

Figure 3. Epr spectrum of $\text{Cu}(\text{OMPA})_3(\text{ClO}_4)_2$ at 297°K.

terested in whether these compounds would give epr spectra similar to those found for $\text{Cu}(\text{OMPA})_3(\text{ClO}_4)_2$. The 88°K spectra for the other organophosphorus chelates have the appearance of intermediate spectra of the type obtained for $\text{Cu}(\text{OMPA})_3(\text{ClO}_4)_2$ at higher temperatures (100–150°K). The spectrum of the latter compound does not become completely anisotropic until 95°K. The other organophosphorus chelates would require lowering the temperature to about 50°K to obtain completely anisotropic spectra.

Table II is a tabulation of g_{\parallel} and g_{\perp} for the tris chelates as determined from the experimental spectra

Table II. Epr Data for Tris Chelates

Compound	297°K	88°K	
	g	g_{\perp}	g_{\parallel}
$\text{Cu}(\text{OMPA})_3(\text{ClO}_4)_2$	2.25	2.08	2.52
$\text{Cu}(\text{NIPA})_3(\text{ClO}_4)_2$	2.26	2.17	2.42
$\text{Cu}(\text{PCP})_3(\text{ClO}_4)_2$	2.24	2.12	2.44
$\text{Cu}(\text{IPCP})_3(\text{ClO}_4)_2$	2.25	2.13	2.47

(see the introduction section for structures of ligands and abbreviations). The g values were calculated from the experimental spectra, since all except $\text{Cu}(\text{OMPA})_3$ -

$(\text{ClO}_4)_2$ give intermediate spectra at 88°K. The values of g_{\parallel} are among the highest known for Cu(II). The only other tris chelates of Cu(II) which have been investigated are dipyrindyl ($g_{\perp} = 2.046$, $g_{\parallel} = 2.268$),¹³ *o*-phenanthroline ($g_{\perp} = 2.064$, $g_{\parallel} = 2.273$),¹⁴ and a mixed complex $\text{Cu}(\text{hfacac})_2(\text{bipy})$, which has $g_{\perp} = 2.056$ and $g_{\parallel} = 2.299$.¹⁵

Another comparison of interest is that of epr data for bis chelates of Cu(II) with organophosphorus ligands. Table III contains g values for these systems. Figure 3

Table III. Epr Data for Bis Chelates at 297°K

Compound	g_{\parallel}	g_{\perp}
$\text{Cu}(\text{OMPA})_2(\text{ClO}_4)_2$	2.44	2.09
$\text{Cu}(\text{NIPA})_2(\text{ClO}_4)_2$	2.45	2.10
$\text{Cu}(\text{PCP})_2(\text{ClO}_4)_2$	2.50	2.08

is a typical anisotropic spectrum at 297°K for the compounds listed in Table III. The X-ray structure of $\text{Cu}(\text{OMPA})_2(\text{ClO}_4)_2$ has been reported.¹⁷ The Cu(II) ion is in a tetragonal environment with equatorial distances of 1.94 Å and an axial distance of 2.55 Å. For a known tetragonal system of OMPA an anisotropic spectrum is observed at 297°K. However, the g values are not very different from those given in Table II for tris chelates.

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A Study of Some Glycine and Leucine Peptide Complexes of Copper, Nickel, and Zinc

M. L. Bair¹ and Edwin M. Larsen*

Contribution from the Department of Chemistry,

University of Wisconsin, Madison, Wisconsin. Received December 4, 1969

Abstract: Some solid complexes of general composition $\text{M}(\text{HAA})^+$ for copper, nickel, and zinc and $\text{M}(\text{HAA})_2$ for nickel and zinc, with glycylglycine, glycyl-L-leucine, and L-leucylglycine, have been prepared. The magnetic susceptibilities over the temperature range 85–300°K indicate that the complexes are magnetically normal and the data are consistent with a coordination number six ligand environment. The infrared spectra of the solid-state and visible spectra of the solutions are consistent with the bonding of the peptide-amide nitrogen in the copper complexes, and the peptide-amide oxygen in the nickel (zinc) complexes.

There have been numerous reports in the literature on solution measurements of the interaction of copper(II), nickel(II), and zinc(II) ions with glycine,

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leucine, and their peptides; for example, see Bryce, *et al.*,² Martin, *et al.*,³ Grant and Hay,⁴ Nancollas, *et*

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al.,⁵ and Kim and Martell.^{6,7} However, few of the peptide complexes studied have been isolated in the solid state and analyzed, and except for those whose structures have been determined (glycylglycinatocopper(II)-3-water,⁸ glycylglycylglycinatocopper(II) chloride-1.5-water,⁹ and bisglycylglycinatozinc(II)-2-water¹⁰), the coordination and bonding are still a question for discussion.^{5,7} Here we present spectral and magnetic measurements on a number of new complexes, on the basis of which conclusions regarding the identity of the ligand atoms are made.

The following abbreviations of the amino acids and peptides are used for convenience: $\text{NH}_3^+\text{-CHR-COO}^-$, HG (R is H), HL (R is isobutyl); $\text{NH}_2\text{-CHR-COO}^-$, G⁻, L⁻; $\text{NH}_3^+\text{-CHR-CO-NH-CHR}'\text{-COO}^-$, H₂GG (R, R' are both H), H₂GL (R is H, R' is isobutyl), H₂LG (R is isobutyl, R' is H); $\text{NH}_2\text{-CHR-CO-NH-CHR}'\text{-COO}^-$, HGG⁻, etc.; $\text{NH}_2\text{-CHR-CO-N-CHR}'\text{-COO}^-$, GG²⁻, etc.; $\text{NH}_3^+\text{-CH}_2\text{-CO-NH-CH}_2\text{-CO-NH-CH}_2\text{-COO}^-$, H₃GGG; $\text{NH}_2\text{-CH}_2\text{-CO-NH-CH}_2\text{-CO-NH-CH}_2\text{-COO}^-$, H₂GGG⁻.

Experimental Section

Reagents. Copper(II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), nickel(II) chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), and zinc(II) chloride ($\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$) were all Baker reagent grade products. The amino acids were obtained from Nutritional Biochemical Co., the peptides from Mann Research Laboratories.

Preparations. In all of the following preparations, water is used as the solvent. As all the complexes except the leucines are very water soluble, it is important to use only the minimum amount of water necessary to dissolve the amino acid or peptide.

Glycinatocopper(II) Chloride-1-Water. A solution made from sodium hydroxide (40.00 mmol) and glycine (40.00 mmol) is mixed with an aqueous solution containing CuCl_2 (85.00 mmol). A blue-green solution results, from which any residue is removed by filtration. Ethanol is added to the filtrate and upon standing, a blue-green precipitate appears, which is filtered, rinsed with ethanol, and dried *in vacuo*. The yield is approximately 80%. *Anal.* Calcd for $\text{CuGCl} \cdot \text{H}_2\text{O}$: N, 7.33; Cu, 33.26. Found: N, 7.15; Cu, 32.88.

Glycylglycinatocopper(II) Chloride-1-Water. To an aqueous solution containing CuCl_2 (1.250 mmol) is added a solution of glycylglycine (1.000 mmol). The resulting blue-green solution is well mixed before adding ethanol. Upon standing, blue-green crystals are deposited which are collected, washed with ethanol, and dried *in vacuo*. A much higher yield (about 90%) is obtained if NaOH (0.900 mmol) is added to the glycylglycine. *Anal.* Calcd for $\text{Cu(HGG)Cl} \cdot \text{H}_2\text{O}$: O, 25.79; N, 11.28; Cl, 14.29; Cu, 25.60. Found: O, 26.20; N, 11.18; Cl, 14.27; Cu, 25.34.

L-Leucylglycinatocopper(II) Chloride-2-Water. To an aqueous solution containing CuCl_2 (1.700 mmol) is added a solution made by mixing H₂LG (1.600 mmol) and NaOH (1.500 mmol). The resulting blue-green solution is evaporated to dryness at room temperature, dissolved in a minimum of water (2-3 ml), and filtered to remove any residue. Ethanol is added to the filtrate and upon standing, a blue-green powder is deposited, which is filtered, rinsed with ethanol, and dried in air. The yield is 70%. *Anal.* Calcd for $\text{Cu(HLG)Cl} \cdot 2\text{H}_2\text{O}$: Cu, 19.72; N, 8.69;

C, 29.80; H, 5.27. Found: Cu, 19.78; N, 8.58; C, 29.41 H, 5.29.

Glycyl-L-leucinatocopper(II) Chloride. To an aqueous solution made from glycyl-L-leucine (3.000 mmol) and NaOH (2.500 mmol) is added a solution of CuCl_2 (3.400 mmol) in water. The resulting blue-green solution is evaporated to dryness, redissolved in a minimum amount of water (2-3 ml), and filtered to remove any residue. Ethanol is added to the filtrate and upon standing, a blue-green powder is deposited, which is collected, rinsed with ethanol, and dried in air. The yield is 80%. *Anal.* Calcd for Cu(HGL)Cl : Cu, 22.20; Cl, 12.39; N, 9.78; H, 5.25. Found: Cu, 22.07; Cl, 12.30; N, 9.80; H, 5.36.

Bis(L-leucylglycinato)nickel(II)-2.5-Water. A water solution containing NiCl_2 (0.9000 mmol) is added to a solution made from L-leucylglycine (1.800 mmol) and NaOH (1.800 mmol). The blue-green solution produced is evaporated to dryness, redissolved in a minimum amount of water, and filtered to remove any residue. The addition of ethanol to the filtrate produces a light blue precipitate, which is collected, rinsed with ethanol, and dried *in vacuo*. The yield is 60%. *Anal.* Calcd for $\text{Ni(HLG)}_2 \cdot 5\text{H}_2\text{O}$: Ni, 12.28; C, 40.16; H, 7.32; N, 11.70. Found: Ni, 12.36; C, 40.72; H, 7.62; N, 11.77.

Glycylglycinatonickel(II) Chloride-1.5-Water. An aqueous solution containing NiCl_2 (3.000 mmol) is added to a solution of glycylglycine (1.000 mmol). A green solution of a slightly different color than NiCl_2 is produced. Ethanol is added and upon standing for several days, a green precipitate is deposited. The precipitate is collected, rinsed with ethanol, and dried *in vacuo*. The yield is approximately 40%. *Anal.* Calcd for $\text{Ni(HGG)Cl} \cdot 1.5\text{H}_2\text{O}$: Cl, 14.09; N, 11.12. Found: Cl, 14.18; N, 11.33.

Glycylglycinatozinc(II) Chloride-0.5-Water. An aqueous solution made from glycylglycine (1.000 mmol) and NaOH (1.000 mmol) is added to a solution of ZnCl_2 (3.0 mmol) in water. The white residue produced upon mixing is removed by filtration and ethanol is added to the filtrate. Upon standing for several days, colorless platelets are deposited. The product is collected, rinsed with ethanol, and dried *in vacuo*. The yield is approximately 60%. *Anal.* Calcd for $\text{Zn(HGG)Cl} \cdot 0.5\text{H}_2\text{O}$: Cl, 14.70; N, 11.61. Found: Cl, 14.54; N, 11.52.

Bis(L-leucinato)zinc(II). To an aqueous solution prepared by mixing L-leucine (20.10 mmol) and sodium hydroxide (16.00 mmol) is added ZnCl_2 (80.00 mmol) in water. A white precipitate appears at once. The mixture is stirred for several hours, filtered, washed well with water, and then dried in air. The yield is quantitative. *Anal.* Calcd for ZnL_2 : N, 8.60; C, 44.21; H, 7.37. Found: N, 8.59; C, 44.15; H, 7.24.

The following compounds were prepared according to previously reported procedures.

cis-Bis(glycinato)copper(II)-1-Water.¹¹ *Anal.* Calcd for $\text{CuG}_2 \cdot \text{H}_2\text{O}$: Cu, 27.66. Found: Cu, 27.65.

trans-Bis(glycinato)nickel(II)-2-Water.¹² *Anal.* Calcd for $\text{NiG}_2 \cdot 2\text{H}_2\text{O}$: N, 11.53; C, 19.77; H, 4.94. Found: N, 11.60; C, 19.89; H, 4.98.

trans-Bis(glycinato)zinc(II)-1-Water.¹³ *Anal.* Calcd for $\text{ZnG}_2 \cdot \text{H}_2\text{O}$: N, 12.09; C, 20.73; H, 4.32. Found: N, 12.16; C, 20.59; H, 4.58.

Bis(L-leucinato)copper(II).¹⁴ *Anal.* Calcd for CuL_2 : Cu, 19.62; N, 8.65; C, 44.46; H, 7.41. Found: Cu, 19.62; N, 8.78; C, 44.23; H, 7.43.

Bis(L-leucinato)nickel(II)-2-Water.¹⁵ *Anal.* Calcd for $\text{NiL}_2 \cdot 2\text{H}_2\text{O}$: Ni, 16.65; N, 7.87; C, 40.60; H, 7.88. Found: Ni, 16.43; N, 7.79; C, 40.80; H, 7.93.

Bis(glycylglycinato)zinc(II)-2-Water.¹⁶ *Anal.* Calcd for $\text{Zn(HGG)}_2 \cdot 2\text{H}_2\text{O}$: C, 26.40; N, 15.40; O, 35.20; Zn, 17.98. Found: C, 26.34; N, 15.26; O, 35.01; Zn, 17.92.

Glycylglycinatocopper(II)-3-Water.¹⁷ *Anal.* Calcd for $\text{CuGG} \cdot 3\text{H}_2\text{O}$: Cu, 25.65; N, 11.31; C, 19.38; H, 4.85. Found: Cu, 25.54; N, 11.62; C, 20.16; H, 5.04. The copper analysis was

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Table I. Magnetic Data for Copper(II) and Nickel(II) Complexes

T, °K	$\chi_{M'} \times 10^6$					
	<i>cis</i> -CuG ₂ ·H ₂ O	CuGCl·H ₂ O	CuL ₂	Cu(HGG)Cl·H ₂ O	CuGG·3H ₂ O	Cu(HGL)Cl
85.8	4894	5360	5156			
86.0					4912	
87.8				4853		
91.2			4876		4667	4509
99.5	4278	4612		4302	4293	4111
116.1		3926	3886		3674	3521
133.0				3228		3060
149.3	2877	3048	3036		2884	2786
166.0				2610		2448
183.9						2268
201.6	2170	2283	2286	2164	2152	2052
219.7						1940
236.8				1852		1788
254.4	1750	1804	1856		1702	
272.4						
293.2				1524		
295.0						
295.8						
296.7					1462	1493
297.2						
298.2	1530			1519		
298.7						
299.2			1616		1452	
299.7		1553				
300.7						
μ_{eff}^b	1.81	1.92	1.86	1.84	1.83	1.83
θ	-1.8	-0.5	+0.6	+1.4	-1.2	+5.5
TIP (obsd) × 10 ⁶	152	9	175	101	58	103

^a The susceptibilities are corrected for diamagnetism (obtained from standard sources). ^b The magnetic moments are also corrected for

done by electrodeposition of a freshly prepared sample; the others were done by standard microtechniques. Presumably in the preparation of the latter samples, dehydration took place.

Glycylglycylglycinatocopper(II)-1.5-Water.⁹ *Anal.* Calcd for Cu(H₂GGG)Cl·1.5H₂O: Cu, 20.25; N, 13.34; Cl, 11.28. Found: Cu, 19.78; N, 13.32; Cl, 11.26.

Bis(glycylglycinato)nickel(II)-2-Water.¹⁷ *Anal.* Calcd for Ni(HGG)₂·2H₂O: C, 26.89; H, 5.04; N, 15.69. Found: C, 26.72; H, 5.18; N, 15.57.

Analytical Methods. Carbon, hydrogen, nitrogen, oxygen, zinc, and nickel were analyzed commercially.¹⁸ The copper analysis was done by electrodeposition. In the absence of chloride ion, standard methods were used; in the presence of chloride, the decomposition was done in HCl solution containing hydroxylamine.¹⁹

Spectra. Visible spectra were obtained using a Cary-14 recording spectrophotometer and a Beckman DB with a recorder. The spectra are of aqueous solutions made by dissolving the solid in doubly distilled water. The concentrations are of the range 1×10^{-2} – 2.5×10^{-2} M for the copper(II) and 2.5×10^{-2} – 4.5×10^{-2} M for the nickel(II) solutions. No adjustments were made in the pH, nor were any buffers added. Infrared spectra were run as mulls (halocarbon and Nujol) on a Beckman IR-10 using NaCl, KBr, and CsI plates and standardized with polystyrene.

Magnetic Measurements. A Gouy balance was used to determine the magnetic susceptibilities over the range of 85–300°K. The balance was equipped with a cryostat similar to that described by Figgis.²⁰ The field was produced by a Varian magnet (Model No. V-4004) using a 2-in. pole gap and was checked by means of a flip coil which varied with the amperage supplied to the magnet by a Varian power supply (Model No. V-2301-A). Mercury tetrathiocyanatocobaltate(II) was used to calibrate the tubes.²¹ The gram susceptibility at 20° was taken to be 17.44×10^{-6} cgs unit. Weight changes were measured at 4.4, 5.4, and 6.2 kg. Several

measurements were made at each temperature and at each field strength; corrections were made for the diamagnetism of the glass tube.

The method of calculation of the magnetic moments is based upon that of Benzie and Cooke.²² The temperature-independent paramagnetism (TIP, N_d) was determined by a least-squares fit of the data to the equation $\chi_{M'} = C_1/T + N_d$ ($\chi_{M'}$ is the susceptibility corrected for diamagnetism). Then, a least-squares fit of $\chi_{M''} = C_2/(T + \theta)$ ($\chi_{M''}$ is the susceptibility corrected for diamagnetism and TIP) gave θ , the Weiss constant. The magnetic moment was calculated from $\mu_{eff} = 2.828[\chi_{M''}(T + \theta)]^{1/2}$. Plots of $\chi_{M'}$ vs. $1/T$ and $1/\chi_{M''}$ vs. T gave straight lines, C_1 and C_2 are identical for the same compound, and the moments do not vary with temperature. The susceptibilities were not field dependent.

Results and Discussion

It is important to note that the solid-state peptide complexes of copper, nickel, and zinc prepared here have retained the peptide-amide proton upon coordination. All the complexes were recovered from solutions with a OH⁻/H₂AA ratio of 0.8 to 1.0, with the exception of Cu(HGG)Cl·H₂O and the corresponding nickel compounds, which were recovered from solutions of the dipeptide and metal salt alone. Because of their high solubility in water, the products were precipitated or crystallized from these solutions by the addition of ethanol. The compound Ni(HGL)₂ could not be isolated in the solid state. Thus the absorption spectrum reported is one of a solution prepared by mixing NiCl₂, H₂GL, and NaOH in the molar ratio 1:2.00:2.00, a procedure justified by the fact that the spectra of solutions of Ni(HLG)₂ prepared in this way and by dissolving the solid complex in water were identical.

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Cu(HLG)Cl· 2H ₂ O	Cu(H ₂ G ₂ GG)Cl· 1.5H ₂ O	<i>trans</i> -NiG ₂ · 2H ₂ O	$X_M' \times 10^6$ NiL ₂ ·2H ₂ O	Ni(HGG)Cl· 1.5H ₂ O	Ni(HGG) ₂ · 2H ₂ O	Ni(HLG) ₂ · 2.5H ₂ O
		14,193	14,425			
4771	4677			14,722	13,626	11,476
4320	4324	12,563	12,497	13,001	13,126	10,616
3769	3715	10,623	10,704		10,310	9,067
3285	3213			9,756		7,977
3000	2856	8,320	8,400		8,064	9,150
2673	2576			7,877		6,466
2438	2349				6,661	5,964
2252	2149	6,195	6,320	6,532		5,438
2035	1987				5,662	5,021
1942	1840					4,662
1793	1733	4,944	4,995	5,228	4,912	4,348
1691	1623				4,591	4,106
	1477					3,815
1526			4,321			
		4,283		4,527	4,341	
1.81	1.83	3.13	3.12	3.20	3.10	2.84
-1.9	+0.8	+0.5	-0.3	+1.3	+2.3	-0.1
146	55	228	246	252	356	394

TIP.

Magnetic Properties. In general, the magnetic moments and TIP values (Table I) of the nickel (II) complexes are consistent with a structure in which nickel(II) is surrounded by six ligand atoms in a somewhat distorted octahedral environment.²³⁻²⁵ In the case of Ni(HLG)·2.5H₂O, the spin-only magnetic moment indicates complete quenching of the orbital contribution and may reflect a ligand geometry with greater than normal distortion from octahedral symmetry.

The magnetic moments of the copper(II) complexes are consistent with structures in which the copper(II) is in a substantially distorted octahedral environment.^{21, 26, 27} Depending upon whether the fifth and sixth ligand atoms are considered to be outside bonding distances, the structures in some instances may be preferentially described as five-coordinate pyramidal or four-coordinate square planar. The large experimental values of the TIP for many of the copper compounds compared to the calculated values of $60 \pm 10 \times 10^{-6}$ cgs unit also suggest that the structures of these compounds deviate substantially from the *O_h* symmetry of the model.

The fact that the nickel(II) and copper(II) complexes have magnetic moments which are essentially independent of temperature and Weiss constants that are small rules out solid-state polymeric structures in which the magnetic dipoles interact with one another either directly or *via* chloride or carboxyl bridging ligands.

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Infrared Spectra. The assignments of the infrared spectra of the peptides and their complexes are based on those of Suzuki, *et al.*, Laulich, *et al.*, Condrate and Nakamoto, and Jackovitz and Walter for glycine,^{28, 29} leucine,³⁰ and their metal complexes,^{11, 30} and Miyazama, *et al.*, for secondary amides.³¹ Only absorptions (Table II) tentatively assigned to the ligand functions of the peptide are included. The complexity of the structures precludes any unambiguous empirical assignment, especially below 1400 cm⁻¹. The extensive hydrogen bonding of the peptides makes it difficult to rationalize frequency shifts upon metal coordination because of the accompanying changes in the extent and nature of the hydrogen bonding. Thus structural interpretations should be viewed as consistent with the assignments but not proved by them.

It is interesting to note that glycylglycine and L-leucylglycine show only the absorptions corresponding to the zwitterion structure, whereas glycyl-L-leucine and glycylglycylglycine show absorptions of nonionized -COOH as observed by Blout and Linsley³² for some dipeptides.

The potential ligand atoms of the coordinated peptide are the terminal NH₂ group, one or both oxygen atoms of the carboxyl group, and either the oxygen or

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Table II. Infrared Spectral Assignments^a of the Peptide and Peptide Complexes (cm⁻¹)

Assignments	H ₂ GG	H ₂ LG	H ₂ GL	H ₃ GGG	CuGG·3H ₂ O	Cu(HGG)Cl·H ₂ O
$\nu(\text{NH})$ amide	3280 s	3350 m	3270 sh ^b 3420 m ^b	3300 s ^b 3260 sh ^b		3160 sh ^d 3110 sh ^d
$\nu(\text{NH}_2)$				3110 sh	3340 s 3300 s 3280 s 3200 s	3330 m 3300 m 3260 m 3220 sh
$\nu_{\text{as}}(\text{NH}_3^+)$	3000 s	3140 w		3040 m		
$\nu_{\text{s}}(\text{NH}_3^+)$	2620 w	2520 w		2680 w		
$\nu(\text{COOH})$			1690 m	1708 sh		
Amide I	1670 sh 1653 s	1658 sh	1675 sh	1676 sh 1645 s	1600– 1550 s,b	1643 sh
$\delta_{\text{d}}(\text{NH}_3^+)$	1628 s	1628 s		1625 sh		
$\delta(\text{NH}_2)$			1622 m	1622 m	1600– 1550 s,b	1608 s
$\nu_{\text{as}}(\text{COO}^-)$	1602 s	1596 s		1582 sh	1600– 1550 s,b	1588 s
Amide II	1573 s	1556 w	1550 sh	1550 s	1442 m	1576 sh 1552 sh
$\delta_{\text{s}}(\text{NH}_3^+)$	1543 sh 1523 s	1515 m		1521 sh		
$\nu(\text{CO}) + \nu(\text{OH})$			1409 w 1259 w	1413 m 1269 w		
$\nu_{\text{s}}(\text{COO}^-)$	1402 s	1402 sh		1413 m	1393 m	1403 s

^a The following abbreviations are used: s, strong; m, medium; w, weak; b, broad; and sh, shoulder; and mode: ν , stretch and δ ,

nitrogen of the peptide group. Additional ligands are the oxygen of water and the chloride ion when present. The generally strong-to-medium absorptions of the N–H stretching mode³³ in the 3000-cm⁻¹ region and the appearance of a generally strong absorption around 1610 cm⁻¹ assigned to the NH₂ deformation, coupled with the disappearance of the bands associated with the zwitterion structure, all are in agreement with the expectation that the terminal NH₂ group of the peptide occupies one of the ligand sites of the metal. This is true for all the complexes examined.

The carboxyl group of di- and tripeptide complexes is generally coordinated,³⁴ an exception being dimeric Zn(HGG)₂·2H₂O, in which both free carboxyl and mono-coordinated carboxyl are present.¹⁰ The mode of the carboxyl bonding may vary among ionic, bonding of one oxygen atom to one metal atom, each oxygen atom to one metal atom, or both oxygen atoms to the same metal atom. Since the early suggestion of Nakamoto³⁵ that the mode of bonding and the shift in frequencies of the asymmetric and symmetric modes of the carboxylate might be used to distinguish monodentate carboxylate bonding from the others, many authors^{36–40} have tried to improve and extend this concept. Edwards and Hayward⁴¹ question the reliability of this generalization, contending that the symmetry of the free ion is so low that no difference in the infrared spectra would be expected for the different types of coordination. In any event, the zinc and nickel compounds prepared here have $\Delta\nu$'s in the range 190–197

cm⁻¹, from which we may conclude that the carboxyl bonding is similar in these cases and probably monocoordinated as in Zn(HGG)₂·2H₂O and Cu(H₂GGG)Cl·1.5H₂O. The uncertainty of such a conclusion is pointed up by the fact that the solid-state structure¹⁰ of Zn(HGG)₂·2H₂O also contains free COO⁻ which is not seen in the infrared spectrum. Hydrogen bonding with the free carboxyl may account for this.

In the case of the series of copper salts, Cu(HLG)Cl·2H₂O, Cu(HGG)Cl·H₂O, and Cu(HGL)Cl, the $\Delta\nu$'s change in the order 167, 185, 203, indicating a substantial change in the nature of the carboxylate bonding. In the two copper compounds for which the structures are known,³⁴ CuGG·3H₂O and Cu(HGGG)Cl·1.5H₂O, the carboxyl groups are monocoordinated, or in the latter case, "bidentate" with one very long M–O distance of 2.82 Å. In the latter case, $\Delta\nu$ is 197 cm⁻¹, similar to that for the zinc and nickel compounds, and we might conclude that the infrared cannot distinguish between mono and "bidentate" carboxylate with one long M–O bond. Comparable data for the CuGG species are not available owing to lack of resolution of the bands in the 1600-cm⁻¹ region. We might also conclude that if there is symmetrical bidentate coordination of the carboxyl group in any case, it will be in Cu(HLG)Cl·2H₂O which has a $\Delta\nu$ of 167. Anhydrous Cu(HGL)Cl, which requires the coordination of both oxygen atoms of the carboxyl group to achieve coordination number five about a copper, shows the largest $\Delta\nu$, 203 cm⁻¹, and presumably the greatest dissymmetry in the carboxyl oxygen–metal bonding.

The bands due to water are not included in Table II, but their presence is an obvious feature of each spectrum except for that of Cu(HGL)Cl, which, in agreement with the analytical data, showed the absence of water. On the basis of the structures which are known for the peptide–metal complexes,³⁴ it seems safe to assume that at least one molecule of water of the hydrated species is coordinated to the metal ion. Similarly, although our

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Cu(HGL)Cl	Cu(HLG)Cl· 2H ₂ O	Cu(H ₂ G ₂ GG)Cl· 1.5H ₂ O	Ni(HGG)Cl· 1.5H ₂ O	Zn(HGG)Cl· 0.5H ₂ O	Ni(HGG) ₂ · 2H ₂ O	Zn(HGG) ₂ · 2H ₂ O	Ni(HLG) ₂ · 2.5H ₂ O
3070 m	3090 m						
3310 m 3240 m	3230 m	3300 sh ^c 3240 s ^c	3360 s ^c 3280 m ^c	3320 s ^c	3350 m ^c 3290 sh ^c 3240 m ^c	3340 m ^c 3330 s ^c	3320 m ^c 3270 m ^c 3240 m ^c
1628 s	1631 sh 1623 sh	1684 (?) 1642 sh	1640 s	1650 s	1651 sh	1658 s 1642 s	1600 s,b
1617 sh	1613 s	1622 s	1618 sh 1601 s	1618 w	1631 s	1620 sh	1600 s,b
1592 s	1580 m	1584 s	1591 s	1592 sh	1602 s	1594 s	1600 s,b
1570 sh	1561 sh 1541 sh	1554 sh	1579 s	1576 s	1576 m	1566 s	1600 s,b
1389 s	1413 m	1387 m	1401 m	1400 m	1405 m	1402 m	1384 m

deformation. ^b Contains a contribution from $\nu(\text{NH}_2)$. ^c Is mixed with $\nu(\text{NH})$ amide. ^d Is mixed with $\nu(\text{H}_2\text{O})$.

infrared data do not extend into the region for M-Cl absorptions, it is reasonable to assume that chloride, when present, also occupies a coordination site.

The changes in the amide I band frequency upon coordination has been variously interpreted, and the amide II band does not seem to be very sensitive to coordination. Infrared spectra of D₂O solutions of the copper(II) complexes with glycylglycine^{6,42} have led to the assignment of the absorption bands at 1670 and 1625 cm⁻¹ to the amide I band of the uncoordinated peptide and the amide I band of the coordinated protonated nitrogen. At pD values of 5.5 and higher only a new band at 1610 cm⁻¹ was observed which was assigned to the amide I band with the deprotonated nitrogen coordinated to the copper. On the other hand, the amide I absorptions of the peptides used in this study fall in the range 1653-1675 cm⁻¹, and decrease in the M(HAA)⁺ copper complexes to 1623-1628 cm⁻¹, consistent with the observations of Martell. In contrast, the zinc and nickel complexes show amide I absorptions in the 1640-1650-cm⁻¹ range. It is clear that the nature of the metal-amide bonding is different in the copper complexes than in the nickel and zinc complexes. Infrared spectra⁴³ of D₂O solutions of 1:1 nickel(II) glycylglycine are similar to those of the ligand alone until a very high pD is reached, indicating weak interaction until the peptide nitrogen is deprotonated. This observation is in agreement with Freeman's data.⁴⁴ Thus in the solid state, the evidence is that the copper complexes are bound through the amide nitrogen, while on the basis of the known structure of Zn(HGG)₂·2H₂O, the zinc and nickel complexes are bound through the amide oxygen. The suggestion that the protonated amide nitrogen is coordinated in the Cu(HAA)⁺ complexes raises problems regarding the

planarity of the chelate ring, the trigonal hybridization of the nitrogen, and the resonance in the peptide bond.^{34,45} It may just be that the ubiquitous proton of the complexes studied here is not bound to the amide nitrogen, but rather to the amide oxygen, as in Co(HGG)₂⁺.⁴⁶ Thus the amide nitrogen would be available for metal bonding by transferring the proton to the oxygen. The Co(HGG)₂⁺ ion is obtained by acidification of solutions containing Co(GG)₂⁻ ions,⁴⁷⁻⁵⁰ while our products are obtained by ethanol precipitation, but the possibility of structural similarities need not be ruled out because of the differences in preparative conditions. More significant is the large shift in the amide I absorption⁴⁶ in the cobalt complex to 1700 cm⁻¹, which is not matched in the copper complexes studied here. Protonation of oxygen has also been observed in nmr studies of protonation of (glycinamidato)tetraamminecobalt(II),⁵¹ so this is not an isolated example of this phenomenon. It might also be well to consider the assertion that dipeptides in aqueous solution exist as cis-trans isomers.⁵² In any event, a single-crystal study of Cu(HGG) Cl·H₂O should be done if suitable crystals can be grown.

Visible Spectra. On occasion arguments have been put forth for the retention of the solid-state configuration of the peptide complexes in aqueous solution. However, there seems to be no evidence that these species are kinetically inert in solution. Therefore, dissolution of the solid in water should yield equilibrium

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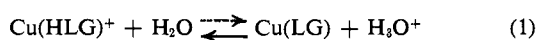
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Table III. Absorption Maxima (kK) and Absorptivity (ϵ) for Copper(II) and Nickel(II) Complexes

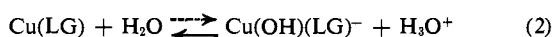
Complex	$\nu(\epsilon)$	Complex	$\nu_1(\epsilon)$	$\nu_2(\epsilon)$	$\nu_3(\epsilon)$
CuG ⁺	14.05 (27.5)				
<i>cis</i> -CuG ₂	15.90 (43.2)	<i>trans</i> -NiG ₂	9.85 (7.05) 8.70 sh 10.50 sh	16.20 (5.07) 13.30 sh	27.20 (9.45)
CuGG	15.68 (81.0)				
CuHGG ⁺	15.40 (35.7)	NiHGG ⁺	9.52 (5.66) 8.77 sh 10.50 sh	15.50 (4.06) 13.60 sh	26.00 (8.20)
		Ni(HGG) ₂	9.83 (7.07) 8.85 sh	16.00 (5.64)	26.50 (10.15)
CuHLG ⁺	15.60 (45.5)	Ni(HLG) ₂	9.94 (9.00) 8.77 sh 10.60 sh	15.90 (7.05) 13.70 sh	26.50 (12.0)
CuHGL ⁺	15.40 (38.8)	Ni(HGL) ₂	9.80 (7.84)	15.90 (6.42)	26.50 (11.4)
CuH ₂ G ₃ GG ⁺	14.60 (34.6)				
Cu(L) ₂ ^a	16.00 17.80 sh	Ni(L) ₂ ^b			
Cu(OH ₂) ₆ ²⁺	12.60 ^c	Ni(OH ₂) ₆ ²⁺	8.50 ^e		
Cu(OH ₂) ₄ (en) ²⁺	15.34 ^d	Ni(OH ₂) ₄ (en) ²⁺	9.80 ^b		
Cu(OH ₂) ₂ (en) ₂ ²⁺	18.20 ^d	Ni(OH ₂) ₄ (en) ₂ ²⁺	10.50 ^b		
		Ni(en) ₃ ²⁺	11.20 ^e		
Cu(DA) ₂ (NO ₃) ₂ ⁱ	13.37 ^{e,k}	Ni(DA) ₃ (ClO ₄) ₂	9.00 ^{i,j}		
Cu(phthalate) ₂ ²⁻	14.50 ^f	Ni(NTA)(OH ₂) ₂ ⁻	9.50 ^{b,k}		

^a ϵ could not be determined, as the complex was only sparingly soluble in water. ^b Complex was insoluble in water. ^c See ref 27. ^d G. Gordon and R. K. Birdwhistell, *J. Amer. Chem. Soc.*, **81**, 3567 (1959). ^e A mull: P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem.*, **28**, 1125 (1966). ^f D. P. Graddon, *ibid.*, **7**, 75 (1958). ^g O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957). ^h C. K. Jørgensen, *ibid.*, **10**, 887 (1956). ⁱ In acetone solution: C. S. Kraihanzel and S. C. Grenda, *Inorg. Chem.*, **4**, 1037 (1965). ^j DA stands for diacetamide. ^k NTA stands for nitrilotriacetato.

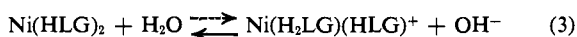
concentrations of all the species compatible with the equilibrium constants for all possible reactions.^{5,6} The lability of the complexes was tested by dissolving samples of Cu(HLG)Cl and Ni(HLG)₂ in water and measuring the pH of the resulting solutions. One-hundredth molar solutions of these complexes gave pH's of 4.6 and 8.4, respectively, consistent with the reactions



and



and in the nickel case



The pH value for the copper system is in the region calculated on the basis of the equilibrium constants for the glycylglycine system.⁵⁻⁷ It seems reasonable to conclude that the carboxyl group in the copper complex is bonded to the metal and thus does not accept the proton. Similarly we conclude that the carboxyl group of the nickel complex is not coordinated to the metal, and that water has taken its place in the coordination sphere. The dipeptides are weak acids ($\text{p}K_{\text{ion}} \sim 8$) and therefore protonated in aqueous solution when the terminal NH₂ is coordinated.

Equilibrium constant data show that dissolution of Cu(HGG)⁺ and Ni(HGG)₂^{4,3} compounds yields major species of the same composition (not necessarily the same coordination), but that Ni(HGG)⁺ is unstable with respect to the reaction



Other species will be present, but these are the most im-

portant contributors to the absorption spectra. It is assumed that the other dipeptides would behave similarly.

By application of the "average environment rule,"⁵³⁻⁵⁵ some information about the identity of the ligand atoms may be obtained from the visible absorption spectra. For a complex containing mixed-ligand groups that are not too far separated in the spectrochemical series, it is possible, within limits, to calculate the prorated contributions of each ligand, δ_l , to the ligand-field separation, Δ . The nickel complexes have less than *O_h* symmetry but as there are no splittings of the peaks, the spectra can be interpreted in terms of an octahedral-type field, and the shoulders assigned to spin forbidden transitions.⁵⁶ For octahedral nickel(II) complexes, three spin-allowed transitions are expected: ³A_{2g}-³T_{2g}, ⁻³T_{1g}(F), ⁻³T_{1g}(P), the energy of the first being taken as Δ . Now by using the Δ_{obsd} (Table III) from the spectrum and the δ_l values (Table IV) of the known coordinating groups (as calculated from similar complexes), the δ_x for an unknown ligand can be determined and the group identified by comparison with other δ_l values.

Previous work^{7,43} on the coordination of nickel(II) with glycine peptides at various pH's by means of visible, infrared, and proton nmr has led to the conclusion that nickel is only weakly coordinated to glycylglycine in a tridentate conformation, except at high pH's, where Ni(GG) is formed. Other workers^{17,37} have concluded

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Table IV. δ Values for Ligands in Copper(II) and Nickel(II) Complexes

Complex	Cu-L distances, Å, in d_{xy} plane		δ_x , calcd ^a		Complex	δ_x , calcd ^a	
	Ligand		Ligand	kK		Ligand	kK
Cu(OH ₂) ₆ ²⁺	O	1.97 ^b	H ₂ O	2.23	Ni(OH ₂) ₆ ²⁺	H ₂ O	1.42
Cu(OH ₂) ₄ en ²⁺	N	2.00 ^c	H ₂ N	3.61	Ni(OH ₂) ₄ (en)	H ₂ N	2.06
Cu(OH ₂) ₂ (en) ₂ ²⁺	N	2.00 ^c	H ₂ N	3.64	Ni(OH ₂) ₂ (en) ₂	H ₂ N	1.92
cis-CuG ₂	N ^{d,e}	2.00			Ni(en) ₃ ²⁺	H ₂ N	1.87
	O	1.95	COO ⁻	2.51	trans-NiG ₂	COO ⁻	1.54
CuGG	H ₂ N ^{d,f}	2.03					
	N ⁻	1.88	N ⁻	3.76			
	COO ⁻	1.98					
	H ₂ O	1.97					
CuG ⁺	N ^g	2.00	H ₂ N'	3.42 ^g	Ni(NH ₂ -CH ₂)(OH ₂) ₆ ²⁺	H ₂ N	2.08 ^h
	O ^e	1.95					
Cu(phthalate) ₂ ²⁻	O	1.97	CO	2.70	Ni(NTA)(OH ₂) ₂ ⁻	(-CH ₂) ₃ N	2.04
Cu(DA) ₂ (NO ₃) ₂	O	1.97	CO	2.43	Ni(DA) ₃ (ClO ₄) ₂	CO	1.50

^a δ_x values for copper complexes contain an approximate error of ± 30 and for nickel complexes of ± 10 , as this was the experimental error in determining ν_{\max} . ^b See ref 30. ^c As there are no X-ray data available for complexes with the above formulas, the values of the copper-nitrogen bond distances were arrived at by averaging various data for known complexes as Cu(en)₂(NO₃)₂: Y. Komiyama and E. C. Lingafer, *Acta Crystallogr.*, **17**, 1145 (1964). ^d δ_{NH_2} value of 3.61 was used. ^e See ref 31. ^f See ref 8. ^g This δ value is for a complex with only one NH₂ group. ^h The variation in δ_{obsd} for the three en complexes led to the calculation of the hypothetical complex Ni(NH₂-CH₂)(H₂O)₅²⁺. The variation in δ for the three en complexes is attributed to cis and trans interactions which were determined to be 20 and 120 cm⁻¹, respectively. Whenever a nitrogen had another nitrogen cis and/or trans to itself, the above values were subtracted from 2.08 cm⁻¹.

that in Ni(HGG)₂ the coordination is bidentate through the terminal NH₂ group and peptide oxygen.

The hydrolysis experiments indicated that the carboxyl groups were not bonded, and therefore that the dipeptide was, at the most, bidentate in solution. We can then assume that the coordination sphere consists of two terminal NH₂ groups, either cis or trans, two water molecules, and either the oxygen or nitrogen of the peptide bond (or two additional waters if the dipeptide should be monodentate). The δ_x 's calculated (using the data in Table IV) for the two unknown ligand positions are 1.44 and 1.54 for the cis and trans isomers, respectively. Clearly, the remaining ligand atoms are oxygens, and if the peptide-amide group is bound it is *via* the oxygen atom. Although no distinction can be made between a pair of monodentate cis dipeptides and a pair of trans bidentate dipeptides, the latter case seems most reasonable. The ν_{\max} 's for solutions of Ni(HGL)₂ and Ni(HLG)₂ are very similar to that for Ni(HGG)₂, so the conclusions regarding the nature of the ligands which are bound are the same for all three dipeptides. From the ν_{\max} values one can conclude that an isobutyl group adjacent to the carboxyl group has little or a slightly negative effect on the ligand-field strength, but when adjacent to the terminal amino group, the isobutyl group has an enhancing effect. This is consistent with the findings in the copper system. Since Ni(HGG)⁺ makes up only at the most 20% of the nickel species in a 0.01 M aqueous solution, analysis of its spectrum is not reliable.

The spectra of the copper(II) complexes investigated here consist of only one broad band (Table III), as found in many copper(II) complexes. There has been considerable discussion⁵³⁻⁶² about the analysis of the broad, often asymmetric, peak, and it is generally concluded that the envelope contains several bands due to

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transitions between the lowest lying ²B_{1g} and the higher lying ²A_{1g}, ²B_{2g}, and ²E_g terms resulting from the splitting of the ²E_g and ²T_{2g} levels in a strong tetragonally distorted field. Regardless of the assignment of the transitions (providing the perturbation in the z direction remains constant), an increase in the perturbing effect of the ligand in the xy direction leads to an increase in the energy of the band maximum compared to Cu(OH₂)₆²⁺. Even though the copper species represent rather severe distortions from O_h symmetry, we have found that additive δ_1 values can be obtained for a ligand in compounds where the crystallographic data are available. The assumptions made are that the average Cu-O distance in the z direction is constant and the same as in CuSO₄·5H₂O, namely 2.40 Å.⁶³ It is also assumed that δ_1 is inversely proportional to the distance of separation, as would be expected for a simple electrostatic model, and that the bond distances in the solid state and in solution are the same. Certainly this approach applies only to those species which have large enough stability constants to preserve the solid-state coordination in solution. Thus, $\delta_{\text{H}_2\text{O}}$ is obtained from the following expression: $12.6 \text{ kK} (\Delta_{\text{H}_2\text{O}}) = 4\delta_{\text{H}_2\text{O}} + (1.97/2.40)\delta_{\text{H}_2\text{O}}$, or $\delta_{\text{H}_2\text{O}} = 2.23 \text{ kK}$. This technique was found to give a good internal check for Cu(II)-ethylenediamine and -ammonia complexes. The δ_1 values reported in Table IV are for the ligand noted at the distance tabulated. As in the case of the nickel(II) complexes, the δ_1 values vary with the type of ligand, the strength of bonding, and the environment. If the environments are properly matched and the bond distances adjusted, the δ_x values can be used to identify the nature of the ligand atoms.

The determination of the ligand environment about Cu(HGG)⁺ is illustrated with the following data. In aqueous solution the complex can be either tridentate (a) or bidentate (b), with the other positions occupied by water molecules. For the calculations, the δ_1 values used were $\delta_{\text{NH}_2} = 3.42$ (selected in the event the unknown ligand atom is oxygen), $\delta_{\text{COO}^-} = 2.51$, and $\delta_{\text{H}_2\text{O}} = 2.23$. The d_{xy} bonding distances for CuGG

(63) C. A. Beevers and H. Lipson, *Proc. Roy. Soc., Ser. A*, **146**, 570 (1934).

were used. For conformation a, δ_x is 3.67; for b, δ_x is 3.92. Values of this magnitude are only consistent with coordination through the peptide nitrogen. With the knowledge that the unknown ligand is a cis nitrogen atom, a better calculation can be made using δ_{NH_2} from $\text{Cu(en)(OH}_2)_4^{2+}$, which gives a δ_x of 3.50 for conformation a and 3.73 for conformation b. It is doubtful whether these values can distinguish between the tridentate and bidentate cases, but they certainly do identify the bound peptide-amide ligand as nitrogen.

Since CuHGL^+ has the same absorption maximum as CuHGG^+ , and CuHLG^+ differs only slightly, the same calculations and conclusions hold. As noted for the nickel complexes, presence of the isobutyl group α to both coordinating nitrogens increases the ligand-field effect. This is also noted in CuG_2 and CuL_2 , where the ν values are 15,900 and 16,000 cm^{-1} , respectively. It is also concluded that coordination of CuL_2 in aqueous solution is the same as in CuG_2 (2NH_2 , 2COO^- , and $2\text{H}_2\text{O}$).

CuH_2GGG^+ in the solid state is known to consist of

infinite copper-peptide chains⁹ of a "six"-coordinate structure involving the terminal NH_2 and peptide oxygen of one peptide, the COO^- terminal of another peptide, Cl^- , and water. The complex dissolves slowly in water and is assumed to form a six-coordinate species in which waters occupy the nonpeptide-ligand positions. Two questions again arise: namely, is the ligand tridentate or bidentate in solution and is the peptide oxygen or peptide nitrogen bound to the metal? The first question cannot be answered unambiguously. In answer to the second, it seems that the peptide oxygen remains bound, since when δ_{OH_2} or δ_{COO^-} was used to calculate δ_x , values of 3060 and 2930, respectively, were obtained, which are consistent with an oxygen atom coordination.

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Hexafluoroacetylacetone and Hexafluoroacetic Anhydride

A. L. Andreassen, D. Zebelman, and S. H. Bauer*

*Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850. Received August 8, 1970*

Abstract: The molecular geometries of a pair of isoelectronic molecules have been determined by gas-phase electron diffraction. Hexafluoroacetylacetone, which exists as the enol tautomer, was found to have a planar symmetric ring with the following r_g values: $\text{C}_1\text{-C}_2 = 1.407 \pm 0.031 \text{ \AA}$, $\text{C}_2\text{-C}_4 = 1.546 \pm 0.008 \text{ \AA}$, $\text{C-O} = 1.259 \pm 0.018 \text{ \AA}$, $\text{C-F} = 1.337 \pm 0.007 \text{ \AA}$, $\angle \text{C}_2\text{C}_1\text{C}_3 = 115.2 \pm 2.3^\circ$, $\angle \text{C}_1\text{C}_2\text{O}_2 = 126.4 \pm 1.3^\circ$, $\angle \text{C}_1\text{C}_3\text{C}_5 = 119.7 \pm 1.5^\circ$, $\angle \text{CCF} = 110.6 \pm 0.8^\circ$. The enol proton appears to lie in the ring plane. The structure of hexafluoroacetic anhydride is best described as two planar halves which pivot about the central oxygen atom. The r_g values for this compound are $\text{O}_1\text{-C}_2 = 1.360 \pm 0.019 \text{ \AA}$, $\text{C}_2\text{-C}_4 = 1.546 \pm 0.010 \text{ \AA}$, $\text{C}_1\text{-O}_2 = 1.203 \pm 0.010 \text{ \AA}$, $\text{C-F} = 1.336 \pm 0.005 \text{ \AA}$, $\angle \text{C}_1\text{O}_1\text{C}_2 = 118.5 \pm 2.6^\circ$, $\angle \text{O}_1\text{C}_2\text{O}_3 = 120.5 \pm 1.9^\circ$, $\angle \text{O}_1\text{C}_1\text{C}_3 = 122.6 \pm 1.1^\circ$, $\angle \text{CCF} = 110.2 \pm 0.6^\circ$; the $\text{C}_2\text{O}_1\text{C}_1\text{O}_2$ dihedral angle is $20.3 \pm 3.6^\circ$. The above error limits are three times the least-squares-calculated uncertainties for fitting the calculated to the observed $qM(q)$ curves. This has been shown to encompass the estimated experimental errors involved in this study.

The effects of fluorine-for-hydrogen substitution in organic molecules have been the subject of several experimental and theoretical studies.¹⁻⁴ The two compounds with which this report is concerned, hexafluoroacetylacetone (HFACT) and hexafluoroacetic anhydride (HFAA), were selected for investigation not only to check whether previously observed trends¹ were followed, but also to determine the structural effects which result from enolization stabilized by intramolecular hydrogen bonding. Indeed, replacement of the central oxygen (O_1) in HFAA with a methylene group leads to significant changes in the central part of the molecule. Also, the structures found for HFACT and HFAA are consistent with published results for related substances.

(1) R. L. Hilderbrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970).

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(3) B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *Spectrochim. Acta*, **13**, 120 (1958).

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Experimental Details and Structure Analysis

Both compounds were obtained from Penninsular ChemResearch, Gainesville, Fla. The samples were distilled and their purities checked by infrared and proton nmr analysis. For each substance two sets of convergent-mode diffraction photographs were obtained with the Cornell dual-mode instrument.⁵ Patterns were recorded for the region $q = 10\text{-}55 \text{ \AA}^{-1}$ at 65 kV with a nozzle-to-plate distance of 253 mm (HVL), and $q = 35\text{-}122 \text{ \AA}^{-1}$ at 65 kV with a distance of 124 mm (HVS). All photographs were taken with 4 in. \times 5 in. Kodak Electron Image plates. The electron beam wavelength and the sample-to-plate distance were determined from measurements of Debye-Scherrer magnesium oxide powder patterns taken concurrently with the gas sample photographs.

The plates were microphotometered on a modified

(5) S. H. Bauer and K. Kimura, *J. Phys. Soc. Jap.*, **17**, 300 (1962).