SCHIFF BASES PREPARED FROM ETHYLENEDIAMINE AND HEXAFLUOROACETYLACETONE*

MARY FRANCES RICHARDSON and ROBERT E. SIEVERS Aerospace Research Laboratories ARC, Wright-Patterson AFB, Ohio 45433

(Received 18 August 1969)

Abstract – Bis(hexafluoroacetylacetone)ethylenediimine(H_2h facen) was prepared by sublimation of the hexafluoroacetylacetone salt of ethylenediamine, en·2Hhfa. In addition to H_2h facen, the sublimation method yields 2,3-dihydro-5,7-bis(trifluoromethyl)-1H-1,4-diazepine(cyclohfa-en) and a hexafluoroacetylacetone salt of 1-amino-2-(trifluoroacetamido)ethane, tfe·Hhfa. H_2h facen is not stable and readily loses a mole of Hhfa to give cyclohfa-en. Attempts to prepare Cu(hfacen) by normal solution methods yielded only solvated Cu(hfa)₂. Gas transport reactions and reactions of CuCl₂ with the ligands in benzene resulted in the synthesis of the following new compounds: CuCl₂·H₂hfacen, Cu(hfa)₂·H₂hfacen, Cu(hfa)₂·cyclohfa-en, and Cu(hfa)₂·2tfe. The structures of the ligands were confirmed by NMR and i.r. spectra. Thermogravimetric data show that some of the Cu complexes are quite volatile. One of the reasons that template synthesis of H_2h facen has failed in solution may be that hydroxylic solvents (water, methanol) add across the carbonyl group to Hhfa to give compounds such as 1,1,1,5,5,5-hexafluoro-2,2,4,4-tetrahydroxypentane and 1,1,1,5,5,5-hexafluoro-2,4-dihydroxy-2,4dimethoxypentane.

PREVIOUS work with β -diketone chelates has shown that the most volatile chelates are those in which specific intermolecular interactions (e.g., polymerization and hydrogen bonding) are minimized and the degree of fluorination of the ligand is high[1].

While a completely satisfying explanation is lacking for the effect of fluorine substitution on volatility, the effects of polymerization and hydrogen bonding are more easily understood. The extent of these intermolecular interactions is ultimately determined by the following factors: the charge and coordination number of the metal ion, the charge on the ligand, and the number of coordination positions the ligand is capable of filling. Thus, metals whose valence is n and whose normal coordination number is 2n form volatile β -diketone chelates† relatively easily; with symmetrical complexes only van der Waals forces need be overcome for the molecules to volatilize. However, considerable difficulty is frequently encountered in preparing volatile β -diketonates of metals whose normal coordination number exceeds 2n. One of two things usually occurs so that the vacant coordination positions are filled. First, a polymeric species may be formed, as in the cases of tetrameric cobalt(II) acetylacetonate[2] and trimeric nickel(II) acetylacetonate[3]. Second, a hydrate or other solvate may be generated. The

*Aerospace Research Laboratories, ARC, Wright-Patterson AFB, Ohio 45433.

†For the present purposes, it is assumed that the β -diketone functions as a bidentate ligand with coordination through both oxygens.

- 1. R. W. Moshier and R. E. Sievers, Gas Chromatography of Metal Chelates. Pergamon Press, Oxford (1965).
- 2. F. A. Cotton and R. C. Elder, J. Am. chem. Soc. 86, 2294 (1964).
- 3. G. J. Bullen, R. Mason, and P. Pauling, Inorg. Chem. 4, 456 (1965).

problems with solvates arise because they are often thermally unstable (e.g., the rare earth acetylacetonate hydrates[4]), and because many of the common solvating agents are capable of hydrogen bonding.

Other things being equal, polymerization and intermolecular hydrogen bonding should reduce volatility since these bonds must be broken before the molecules volatilize, or else polymeric units must volatilize. Both of these processes require greater energy than the vaporization of single molecules which are not strongly bonded to their neighbors.

There are two ways of overcoming these difficulties. The first is to use β -diketones or other ligands with bulky substituents so that the metal is "shielded" from interactions with other molecules. Application of this reasoning resulted in the first volatile, thermally stable rare earth chelates, those of 2,2,6,6-tetramethyl-3,5heptanedione (thd)[5]. The second method is to develop ligands which can simultaneously satisfy the valence of the metal ion and exhibit coordination numbers greater than 2*n*. Schiff bases derived from polyamines and β -diketones comprise one type of ligand which meets these requirements. The coordination number and stereochemistry of the resulting complex can be controlled by proper choice of the polyamine; e.g. ligands derived from β -diketones and tris(2aminoethyl)-amine are expected to give neutral, 7-coordinate complexes with trivalent metal ions[6]. In a similar fashion, the condensation of triethylenetetramine with two β -diketone groups should yield a Schiff base that can act as a sexadentate ligand and form neutral complexes with divalent ions[7].

In the present work, ethylenediamine and hexafluoroacetylacetone were chosen as a model system to examine the possibility of condensing highly fluorinated β -diketones with polyamines. Previous attempts to condense ethylenediamine with hexafluoroacetylacetone have been unsuccessful[8–10].

EXPERIMENTAL

Hexafluoroacetylacetone, trifluoroacetic acid, and trifluoroacetic anhydride were obtained from the Pierce Chemical Company, Rockford, Ill. Other compounds were standard laboratory chemicals.

Analyses for C, H, N, F, and Cu, and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tennessee. I.R. spectra were recorded in mineral oil mulls on a Perkin-Elmer Infracord spectrophotometer. NMR spectra were recorded on the Varian A-60 spectrometer. Mass spectra were taken with an LKB-9000 mass spectrometer.

Thermogravimetric curves were recorded on a DuPont Model 950 Thermogravimetric Analyzer. The sample sizes were approximately 10 mg (except for $Cu(hfa)_2 \cdot H_2hfacen$ and $Cu(hfa)_2 \cdot cyclohfa-en$,

- 4. M. F. Richardson, W. F. Wagner and D. E. Sands, Inorg. Chem. 7, 2495 (1968).
- 5. (a) K. J. Eisentraut and R. E. Sievers, J. Am. chem. Soc. 87, 5254 (1965); J. Am. chem. Soc. 91, In press (1969); (b) A crystal structure determination has shown that Pr(thd)₃ is dimerized in the solid state with Pr atoms bridged by carbonyl oxygens (C. S. Erasmus and J. C. A. Boeyens, Abstracts, 8th International Union of Crystallography Congress, Stony Brook, New York, August, 1969). The molecules composing the dimers cannot be very strongly linked, however, since molecular weight measurements show that Pr(thd)₃ is monomeric in non-polar solvents.
- 6. L. J. Wilson and N. J. Rose, J. Am. chem. Soc. 90, 6041 (1968).
- 7. S. C. Cummings and R. E. Sievers, To be published.
- 8. A. E. Martell, R. Linn Belford and M. Calvin, J. inorg. nucl. Chem. 5, 170 (1958).
- 9. E. J. Olszewski and D. F. Martin, J. inorg. nucl. Chem. 27, 1043 (1965).
- 10. D. F. Martin and E. J. Olszewski, J. inorg. nucl. Chem. 28, 1073 (1966).

Schiff bases

for which they were 5 mg). The helium flow rate was 60 cc/min; the heating rate was $\sim 10^{\circ}$ /min. The samples were contained in open platinum pans.

X-ray powder diffraction patterns (Table 1) were obtained with nickel-filtered CuK α radiation in a 115.9 mm Debye-Scherrer camera. The powdered samples were packed in 0.5 mm glass capillaries. Line positions were determined to the nearest 0.05 mm; intensities were estimated visually.

| Table 1. | X-ray power patterns* | ler diffraction |
|----------|--------------------------|-----------------|
| en∙2Hhfa | H ₂ hfacen | cyclohfa-en |
| 11·43 m† | 14·90 vw | 8·43 m |
| 7∙74 m | 9∙09 m | 7·20 vw |
| 6·37 vw | 6·07 m | 5∙94 w |
| 5·74 m | 5·75 w | 5·57 m |
| 4∙95 vw | 5·27 w | 5.30 st |
| 4∙44 st | 5·01 w | 4·71 m |
| 3-90 vst | 4·79 st | 4∙03 m |
| 3∙58 w | 4∙59 w | 3.68 vst |
| | 4·37 m | |
| | 3·87 m | |

*Abbreviations: w, weak; m, medium; st, strong; v, very.

†d_{hki} in Angstroms.

Ethylenediammonium hexafluoroacetylacetonate, $en \cdot 2Hhfa$. Ethylenediamine (0·1 mole in 100 ml benzene) was added slowly to hexafluoroacetylacetone (0·2 mole in 100 ml benzene). Heat was evolved and a white solid precipitated. Prolonged boiling of this suspension did not result in any noticeable change in the solid.*

The suspension was filtered while hot, washed with hot benzene, and air dried. The salt melts at $133-135^{\circ}$ (dec). Anal. Calcd. for $C_{12}H_{12}F_{12}N_2O_4$: C. 30·26; H. 2·54; N. 5·88; F. 47·88 per cent. Found: C, 30·01; H. 2·53; N. 5·73; F. 47·63 per cent.

Bis(hexafluoroacetylacetone)ethylenediimine, $H_2hfacen$. 5 g en·2Hhfa was placed in a vacuum sublimator, the vessel was evacuated, and the temperature was raised to 80–100°. The sublimator was immediately thereafter sealed off from the vacuum. Large shiny white feathery needles and a microcrystalline substance collected on the cold finger maintained at ~ 15°. The large needles were separated manually as best as possible from the small crystals and submitted for analysis. *Anal.* Calcd. for $C_{12}H_8F_{12}N_2O_2$: C. 32·74; H. 1·83; N. 6·36; F, 41·80 per cent. Calcd. for $C_7H_8F_6N_2$ (cyclohfa-en): C. 36·22; H, 2·60; N, 12·06; F, 49·11 per cent. Found: C, 33·61; H, 2·03; N, 8·39; F, 49·64 per cent. The analytical data correspond to a mixture of 65 per cent H_2 hfacen and 35 per cent cyclohfa-en. The sample contained no cyclohfa-en before being sent for analysis (i.e., there was no i.r. peak at 1020 cm⁻¹), but H_2 hfacen cyclizes spontaneously to give cyclohfa-en (see below) so this could easily occur while the sample was in transit.

Decomposition of $H_2hfacen$. The large needles obtained during sublimation turn opaque, rapidly in air and slowly in a closed vial. A fresh batch (0.2276 g) of $H_2hfacen$, judged to be nearly pure from its i.r. spectrum, was exposed to air until a constant weight (0.1254 g) was reached. The faint smell of Hhfa was detectable until weight loss creased. During this time, the needle-shaped crystals changed to small prisms. Analytical data and i.r. spectra showed that the product is cyclohfa-en. The weight loss expected for the reaction given by Equation (2) (assuming volatilization of the Hhfa) is 47.3 per cent; the weight loss actually observed was 44.9 per cent.

*When the analogous reaction is carried out with acetylacetone or trifluoroacetylacetone, the heat generated from salt formation is sufficient to start the condensation; droplets of water appear and additional heating results in complete "solution" of the salt initially formed. Cooling yields the Schiff bases, H_2 acen and H_2 tfacen.

2,3-dihydro-5,7-bis(trifluoromethyl)-1H-1,4-diazepine (cyclohfa-en). This compound is readily prepared by sublimation of H₂hfacen (maintaining a constant vacuum to remove Hhfa), by repeated recrystallization of H₂hfacen from hexane, or by exposure of H₂hfacen to air for several days. Anal. Calcd. for C₇H₆F₆N₂: C, 36·22; H, 2·60; N, 12·06; F, 49·11 per cent; mol. wt. 232. Found: C, 36·24; H, 2·53; N, 11·95; F, 49·31 per cent; mol. wt. 256 (in benzene).

Hexafluoroacetylacetone salt of 1-amino-2-(trifluoroacetamido) ethane, tfe Hhfa. This compound is sometimes obtained as the major product of sublimation of en 2Hhfa. It is also obtained when en 2Hhfa is boiled in benzene and filtered; the cooled filtrate yields small amounts of tfe Hhfa. A third method of preparation involves adding a solution of ethylenediamine (0·1 mole in 100 ml benzene) to a solution of 0·1 mole CF_3CO_2H and 0·1 mole Hhfa in 100 ml benzene, boiling the mixture, filtering off the unreacted salt, and cooling the filtrate. Repeated boiling of the salt in benzene effects complete transformation of the salt into tfe Hhfa. Anal. Calcd. for $C_9H_9F_9N_2O_3$: C, 29·68; H, 2·49; N, 7·68; F, 46·96 per cent. Found: C, 29·99, H, 2·70; N, 7·73; F, 46·84 per cent.

Bis(trifluoroacetato)ethylenediamide, entfam. A solution of 0.033 mole trifluoroacetic anhydride (2-fold excess) in 10 ml benzene was added to 0.016 mole ethylenediamine in 10 ml benzene. The reaction was practically instantaneous and proceeded with the evolution of heat. The filtrate yielded the diamide when cooled, m.p. 198-201°. Anal. Calcd. for $C_6H_6F_6N_2O_2$: C, 28.58; H, 2.40; N, 11.11; F, 45.22 per cent. Found: C, 28.48; H, 2.44; N, 10.93; F, 45.39 per cent.

1,1,1,5,5,5-Hexafluoro-2,4-dihydroxy-2,4-dimethoxypentane. Hhfa·2CH₃OH. 2 ml Hhfa was added to 5 ml CH₃OH. Considerable heat was evolved. Upon cooling, large, platelike crystals were obtained. Anal. Calcd. for C₇H₁₀F₆O₄: C, 30·89; H, 3·74; F, 41·89; H₂O, 0·00 per cent. Found: C, 30·68; H, 3·63; F, 41·69; H₂O, 0·0 per cent (Karl Fischer titration).

Copper chelates. Standard methods of preparing the chelates, i.e., mixing methanol or dioxane solutions of a copper salt and the ligand[8], yielded only solvated $Cu(hfa)_2$. New compounds were obtained either by transport reactions (sublimation of the chelate from a mixture of the copper salt and ligand) or by boiling a suspension of the ligand and copper salt in benzene.

CuCl₂·H₂hfacen^{*}. The "Schiff base", actually a mixture of H₂hfacen and en·2Hhfa, was ground with a large excess of anhydrous CuCl₂ in an agate mortar. The brown mixture was placed in a vacuum sublimator and the temperature was raised to 90°. A white sublimate (mostly Hhfa·2H₂O) first appeared. The sublimator was removed from the oil bath and allowed to stand overnight, during which time the brown residue turned green. Vacuum sublimation was begun again at 100°. A green powder, which seemed to be "wet", collected on the cold finger. It was scraped off and dried in air; the resulting yellow product was analyzed. *Anal.* Calcd. for C₁₂H₈Cl₂CuF₁₂N₂O₂: Cu, 11·06; Cl, 12·34; C, 25·08; H, 1·40; N, 4·87; F, 39·68 per cent. Found: Cu, 10·93; Cl, 12·23; C. 24·97; H, 1·49; N, 4·83; F, 39·64 per cent.

Cu(*hfa*)₂·H₂*hfacen*. Two-tenths of a gram of the "Schiff base", a mixture of H₂*hfacen* and en·2Hhfa, was ground with 0.067 g (10 per cent excess) CuCl₂. The mixture was placed in 10 ml benzene, boiled for 1 min, and filtered. The bright yellow residue had a Cl:Cu ratio of 2.9:1 (38.91 per cent Cl, 23.89 per cent Cu). Chartreuse crystals precipitated from the cool filtrate. *Anal.* Calcd. for C₂₂H₁₀CuF₂₄N₂O₆: Cu, 6.92; C, 28.79; H, 1.10; N, 3.05; F, 49.68 per cent. Found: Cu, 7.09; C, 28.90; H, 1.01; N, 3.17; F, 49.03 per cent. A chloride test was negative.

 $Cu(hfa)_2 \cdot cyclohfa$ -en. The filtrate obtained after removing the chartreuse crystals of $Cu(hfa)_2 \cdot H_2hfacen$ was evaporated to give a sticky green residue which contained $Cu(hfa)_2 \cdot cyclohfa$ -en, $H_2hfacen$, cyclohfa-en, and small amounts of tfe·Hhfa. Repeated crystallization from hexane yielded chartreuse crystals of $Cu(hfa)_2 \cdot cyclohfa$ -en. In subsequent preparations of $Cu(hfa)_2 \cdot H_2hfacen$ and $Cu(hfa)_2 \cdot cyclohfa$ -en, $CuCl_2$ was present in great excess, thus largely eliminating many of the separation problems caused by excess ligand. $Cu(hfa)_2 \cdot cyclohfa$ -en is also obtained upon the slow, repeated vacuum sublimation of $Cu(hfa)_2 \cdot H_2hfacen$. Anal. Calcd. for $C_{17}H_8CuF_{18}N_2O_4$: Cu, 8.95; C, 28.77; H, 1.14; N, 3.95; F, 48.19 per cent. Found: Cu, 8.45; C, 29.26; H, 1.24; N, 4.03; F, 48.00 per cent.

 $Cu(hfa)_2 \cdot en$ and $Cu(hfa)_2 \cdot 2en$. The mono(ethylenediamine) adduct was prepared by adding ethylenediamine (2 m-mole in 10 ml benzene) to a warm solution of 2 m-mole $Cu(hfa)_2 \cdot H_2O$ in 40 ml

*For convenience, and because the detailed structures are not generally known, the formulas for the copper chelates have been written as $CuL_2 \cdot nD$. These formulas are not intended to imply that L is coordinated to Cu and D is not; indeed, in the case of $Cu(hfa)_2 \cdot 2en$, it seems that both ethylenediamines are coordinated, while the hexafluoroacetylacetonates are not (see below).

Schiff bases

warm benzene. The green solution was partially evaporated at room temperature, whereupon large green crystals of $Cu(hfa)_2 \cdot en \cdot C_6H_6$ were obtained. These crystals turned opaque fairly rapidly in air. A sample weighting 0.2391 g came to a constant weight of 0.2077 g in 2 hr for a weight loss of 13.1 per cent; the calculated weight loss for 1 mole of benzene is 12.7 per cent. The opaque green residue was analyzed. Anal. Calcd. for $C_{12}H_{10}CuF_{12}N_2O_4$: Cu, 11.82; C, 26.80; H, 1.87; N, 5.21; F, 42.40 per cent. Found: Cu, 11.97; C, 27.03; H, 1.85; N, 5.30; F, 42.55 per cent.

The bis adduct was prepared analogously, using 4 m-mole ethylenediamine and 2 m-mole $Cu(hfa)_2$. H₂O. The violet crystals are insoluble in benzene. *Anal.* Calcd. for $C_{14}H_{18}CuF_{12}N_4O_4$: Cu, 10.63; C, 28.13; H, 3.03; N, 9.37; F, 38.15 per cent. Found: Cu, 10.80; C, 28.27; H, 3.14; N, 9.48; F, 38.10 per cent.

 $Cu(hfa)_2 \cdot 2tfe$. Only $Cu(hfa)_2 \cdot H_2O$ was obtained when $CuCl_2$ was boiled with tfe \cdot Hhfa in benzene. A gas transport reaction yielded the desired Cu complex. Tfe \cdot Hhfa (0 · 432 g) was ground with excess $Cu(OAc)_2 \cdot H_2O$ (0 · 494 g) and placed in a vacuum sublimator at 100°. A green compound (0 · 1 g, 20 per cent) sublimed. *Anal.* Calcd. for $C_{18}H_{16}CuF_{18}N_4O_6$: Cu, 8 · 04; C, 27 · 37 H, 2 · 04 N, 7 · 09; F, 43 · 29 per cent. Found: Cu, 7 · 94; C, 27 · 62; H, 2 · 16; N, 7 · 20; F, 43 · 08 per cent. Substitution of $CuCl_2$ for Cu (OAc)₂ · H₂O in the transport reaction resulted in the sublimation of most of the ligand, only a small amount of $Cu(hfa)_2 \cdot 2tfe$ being obtained.

Attempted reaction of $CuCl_2$ with pure $H_2hfacen$. Anhydrous $CuCl_2$ was ground with $H_2hfacen$ and mixture was boiled with benzene as described for $Cu(hfa)_2 \cdot H_2hfacen$. Only a very faint green coloration appeared in the benzene. Cooling yielded the starting ligand and cyclohfa-en. However, when a 1:1 mixture of $H_2hfacen$ (0.159 g; 0.36 m-mole) and en 2Hhfa (0.170 g; 0.36 m-mole) was used, $Cu(hfa)_2 \cdot H_2hfacen$ was obtained.

Attempted reaction of $CuCl_2$ with cyclohfa-en. No reaction occurred when $CuCl_2$ was boiled with cyclohfa-en in benzene as described in the synthesis of $Cu(hfa)_2 \cdot H_2hfacen$.

RESULTS AND DISCUSSION

In this work, H_2 hfacen (1) has been prepared during sublimation (in a sealed system, after evacuation) of the salt, en·2Hhfa (Equation (1)).



Several other products are obtained in addition to the Schiff base, including cyclohfa-en (2), tfe·Hhfa (3), Hhfa· $2H_2O$, and some unreacted salt, en·2Hhfa. It is difficult to separate the components, particularly since a glass frequently forms on the cold finger instead of crystals which could be hand-separated. Sublimation fractions which contained significant amounts of cyclohfa-en, tfe·Hhfa, and Hhfa· $2H_2O$ were not used in the chelate syntheses*. However, it was not discovered until late in the work that the salt, en·2Hhfa, also sublimes. The significance of this is that, in most of the work, mixtures of H_2 hfacen and en·2Hhfa

*Hhfa·2H₂O reveals its presence in the Schiff base fraction by peaks at 910 and 985 cm⁻¹; tfe·Hhfa by a peak at 1700 cm⁻¹; and cyclohfa-en by a peak at 1020 cm⁻¹.

were used instead of pure H_2 hfacen. In retrospect, this was fortunate since it was found that the essentially pure Schiff base does not undergo reaction with CuCl₂.

The structure 1 proposed for H₂hfacen is supported by i.r. and NMR spectral evidence. The three peaks in the NMR spectrum at 3.87, 5.49, and 9.85 ppm (Table 2) are due to $-CH_2CH_2-$, =CH-, and -OH (hydrogen bonded). There is a strong peak in the i.r. spectrum at ~ 2700 cm⁻¹, which corresponds to hydrogen-bonded OH. There are no strong C=O peaks, which indicates that the ligand exists primarily in the enol form.

 H_2 hfacen is not very stable. In solution it is subject both to hydrolysis (to give the starting materials, Hhfa and en) and to cyclization to give 2; in air it spontaneously loses a mole of Hhfa to give 2 (Equation (2)). The success of the sublimation method for synthesis apparently lies in the fact that the system is sealed, allowing an equilibrium to be established between H_2 hfacen and cyclohfa-en. It may be noted that cyclization also occurs during the sublimation of Cu(hfa)₂. H_2 hfacen; the product is Cu(hfa)₂ cyclohfa-en.

The mass spectrum of H₂hfacen is practically identical to the spectrum of cyclohfa-en (see below), except the spectrum of H₂hfacen contains a medium peak at m/e = 208 (Hhfa). This shows that H₂hfacen decomposes to cyclohfa-en and Hhfa in the mass spectrometer, just as it does spontaneously in air (Equation (2)).



Cyclohfa-en, in which both carbonyl groups in Hhfa have condensed with ethylenediamine, was an entirely unexpected reaction product although the analogous compound with acetylacetone and ethylenediamine is known[11]. The structure 2 proposed for cyclohfa-en is consistent with the i.r., NMR, and mass spectra. There are no OH or C=O frequencies in the i.r. spectrum, while there are frequencies attributable to the NH, C=C, and C=N vibrations (Table 3). The NMR peaks at 3.79, 5.48 and 5.93 ppm are assigned to the $-CH_2CH_2$ -, =CH- and -NH- groups in 2. The other tautomeric form of 2 (the diimine) apparently does not exist in significant concentrations.

11. D. Lloyd and D. R. Marshall, J. chem. Soc. 2597 (1956) and references cited therein.

| | | | | | | , | | | | | |
|------------------------|----------------|---|----------------|-----------------|----------------|---------------|----------------|--------------------|----------------|--------------------|----------------|
| en∙2Hhfa* ð§ | Inten- sity | H₂hfacen* δ§ | Inten- sity | tfe-Hhfa* ð§ | Inten- sity | entfam* δ§ | Inten- sity | Cyclohfa-en⁺ δ§ | Inten- sity | Hhfa·2CH₃OH‡ δ§ | Inten- sity |
| 3.22 | 2.2 | 3.87 | 2.0 | 3-03 | - | 3.40 | 5·1 | 3.79 | 3-9 | 2.32 | 1.0 |
| 5.58 | 1.0 | 5.49 | 1.0 | 3.50 | F | 9.54** | 1.0 | 5.48 | Ŀ | 3.22 | 3.0 |
| 8-32** | 3-0 | 9.85 | l·1 | 5.50 | 1.0 | | | 5.93 | 1.0 | 5.83 | 1.0 |
| | | | | 8.15** | 3.8 | | | | | | |
| | | | | 9.48** | 1.0 | | | | | | |
| * Measure † Measure | d in (CE | 0 ₃),s0. Cl ₃ . | | | | | | | | | 1 |
| ‡Measure(| d in ben: | zene. | | | | | | | | | |
| §Parts per | million | downfield frc | om an int | ternal refere | ence of te | etramethyl | lsilane. | | | | |

Table 2. Nuclear magnetic resonance spectra

Frans per minuon Not measured. **Broad.

| Probable | | | | |
|-------------------|--------------------------|--|-----------------------|---------------|
| assignment | en·2Hhfa† | H ₂ hfacen† | tfe∙Hhfa | cyclohfa-en |
| | | | | |
| N-H str. | | 3250 w, sp‡ | 3250 m, sp | 3250 m, sp |
| | | | | |
| NH3+ | 3050 m | | 3000 m, br | |
| OH str. | | 2700 m, br | | |
| =CH- str. | | 3150 w | | 3100 m |
| | 1640 m | 1670 w | 1700 st | 1650 m |
| C==0, | 1600 m | 1640 w | 1655 m | 1575 st |
| C==N, | 1555 w | 1560 m | 1590 w | |
| C=C | 1525 w | 1550 m | 1555 st | |
| | | 1540 m | 1535 w | |
| | 1460 m | 1430 w | 1365 w | 1360 m |
| | 1330 w | 1350 w | 1330 w | 1340 m |
| | 1550 ₩ | 1330 m | 1305 w | 15 10 11 |
| | | | | |
| | 1250 st | 1295 m | 1290 w | 1295 st |
| | 1225 st | 1255 m | 1255 st | 1280 st |
| C—F | 1190 m | 1180 vst | 1215 st | 1250 st |
| | 1140 st | 1150 st | 1180 vst | 1210 st |
| | 1130 vst | 1130 st | 1140 st | 1190 vst |
| | | | 1115 st | 1140 Vst |
| | 1080 w | 1075 w | 1070 w | 1030 w |
| | 1010 w | 1025 vw‡ | 975 w | 1020 m |
| | 805 w | 980 w | 950 vw | 970 w |
| | 797 m | 940 w | 935 vw | 828 m |
| | 768 w | 830 w | 870 w | 795 m |
| | 735 w | 795 w | 810 m | 735 m |
| | | 790 m | 795 m | 688 m |
| | | 780 w | 765 w | |
| | | 755 vw | 738 w | |
| | | 735 w | 725 m | |
| | | 690 w | 690 w | |
| | 10.6. 2011 OF | | Out (hfter) | (hf-) |
| entiam | Hhfa-2CH ₃ OH | CuCl ₂ ·H ₂ hfacen | $Cu(nfa)_2$ | $Cu(nra)_2$. |
| | | | H ₂ nfacen | cyclonfa-en |
| 3330 m. sp | | | | 3400 m. sp |
| 3130 w | | | | - |
| | 3300 m | 3400 w, br | 3350 w, 3225 | w |
| | | 3150 w | 3100 w | |
| 1715 st | | 1650 m | 1655 m | 1680 m |
| 1715 SL 1575 m | | 1580 m | 1615 w | 1620 w |
| 137311 | | 1,500 III | 1590 w | 1560 m |
| | | | 1570 m | 1535 m |
| | | | 1540 m | |
| | | | 1.405 | 1.470 |
| 1360 w | 1460 m | 1480 m | 1495 m | 1470 m |
| 1320 w | 1255 m | 1360 w | 1465 m | 1450 m |
| | | 1330 m | 1420 W | 1330 W |
| | | | 1340 m | 1340 W |
| | | | | 1520 W |

Table 3. I.R. spectra in mineral oil mulls*

| 1245 m | 1255 m | 1295 m | 1290 m | 1290 m |
|----------------------------|--------------------------|---------------------------|---------|---------|
| 1180 vst | 1230 m | 1260 st | 1260 st | 1255 st |
| | 1165 vst | 1220 st | 1225 st | 1220 st |
| | 1100 st | 1200 vst | 1195 st | 1190 st |
| | | 1150 vst | 1160 st | 1145 st |
| | | | 1140 st | |
| 1040 w | 1050 m | 1110 w | 1090 w | 1110 m |
| 900 m | 1030 w | 1060 w | 1030 vw | 1095 m |
| 765 w | 960 m | 1025 w | 950 w | 1015 w |
| 710 m | 950 m | 915 vw | 805 m | 980 vw |
| 690 w | 875 m | 835 w | 765 w | 835 vw |
| | 765 w | 805 m | 742 w | 805 m |
| | 735 w | 745 w | 695 w | 800 m |
| | | 678 m | 670 m | 740 w |
| | | | | 725 w |
| | | | | 700 w |
| | | | | 690 w |
| | | | | 670 m |
| Cu(hfa) ₂ ·2tfe | Cu(hfa) ₂ ·en | Cu(hfa) ₂ ·2en | | |
| 3375 m. sp | 3450 m. sp | 3400 m. sp | | |
| 3250 w. sp | 3350 m. sp | 3300 m. sp | | |
| 3150 w, sp | 3200 w | 3225 m, sp | | |
| 1710 m | 1670 st | 1675 st | | |
| 1660 m | 1610 m | 1620 w | | |
| 1600 w | 1570 st | 1600 w | | |
| 1570 m | 1540 st | 1530 st | | |
| 1540 m | | 1520 st | | |
| 1480 m | 1490 vst | 1330 w | | |
| 1360 w | 1345 w | 1280 w | | |
| 1320 w | 1330 w | | | |
| 1260 st | 1260 vst | 1260 st | | |
| 1240 st | 1220 vst | 1200 st | | |
| 1190 vst | 1200 vst | 1150 st | | |
| 1155 st | 1150 vst | 1125 st | | |
| 1145 st | | | | |
| 1080 w | 1080 m | 1080 w | | |
| 1020 w | 1045 m | 1045 m | | |
| 880 w | 1015 m | 985 w | | |
| 815 w | 980 vw | 945 vw | | |
| 805 m | 945 vw | 795 w | | |
| 770 w | 874 w | 790 m | | |
| 745 w | 807 m | 765 w | | |
| 730 m | 800 st | 740 w | | |
| | 765 w | 730 w | | |

Table 3 (Contd.)

*Abbreviations: st, strong; m, medium; w, weak: v, very; sp, sharp; br, broad.

†Spectrum also obtained for a Fluorlube mull.

740 w

‡Probably due to cyclohfa-en impurity.

In the mass spectrum of cyclohfa-en, the parent peak (m/e = 232) was among the most prominent peaks. Other strong peaks were found at m/e = 204 $(CF_3 - C - CH = C - CF_3)$, 69 (CF₃), and 57 (= N CH₂ CH₂ NH--). \parallel NH

The structure of tfe·Hhfa (3) was deduced primarily from its NMR spectrum (Table 2), which not only has the correct peak areas, but also generally resembles a superposition of the spectra of en·2Hhfa and entfam. The peaks at 5.50, 8.15, and 9.48 ppm are due to the =CH-, NH₃⁺, and -NH-groupings. The -CH₂CH₂- region is complex, the peak at 3.03 ppm having three components, while the peak at 3.50 ppm has four. Part of the complexity may be due to long-range coupling with the CF₃ groups (see the discussion of the NMR spectrum of Hhfa·2CH₃OH, below).



Copper chelates with the formula Cu(hfacen) could not be made by the methods employed herein, although the adducts $CuCl_2 \cdot H_2hfacen$ and $Cu(hfa)_2 \cdot H_2hfacen$ were isolated. The structure of $Cu(hfa)_2 \cdot H_2hfacen$ is of special interest, since it seems unlikely that the Schiff base is acting as a tetradentate ligand. The tendency of $Cu(hfa)_2$ to become 5- and 6-coordinate is well-known[12], and it is probable that $H_2hfacen$ is bonded to the Cu ion through one or both of its nitrogens.

The compound $Cu(hfa)_2$ cyclohfa-en is also of interest. Judging from the color[11], the cyclohfa-en behaves at least as a monodentate ligand to give 5-coordinate copper. If cyclohfa-en functions as a bidentate chelating ligand, it should be a highly effective shielding group since in place of a single chelate ring there would be two fused chelate rings. However, Fisher-Hirshfelder models suggest that it would be difficult for both nitrogens to coordinate to the same copper ion.

Both $Cu(hfa)_2 \cdot H_2hfacen$ and $Cu(hfa)_2 \cdot cyclohfa-en$ sublime quantitatively (Fig. 1, curves 4 and 5). The slight break at ~120° on the curve for $Cu(hfa)_2 \cdot H_2hfacen$ is undoubtably due to cyclization of $H_2hfacen$ and loss of Hhfa, which occurs before the complex begins to volatilize appreciably. These adducts begin to sublime at higher temperatures than $Cu(hfa)_2 \cdot H_2O$, but $Cu(hfa)_2 \cdot H_2O$ undergoes some decomposition during sublimation (curve 1).

The mass spectra of $Cu(hfa)_2 \cdot H_2hfacen$ and $Cu(hfa)_2 \cdot cyclohfa-en$ are quite similar; neither contained significant peaks above m/e 477/479 [Cu(hfa)₂]. The 477/479 pair, along with peaks at 408/410 [Cu(hfa)(hfa-CF₃)], 339/341 [Cu(hfa-CF₃)₂], 201/203 [Cu(hfa-CF₃)], and 232 (cyclohfa-en) were among the strongest peaks above m/e 200 in both spectra. No peaks were found which might indicate a Cu—N linkage [e.g. Cu(cyclohfa-en), Cu(hfacen), Cu(H₂hfacen)]. The complete absence of a peak due to H₂hfacen in the spectrum of Cu(hfa)₂·H₂hfacen, and

12. e.g. see L. L. Funck and T. R. Ortolano, Inorg. Chem. 7, 567 (1968).

1904



Fig. 1. Thermogravimetric curves for some adducts of Cu(hfa)₂.

the similarity between the mass spectra of $Cu(hfa)_2 \cdot cyclohfa-en$ and $Cu(hfa)_2 \cdot H_2hfacen$, is apparently due to the previously observed fact that $Cu(hfa)_2 \cdot H_2hfacen$ is readily transformed to $Cu(hfa)_2 \cdot cyclohfa-en$ with the loss of Hhfa.

The ethylenediamine adducts of $Cu(hfa)_2$ were synthesized to examine the possibility of gas phase template synthesis (e.g., $Cu(hfa)_2 \cdot en \rightarrow Cu(hfacen) + 2H_2O$). Vacuum sublimation of $Cu(hfa)_2 \cdot en$ at 145° yielded a nonstoichiometric green sublimate (whose composition failed to become constant after repeated sublimations) and a violet residue, $Cu(hfa)_2 \cdot 2en$. $Cu(hfa)_2 \cdot 2en$ (which is better written as $[Cu(en)_2](hfa)_2$ in view of its violet color and the well-known preference of copper for nitrogen donors) sublimes with partial decomposition, and there is no evidence that template synthesis occurs. The thermogravimetric curves for these compounds are shown in Fig. 1, curves 2 and 3.

The compound, $Cu(hfa)_2$ ·2tfe, partially decomposes upon sublimation (Fig. 1, curve 6).

The reaction of hexafluoroacetylacetone with methanol is of interest, since it may be one of the reasons that template synthesis fails in solution. Methanol apparently adds across the carbonyl group to give 4, similar to the structures proposed for Hhfa·2H₂O[13] and Hhfa·HOCH₂CH₂OH[14]. The structure of the methanol solvate was deduced from i.r. and NMR spectral data. The C==O frequencies observed at 1680–1790 cm⁻¹ in Hhfa are absent in Hhfa·2CH₃OH (the highest frequency band, other than OH, is 1460 cm⁻¹). The ¹H NMR spectrum has peaks at 2·32, 3·22 (quartet, J = 1.55 Hz), and 5·93 ppm (structured), which correspond to the --CH₂--, -OCH₃, and OH protons in 4. The ¹⁹F NMR

13. B. G. Schultz and E. M. Larsen, J. Am. chem. Soc. 71, 3250 (1949).

14. K. Sata and K. Arakawa, J. chem. Soc. Japan 88, 470 (1967); Chem. Abstr. 68, 87283 (1968).

spectrum (in CFCl₃) has a structured peak 82.35 ppm upfield from CFCl₃. There thus seems to be long range coupling between the CF₃ and the OH and OCH₃ groups.



Acknowledgements – We thank Dr. John Fortman and Dr. Gordon Skinner for use of the X-ray diffraction equipment at Wright State University, Dr. Charles Springer for measuring the ¹⁹F NMR spectrum of Hhfa·2CH₃OH, and Dr. Ashley S. Hilton and Dr. Sue C. Cummings for helpfúl discussions of the work. We also thank Mr. G. Nicholson for obtaining the mass spectra.