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Is CrF_6 Octahedral? Experiment Still Suggests "Yes!"

The synthesis of CrF_6 was first reported in 1963 by Glemser et al.,[1] who prepared a volatile yellow material with a Cr:F atom ratio of ca.1:6 from the reaction between chromium and fluorine at high temperature and pressure (400 °C/ca. 300 atm). This synthesis does not appear to have been successfully repeated, but in 1985, Hope et al.[2] prepared a very similar material (yellow, volatile, Cr:F = 1:5.7) from the fluorination of CrO_3 and obtained IR and UV/vis data consistent with those expected for octahedral CrF_6. Since this latter characterization, two papers have appeared which cast doubt on the existence of this molecule. The first of these was by Jacob and Willner[3] (J&W), who concluded that the yellow material was CrF_5, while a theoretical paper by Marsden and Wolynec[4] predicted that if CrF_6 were to exist, its ground-state geometry would be a trigonal prism. The purpose of this communication is to reaffirm our belief that the yellow volatile material is indeed CrF_6 and that it is almost certainly octahedral.

First, we examine the spectroscopic arguments put forward by J&W and suggest that their characterization of this material as CrF_5 is not consistent with the experimental data. Second, we examine whether the results may be interpreted on the basis of the predicted[4] prismatic structure for CrF_6.

Before embarking on this discussion however, it is important to stress the very satisfactory agreement between our original[2] spectroscopic data and the results subsequently reported by J&W.[3] Both research groups carried out matrix isolation studies on a volatile yellow fluoride of chromium and obtained IR spectra showing a single intense absorption in the Cr–F stretching region at ca. 760 cm^{-1}. Both groups observed chromium isotope structure on this feature, and J&W also reported a weaker absorption in the bending region close to the frequency predicted in the initial matrix study.[2] There is no question but that we are discussing the same species.

Our results[2] were obtained from a yellow volatile material with a stoichiometry of Cr:F = 1:5.7, but our assignment of the 760-cm^{-1} band as the T_{1u} stretch in octahedral CrF_6 is based primarily on the observed spectrum and does not rely upon the identity of the starting material. Figure 1a reproduces our high-resolution nitrogen matrix spectrum in which the experimental bandwidths for the ^{50}Cr, ^{53}Cr, and ^{54}Cr isotopic features are all ca. 0.5 cm^{-1}. Figure 1b shows the corresponding spectrum calculated for octahedral CrF_6 by assuming no coupling with the T_{1u} bend. The agreement is very satisfactory.

J&W obtained a very similar neon matrix spectrum[5] and also obtained isotope structure on the bending mode at ca. 332 cm^{-1}, but as they were unable to derive a unique force field for the T_{1u} block, they rejected our O_h CrF_6 model. However, in so doing, they neglected to take account of the possible effects of anharmonicity on the chromium isotope shifts, and when due allowance[6] is made for this, it may be shown[7] that rejection of the O_h model is premature.

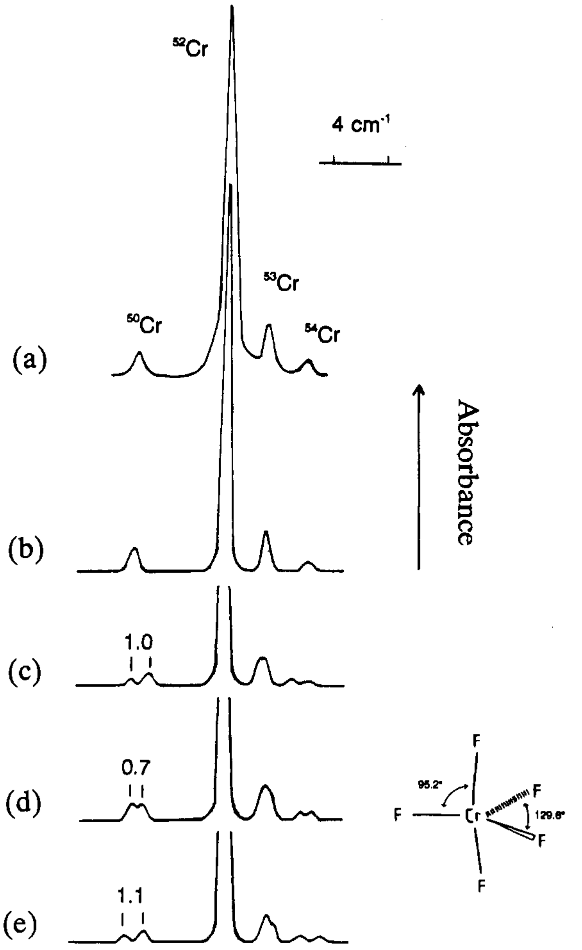

Figure 1. Observed and calculated Cr isotope patterns for the band at ca. 760 cm^{-1}, showing the effect of differential shifts: (a) high-resolution N_2 matrix IR spectrum, assigned to ν_3 O_h CrF_6; (b) spectrum calculated for ν_3 O_h CrF_6; (c) spectrum calculated for D_{3h} CrF_5 by assuming overlap of E′ and A_2'' stretching modes; (d) spectrum calculated for C_{2v} CrF_5 (model inset) by assuming overlap of B_1 and B_2 stretching modes; (e) spectrum calculated for D_{3h} CrF_6 (trigonal prism) by assuming overlap of E′ and A_2'' stretching modes.

As an alternative to O_h CrF_6, J&W propose that CrF_5 is the species responsible for the single IR-active stretch at ca. 760 cm^{-1}. Following normal convention, we therefore consider whether there is a reasonable structural model for CrF_5 which yields *one* intense IR feature in the Cr–F stretching region and also exhibits the observed isotope structure (Figure 1a). The D_{3h} trigonal bipyramid and the C_{4v} square pyramid clearly deserve consideration, and lower symmetry structures such as the C_{2v} model favored by J&W must also be examined. However, group theory predicts that all these structures will show at least *two* IR-active Cr–F stretching modes, and we must therefore consider the likelihood that two ^{52}Cr–F modes of different symmetries are separated by less than ca. 1.0 cm^{-1}.

In D_{3h} VF_5, the IR-active E′ and A_2'' stretches lie[8] at ca. 810 and 784 cm^{-1}, while, in UF_5, ClF_5, and BrF_5 (all C_{4v}), the two most intense stretches[9] are similarly separated by over 20 cm^{-1}. In view of this, we believe it to be most unlikely that there would be a near overlap of fundamentals if CrF_5 had either of these

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structures. We also note that this presumed coincidence must be invoked in neon, argon, and nitrogen matrix environments.

However, let us for the moment accept that there *is* an exact overlap for one of these models—the trigonal bipyramid—and proceed to calculate the isotope structure expected for the E′ and A_2'' modes. Assuming that these two stretching modes are effectively uncoupled from bends of the same symmetry, the positions of the ^{50}Cr, ^{53}Cr, and ^{54}Cr absorptions are determined solely from the appropriate **G** matrix terms, within the harmonic oscillator approximation. The relevant expressions are

$$G_{E'} = (1/M_F) + (3/2M_{Cr}) \qquad G_{A_2''} = (1/M_F) + (2/M_{Cr})$$

and as these are clearly different, one must anticipate differences in the isotope shifts for the two modes. The resulting spectrum will therefore be a superposition of two distinct isotope patterns. Figure 1c summarizes the results of our isotope calculations, and it is clear that, at the resolution of our spectrum (Figure 1a), we should observe *doublets* for the ^{50}Cr and ^{54}Cr components (separation 1.0 cm^{-1}) and a broadening of the ^{53}Cr absorption(s) if this spectrum were due to D_{3h} CrF_5.

The C_{2v} model proposed by J&W is derived from electron diffraction studies[10] and accompanies Figure 1d. It contains three independent sets of Cr–F bonds and is expected[7] to show *three* prominent IR stretches. This model thus requires the accidental overlap of *three* IR stretches to better than ca. 1.0 cm^{-1} in three different matrix environments, and is even less likely! More significantly, this structure can also be rejected on the basis of differential isotope shifts for the proposed[3] B_1 and B_2 modes. This C_{2v} model contains two pairs of equivalent CrF_2 units with interbond angles of 169.6° (axial) and 129.6° (equatorial). The Cr isotope shifts for these antisymmetric stretching modes are angle dependent, and Figure 1d shows the patterns computed by assuming an exact overlap of the ^{52}Cr B_1 and B_2 components. The outer isotopic components again appear as doublets, and this model is therefore also inconsistent with the observed spectrum. In a similar way, we are able to reject the C_{4v} structure.

We therefore believe, first, that there are no compelling grounds on which to reject the assignment of this IR spectrum to O_h CrF_6 and, more importantly, that the observed spectrum cannot be due to a CrF_5 molecule with the above D_{3h}, C_{4v}, or C_{2v} shape.

We now examine the suggestion made by Marsden and Wolynec (M&W)[4] that our spectrum could arise from molecular CrF_6 which has a trigonal-prismatic geometry, where the angle between each Cr–F bond and the C_3 axis is 50.5°. This structure also yields two IR-active stretches (E′ + A_2''), and Figure 1e shows the isotope pattern calculated by assuming an exact overlap (at 760 cm^{-1}) of the ^{52}Cr components. Once again, it turns out that we should observe *doublets* for the ^{50}Cr and ^{54}Cr components, and this model must similarly be rejected. However, since the basic prismatic structure still retains some flexibility with respect to the F–Cr–F bond angles, it is interesting to examine whether a *specific* geometry exists for which the E′ and A_2'' isotope patterns *would* be indistinguishable from those of the octahedron. For this, it is necessary that the **G** matrix terms for these two stretches should *both* be equivalent to the $G_{T_{1u}}$ stretch in O_h CrF_6. This may seem an unlikely event, but it in fact occurs when each Cr–F bond is at an angle of 54° 44′ to the C_3 axis. For this specific geometry, the observed isotope splittings could correspond to either a D_{3h} or an O_h structure, but for the prism, the assumption of band overlap in three different matrices would remain....

Finally, we note that Edwards clearly states[11] that CrF_5 vapor is *crimson* and that all the above studies have been carried out on a *yellow* vapor. J&W do not give detailed analytical figures for their product, but we believe that they may have prepared samples which are *primarily* red, less volatile CrF_5 but which contain some yellow, volatile CrF_6. Their observations on the *condensed-phase* material would thus be consistent with previous reports[12] on liquid or solid CrF_5, but their *vapor-phase* and matrix studies would be dominated by the more volatile CrF_6. In his original paper describing the synthesis of CrF_6, Glemser[1] states that the reaction between fluorine and chromium gives a mixture of *red* and *yellow* products, and we remain convinced that the yellow material is chromium hexafluoride.

Registry No. CrF_6, 13843-28-2; Cr, 7440-47-3; CrO_3, 1333-82-0; CrF_5, 14884-42-5.

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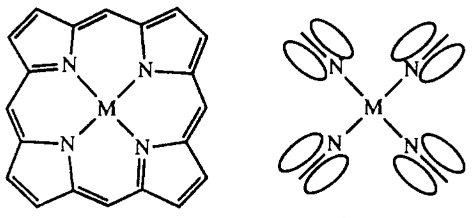
A New Class of Tetrapodal Ligands

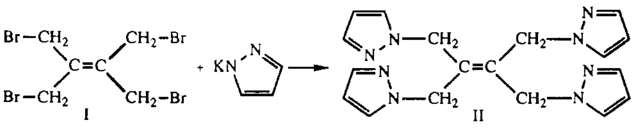
There are known large numbers of planar tetradentate and several types of tripodal ligands for metals. However, tetrapodal heterocyclic ligands seem to be unknown. In probing the reasons for the seemingly special characteristics of porphyrins, we have sought ways of preparing complexes having the four heterocyclic rings turned 90° from their positions in porphyrins, illustrated with π-orbital sketches:



Porphyrin **Tetrapod**

This change would allow us to test the effects of porphyrin delocalization, introduce a different kind of dpπ overlap, and perhaps provide novel biomimetic model systems. While tripod ligands are available by attaching heterocycles to a tetrahedral atom[2-4] tetrapodal ligands provide an additional problem in that a square base is needed and the lone pairs on each nitrogen would be directed toward the metal so that the four heterocycles are in parallel planes.

We approached this design using the slightly rectangular (2.8 Å × 2.7 Å) tetramethyleneethene structure to provide a square framework for the four pendant ligands. This has the advantage and/or disadvantage of possible interaction of the metal with the double bond but protection of one coordination site is assured if chelation occurs. Importantly, the syntheses are straightforward as illustrated in



As a first example, a suspension of potassium pyrazolide in tetrahydrofuran was treated with 1,4-dibromo-2,3-di(bromo-

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