Is $CrCl_2$ Linear or Bent? An *Ab Initio* MO Study

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Ab initio MO calculations of the electronic and geometric structure of $CrCl_2$ predict the ground state to be linear with an electronic configuration . . . $1\delta_g{}^2 3\pi_g{}^2$.

There is some confusion over the shape of monomeric $CrCl_2$. A recent gas-phase electron diffraction study of Hargittai *et al.*[1] proposes a significantly bent structure with a Cl–Cr–Cl angle of approximately 110°, whilst a matrix isolation i.r. study of Ogden and Wyatt[2] concludes that analysis of the spectra of isotopomers indicates a linear or near-linear structure. However, in a recent review[3] Hargittai states that 'a reanalysis of the electron diffraction data[1] is underway allowing for the presence of trimeric species, in which case evidence points to the linearity of $CrCl_2$.'

In an attempt to resolve this problem, here we describe all-electron *ab initio* calculations of the electronic structure and geometry of $CrCl_2$. The chromium basis used was the (14s9p5d) set of Wachters,[4] augmented by two p functions of exponent 0.192 and 0.075[5] and by an additional diffuse d function of exponent 0.0912.[6] This basis was contracted (10s8p3d). The chlorine basis used was (12s9p) contracted to (6s5p).[7]

A d^4 $CrCl_2$ species with the electronic configuration . . . $1\delta_g{}^2 3\pi g^2$ (where the $1\delta_g$ and $3\pi_g$ MOs have mainly Cr 3d character) would most likely be linear.[8] In addition to this configuration, we have investigated the alternative configuration . . . $1\delta_g{}^2 3\pi_g{}^1 9\sigma_g{}^1$. Arguments[9] based on a Walsh diagram[10] suggest that this latter configuration may give rise to a bent structure. For a number of Cl–Cr–Cl angles the Cr–Cl bond length was optimised at the restricted Hartree Fock (RHF) level using the program GAMESS.[11] The linear configuration . . . $1\delta_g{}^2 3\pi_g{}^2$ ($^5\Sigma_g{}^+$) becomes $^5A_1$ in C_{2v} symmetry, whilst the $^5\Pi_g$ state having the configuration $1\delta_g{}^2 3\pi_g{}^1 9\sigma_g{}^1$ splits into a $^5B_2$ and $^5A_2$ state on bending. Correlation effects were estimated by performing configuration interaction (CI) calculations at the RHF geometries. The CI expansion included all single and double excitations of the valence electrons plus Cr 3s and 3p electrons from the RHF configuration, to the lowest 55 virtual orbitals. The results of these calculations are summarised in Table 1. Here we quote only results for Cl–Cr–Cl bond angles of 180° and 120°, although calculations at a range of intermediate values were also carried out.

It can be seen that for both possible electronic configurations . . . $1\delta_g{}^2 3\pi_g{}^2$, and $1\delta_g{}^2 3\pi_g{}^1 9\sigma_g{}^1$, the linear structure is preferred, with the . . . $1\delta_g{}^2 3\pi_g{}^2$ being of lowest energy. The calculated correlation energy is found to be essentially independent of bond length, bond angle, and electronic configuration for the cases studied here. Thus, although our optimisation studies were carried out at the RHF level, our conclusions are unlikely to be altered if optimisation were to be carried out at the CI level. The results of Table 1 show that the potential energy curve for bending $CrCl_2$ is quite shallow for all states studied. However, the curve for bending the $^5\Pi_g$ state to give the $^5B_2$ state is noticeably flatter than the other two, in line with arguments based on a Walsh diagram.[9] For the predicted linear configuration (. . . $1\delta_g{}^2 3\pi_g{}^2$; $^5\Sigma_g{}^+$) we have calculated the harmonic frequencies for $^{52}Cr^{35}Cl_2$ at the RHF level. The values obtained are 92 cm^{-1} (degenerate bend), 320 cm^{-1} (symmetric stretch) and 464 cm^{-1} (asymmetric stretch). The latter value is a good agreement with a value of 457 cm^{-1} reported by Ogden and Wyatt.[2]

Table 1. Optimised bond lengths (Å)[a] and calculated energies (a.u.) for different bond angles of $CrCl_2$.

			Energy	
State	Cl–Cr–Cl(°)	Cr–Cl	RHF	CI
$^5\Sigma_g{}^+$	180	2.315	−1962.48554	−1962.79854
$^5A_1$	120	2.326	−1962.46001	−1962.77584
$^5\Pi_g$	180	2.309	−1962.47516	−1962.79419
$^5B_2$	120	2.298	−1962.46764	−1962.78790
$^5A_2$	120	2.327	−1962.45226	

[a] Bond lengths were optimised at the RHF level.

The calculations reported herein thus favour a linear structure for gaseous $CrCl_2$ in line with both matrix isolation i.r. studies[2] and with a possible reinterpretation of electron diffraction data.

We thank the S.E.R.C. for support of this research.

Received, 13th December 1988; Com. 8/04901G

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