



Universiteit
Leiden
The Netherlands

Reactivity of cobalt(II)-dichalcogenide complexes: correlation between redox conversion and ligand-field strength

Marvelous, C.

Citation

Marvelous, C. (2022, July 5). *Reactivity of cobalt(II)-dichalcogenide complexes: correlation between redox conversion and ligand-field strength*. Retrieved from <https://hdl.handle.net/1887/3421554>

Version: Publisher's Version

[Licence agreement concerning inclusion of doctoral
thesis in the Institutional Repository of the University
of Leiden](#)

License: <https://hdl.handle.net/1887/3421554>

Note: To cite this publication please use the final published version (if applicable).

**Reactivity of Cobalt(II)-Dichalcogenide Complexes:
Correlation between Redox Conversion
and Ligand-field Strength**

Proefschrift

ter verkrijging van
de graad van doctor aan de Universiteit Leiden,
op gezag van rector magnificus prof.dr.ir. H. Bijl,
volgens besluit van het college voor promoties
te verdedigen op dinsdag 5 Juli 2022

klokke 10:00 uur

door

Christian Marvelous

geboren te Malang, Indonesië

in 1994

Promotores:

Prof.dr. E. Bouwman

Prof.dr. C. Fonseca Guerra

Promotiecommissie:

Prof.dr. H.S. Overkleeft

Prof.dr. S.A. Bonnet

Prof.dr. B. de Bruin (University of Amsterdam)

Dr. C. Duboc (Université Grenoble Alpes, France)

Dr.ing. D.L.J. Broere (Utrecht University)

“If you wish to succeed in life, make perseverance your bosom friend, experience your wise counselor, caution your elder brother, and hope your guardian genius.”

Joseph Addison

To my parents and to my future self,

As a reminder that persistence is almost always rewarding.

Table of Contents

List of Abbreviations	5
Chapter 1 Biomimetic Models of Sulfur-containing Enzymes and a Bioinspired Redox-conversion Reaction.....	7
Chapter 2 Probing The Redox-conversion of Co(II)-disulfide to Co(III)-thiolate Complexes: The Effect of Ligand-Field Strength	25
Chapter 3 Cleaner and Stronger: How 8-quinolinolate Facilitates Formation of Co(III)-thiolate from Co(II)-disulfide Complexes.....	47
Chapter 4 Redox-conversion Reactivity of The Chalcogen Family: Selenium vs Sulfur	67
Chapter 5 Structural Investigations and Reactivity of Cobalt(II)-Disulfide Complexes.....	89
Chapter 6 Summary, Conclusions, and Outlook.....	107
Appendix I Supplementary Information for Chapter 2	115
Appendix II Supplementary Information for Chapter 3	129
Appendix III Supplementary Information for Chapter 4	143
Appendix IV Supplementary Information for Chapter 5	157
Samenvatting	173
Summary in Indonesian	179
Curriculum Vitae	185
List of Publications	187
Acknowledgements.....	189

List of Abbreviations

ATP	adenosine triphosphate	mer	meridional
a.u.	arbitrary units	Met	methionine
bpy	2,2'-bipyridine	MO	molecular orbital
br	broad	MS	mass spectrometry
calcd.	calculated	N(nBu ₄)I	tetrabutylammonium iodide
CcO	cytochrome c oxidase	NEt ₄ Cl	tetraethylammonium chloride
Cys	cysteine	(NGuaS) ₂	2',2'-(2,2'-dithiodiphenyl)bis(1,1,3,3-tetramethylguanidine)
d	doublet (NMR)	NHase	nitrile hydratase
DCM	dichloromethane	NMR	nuclear magnetic resonance
dd	double doublet	Ph	phenyl
DFT	density functional theory	phen	1,10-phenanthroline
DIPEA	diisopropylethylamine	ppm	parts per million
DMF	dimethylformamide	Py	2-pyridyl
DMSO	dimethylsulfoxide	q	quartet
equiv.	equivalent	Hquin	8-quinolinol
ESI	electrospray ionization	RT	room temperature
fac	facial	s	singlet (NMR), strong (IR)
Glu	glutamic acid	Sec	selenocysteine
His	histidine	Ser	serine
HOTf	trifluoromethanesulfonic acid	SOMO	singly occupied molecular orbital
IR	infrared	t	triplet
Leu	leucine	TDDFT	time-dependent density functional theory
LMCT	ligand-to-metal charge transfer	UV-vis	ultraviolet -visible
m	multiplet (NMR), medium (IR)	vs	very strong
Me	methyl	w	weak

