

Is CrF₆ Octahedral? Theory Confirms "Yes!"

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The molecular structure of the volatile material CrF₆ has been debated in two recent communications to this journal.^{1,2} CrF₆ was first synthesized by Glemser et al.³ in 1963. A new synthesis was performed by Hope et al.^{4,5} in 1984. On the basis of an analysis of the matrix isolation IR spectrum they concluded that CrF₆ has an octahedral structure. They also measured the UV-visible spectrum and found two prominent CT bands at 38 450 and 26 700 cm⁻¹.

Theoretically CrF₆ was first studied by Miyoshi et al.⁶ using a configuration interaction (CI) technique with a model potential for the core electrons. At the SDQ-CI level they computed the bond distance to be 1.747 Å. An octahedral structure was assumed.

Kang et al.⁷ in 1989 argued that second-order Jahn-Teller effects might for certain d⁰ complexes lead to distortion from octahedral symmetry. The surmise was tested using Hartree-Fock (HF/SCF) and second-order Møller-Plesset (MP2) theory with a limited basis set. It was found, however, that the octahedral structure was the most stable with the trigonal prismatic (D_{3h}) structure 18.5 kcal/mol higher (MP2). The bond distance for the octahedral complex was calculated to be 1.71 Å.

In 1990 Jacob and Willner⁸ performed new matrix-isolation IR studies and concluded that the spectrum measured by Hope et al.^{4,5} was due to the more stable species CrF₅ rather than CrF₆. They thus questioned the mere existence of CrF₆. A new theoretical study appeared in 1991:¹ Marsden and Wolyneć performed SCF, MP4, and coupled-cluster (CCD) calculations on O_h, D_{2d}, and D_{3h} symmetries. Somewhat larger, but still rather limited, basis sets were used. The geometry was optimized at the SCF level. The Cr-F distance in O_h symmetry was calculated to be 1.698 Å, which increased to 1.716 Å in D_{3h}. The D_{2d} structure was unstable. At the SCF level they found the O_h structure to be 2.9 kcal/mol more stable than D_{3h}. The MP_n (n = 2, 3, 4) series gave rise to wild oscillations in the relative energy: MP2, 17.0 kcal/mol; MP3, +20.3 kcal/mol; and MP4DQ, -0.3 kcal/mol. Thus the D_{3h} structure is slightly more stable at the MP4 level of theory. However, they conclude from these calculations, that "a single-reference description of CrF₆ is poor and perturbation based correlation energies are unreliable". Instead they used CCD, which, even if it is also a single-configuration based approach, was believed to be more accurate. Calculations predicted the trigonal prismatic structure to be 4.7 kcal/mol more stable than O_h. However, this result can be criticized on the same grounds as the MP calculations. The CCD method cannot be expected to account in a proper way for the

near-degeneracy effects, especially when single- and triple-excitation amplitudes are not included in the cluster expansion.

As an answer to the theoretical study discussed above and the experimental work by Jacob and Willner⁸, Hope and co-workers² re-analyzed their matrix IR spectrum and showed that the only consistent interpretation is an octahedral structure.

Here we shall present theoretical results that confirm the analysis of Hope et al. and show that CrF₆ is most certainly octahedral. The treatment is based on an approach that properly accounts for the near-degeneracies in the electronic structure. An extended basis set of the ANO type was used: for Cr 5s4p3d2f, ANOs were selected from a primitive set of 17s12p9d4f GTOs; for F, 4s3p1d from 10s6p3d was used.⁹ Complete active space SCF calculations¹⁰ were carried out with 10 electrons in 10 active orbitals: The bonding and antibonding combinations of Cr(3d) and F(2p). For O_h this gives 2 × 3 orbitals of t_{2g} and 2 × 2 orbitals of e_g symmetry, and for D_{3h} 2 × 2 e', 2 × 2 e'', and a₁' orbitals. This wave function accounts well for the multiconfigurational character of the electronic structure, which manifests itself by a relatively large occupation of the antibonding orbitals. The bonding is then described as taking place primarily between the Cr 3d orbitals and F orbitals of corresponding symmetries. Such an active space does not of course exclude delocalization of fluorine lone-pair orbitals of other symmetries onto Cr 4s and 4p orbitals, but the occupation of the corresponding antibonding orbitals is assumed to be small. Several preliminary test calculations with other active spaces have been performed to check this. Fluorine is normally assumed to be a weak π-donor in transition metal complexes. However, in CrF₆ it seems that F π-orbitals play an equally important role in the Cr-F bonds as the σ-orbitals. Excitations out of all F lone pairs (also those which are inactive in the CASSCF calculation) are, of course, included in the treatment of the dynamical correlation effects by the perturbation calculation (see below). The result of this calculation gives further support of the choice of active space, since no other configurations appeared in the first-order perturbed wave function with large coefficients. We are thus confident that the dominant electronic configurations are included in the CASSCF reference function, which is a prerequisite for the present method to work well. Note that all orbitals (inactive and active) are optimized in the CASSCF calculation.

Remaining correlation effects were treated using multiconfigurational second order perturbation theory (CASPT2),^{11,12} where the CASSCF wave function constitutes the reference function and the first-order wave function is expanded in the interacting subspace of the full space of configurations generated by the basis set. The approach was tested in calculations of binding energies and equilibrium geometries of a large number of

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molecules.¹³ It is a surprisingly accurate method for both structure determination and for relative energies, especially in cases where the number of electron pairs does not change. The same approach has in addition been tested in calculations of binding energies for transition metal compounds: for both Ni(C₂H₄) and Ni(CO)_x (x = 1–4) results in good agreement with experiment are obtained.¹⁴ On the basis of this experience, we are confident that the approach will also in the present case give relative energies with an accuracy that is high enough to allow a conclusive prediction of the minimum structure of CrF₆. A parallel calculation on tetrahedral CrF₄ confirms that equilibrium geometries are predicted with good accuracy with the present approach¹⁵ (calculated value for r(Cr–F) is 1.712 Å, while the experimental value¹⁶ is 1.706 Å). The results of our calculations are presented in the table. Computed bond distances are considerably longer than earlier estimates,^{1,7} while the bond angle θ for the D_{3h} structure is essentially the same as that obtained by Kang et al.⁷ in the MP2 calculation. Contrary to their results (and also to the SCF results of Marsden and Wolyneć¹) we find that the Cr–F distance is shorter in the D_{3h} structure. The longer bond distances obtained here are due to the large populations of the Cr(3d)–F(2p) antibonding orbitals in the multiconfigurational wave function: the total occupation of these orbitals (CASSCF) is 0.14 (e_g) and 0.18 (t_{2g}) for the O_h structure. The corresponding numbers in the D_{3h} structure are 0.03 (a₁'), 0.21 (e'), and 0.21 (e''). This gives a total occupation of 0.32 and 0.46 electron in O_h and D_{3h}, respectively. Notice that the less stable D_{3h} structure has a larger occupation of the antibonding orbitals. From these results it is clear that single-configuration-based methods will not be adequate for the treatment of electron correlation of CrF₆.

CrF₆ is less stable than the other chromium fluorides and is therefore expected to have a longer CrF bond length: CrF₃, 1.732 Å;¹⁷ CrF₄, 1.706 Å;¹⁶ and CrF₅, 1.70 and 1.74 Å.¹⁸ We expect the present bond distance for the octahedral complex to be in error with not more than a few hundreds of an angström. The polarization functions (Cr(4f) and F(3d)) are essential for the bond strength. Excluding them from the basis sets leads to considerably longer Cr–F distances. The Mulliken populations (CASSCF) of the f-type orbitals on Cr are also rather large, as the numbers in the table show. It is probable that the basis set

Table I. Calculated Equilibrium Parameters, Total Energies, and Relative Energies for CrF₆ (CASPT2 Results)

	O _h	D _{3h}
r(Cr–F) (Å)	1.754	1.727
θ° (deg)	(54.74)	50.0
tot. energy (CASPT2) (au)	-1641.216736	-1641.137194
relative energy (kcal/mol)	–	+49.9
Mulliken populations		
Cr(3d)	3.38	3.68
Cr(4s)	0.14	0.17
Cr(4p)	0.40	0.29
Cr(4f)	0.45	0.41
tot. charge	Cr +1.63	+1.45
	F(2s) 1.97	1.97
	F(2p) 5.29	5.27
	F(3d) 0.01	0.01
tot. charge	F -0.27	-0.24

^a The angle between the Cr–F bond and the 3-fold symmetry axis is not fully saturated and that addition of more polarization functions (g-type on Cr and f-type on F) would lead to somewhat shorter bond distances. But why has the less stable D_{3h} structure a shorter bond distance than the O_h structure? The Mulliken populations show some striking differences: the Cr(3d) population is 0.3 electron larger in D_{3h}, while the 4p and 4f populations are smaller. This structure is also less ionic. The bonds thus have larger 3d character and are hybridized to a smaller extent. This could lead to somewhat shorter bonds, due to the more compact nature of the 3d orbitals in combination with the attractive ionic force, without necessarily giving a stronger bond.

The relative energy between the octahedral and the trigonal prismatic structure was calculated to be 49.9 kcal/mol. This result confirms that CrF₆ has an octahedral structure. The energy difference is large enough to be outside the error limits of the present approach. One reason for the difference between the present and earlier results is the larger basis set used here, with the Cr(4f) functions playing a crucial role for the bond formation. But equally important is the use of a method that properly treats the near-degeneracy of the wave function and accounts for electron correlation between all valence electrons.

Note Added in Proof

Preliminary results obtained with a larger active space indicate that the energy difference between O_h and D_{3h} structures may be somewhat smaller than is reported in Table I. These calculations do not change the main conclusion of the report, that O_h is a more stable structure than D_{3h}. These new calculations also indicate that CrF₆ is a very unstable system.

Registry No. CrF₆, 13843-28-2.

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