

Received: May 17, 1984; accepted: December 29, 1984

SYNTHESIS AND CRYSTAL STRUCTURE OF 1,1,1,5,5,5-HEXAFLUORO-2-AMINOPENTAN-4-ONE (HFAP)

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SUMMARY

The vapour phase reaction of ammonia and hexafluoroacetylacetone leads to the formation of the new β -keto-amine $C_5H_3F_6NO$. Crystals of the compound are monoclinic, space group $P2_1/n$, $a = 10.01(2)$, $b = 19.33(3)$, $c = 8.40(1)$ Å, $\beta = 82.27(6)^\circ$; final R = 0.044.

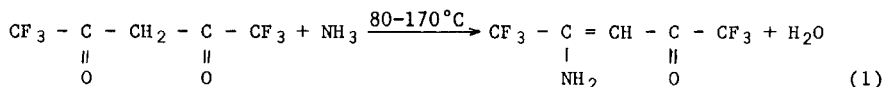
INTRODUCTION

Hexafluoroacetylacetone (HHFA) and ammonia undergo an acid-base reaction at room temperature to form NH_4HF_6 , a sublimable white solid [1,2]. This salt has been shown [3] by I.R. spectroscopy to dissociate in the vapour phase to the starting materials NH_3 and HHFA.

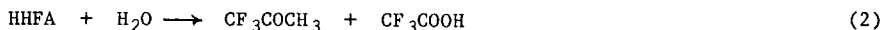
Fluorinated β -diketonates have been employed in laser photochemistry studies directed towards uranium and vanadium enrichment [4,5,6]. The present study was undertaken to prepare fluorinated keto-amine complexes which would be volatile but have a lower thermal stability than the diketonates.

RESULTS AND DISCUSSION

In the present study, it was observed that if NH_4HF_6 was heated to $80^\circ C$ for 3 hours or $170^\circ C$ for 30 min in a sealed evacuated tube, there was a condensation reaction between NH_3 and a keto group in HHFA, according to the reaction :



A secondary reaction occurs between the H₂O produced from reaction (1) and HHFA producing trifluoroacetone and ammonium trifluoroacetate. The latter compound is formed from the ammonia/trifluoroacetic acid reaction. The reaction with water was confirmed by heating HHFA.2H₂O crystals which formed trifluoroacetone and trifluoroacetic acid:-



Small amounts of three compounds of higher molecular weight were detected by gas chromatography and mass spectrometry. Prolonged heating or liquid phase reactions resulted in greater proportions of these compounds. Reactions carried out solely in the gas phase gave yields of up to 85 percent HFAP. The remaining 15 percent consisted of NH₄HFA and trifluoroacetone with a trace amount of the higher molecular weight compounds.

Trifluoroacetone was removed under vacuum at -35°C. Further fractionation at 0°C yielded relatively pure HFAP, free of NH₄HFA. Samples for characterization were further purified by gas chromatography using a Poropak Q column at 230°C.

HFAP is a colourless crystalline solid, soluble in most organic solvents and having a vapour pressure of 100 Pa at 20°C. The gas phase UV absorption maximum occurs at 288 nm. The infra-red spectrum of a mull (fluorolube) shows strong absorptions at 3480 cm⁻¹ (m) and 3300 cm⁻¹ (s) due to the asymmetric and symmetric N-H stretches respectively. These bands occur at 3490 cm⁻¹ and 3280 cm⁻¹ in a spectrum of the melt with additional absorptions due to association at 3370 cm⁻¹ and 3200 cm⁻¹.

In the vapour phase asymmetric -NH vibrations occur at higher frequencies [7]. The absorptions for HFAP in this phase occur at 3540 cm⁻¹ (s) and 3300 cm⁻¹ (w).

Gas phase infra-red absorption frequencies of HFAP in cm⁻¹

3540(s), 3300(w), 1683(s), 1634(vs), 1563(s), 1450(s), 1370(s), 1280(vs), 1218(vs), 1175(vs), 1120(s), 1062(s), 803(m), 735(m), 635(m), 585(w), 575(w).

Positive ion mass spectrum of HFAP

The positive ion mass spectrum of the ligand shows a parent ion at $m/e = 207$. The fragmentation pattern is similar to that of HHFA with losses of fluoride ions and the CF_3 group. It has been shown that the large $m/e = 69$ peak in HHFA was due to both CF_3 and C_3O_2H , with this ligand the $m/e = 69$ is small and an equal height peak at $m/e = 68$ is found presumably due to C_3ONH_2 .

m/e	138	207	68	96	69	91	90	43	169	188
I/I_0	100	33	29	28	27	22	17	17	5	4

Elemental analysis of HFAP - $C_5H_3F_6NO$

	C	F	H	N
Found	28.98	55.07	1.45	6.76
Calc.	28.82	55.30	1.50	6.71

HFAP complexes

The copper(II) complex of HFAP was prepared by shaking an excess of a Cu(II) acetate solution with a chloroform solution of the ligand. Dark green crystals were obtained by evaporation and purified by vacuum sublimation. Attempts to prepare Fe(II), Co(II), oxo V(IV) and oxo U(VI) by the same procedure were unsuccessful.

The copper complex of this ligand shows a single absorption in the N-H stretching region at 3360 cm^{-1} . Thermal decomposition of the vapour of the copper complex occurred at 330°C and deposited a copper film on the glass surface. The crystals were green needles, which gave apparent monoclinic symmetry with $a = 8.80(4)$, $b = 10.61(4)$, $c = 8.79(4)$ Å, $\beta = 89.85(5)^\circ$, but as the spots were elongated and the crystal texture appeared fibrous, a complete structure analysis was not undertaken.

Elemental analysis of copper complex $Cu(HFAP)_2$

	C	F	H	N	Cu
Found	25.17	47.5	0.84	5.54	13.25
Calc.	25.21	47.9	0.84	5.88	13.45

X-ray data collection

For diffractometry, a single crystal of dimensions 0.50 x 0.20 x 0.20 mm was mounted in a glass capillary. Unit cell dimensions were obtained from a least-squares fit to the setting parameters of 25 reflections. The intensities of 1895 unique reflections in the range $2<\theta<22^\circ$ were measured on an automatic four-circle diffractometer using Zr filtered MoK α radiation. Intensities were measured in the ω - 2θ mode over 200 steps of 0.005 degrees, and backgrounds were measured at each extreme of the scan width. The intensity of a standard reflection monitored throughout the data collection, indicated that there was no decomposition. The data were corrected for Lorentz, polarization and absorption effects resulting in 1266 reflections with $I > 2.5\sigma(I)$.

Crystal data

C₅H₃F₆NO, M_r 207.07; monoclinic, space group $P2_1/n$; $a = 10.01(2)$, $b = 19.33(3)$, $c = 8.40(1)$ Å, $\beta = 82.27(6)^\circ$; $V = 1611$ Å³, $Z = 8$, $D_c = 1.707$ g cm⁻³, $\lambda(\text{MoK}\alpha) = 0.7107$ Å, $\mu(\text{MoK}\alpha) 1.56$ cm⁻¹, $F(000) = 816$ electrons.

Structure solution and refinement

The structure was solved by direct methods using SHELX-76 [8] and all expected hydrogen atoms were located from difference Fourier. The CF₃ groups are rotationally disordered and were modelled as two separate sites. All non-hydrogen atoms were refined anisotropically; the fluorine atoms yielded large thermal parameters suggesting that the disorder of the CF₃ groups approaches free rotation about the carbon-carbon bond.

Blocked-matrix least-squares refinement of all positional and thermal parameters, an overall scale factor and a weighting scheme converged with $R = 0.044$, $R_w = 0.049$ and $\bar{w} = 0.75/(\sigma_{F_0}^2 + 0.0048 F_0^2)$.

Final atomic coordinates are listed in Table 1.

TABLE 1

Final positional parameters for HFAP; by 10^3 for hydrogen,
 10^4 for all others

	x	y	z
C(11)	1024(3)	3133(2)	8738(6)
C(12)	2204(2)	3635(2)	8702(3)
C(13)	3468(3)	3361(1)	8802(3)
C(14)	4594(2)	3770(1)	8616(3)
C(15)	5966(3)	3448(2)	8612(5)
O(11)	1946(2)	4253(1)	8557(3)
N(11)	4607(3)	4441(1)	8417(3)
F(11)	341(28)	3263(9)	7539(24)
F(12)	1328(9)	2474(3)	8606(49)
F(13)	146(20)	3204(14)	10009(38)
F(11')	-104(7)	3464(5)	8996(34)
F(12')	972(14)	2717(11)	9856(25)
F(13')	1057(24)	2834(14)	7443(20)
F(14)	6618(22)	3706(20)	9739(34)
F(15)	6741(20)	3616(12)	7271(46)
F(16)	5956(20)	2797(12)	8607(75)
F(14')	6765(11)	3829(3)	9248(38)
F(15')	6505(29)	3294(21)	7247(15)
F(16')	5882(28)	2866(8)	9474(23)
C(21)	1201(3)	5881(2)	6559(5)
C(22)	-225(2)	5630(1)	7055(3)
C(23)	-1279(2)	6000(1)	6641(3)
C(24)	7393(2)	5778(1)	7025(3)
C(25)	6274(4)	6207(2)	6450(5)
O(21)	7030(1)	5255(1)	7803(2)
N(21)	-321(2)	5046(1)	7836(3)
F(21)	1265(5)	6497(3)	6120(21)
F(22)	1867(5)	5821(6)	7892(7)
F(23)	1849(8)	5455(5)	5570(12)
F(21')	2064(14)	5489(9)	6263(67)
F(22')	1286(13)	6245(20)	5080(31)
F(23')	1517(23)	6357(29)	7422(38)
F(24)	5120(5)	6046(5)	7163(27)
F(25)	6402(8)	6873(2)	6912(22)
F(26)	6305(27)	6190(12)	4976(11)
F(24')	5647(21)	5764(8)	5518(38)
F(25')	6621(9)	6655(8)	5395(20)
F(26')	5432(21)	6410(14)	7489(10)
H(11)	355(3)	286(2)	894(3)
H(12)	536(4)	471(2)	832(4)
H(13)	383(4)	465(2)	834(3)
H(21)	-108(3)	637(2)	600(3)
H(22)	43(4)	481(2)	799(4)
H(23)	-115(4)	487(2)	813(3)

TABLE 2
Geometry of HFAP

C(11) - C(12)	1.526(5) Å	C(14) - C(15)	1.508(4)
C(12) - C(13)	1.384(4)	C(14) - N(11)	1.307(4)
C(12) - O(11)	1.233(4)	N(11) - H(12)	0.88(4)
C(13) - H(11)	0.97(4)	N(11) - H(13)	0.91(4)
C(13) - C(14)	1.367(4)	C - F	1.283(av.)
C(11) - C(12) - C(13)	117.9(3)°	C(13) - C(14) - C(15)	119.8(3)
C(11) - C(12) - O(11)	116.5(3)	C(13) - C(14) - N(11)	125.6(3)
C(13) - C(12) - O(11)	125.6(3)	C(15) - C(14) - N(11)	114.6(3)
C(12) - C(13) - C(14)	121.2(3)		

Intra and intermolecular hydrogen bonds

N(11) - O(11)	2.67(4) Å	N(11) - O(21)	2.879(4) Å
H(13) - O(11)	2.02(4)	H(12) - O(21)	1.98(4)
N(21) - O(21)	2.684(4)	N(21) - O(11)	2.869(4)
H(23) - O(21)	2.02(4)	H(22) - O(11)	1.97(4)

Description of the structure

There are two independent molecules in the unit cell (Table 1). These have very similar geometries, and are essentially planar, with no C, H, N or O atom deviating more than 0.08 Å from the least-squares plane through these atoms. The first molecule in the unit is shown in Figure 1, the second fluorine of each pair being omitted. Bond lengths and angles for this molecule are given in Table 2, uncorrected for the effects of thermal motion; these distances and angles are normal. There is a reasonably strong N-H...O intra-molecular hydrogen bond in each independent molecule of length 2.7 Å.

The molecules pack in planes roughly parallel to the C-axis and adjacent independent molecules are linked by two types of N-H...O intermolecular hydrogen bonds of length 2.879(4) and 2.869(4) Å. The molecular packing is shown in a stereo diagram in Figure 2 (second fluorine pair omitted).

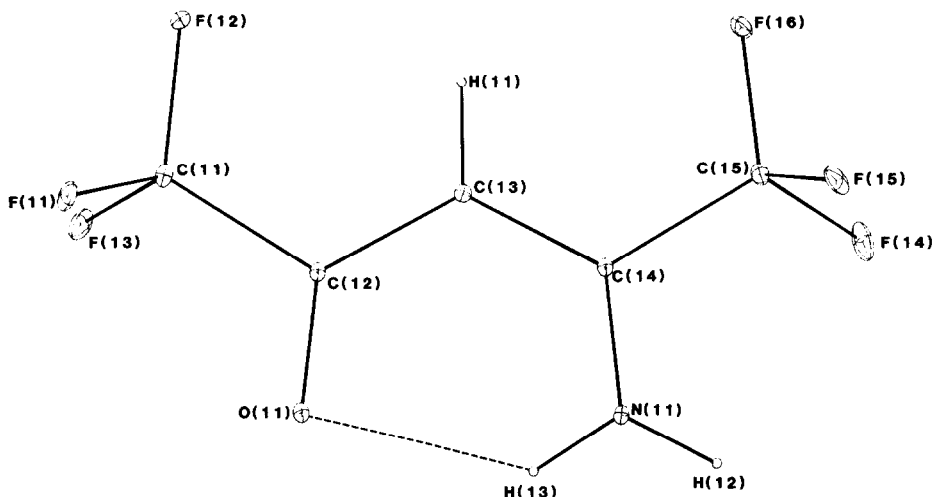


Fig.1 Thermal ellipsoid plot of HFAP Molecule 1 giving the atom numbering scheme. Second pair of partial fluorine atoms omitted.

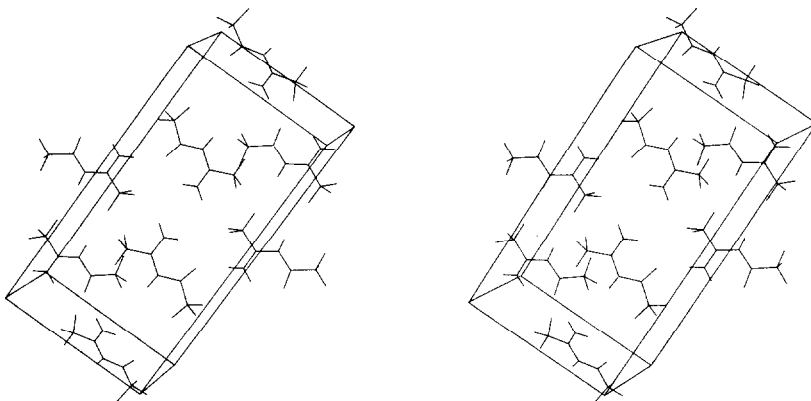


Fig.2 Stereo pair showing the crystal packing of HFAP, as seen down the *c*-axis.

DISCUSSION

Condensation reactions of β diketones with amines or ammonia are not unusual however this is the first product isolated with both fluorinated-end-alkyl groups. Normally with such condensation reactions a β ketoimine results not a β ketoamine and this probably reflects the electronegativity of the terminal CF_3 groups. The amine group (NH_2) was confirmed in the

solid state by structural studies and in the gas phase by infrared measurements. As might be expected this ligand resembles HHFA, particularly in its mass spectrum fragmentation pattern.

Complex formation was evident with many metals using the organic extraction method but only the copper complex was isolated, this is not unusual and often occurs with HHFA complexes. Other preparative techniques may be more suitable for isolating metal complexes. The thermal stability of $\text{Cu}(\text{HFA})_2$ is only 250°C whereas $\text{Cu}(\text{HFAP})_2$ is stable up to 330°C . Both give Cu metal as one product and a mixture of organic products. This difference in thermal stability can be explained by the fact that Cu-N bonds are more highly favoured than Cu-O bonds, however it is felt that with complexes which favour metal-oxygen bonds then the HHFA complexes will show a greater thermal stability than HFAP complexes for example iron and uranyl complexes.

ACKNOWLEDGEMENT

T.W.H. acknowledges the Australian Institute of Nuclear Science and Engineering for the Award of a Postdoctoral Fellowship.

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