Structural Study of Enantiomeric Schiff Bases Derived from S-Substituted Dithiocarbazates and Their Metal Complexes

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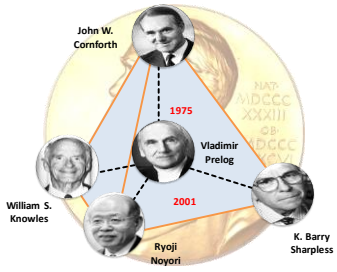
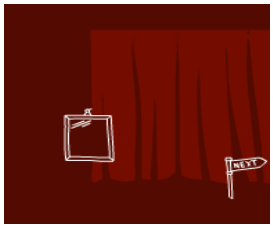
Introduction to Chirality



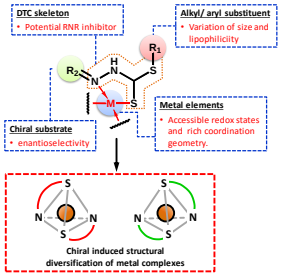
Introduction to Chirality (Cont)



- Chiral molecules can be used to control or speed up different chemical reactions
- Enantiomers may react differently in biological system with intrinsic chiral nature.

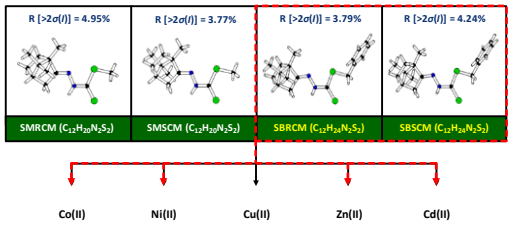
Source: https://www.nobelprize.org/educational/chemistry/chiral/

Objectives

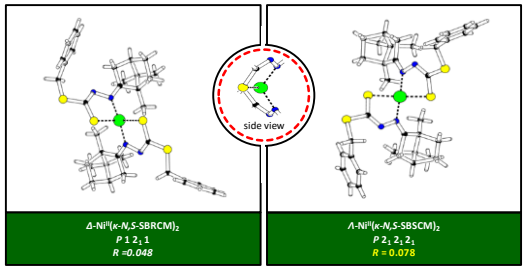


- To study the effect on the use of chiral ligand to the formation of complexes.
- To study the geometrical and structural differences between different complexes with same coordinating ligand.
- To compare the crystallographic properties between enantiomeric and racemic structures.

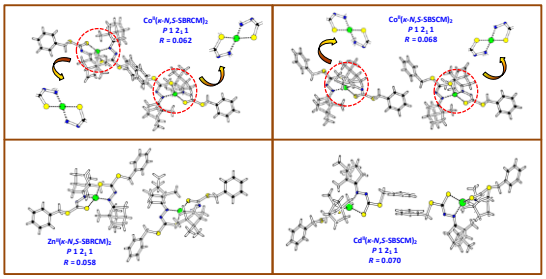
Research Settings



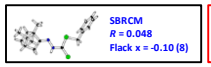
Part I – Absolute Structure of Metal Complexes



Absolute Structure of Metal Complexes (Cont)

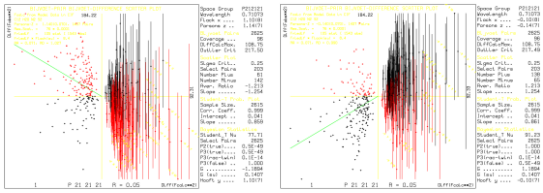


Absolute Structure Determination



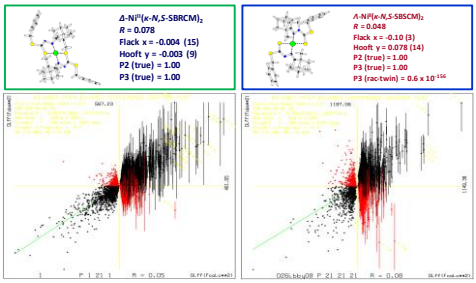
SBRCM
R = 0.048
Flack x = -0.10 (8)

For a Flack's x value to reliably determine the absolute configuration:
0 < x < 1, -3u < x < 3u;
Confidence limit for u < 0.10



Flack, H.D. and Bernardinelli, G. (2000) *J. Appl. Crystallogr.* 33, 1143-1148.

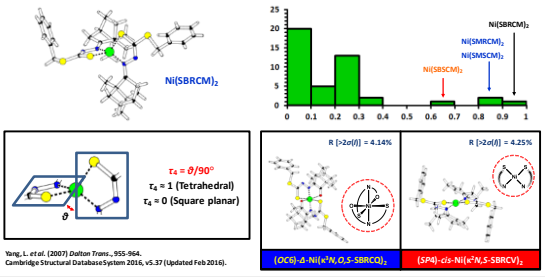
Absolute Structure Determination (Cont)



Absolute Structure Determination (Cont)

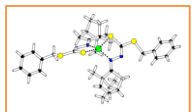
Parameter	Co^{II}(*κ*-N,S-SBRCM)$_2$	Co^{II}(*κ*-N,S-SBSCM)$_2$	Zn^{II}(*κ*-N,S-SBRCM)$_2$	Zn^{II}(*κ*-N,S-SBSCM)$_2$	Cd^{II}(*κ*-N,S-SBRCM)$_2$
Flack *x* (su)	-0.036 (17)	0.016 (26)	0.017 (15)	0.062 (17)	-0.04 (4)
Hooft *y* (su)	-0.003 (9)	-0.014 (23)	0.029 (10)	0.059 (9)	-0.02 (3)
P2 (true)	1.00	1.00	1.00	1.00	1.00
P3 (true)	1.00	1.00	1.00	1.00	1.00
P3 (rac-twin)	0	0	0	0	0.3 x 10^{-52}
P3 (false)	0	0	0	0	0.5 x 10^{-180}

Part II – Geometrical Property of Metal Complexes



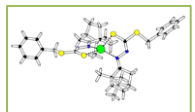
Yang, L. *et al.* (2007) *Dalton Trans.*, 955-964.
Cambridge Structural Database System 2016, v5.37 (Updated Feb 2016).

Geometrical Property of Metal Complexes (Cont)



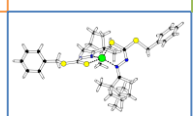
Co^{II}(*κ-N,S*-SBRCM)$_2$

τ$_4$ index		Average *ϑ* in CSD
R	*S*	
0.99	0.99	0.92



Cd^{II}(*κ-N,S*-SBRCM)$_2$

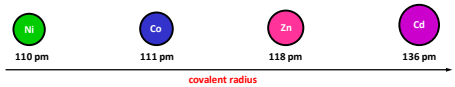
τ$_4$ index		Average *ϑ* in CSD
R	*S*	
0.97	0.97	0.91



Zn^{II}(*κ-N,S*-SBRCM)$_2$

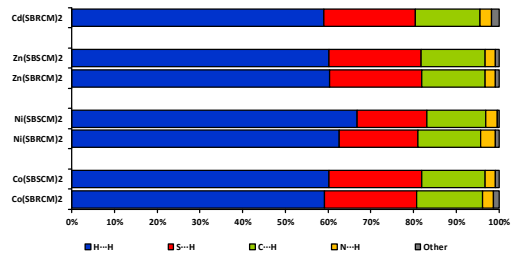
τ$_4$ index		Average *ϑ* in CSD
R	*S*	
0.99	0.97	0.92

Geometrical Differences between Metal Complexes

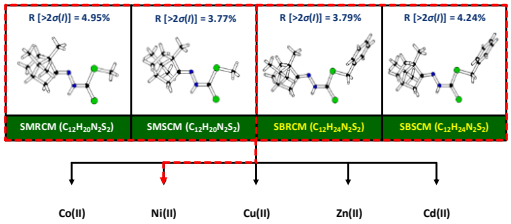


Parameter (average)	Ni(SBSCM)$_2$	Ni(SBRCM)$_2$	Co(SBRCM)$_2$	Co(SBSCM)$_2$	Zn(SBRCM)$_2$	Zn(SBSCM)$_2$	Cd(SBRCM)$_2$
τ_4 index	0.60	0.90	0.97	0.97	0.99	0.99	0.99
M-N/ Å	1.901	1.988	2.041	2.040	2.060	2.061	2.284
M-S/ Å	2.211	2.255	2.279	2.277	2.292	2.293	2.462
S-M-N/ °	85.1	86.8	87.8	87.7	88.3	88.6	81.9
N-M-N/ °	177.8	142.7	124.9	125.0	123.3	123.1	123.3
S-M-S/ °	153.8	111.5	114.4	114.6	118.1	118.1	125.4

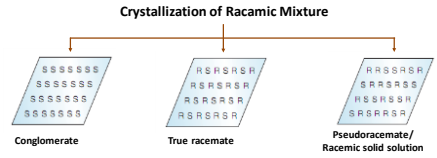
Comparison of Intermolecular Close Contacts between Metal Complexes



Part III – Racemates and Enantiopure Crystals



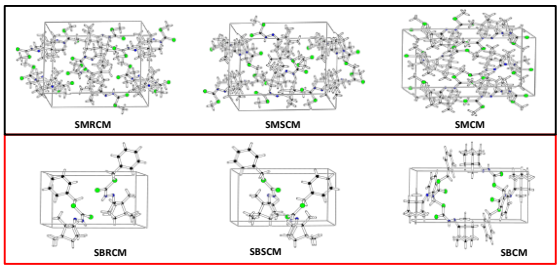
Crystallization of Racemic Compounds



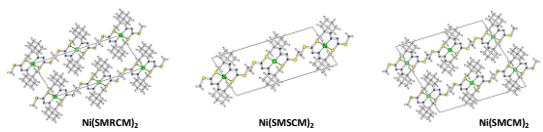
Knowledge in understanding the differences of crystallization between enantiopure and racemic compounds is essential for rational design of chiral resolution and purification processes.

Picture credit: Datta, S. and Grant, D.J.W. (2004) *Nat. Rev. Drug Discov.* 3, 42-57.

Crystal Packing of Racemic and Enantiopure Crystals

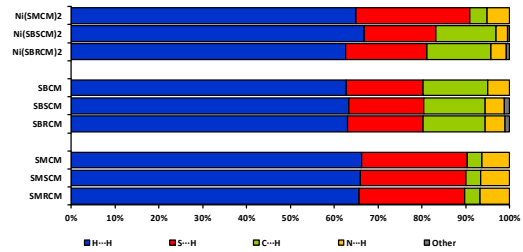


Crystal Packing and Some Physical Properties of Racemic and Enantiopure Crystals

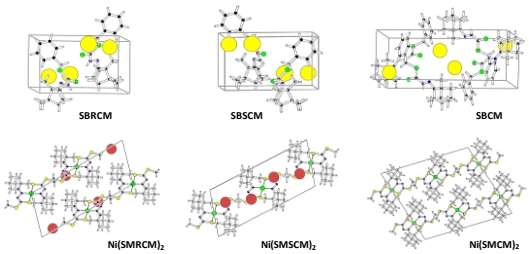


Parameter	SMRCM	SMSCM	SMCM	SBRCM	SBSCM	SBCM	Ni(SMRCM)$_2$	Ni(SMSCM)$_2$	Ni(SMCM)$_2$
Space Group	$P2_12_12_1$	$P2_12_12_1$	*Pcab*	$P1\,2_1\,1$	$P1\,2_1\,1$	$P1\,2_1/c\,1$	$C1\,2\,1$	$C1\,2\,1$	$C1\,2/c\,1$
Z	8	8	8	2	2	4	2	2	4
Cell Volume, Å^3	2715.42	2720.00	2723.75	913.81	913.08	1775.35	1391.69	1395.81	2777.58
Density, g/cm^{-3}	1.254	1.252	1.251	1.208	1.209	1.244	1.359	1.355	1.362
KPL %	67.1	67.1	66.9	64.9	65.0	67.1	65.9	65.9	66

Comparison of Intermolecular Close Contacts between Racemic and Enantiopure Crystals



Presence of Crystal Voids in Racemic and Enantiopure Crystals



Min cavity radius = 1.2 Å

Conclusions

- The use of chiral ligand have resulted in formation of metal complexes with inherited chiral property, although the helicity around the metal center remains unresolved for some complexes.
- All complexes adopted a pseudo-tetraheral geometry, with the Ni(II) complexes being the first on its kind as found in the database.
- Racemic compounds are generally found to agree with Wallach's rule in which they are denser and more closely packed than their enantiopure counterparts.

Acknowledgements

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Thank You