

Yingzhao Ma

The Reduction of Elemental Chalcogens and Their Derivatives by Divalent Lanthanide Complexes

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13	14																	7
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17	18																	9
19	20																	10
21	22																	11
23	24																	12
25	26																	13
27	28																	14
29	30																	15
31	32																	16
33	34																	17
35	36																	18
37	38																	19
39	40																	20
41	42																	21
43	44																	22
45	46																	23
47	48																	24
49	50																	25
51	52																	26
53	54																	27
55	56																	28
57	58																	29
59	60																	30
61	62																	31
63	64																	32
65	66																	33
67	68																	34
69	70																	35
71	72																	36
73	74																	37
75	76																	38
77	78																	39
79	80																	40
81	82																	41
83	84																	42
85	86																	43
87	88																	44
89	90																	45
91	92																	46
93	94																	47
95	96																	48
97	98																	49
99	100																	50
101	102																	51
103	104																	52



Cuvillier Verlag Göttingen
Internationaler wissenschaftlicher Fachverlag



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The Reduction of Elemental Chalcogens and Their Derivatives by Divalent Lanthanide Complexes

Zur Erlangung des akademischen Grades eines
DOKTORS/DOKTORIN DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

der KIT-Fakultät für Chemie und Biowissenschaften
des Karlsruher Instituts für Technologie (KIT)

vorgelegte

DISSERTATION

von

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Tag der mündlichen Prüfung: 16.04.2018



Die vorliegende Arbeit wurde in der Zeit vom 01. September 2014 bis zum 07. März 2018 am Institut für Anorganische Chemie des Karlsruher Instituts für Technologie (KIT) unter der Leitung von Herrn Prof. Dr. Peter W. Roesky durchgeführt.

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Bibliografische Information der Deutschen Nationalbibliothek

Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.d-nb.de> abrufbar.

1. Aufl.-Göttingen: Cuvillier, 2018

Zugl.: Karlsruhe (KIT), Univ., Diss., 2018

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1. Auflage, 2018

Gedruckt auf umweltfreundlichem, säurefreiem Papier aus nachhaltiger Forstwirtschaft.

ISBN 978-3-7369-9821-6

eISBN 978-3-7369-8821-7



Dedicated to my Grandma





List of content

1 Introduction.....	1
1.1 Chalcogen.....	1
1.1.1 General.....	1
1.1.2 Physical and Chemical Properties.....	2
1.2 Rare earth elements.....	4
1.2.1 General.....	4
1.2.2 Physical and chemical properties.....	5
1.3 Lanthanide chalcogenide complexes derived from the reduction of chalcogen(ide)s by divalent lanthanide complexes.....	7
2 Aim of the project	13
3 Results and discussion	14
3.1 Polysulfide coordination clusters of the lanthanides.....	14
3.1.1 Synthesis	15
3.1.2 Structure.....	18
3.1.3 NIR analysis.....	22
3.2 Synthesis of dinuclear chalcogenides from the reduction of chalcogens by <i>N,N'</i> -chelating ligand supported low-valent metal complexes.....	24
3.2.1 Synthesis	25
3.2.2 Structure.....	27
3.3 Synthesis of lanthanide (Sm, Yb) aryl chalcogenides by redox reactions.....	34
3.3.1 Synthesis	35
3.3.2 Crystal structures.....	38
3.3.3 IR analysis.....	46
4 Experimental sections	48
4.1 General considerations.....	48
4.2 Synthesis of polysulfide clusters.....	48
4.2.1 Synthesis of [(DippForm) ₃ Sm ₃ S ₁₂ (THF) ₂] (1).....	48
4.2.2 Synthesis of [(DippForm) ₃ Yb ₃ S ₁₂ (THF) ₂]·2(C ₇ H ₈)·S ₈ (2).....	50
4.2.3 Synthesis of [(DippForm) ₂ YbCl(THF)] (3)	50
4.3 Synthesis of dinuclear chalcogenides.....	51
4.3.1 General procedure for the Synthesis of [{(DippForm) ₂ LnE} ₂] (4-6).....	51
4.3.2 General procedure for the Synthesis of [(DippNafnaf)FeE] ₂] (7-9).....	52
4.4 Synthesis of lanthanide (Sm, Yb) aryl chalcogenides.....	53
4.4.1 General procedure for the Synthesis of [(DippForm) ₂ Ln(EPh)(THF)] (10-15).....	53
5 Crystal structure measurements	56
5.1 Data collection and refinement	56
5.2 Crystal Data.....	58
5.2.1 [(DippForm) ₃ Sm ₃ S ₁₂ (THF) ₂]·2(C ₇ H ₈)·S ₈ (1 Method A).....	58
5.2.2 [(DippForm) ₃ Sm ₃ S ₁₂ (THF) ₂]·3(C ₇ H ₈) (1 Method B).....	59
5.2.3 [(DippForm) ₃ Yb ₃ S ₁₂ (THF) ₂]·2(C ₇ H ₈)·S ₈ (2)	60
5.2.4 [(DippForm) ₂ YbCl(THF)] (3).....	61
5.2.5 [{(DippForm) ₂ SmSe} ₂]·0.5(C ₇ H ₈) (4)	62



5.2.6 [(DippForm) ₂ SmTe ₂](C ₇ H ₈) (5)	63
5.2.7 [(DippForm) ₂ YbSe ₂](C ₇ H ₈) (6)	64
5.2.8 [(DippNafnaf)FeS ₂] (7)	65
5.2.9 [(DippNafnaf)FeSe ₂] (8)	66
5.2.10 [(DippNafnaf)FeTe ₂](C ₇ H ₈) (9)	67
5.2.11 [(DippForm) ₂ Sm(SPh)(THF)] (10)	68
5.2.12 [(DippForm) ₂ Yb(SPh)(THF)](C ₇ H ₈) (11)	69
5.2.13 [(DippForm) ₂ Sm(SePh)(THF)](C ₇ H ₈) (12)	70
5.2.14 [(DippForm) ₂ Yb(SePh)(THF)](C ₇ H ₈) (13)	71
5.2.15 [(DippForm) ₂ Sm(TePh)(THF)](C ₇ H ₈) (14)	72
5.2.16 [(DippForm) ₂ Yb(TePh)(THF)](C ₇ H ₈) (15)	73
5.2.17 [(DippForm) ₂ Sm(SeC ₆ F ₅)(THF)](C ₆ H ₁₂) (16)	74
5.2.18 [(DippForm) ₂ Yb(SeC ₆ F ₅)]·0.5(C ₆ H ₁₂) (18)	75
5.2.19 [(DippForm) ₂ Sm(SeC ₆ F ₄ OMe)(THF)](C ₆ H ₁₂) (19)	76
5.2.20 [(DippForm) ₂ Yb(SeC ₆ F ₄ OMe)(THF)] (20)	77
5.2.21 [(DippForm) ₂ Yb(SeC ₆ F ₄ OMe)] (21)	78
5.2.22 (BBED ₂ Sm ₂) (22)	79
5.2.23 [BABCD{SmI(BTSA)(THF)} ₂] (23)	80
5.2.24 [BAPCD{Sm(BTSA) ₂ } ₂] (24)	81
6 Summary	82
6 Zusammenfassung	85
7 References	88
8 Appendix	95
8.1 Preliminary Results	95
8.1.1 Synthesis	95
8.1.2 Structure	97
8.2 Directory of abbreviations	100
8.3 NMR abbreviations	101
8.4 IR abbreviations	101
8.5 Directory of compounds	101
9 Acknowledgements	103
10 Curriculum Vitae	105
11 Publications	106

1 Introduction

1.1 Chalcogen

1.1.1 General

The word "chalcogen" is derived from a combination of the Greek word *khalkós* principally meaning copper (the term was also used for bronze/brass, any metal in the poetic sense, ore or coin), and the latinized Greek word *genēs*, meaning born or produced.^[1] Chalcogens are known as oxygen, sulfur, selenium, tellurium and radioactive element polonium, which are group 16 elements. According to Emsley John, the chemically uncharacterized synthetic element livermorium (Lv) is predicted to be a chalcogen as well.^[2] Oxygen was recognized as an element in the 18th century. Sulfur has been known since antiquity as well. Selenium, tellurium and polonium were synthesized in the 19th century, and livermorium in 2000. Almost all the chalcogens can find their roles in biological functions. Typically, lighter chalcogens (oxygen and sulfur) are rarely toxic in their elemental form, and are often critical to life, while the heavier chalcogens (selenium and tellurium) are often toxic.^[3] Commercially, selenium is used for glassmaking and pigments. Moreover, selenium is a semiconductor used in photocells electronics. Tellurium is extremely rare in earth's crust. Compounds bearing tellurium were first discovered in Zlatna, Romania by Austrian mineralogist Franz-Joseph Müller von Reichenstein in 1782 in a gold mine, and subsequently, this new element was named by Martin Heinrich Klaproth in 1798. Tellurium has no biological function, although fungi can use it in place of sulfur and selenium in amino acids such as tellurocysteine and telluromethionine.^[4] The primary use of tellurium is in copper and steel alloys, in which it provides improved machinability. Other applications namely CdTe solar panels and semiconductors also consume a significant portion of tellurium production. Polonium was discovered by Marie and Pierre Curie in 1898 from uranium ore and identified solely by its strong radioactivity and this makes polonium dangerously toxic. Polonium has few applications (heaters in space probes, antistatic



devices, and sources of neutrons and alpha particles) except for those related to its radioactivity.

1.1.2 Physical and Chemical Properties

Table 1.1 shows selected physical properties of the group 16 elements. The trend in electronegativity values has important consequences as regards the ability of O-H bonds to form hydrogen bonds. This pattern follows that in group 15. Of all the group 16 elements, there are nonmetals (oxygen, sulfur, and selenium) and metalloid (tellurium).^[5] Polonium possesses some metallic properties, however, some sources also refer to polonium as a metalloid.^[3,6] It is also notable that some selenium allotropes show metalloid characteristics. Even though the group 16 is also named as the oxygen group. Oxygen has very different chemical properties from those of the other chalcogens. This owes not only to the fact that heavier chalcogens possess vacant *d*-orbitals, but also to oxygen's distinctly higher electronegativity, which makes the electric polarizability of oxygen multiple times lower compared to the other chalcogens.^[7] The most common oxidation number of chalcogens is -2, though chalcogens' tendency forming -2 state compounds decreases towards the heavier ones. The highest oxidation number is +6,^[8] found in sulfates, selenates, tellurates, polonates, and, their corresponding acids. In terms of oxygen, the second most electronegative element, it participates into the formation of compounds with almost all elements (namely water, metal/metalloid-oxide and ubiquitous organic oxygen compounds) with its common oxidation state being -2 and -1.^[8] When it comes to sulfur, whose most common oxidation states are -2, +2, +4 and, +6, the chemistry is in multiple ways similar to that of oxygen.

However, sulfur-sulfur double bonds are far weaker than that of oxygen-oxygen while the corresponding single bonds are just on the contrary. Organic sulfur compounds normally have obvious specific smell, and a good case in point is thiols. It is worth mentioning that some organic sulfur compounds are of great significance to humans and utilized by some organisms.^[3]

**Table 1.1** Some physical properties of the group 16 elements and their ions.^[9]

Property	O	S	Se	Te	Po
Atomic number, Z	8	16	34	52	84
Ground state electronic configuration	[He]2s ² 2p ⁴	[Ne]3s ² 3p ⁴	[Ar]3d ¹⁰ 4s ² 4p ⁴	[Kr]4d ¹⁰ 5s ² 5p ⁴	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
Enthalpy of atomization, $\Delta_a H^\circ(298\text{K})/\text{kJ mol}^{-1}$	249 [‡]	277	227	197	≈146
Melting point, mp/K	54	388	494	725	527
Boiling point, bp/K	90	718	958	1263*	1235
Standard enthalpy of fusion, $\Delta_{\text{fus}} H^\circ(\text{mp})/\text{kJ mol}^{-1}$	0.44	1.72	6.69	17.49	-
First ionization energy, $IE_1/\text{kJ mol}^{-1}$	1314	999.6	941.0	869.3	812.1
$\Delta_{\text{EA}} H^\circ_1(298\text{K})/\text{kJ mol}^{-1**}$	-141	-201	-195	-190	-183
$\Delta_{\text{EA}} H^\circ_2(298\text{K})/\text{kJ mol}^{-1**}$	+789	+640			
Covalent radius, r_{cov}/pm	73	103	117	135	-
Ionic radius, r_{ion} for X ²⁻ /pm	140	184	198	211	-
Pauling electronegativity, χ^{P}	3.4	2.6	2.6	2.1	2.0
NMR active nuclei(% abundance, nuclear spin)	¹⁷ O (0.04, $I = 5/2$)	³³ S (0.76, $I = 3/2$)	⁷⁷ Se (7.6, $I = 1/2$)	¹²³ Te (0.9, $I = 1/2$) ¹²⁵ Te (7.0, $I = 1/2$)	

[‡] For oxygen, $\Delta_a H^\circ = 1/2 \times$ dissociation energy of O₂.

* For amorphous Te.

** $\Delta_{\text{EA}} H^\circ_1(298\text{K})$ is the enthalpy change associated with the process $\text{X}(\text{g}) + \text{e}^- \rightarrow \text{X}^-(\text{g}) \approx -\Delta U(0 \text{ K})$; $\Delta_{\text{EA}} H^\circ_2(298\text{K})$ refers to the process $\text{X}^-(\text{g}) + \text{e}^- \rightarrow \text{X}^{2-}(\text{g})$

As is often the case, the most common oxidation states of selenium are -2, +4 and +6 and selenium can bond to oxygen.^[3] Organic selenium compounds do exist, for example, selenoproteins. Tellurium commonly possesses -2, +2, +4 and +6 oxidation states and forms tellurium mono/di/tri-oxide compounds. Polonium's oxidation states are +2 and +4.^[8] Although O, Se, Te, Po (and Lv) can be defined as chalcogens, oxygen and oxides are normally distinguished from chalcogens and chalcogenides. The term