

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

The Electronic, Structural, and Magnetic Properties of
the Chromium Dihalides - from the Gas-phase to the
Solid-state

A thesis submitted in partial fulfillment of the requirements of the degree
of
Doctor of Philosophy
in
Theoretical Chemistry
at
Massey University, Albany
New Zealand

Brian Michael Vest

June 10, 2008

Contents

1	Introduction	9
2	Theory	13
2.1	Quantum Mechanics and Molecules	13
2.2	Variational Principle	16
2.3	Hartree-Fock Theory	16
2.4	Møller-Plesset Perturbation Theory	17
2.5	Coupled-Cluster Theory	19
2.6	Configuration Interaction	21
2.7	Complete Active Space SCF	22
2.8	Density Functional Theory	24
2.8.1	Local Density Methods	26
2.8.2	Gradient Corrected Methods	27
2.8.3	Hybrid Methods	28
2.8.4	Broken Symmetry DFT	29
2.9	Basis Set Superposition Errors	30
2.10	The Pseudopotential Approximation	32
2.10.1	Introducing Pseudopotentials into the Hartree-Fock Equations . . .	34
2.11	Gas-phase Electron Diffraction	37
2.12	Computational Details	41
2.13	Solid-state Calculations	44
2.14	Electron Diffraction Analysis	44
2.14.1	Experimental Details	45
2.14.2	Least-Squares Refinement	45
2.15	Thermodynamic Analysis	47

3	Results	48
3.1	Monomers	48
3.1.1	Infrared Analysis	64
3.2	Clusters	66
3.2.1	Dimers	66
3.2.2	Trimers	73
3.2.3	Tetramers	81
3.2.4	Basis Set Superposition Errors	88
3.2.5	Thermodynamics	92
3.2.6	Infrared Analysis	100
3.3	Gas-Phase Electron Diffraction Analysis of CrCl_2	103
3.4	The Solid State of CrCl_2	108
4	Trends among the Chromium Dihalides	115
5	Conclusions	122
6	Appendix	128
6.1	Cartesian Coordinates of the Low-energy Structures	128
6.2	Experimental Electron Diffraction Molecular Intensities	160
6.3	Modified Basis Sets for Cr, Br, and I	161

List of Figures

2.1	Scheme of an apparatus for gas-phase electron diffraction	38
3.1	DFT bending potential curves for the 5B_2 and 5A_2 states of the chromium dihalides	49
3.2	APES of a linear molecule in a doubly-degenerate ground state	60
3.3	Initial dimer structures used in the preliminary analysis	67
3.4	Representations of the low-energy minima for the dimers	68
3.5	Initial trimer structures used in the preliminary analysis	74
3.6	Representations of the low-energy minima for the trimers	76
3.7	Overlap of the d_{z^2} orbitals in the tridecet state of Cr_3Br_6	80
3.8	BS spin-coupling patterns for the trimer global minima	80
3.9	Initial tetramer structures used in the preliminary analysis	82
3.10	Representations of the low-energy minima for the tetramers	83
3.11	BS spin-coupling patterns for the tetramer global minima	88
3.12	Experimental and theoretical electron diffraction molecular intensity curves	104
3.13	Experimental and theoretical electron diffraction radial distribution curves	105
3.14	Thermal-averaged dimer and trimer structures for CrCl_2	107
3.15	Magnetic unit cell of the anti-ferromagnetically coupled $\alpha\text{-CrCl}_2$	109
3.16	Different intra and interchain coupling schemes examined for $\alpha\text{-CrCl}_2$. . .	110
3.17	$E(\Omega_o)$ -curves	111
3.18	Magnetic coupling constants from hybrid-DFT calculations	114
4.1	Comparison of the Cr-X bond lengths and angles among the different monomers	116
4.2	Comparison of the Cr-Cr distances and Mulliken spin densities for the singlet state dimers	118

4.3	Gas-phase Cr- X_b distances for the dihalide-bridged, anti-ferromagnetically coupled oligomers	119
4.4	Dissociation energies for the different chromium dihalide oligomers obtained from DFT calculations	120

List of Tables

3.1	Relative energies, geometrical parameters, and vibrational frequencies of CrF_2 in different electronic states	50
3.2	Relative energies, geometrical parameters, and vibrational frequencies of CrCl_2 in different electronic states	52
3.3	Relative energies, geometrical parameters, and vibrational frequencies of CrBr_2 in different electronic states	54
3.4	Relative energies, geometrical parameters, and vibrational frequencies of CrI_2 in different electronic states	56
3.5	Contributions from the major configurations within the active space of the $^3\Sigma_g^-$, $^1\Sigma_g^+$, and $^5\Pi_g$ states from CASPT2(4,5) geometry optimizations . . .	63
3.6	Mulliken charges and spin densities for the chromium dihalide monomers .	65
3.7	Relative energies among the dimer minima from various geometry optimizations	69
3.8	Geometrical parameters for the lowest energy singlet and nonet dimers obtained from intensive geometry optimizations	71
3.9	Mulliken charges and spin densities for the lowest energy singlet and nonet dimers obtained from the intensive geometry optimizations	72
3.10	Relative energies among the low energy trimers from various geometry optimizations	77
3.11	Geometrical parameters for the trimer global minima obtained from intensive geometry optimizations	79
3.12	Relative energies among the low energy tetramers from various geometry optimizations	84
3.13	Selected geometrical parameters for the tetramer global minima obtained from intensive geometry optimizations	86

3.14	Calculated BSSE for the oligomer global minima	90
3.15	Comparison of the counterpoise-corrected binding energies of the global minima with other low-lying states	91
3.16	Dissociation energies for the global minima of the CrF_2 clusters for each spin state	92
3.17	Thermodynamic properties for the CrF_2 nucleation	93
3.18	Dissociation energies for the global minima of the CrCl_2 clusters for each spin state	94
3.19	Thermodynamic properties for the CrCl_2 nucleation	95
3.20	Dissociation energies for the global minima of the CrBr_2 clusters for each spin state	97
3.21	Thermodynamic properties for the CrBr_2 nucleation	97
3.22	Dissociation energies for the global minima of the CrI_2 clusters for each spin state	98
3.23	Thermodynamic properties for the CrI_2 nucleation	99
3.24	Calculated vibrational frequencies and IR intensities for the chromium dihalide global minima	101
3.25	Geometrical parameters and vapor composition for CrCl_2 from electron diffraction	106
3.26	Comparison of the intrachain Cr-Cl bond lengths from crystalline α - CrCl_2 with our gas-phase structures	112
3.27	Spin coupling constants for α - CrCl_2 , calculated at experimental and theoretical geometries	113
6.1	Cartesian coordinates and energies of the optimized CrF_2 oligomers	128
6.2	Cartesian coordinates and energies of the optimized CrCl_2 oligomers	135
6.3	Cartesian coordinates and energies of the optimized CrBr_2 oligomers	144
6.4	Cartesian coordinates and energies of the optimized CrI_2 oligomers	151
6.5	Electron diffraction molecular intensities for two camera ranges for CrCl_2 .	160
6.6	Modified basis set for Cr	161
6.7	Modified basis set for Br	162
6.8	Modified basis set for I	163

Abstract

Unrestricted Kohn-Sham (broken symmetry) density functional calculations have been used to determine the low-energy geometries of the chromium dihalide molecules (CrX_2) and their clusters, Cr_2X_4 , Cr_3X_6 , and Cr_4X_8 . The monomers are also investigated at a higher level, including coupled-cluster and state-average CASSCF computations. Our calculations show that the monomers have a 5B_2 ground state arising from the Renner-Teller distorted ${}^5\Pi_g$ transition state, leading to a bent geometry. The global minima of the gas-phase clusters of CrF_2 and CrCl_2 consist of two-dimensional, anti-ferromagnetically coupled chains of CrX_2 units forming four-membered, doubly bridged Cr_2X_2 rings, closely resembling their solid-state structures. The global minima of the CrBr_2 and CrI_2 clusters consist of the same two-dimensional chain-like structures for their dimers, but their trimers and tetramers consist of three-dimensional 'triangular' structures which contain two capping ligands bound to three chromium atoms along with a Cr-Cr bond. Each Cr atom within these clusters has spin quantum number $S=2$. There is approximately a constant change in energy, between 45-55 kcal/mol, with every new CrX_2 unit during cluster formation.

Information about the structure of the CrCl_2 clusters is used in the reanalysis of high-temperature electron diffraction data. The vapor at 1170 K contains about 77% monomeric molecules, 19% dimers, and a small amount of trimers. Monomeric CrCl_2 is found to be bent with a bond angle of $149(10)^\circ$, in good agreement with our computations.

Solid-state DFT calculations are performed on $\alpha\text{-CrCl}_2$ to determine the lattice structure and spin-coupling constants for the Cr atoms within the crystals. The GGA (PW91) method produces a structure in good agreement with the literature. In the lowest energy structure, the spins of the Cr atoms within the chains along the crystallographic c -axis are anti-ferromagnetically coupled with four parallel spins situated almost exclusively in the d -bands of Cr along these chains. This anti-ferromagnetic coupling is also seen in the CrX_2 clusters.

Acknowledgements

First and foremost, I would like to give many thanks to my advisor Prof. Peter Schwerdtfeger. He has helped me more times than I can count with getting this thesis written and encouraged me to see the entire forest and not just the trees. I also want to thank him for his guidance, encouragement, and wonderful sense of humour. I would also like to thank Behnam Assadollahzadeh for his help with Gaussian and L^AT_EX templates and commands. He has also provided me with invaluable knowledge of various fishing spots around New Zealand and has taught me how to speak “proper” German. I want to also thank Andreas Hermann for his help with the solid-state of CrCl₂ and creating nice EPS files. Christian Thierfelder also deserves my thanks for helping me with various physics, mathematics, and Xmgrace problems. Lastly, I would like to thank Dr. Magdolna Hargittai for her help in understanding gas-phase electron diffraction.