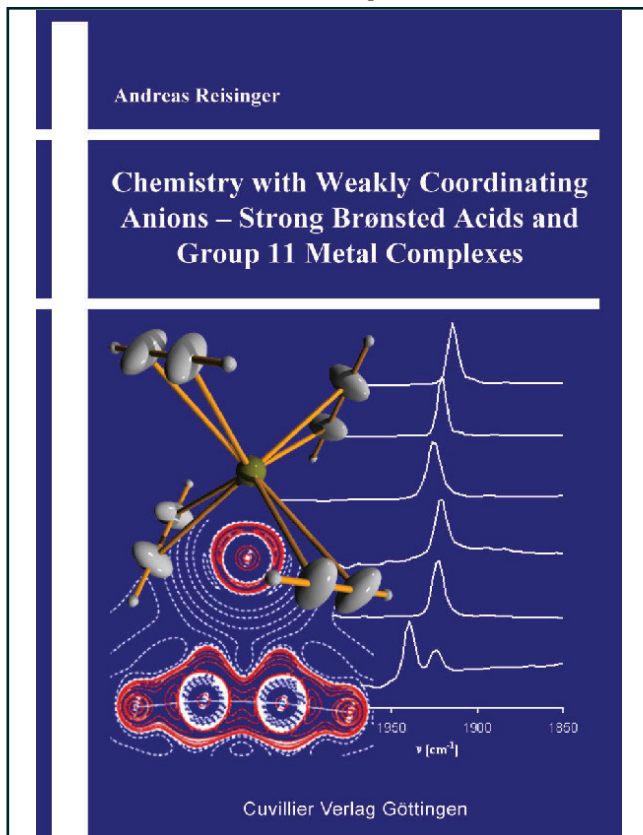




Andreas Reisinger (Autor)

Chemistry with Weakly Coordinating Anions - Strong Brønsted Acids and Group 11 Metal Complexes



<https://cuvillier.de/de/shop/publications/1810>

Copyright:

Cuvillier Verlag, Inhaberin Annette Jentsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen, Germany

Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

Table of Contents

1. CHEMISTRY WITH WEAKLY COORDINATING ANIONS – INTRODUCTION AND THEORETICAL BACKGROUND	7
2. OBJECTIVES OF THE THESIS	21
3. STRONG BRØNSTED ACIDS	23
3.1. Known Brønsted acids of type $[\text{H}(\text{L})_2]^+$ ($\text{L} = \text{Me}_2\text{O}, \text{Et}_2\text{O}, \text{THF}$)	23
3.2. Synthesis and characterization of $[\text{HL}_2]^+[\text{Al}(\text{OR})_4]^-$ ($\text{L} = \text{Me}_2\text{O}, \text{Et}_2\text{O}, \text{THF}; \text{R} = \text{C}(\text{CF}_3)_3$)	24
3.2.1. Synthesis	24
3.2.2. Thermodynamics of the Formation of 1 to 3	26
3.2.3. NMR Spectroscopy	27
3.2.4. Vibrational Spectroscopy	30
3.2.5. Solid State Structures	38
3.3. On the structure of $[\text{H}(\text{Et}_2\text{O})_2]^+$	40
3.4. Lewis acid-base complexes $\text{L-Al}(\text{OR})_3$ ($\text{L} = \text{Me}_2\text{O}, \text{Et}_2\text{O}; \text{R} = \text{C}(\text{CF}_3)_3$) – Decomposition products on the way to Brønsted acid salts	45
4. SILVER ETHENE COMPLEXES	49
4.1. Known Alkene complexes of group 10 and 11 metals	49
4.2. Synthesis and Characterization	51
4.2.1. Synthesis	51
4.2.2. NMR Spectroscopy	53
4.2.3. Vibrational Spectroscopy	61
4.2.4. Solid State Structures	63

4.3.	Calculated structures of the cations $M(C_2H_4)_n$ ($M = Na^+, Pd, Ag^+$; $n = 1 - 3$)	71
4.4.	Thermodynamic considerations based on Born-Haber Cycles: Implications for the gas phase....	75
4.5.	The C=C Bond Distances of coordinated C_2H_4 : X-ray Data vs. Stretching Frequency and Experiment vs. Theory	78
4.6.	Structure of $Ag(C_2H_4)_3^+$ in comparison to $M(C_2H_4)_3$ ($M = Cu^+, Ni, Pd, Pt$)	85
4.7.	Bonding in $Ag(C_2H_4)_3^+$ in comparison to $M(C_2H_4)_3$ ($M = Pd, Na^+$)	86
5.	SILVER ETHYNE COMPLEXES	95
5.1.	Known Alkyne complexes of group 10 and 11 metals	95
5.2.	Synthesis and Characterization of $Ag(C_2H_2)_n^+$ ($n = 1 - 4$)	96
5.2.1.	Synthesis	96
5.2.2.	NMR Spectroscopy	98
5.2.3.	Vibrational Spectroscopy	100
5.2.4.	Solid State Structures	103
5.3.	Calculated Molecular Geometries of $Ag(C_2H_2)_n^+$	111
5.4.	Complexation energies	121
5.5.	Thermodynamic considerations based on Born-Haber Cycles: Implications for the gas phase..	125
5.6.	$C\equiv C$ Bond Distance and Stretching Frequency – Theory vs. Experiment	127
5.7.	Experimental charge density study of $AgC_2H_2Al(OC(CH_3)(CF_3)_2)_4$ (1)	135
5.8.	Structural preferences and relations of the $Ag(C_2H_2)_n^+$ complexes	139
5.9.	Nature of the bonding in $Ag(C_2H_2)_2^+$	141
5.10.	Comparison of ML_2 ($M = Ag^+, Pd, Na^+$)	145
5.11.	Bonding in $Ag(C_2H_2)_n^+$ ($n = 1 - 4$)	146

6. FURTHER WEAKLY BOUND LEWIS ACID-BASE COMPLEXES

WITH L = CH₂CL₂, C₄H₈ AND CO 149

- 6.1. Reactions of Ag[Al(OR^F)₄] with CO - Synthesis and characterization of Ag(CO)[AlOC(CH₃)(CF₃)₂]₄ and Ag(CH₂Cl₂)₂[AlOC(H)(CF₃)₂]₄ 150
- 6.2. Reactions of Ag[AlOC(CH₃)(CF₃)₂]₄ with 1,1-C₂H₂F₂ - Synthesis and characterization of Ag(CH₂Cl₂)[AlOC(CH₃)(CF₃)₂]₄ 153
- 6.3. Reactions of Ag[AlOC(CH₃)(CF₃)₂]₄ with 1,1-C₂H₂Me₂ - Synthesis and characterization of Ag(C₂H₂Me₂)[AlOC(CH₃)(CF₃)₂]₄ 155
- 6.4. Trends in solid state structures of various Ag⁺ complexes – Anion Effects and Silver Ion Affinity 157

7. INTRODUCTION OF NEW METAL CATIONS – CU(I) HALIDE

METATHESIS 163

- 7.1. General considerations based on Born Haber cycles and *ab initio* calculations 163
- 7.2. Synthesis and Characterization of Cu(C₂H₄)₃[Al(OC(CF₃)₃)₄] 165
- 7.2.1. Synthesis 165
- 7.2.2. NMR Spectroscopy 166
- 7.2.3. Vibrational Spectroscopy 167
- 7.2.4. Solid State Structure 170

8. SYNTHESIS AND APPLICATIONS OF AGOC(CF₃)₃ – THE FIRST

SILVER ALKOXIDE 173

- 8.1. Introduction to group 11 metal alkoxides and [M₃X₂] (M = group 10, 11) cage compounds 173
- 8.2. Syntheses 175

8.3.	Characterization of MOC(CF₃)₃ (M = Li, Ag)	178
8.3.1.	NMR spectroscopy	178
8.3.2.	Vibrational Spectroscopy	179
8.3.3.	Solid State Structures	181
8.4.	Characterization of [(AgL)₃(OR^F)₂][Al(OR^F)₄] (L = C₂H₄, C₄H₈)	186
8.4.1.	NMR Spectroscopy	186
8.4.2.	Vibrational Spectroscopy	188
8.4.3.	Solid State Structures	192
8.5.	On the structure of Ag₃X₂⁺	195
9.	SUMMARY AND OUTLOOK	197
10.	EXPERIMENTAL PART	205
10.1.	General procedures	205
10.2.	Syntheses of the compounds described in section 3	213
10.2.1.	[H(OEt ₂) ₂] ⁺ [Al(OC(CF ₃) ₃) ₄] ⁻ (1)	213
10.2.2.	[H(THF) ₂] ⁺ [Al(OC(CF ₃) ₃) ₄] ⁻ (2)	214
10.2.3.	[H(OMe ₂) ₂] ⁺ [Al(OC(CF ₃) ₃) ₄] ⁻ (3)	215
10.2.4.	Et ₂ O-Al(OC(CF ₃) ₃) ₃ (4)	216
10.3.	Syntheses of the compounds described in section 4	216
10.3.1.	Ag(C ₂ H ₄)[Al(OC(CH ₃)(CF ₃) ₂) ₄] (6)	217
10.3.2.	Ag(C ₂ H ₄) ₂ [Al(OC(H)(CF ₃) ₂) ₄] (7)	217
10.3.3.	Ag(C ₂ H ₄)(CH ₂ Cl ₂) ₂ [Al(OC(CF ₃) ₃) ₄] (8)	218
10.3.4.	Ag(C ₂ H ₄) ₃ [Al(OC(CF ₃) ₃) ₄] (9)	218
10.3.5.	Ag(C ₂ H ₄) ₃ [((F ₃ C) ₃ CO) ₃ Al-F-Al(OC(CF ₃) ₃) ₃] (10)	219
10.4.	Syntheses of the compounds described in section 5	220
10.4.1.	Ag(C ₂ H ₂)[Al(OC(CH ₃)(CF ₃) ₂) ₄] (11)	220
10.4.2.	Ag(C ₂ H ₂) ₂ [Al(OC(H)(CF ₃) ₂) ₄] (12)	221

10.4.3.	$\text{Ag}(\text{C}_2\text{H}_2)_3[(\text{F}_3\text{C})_3\text{CO})_3\text{Al-F-Al}(\text{OC}(\text{CF}_3)_3)_3]$ (13)	221
10.4.4.	$\text{Ag}(\text{C}_2\text{H}_2)_2(\text{CH}_2\text{Cl}_2)[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (14)	222
10.4.5.	$\text{Ag}(\text{C}_2\text{H}_2)_3[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (15)	222
10.4.6.	$\text{Ag}(\text{C}_2\text{H}_2)_4[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (16)	223
10.5.	Syntheses of the compounds described in section 6	223
10.5.1.	$\text{Ag}(\text{CO})[\text{Al}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4]$ (17)	223
10.5.2.	$\text{Ag}(\text{CH}_2\text{Cl}_2)_2[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]$ (18)	224
10.5.3.	$\text{Ag}(\text{CH}_2\text{Cl}_2)_3[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (19)	224
10.5.4.	$\text{Ag}(\text{CH}_2\text{Cl}_2)[\text{Al}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4]$ (20)	224
10.5.5.	$\text{Ag}(\text{C}_4\text{H}_8)[\text{Al}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4]$ (21)	225
10.6.	Synthesis of $\text{Cu}(\text{C}_2\text{H}_4)_3[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$	225
10.7.	Syntheses of the compounds described in section 8	226
10.7.1.	$\text{LiOC}(\text{CF}_3)_3$ (23)	226
10.7.2.	$\text{AgOC}(\text{CF}_3)_3$ (24)	226
10.7.3.	$[(\text{Ag}(\text{C}_2\text{H}_4))_3(\text{OC}(\text{CF}_3)_3)_2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (25)	227
10.7.4.	$[(\text{Ag}(\text{C}_4\text{H}_8))_3(\text{OC}(\text{CF}_3)_3)_2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (26)	228
10.8.	Quantum chemical calculations	230
11.	ANNEX	233
11.1.	Numbering of all compounds	233
11.2.	Experimental anion NMR signals and calculated chemical shifts	234
11.3.	Experimental bands and calculated frequencies of $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$	235
11.4.	Experimental IR and Raman bands of $[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$	239
11.5.	Experimental IR and Raman bands of $[\text{Al}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4]^-$	240
11.6.	IR and Raman bands of $[(\text{RO})_3\text{Al-F-Al}(\text{OR})_3]^-$ ($\text{R} = \text{C}(\text{CF}_3)_3$)	241

11.7.	Computational data of all calculated species	242
11.8.	Crystal data of 1 to 26	251
11.9.	Abbreviations	281
11.10.	Publications and Poster contributions	283
12.	LITERATURE	285