set as the unlike configuration). Bold lines separate the families of isomers described in the preceding text. There is extensive color coding that carries over to Table s1, but the conventions are left to be empirically discerned.



Λ

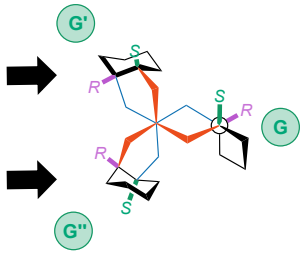
lelob$_2$



Λ-*fac*-δλλ
SR/SR/SR
***lelob*$_2$**
C_1

3

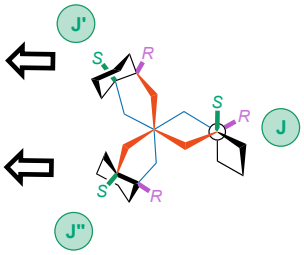
B'
B''
D



Λ-*mer*-δλλ
*SR/SR/**RS***
***lelob*$_2$**
C_1

7

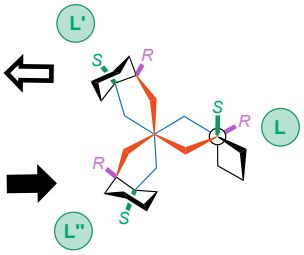
H
K'
I'



Λ-*mer*-δλλ
*SR/**RS**/SR*
***lelob*$_2$**
C_1

10

F''
H'
K''

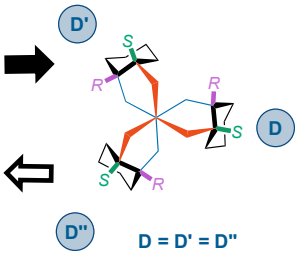


Λ-*mer*-δλλ
*SR/**RS**/RS*
***lelob*$_2$**
C_1

12

F'
H''
I''

ob$_3$

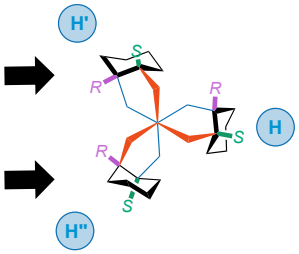


D = D' = D''

Λ-*fac*-λλλ
SR/SR/SR
***ob*$_3$**
C_3

4

C



Λ-*mer*-λλλ
*SR/SR/**RS***
***ob*$_3$**
C_1

8

G
J
L

Δ

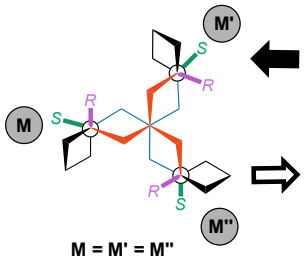
Family III — *fac*

lel_3

N

Δ-*fac*-λλλ
RS/RS/RS
***lel*$_3$**
C_3

13



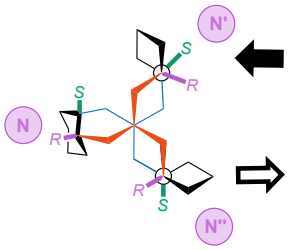
M = M' = M''

lel_2ob

M
O'
O''

Δ-*fac*-δλλ
RS/RS/RS
lel*$_2$*ob
C_1

14

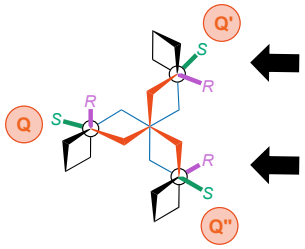


Family IV — *mer*

R
U
W

Δ-*mer*-λλλ
RS/RS/SR
***lel*$_3$**
C_1

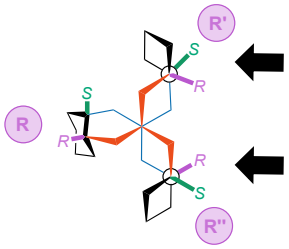
17



Q
V'
X'

Δ-*mer*-δλλ
RS/RS/SR
lel*$_2$*ob
C_1

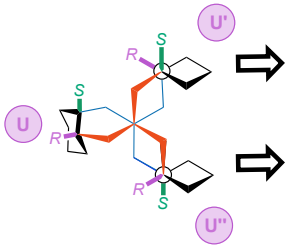
18



Q'
S''
X''

Δ-*mer*-δλλ
RS/SR/RS
lel*$_2$*ob
C_1

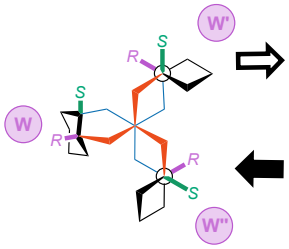
21



Q''
S'
V''

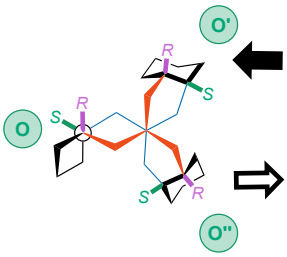
Δ-*mer*-δλλ
RS/SR/SR
lel*$_2$*ob
C_1

23



Δ

lelob$_2$

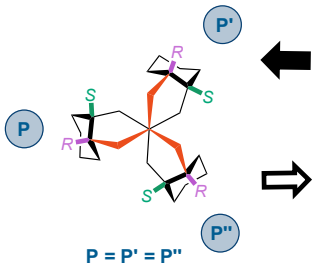


Δ-*fac*-λδδ
RS/RS/RS
***lelob*$_2$**
C_1

15

N'
N''
P

ob$_3$

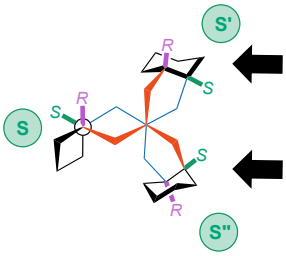


P = P' = P''

Δ-*fac*-δδδ
RS/RS/RS
***ob*$_3$**
C_3

16

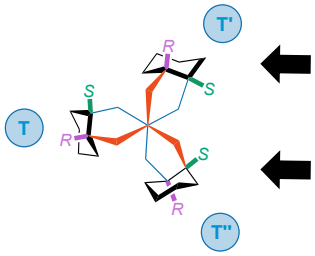
O



Δ-*mer*-λδδ
RS/RS/SR
***lelob*$_2$**
C_1

19

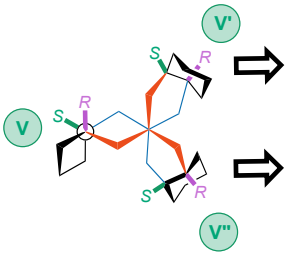
T
W'
U'



Δ-*mer*-δδδ
RS/RS/SR
***ob*$_3$**
C_1

20

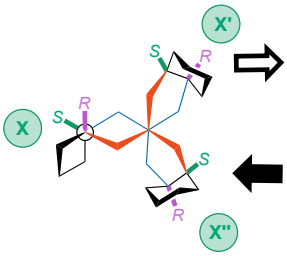
S
V
X



Δ-*mer*-λδδ
RS/SR/RS
***lelob*$_2$**
C_1

22

R''
T'
W''



Δ-*mer*-λδδ
RS/SR/SR
***lelob*$_2$**
C_1

24

R'
T''
U''

Table s1. Summary of the stereoisomers of the $[Co(cis\text{-chxn})_3]^{3+}$ trication depicted in Figure s4.

structure number (Figure s4)	cobalt configuration	ligand configurations	chelate conformations	perspective down the C_3 axis[a]	geometrical type isomers
1	Λ	*SR/SR/SR*	δδδ	***lel*$_3$**	*fac*
5	Λ	*SR/SR/**RS***	δδδ		*mer*
17	Δ	***RS**/**RS**/SR*	λλλ		*mer*
13	Δ	***RS/RS/RS***	λλλ		*fac*
2	Λ	*SR/SR/SR*	λδδ	***lel*$_2$*ob***	*fac*
6	Λ	*SR/SR/**RS***	λδδ		*mer*
9	Λ	*SR/**RS**/SR*	λδδ		*mer*
11	Λ	*SR/**RS/RS***	λδδ		*mer*
23	Δ	***RS**/SR/SR*	δλλ		*mer*
21	Δ	***RS**/SR/**RS***	δλλ		*mer*
18	Δ	***RS**/**RS**/SR*	δλλ		*mer*
14	Δ	***RS/RS/RS***	δλλ		*fac*
3	Λ	*SR/SR/SR*	δλλ	***lelob*$_2$**	*fac*
7	Λ	*SR/SR/**RS***	δλλ		*mer*
10	Λ	*SR/**RS**/SR*	δλλ		*mer*
12	Λ	*SR/**RS/RS***	δλλ		*mer*
24	Δ	***RS**/SR/SR*	λδδ		*mer*
22	Δ	***RS**/SR/**RS***	λδδ		*mer*
19	Δ	***RS**/**RS**/SR*	λδδ		*mer*
15	Δ	***RS/RS/RS***	λδδ		*fac*
4	Λ	*SR/SR/SR*	λλλ	***ob*$_3$**	*fac*
8	Λ	*SR/SR/**RS***	λλλ		*mer*
20	Δ	***RS**/**RS**/SR*	δδδ		*mer*
16	Δ	***RS/RS/RS***	δδδ		*fac*

[a] Or an equivalent axis as defined in the text.

Table s2. A grid of the structure numbers for the 24 stereoisomers in Figure s4 with "×" indicating those that can be interconverted by a single cyclohexane "ring flip". The specific ring can be inferred from additional coding in Figure s4. The sets of structures interconverted by "×" are considered families of conformational stereoisomers.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1		×																						
2	×		×																					
3		×		×																				
4			×																					
5						×			×		×													
6					×					×		×												
7								×	×		×													
8							×			×		×												
9					×		×					×												
10						×		×			×													
11					×		×			×														
12						×		×	×															
13														×										
14													×		×									
15														×		×								
16															×									
17																		×			×		×	
18																	×					×		×
19																				×	×		×	
20																			×			×		×
21																	×		×					×
22																		×		×			×	
23																	×		×			×		
24																		×		×	×			