0.25 in. copper column packed with 25% Kel-F No. 10 oil on 60–80 mesh Chromosorb P and a helium flow rate of 60 cc/min. Preparative separations were also performed at ambient temperatures with an 8 ft × 0.5 in. column containing 20% Kel-F No. 10 oil on 60–80 mesh Chromosorb P and a carrier gas flow of 200 cc/min. The molecular weights of volatile compounds were determined by gas density.

The CF_3CN and C_2F_5CN were purchased from Columbia Organic Chemicals Co. while the preparations of $CClF_2CN$[7] and $CF_2(CN)_2$[8] have been described in recent papers. The ClF was purchased from the Ozark-Mahoning Co.

The Reaction of ClF with CF_3CN.—Into the 150-cc cylinder were condensed successively 10 mmoles of CF_3CN and 20 mmoles of ClF. The vessel was then warmed from −196 to −78° and maintained at this temperature for approximately 10 hr after which it was allowed to warm gradually to 0°. The contents of the reactor were degassed at −78° and there remained 0.75 ml of light yellow liquid which was shown chromatographically to be better than 95% $C_2F_5NCl_2$ (estimated yield 75%). A sample purified by preparative chromatography, boiled at 44° (760 mm) (the literature reports 44°[1]), had a molecular weight of 206 (calcd 204), and an ultraviolet absorption maximum at 294 mμ (vapor phase). Its major gas phase infrared bands were located at 1348 (m), 1241 (vs), 1217 (s), 1158 (s), 1075 (vs), 968 (w), 842 (w), 780 (w), 719 (m), and 663 (w) cm^{-1}. The F^{19} nmr spectrum exhibited two peaks, one at +78.4 ppm (CF_3) and the other at +101.2 ppm (CF_2), the relative areas of which were in the ratio of 3.00:2.15.

An analogous experiment was performed using equal molar quantities of the reactants in the hope of preparing the known 1:1 addition compound, $CF_3CF{=}NCl$.[1] However, the resulting mixture was found to contain only $C_2F_5NCl_2$ and CF_3CN and traces of unreacted ClF.

The Reaction of ClF with C_2F_5CN.—Using the same procedure employed with CF_3CN, 10 mmoles of nitrile and 20 mmoles of ClF were allowed to react to produce, after degassing at −78°, 0.8 ml of light yellow liquid. Analysis by infrared and chromatography showed that, in addition to $C_3F_7NCl_2$, a small amount (5–10%) of an unidentified compound exhibiting an absorption band at 1613 cm^{-1} was also produced. Purification by preparative chromatography eliminated this impurity and yielded $C_3F_7NCl_2$ which boiled at 66.2° (757 mm), had a molecular weight of 246, 257 (calcd 254), and a vapor phase ultraviolet absorption maximum at 294 mμ, the estimated yield being 65%. Its nmr spectrum exhibited peaks at +82.4 ppm (CF_3), +97.7 ppm (α-CF_2), and +121.8 ppm (β-CF_2), the areas of which were in the ratio of 3.00:1.96:1.92. The gas phase infrared spectrum showed the following major peaks: 1348 (m), 1289 (w), 1250–1240 (vs), 1205 (s), 1143 (s), 1115 (s), 1035 (s), 990 (s), 968 (s), 833 (w), 767 (w), 735 (m), 709 (m), and 632 (w) cm^{-1}.

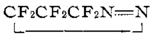
The Reaction of ClF with $CClF_2CN$.—This reaction was conducted in a like manner using 10 mmoles of $CClF_2CN$ and 20 mmoles of ClF. However, the resulting reaction mixture was allowed to remain at ambient temperature for 2 days. After degassing several times at −78°, 0.85 ml of liquid product remained in the reactor. The $CClF_2CF_2NCl_2$ was purified from several trace impurities by preparative gas chromatography, the estimated yield being 70%. The purified compound boiled at 85° (760 mm), had a molecular weight of 215 (calcd 220.5), and exhibited a vapor phase ultraviolet absorption maximum at 296 mμ. The F^{19} nmr spectrum showed peaks at +64.2 ppm ($CClF_2$) and +99.1 ppm (CF_2), the relative areas of which were in the ratio of 2:2.04. Its gas phase infrared spectrum showed major peaks at 1276 (m), 1198 (s), 1184 (s, sh), 1150 (s), 1102 (s), 988 (s), 943 (m), 830 (w), 752 (w), 720 (s), 672 (w), and 642 (w) cm^{-1}.

The Reaction of ClF with $CF_2(CN)_2$.—A 4-mmole sample of $CF_2(CN)_2$ and 16 mmoles of ClF were condensed successively into the reactor. After being held at −78° for 10 hr the reactor was allowed to warm slowly to room temperature and left at ambient temperature for 24 hr. After degassing at −78° to remove traces of $CF_2(CN)_2$, the product was transferred with pumping and heating to a glass system yielding 0.45 ml of high-boiling yellow liquid. Analytical chromatography on a 6 ft × 0.25 in. o.d. column packed with 20% Kel-F grease on 60–80 mesh Chromosorb P maintained at 70° showed only one significant component. Vacuum distillation produced a single fraction boiling at 77–78° (28 mm) with an ultraviolet absorption maximum at 298 mμ (CCl_4) and a molecular weight (cryoscopic in benzene) of 296 (calcd 320). Its infrared spectrum (liquid film) showed bands at 1290 (w), 1257 (m), 1191 (vs), 1148 (s), 1113 (m), 1088 (s), 968 (m), 948 (s), 935 (m), 834 (m), 818 (m), 749 (m), 712 (m), 677 (m), and 633 (m) cm^-. The F^{19} nmr spectrum exhibited peaks at +97.0 ppm (α-CF_2) and +112.7 ppm (β-CF_2), the relative areas of which were in the ratio of 4.10:2.

Thermal Decomposition of N,N-Dichloramines.—The pyrolytic reactions were conducted in a 150-cc Pyrex vessel equipped with a Fischer and Porter high-pressure needle valve. In each case approximately 0.25 ml of liquid compound was used and the resulting gaseous mixtures were analyzed chromatographically, the products being identified by their known infrared spectra. In all cases chlorine and an azo compound were the principal products, although traces of by-products (<5%) were detected in several cases.

TABLE I

CONDITIONS AND RESULTS OF THE PYROLYSIS OF FLUORINATED N,N-DICHLORAMINES

Reactant	Temp, °C	Duration hr	% reacted	Azo products
$CClF_2CF_2NCl_2$	110	20	0	. . .
$CClF_2CF_2NCl_2$	160 ± 10	63	45	$CClF_2CF_2N{=}NCF_2CClF_2$[3]
$CClF_2CF_2NCl_2$	200 ± 10	24	>95	$CClF_2CF_2N{=}NCF_2CClF_2$[3]
$C_3F_7NCl_2$	205 ± 5	20	85	$C_3F_7N{=}NC_3F_7$[1]
$C_2F_5NCl_2$	200 ± 10	30	90	$C_2F_5N{=}NC_2F_5$[4]
$NCl_2CF_2CF_2CF_2NCl_2$	200–215	63	>95	 $CF_2CF_2CF_2N{=}N$[3]

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[7] B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Am. Chem. Soc.*, **86**, 1827 (1964).

[8] B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *ibid.*, **85**, 1606 (1963).

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
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A Study of Bis(hexafluoroacetylacetonato)copper(II)[1]

BY J. A. BERTRAND AND ROY I. KAPLAN

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Although bis(hexafluoroacetylacetonato)copper(II) has been the subject of several studies,[2-4] there appears to be some confusion about the characterization

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[1] Supported by the Petroleum Research Fund of the American Chemical Society under Grant No. 1836-A1. Presented at the Southeast–Southwest Regional American Chemical Society Meeting, Memphis, Tenn., Dec. 1965.

[2] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

[3] J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

[4] M. L. Morris, R. W. Moshier, and R. E. Sievers, *ibid.*, **2**, 411 (1963).

of this substance. In the first published report[2] of this compound, the carbon and hydrogen analyses of the green, sublimed product checked for a dihydrate; however, no absorptions characteristic of water were present in the infrared spectrum and the substance was, thus, characterized as the anhydrous compound; in a later study,[3] analytical data for copper checked very well with the value expected for the anhydrous chelate.

In both studies,[2,3] the visible spectrum reported for this compound was considerably different from the spectra of chelates of copper(II) with other substituted acetylacetonates—not only in the position of absorption, which would be indicative of a different ligand field, different π bonding, etc., but a pronounced shoulder on the high-energy side of the visible band of all of the other chelates was not observed in the spectrum of the hexafluoroacetylacetonate.

A more recent study[4] of the infrared spectra of metal hexafluoroacetylacetonates reports absorption characteristic of water for the copper compound and characterizes the compound as a monohydrate; no analytical data were given.

In the course of preparing several copper chelates for further studies, we prepared the hexafluoroacetylacetone compound. Instead of purifying the initial product by sublimation, we first recrystallized it from methanol and then sublimed; the sublimed material was a mixture of green and blue crystals. Since previous studies indicate only a green sublimate, we have carried out further studies on the system.

Experimental Section

Preparation of Bis(hexafluoroacetylacetonato)diaquocopper(II).—Copper nitrate trihydrate (0.09 mole) was dissolved in water (200 ml); to this was added, with mixing, hexafluoroacetylacetone (0.18 mole) and sodium acetate (0.18 mole) in water (20 ml). The green needles which precipitated were filtered and dried in air; the product was further purified by sublimation; mp 134–136°.

Anal. Calcd for $CuC_{10}H_6F_{12}O_6$: C, 23.4; H, 1.17; Cu, 12.4. Found: C, 23.7; H, 1.01; Cu, 12.5.

Preparation of Bis(hexafluoroacetylacetonato)copper(II).—A portion of the dihydrate was placed in a vacuum desiccator over sulfuric acid; the color gradually changed from green to purple. The purple solid melted at 95–98°.

Anal. Calcd for $CuC_{10}H_2F_{12}O_4$: C, 25.1; H, 0.42; Cu, 13.4. Found: C, 23.7; H, 0.60; Cu, 13.4.

A sample of 1.081 g of the purple solid was exposed to the atmosphere until repeated weighings showed no further change in weight. The final weight, 1.158 g, indicated 6.64% water (calculated for the dihydrate, 7.01%).

Anal. Found (after hydration): C, 23.7; H, 1.09; Cu, 12.5.

Physical Measurements.—Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer. The spectra of the two compounds were identical with the reported spectrum of bis(hexafluoroacetylacetonato)copper(II) except for a band at 3430 cm^{-1} in the dihydrate spectrum.

Visible and near-infrared spectra were obtained using a Cary Model 14 spectrophotometer. Spectra of the two compounds in chloroform were identical with the spectrum previously reported. The spectra of the two compounds in carbon tetrachloride are shown in Figure 1.

Room temperature magnetic moments were obtained using a Gouy balance; values of 1.9 BM were obtained for both compounds.

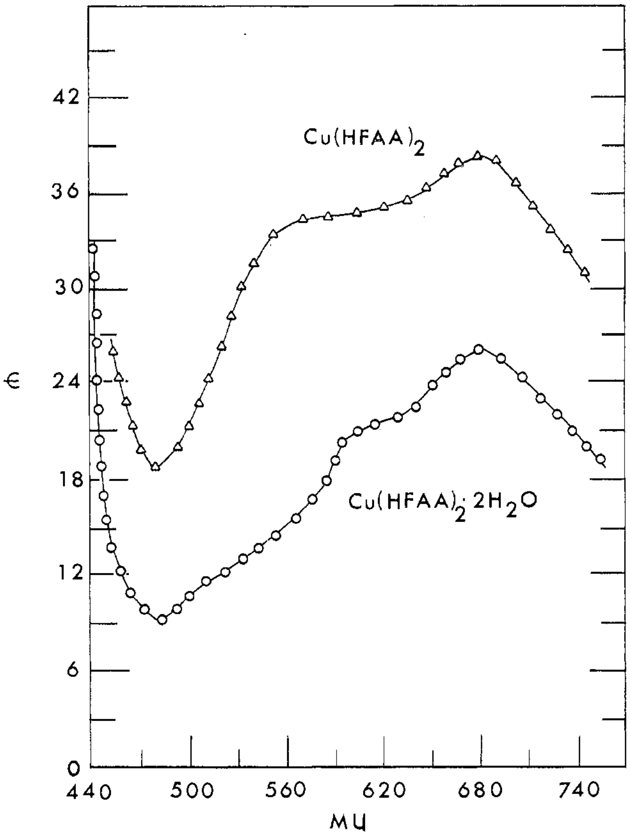

Figure 1.—Visible spectra of carbon tetrachloride solutions of bis(hexafluoroacetylacetonato)copper(II) and its dihydrate.

Molecular weights were obtained using a Mechrolab Model 301A vapor pressure osmometer; carbon tetrachloride was used as solvent. No concentration dependence was noted for any of the compounds; average values of 473 and 496 were obtained for the anhydrous material and the dihydrate, respectively.

Results and Discussion

The previously reported green solid[2,3] appears to be bis(hexafluoroacetylacetonato)diaquocopper(II); although the dihydrate sublimed unchanged, it is dehydrated over sulfuric acid under vacuum to the purple anhydrous material. These conclusions are supported by the analytical data and by infrared spectra of the two compounds which show absorptions characteristic of water in the spectrum of the green compound but not in the spectrum of the purple compound.

The stability of the dihydrate is surprising when compared to the tendency of other β-dicarbonyl chelates of copper(II) to form adducts. Although such adducts have been noted in solution[5] and a few have been isolated as solids,[6] the stability of square-planar copper(II) complexes causes a marked decrease in the tendency to form octahedral adducts as are common, for example, with cobalt(II) and nickel(II) β-dicarbonyl compounds. It has been noted[4] that the hexafluoroacetylacetonates of these metals form very stable hydrates whereas the acetylacetonates form hydrates which are readily dehydrated.

Both the anhydrous compound and the dihydrate

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(5) D. P. Graddon, *Nature*, **183**, 1610 (1959).

(6) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5399 (1963), and references cited therein.

were found to be monomeric and both exhibited normal magnetic moments. The visible spectrum of the anhydrous material in carbon tetrachloride, Figure 1, shows a well-separated shoulder on the high-energy side of the visible band; the spectrum of the dihydrate in the same solvent shows a less pronounced shoulder much closer to the main band. Since a well-separated shoulder is present on the high-energy side of the main band in the spectra of all other β-dicarbonyl complexes of copper(II), this shoulder probably results from further splitting of the d orbitals as the symmetry is decreased from octahedral to square-planar; such an assignment has been discussed for bis(acetylacetonato)-copper(II).[7] The position of this band, nearer the main band, in the dihydrate spectrum is probably due to a less pronounced tetragonal distortion and, thus, suggests that the waters are coordinated to the copper to give a distorted octahedron.

[7] T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

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Magnetic Circular Dichroism for Tetrachloroplatinate(II) Ion[1]

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Magnetic circular dichroism (MCD) has been observed for solutions of K_2PtCl_4 in dilute HCl which provides information relevant to the assignment of energy levels of the square-planar $PtCl_4^{-2}$ ion. The energy level scheme of this ion has recently been discussed on the basis of polarized single-crystal spectra recorded at 15°K.[2] The experimental arrangement for the determination of circular dichroism was described earlier.[3] Modifications have included: (1) a 30-fold electrical expansion of the recorder scale which does not appreciably alter the signal-to-noise ratio, (2) the replacement of the Jouan monochromator by an Applied Physics Corp. Model 15 monochromator, (3) the use of a 500-w xenon arc light source, (4) a change of the crystal modulation frequency in the dichrograph from 60 to 82 cps, (5) the use of an electromagnet to provide a magnetic field of 12,000 gauss in which the light beam travels from the south toward the north pole. A clockwise rotation for an observation toward the light source is called positive. Under these experimental conditions the MCD near 500 mμ for an aqueous cobalt(II) chloride solution is positive, in agreement with the normal convention and contrary to that employed by Schooley, *et al.*[4]

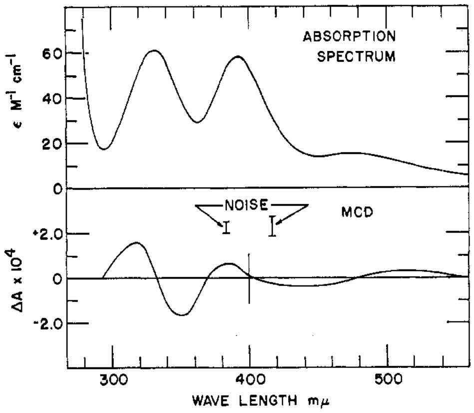

Figure 1.—Absorption spectrum and magnetic circular dichroism for a solution of K_2PtCl_4 in dilute aqueous HCl. Cell length = 1.00 cm; concentration of K_2PtCl_4 0.015 *M*.

The MCD for a solution of K_2PtCl_4 in dilute HCl is shown in Figure 1 together with a plot of its absorption spectrum. A reference trace was obtained with the light passing through the solution in the absence of a magnetic field. An MCD appears clearly to be associated with the absorption band having a maximum at 330 mμ. There is a distinct positive lobe at shorter wavelengths. The MCD trace crossed the reference at 332 mμ to give a negative lobe at longer wavelengths. The small positive lobe from 370 to 400 mμ is at most only slightly greater than the noise. Beyond 400 mμ, there was no deviation of the MCD from the reference line greater than the noise level. The MCD peaks correspond to a $\Delta A/A_{\max}$ of 1.5×10^{-4} where ΔA is the difference in absorbance between right- and left-handed light and $A_{\max}$ is the absorbance at the band maximum.

The MCD may arise from the Zeeman splitting of two transitions which possess different absorptions for the right- and left-handed light. If the transitions may each be represented by a Gaussian function whose central frequencies differ by the Zeeman splitting, 2δ, the amplitudes of the MCD lobes will be proportional to δ and inversely proportional to the width of the band.[3]

The two transitions may, in general, proceed from separate states differing by an energy $2\delta_g$ and initially filled according to a Boltzmann distribution and terminate in separate excited states differing by an energy, $2\delta_m$. Thus $\delta = \delta_m \pm \delta_g$. A least-squares method was utilized to fit the experimental MCD to separate values of δ_g and δ_m, based on the assumption that each of the two transitions is circularly polarized completely.[5] From the curve in Figure 1, the least-squares program gave splittings of 0.00 and 0.45 cm^{-1} for the ground and excited states, respectively.

The result, $\delta_g = 0$, is gratifyingly consistent with the

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[1] Work was performed in part in the Ames Laboratory of the Atomic Energy Commission and in part under support by a grant from the United States Public Health Service, Contribution No. 1801.

[2] D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, (1965).

[3] J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.*, **87**, 228 (1965).

[4] D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci.*, **53**, 579 (1965).

[5] J. G. Foss and M. E. McCarville, submitted for publication.