The Structures and Spectra of Bis(*dl*-N,N-diethyl-α-alaninato)copper(II) and Related Complexes

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Abstract: The red complex bis(N,N-diethyl-α-alaninato)copper(II), $[(C_2H_5)_2NCHCH_3CO_2]_2Cu$, crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a = 9.684$ (6), $b = 7.495$ (6), $c = 8.101$ (7) Å, $\alpha = 100.57$ (5)°, $\beta = 106.85$ (4)°, $\gamma = 124.01$ (4)°. The density measured by flotation is 1.40 (1) g/cm^3 and the calculated density is 1.39 g/cm^3. There is one molecule in the cell. The structure was solved by Fourier techniques and refined by three-dimensional, least-squares calculations based on 1294 reflections collected with copper radiation on a Picker automatic diffractometer to a conventional R index of 0.063. The coordination about the copper atom is *trans* square planar with a Cu–O distance of 1.911 (5) Å, a very short value. In benzene solution the carboxylate antisymmetric stretching frequency is found at 1684 cm^{-1}, the highest frequency yet reported for amino acid chelates of copper. This frequency may be lowered by 30 cm^{-1} upon forming hydrogen bonds to the carbonyl oxygen. When the carboxylate function forms a bridge, as in the blue polymeric aggregates of N,N-di-*n*-butylglycinatocopper(II), the antisymmetric stretching frequency is lowered to 1645 cm^{-1}.

In recent years a number of studies have been conducted on the infrared spectra[2-7] and the structures[8,9] of complexes of the first-row transition metals with amino acids, both natural and synthetic. All of these studies have concerned processes occurring in, or complexes precipitated from, aqueous solution. Moreover, with the single exception of N,N-dimethylglycine,[2] all the ligands have been primary or secondary amino acids, and hence the systems have all been subject to complications arising from hydrogen bonding.

In the course of investigations of the physical chemistry of solutions of N,N-dialkylated amino acids, we noted that in benzene solution at elevated temperatures a reaction occurred between metallic copper and three different N,N-dialkylated-α-amino acids which produced superficially identical red solutions. Both the visible and infrared spectra of these solutions were sufficiently unusual to prompt the detailed investigations we report here.

Experimental Section

Ligand Syntheses. *d,l*-N,N-Diethyl-α-alanine was prepared by the method of Bowman[10] with some modifications. *d,l*-α-Alanine (3 g) was mixed with 35 ml of acetaldehyde, 8 g of 5% palladium on barium sulfate, and 200 ml of 50% aqueous ethanol. The reaction mixture was shaken under 2 atm of hydrogen for 4 days. Volatiles were stripped and the residue was refluxed with acetone; the hot acetone solution was filtered, concentrated, and allowed to stand overnight. The crystalline product weighed 1.2 g (30% yield) and melted at 137–139°. *Anal.* Calcd for $C_7H_{15}O_2N$: C, 58.0; H, 10.4; N, 9.6. Found: C, 57.7; H, 10.3; N, 9.4.

To prepare N,N-di-*n*-butylglycine a twofold excess of dibutylamine was mixed with ethyl chloroacetate in absolute alcohol. During the 15 hr the reaction mixture was refluxed, crystals of the amine hydrochloride were formed. The reaction mixture was filtered and fractionally distilled. The ester of the desired amino acid boiled at 76° (1 mm). The ester was refluxed with 100 parts of water containing a trace of hydrochloric acid for 10 hr. The solution was evaporated to dryness and the amino acid was dissolved in chloroform. It was then recrystallized twice from benzene, mp 137–138°. *Anal.* Calcd for $C_{10}H_{21}ON$: C, 64.1; H, 11.3; N, 7.5. Found: C, 64.0; H, 11.3; N, 7.4.

The sodium salt of N,N-diethylglycine was purchased from Eastman (White Label).

Preparation of Complexes in Solution. The ligands were converted to their respective sodium salts by the addition of an equivalent amount of aqueous sodium hydroxide to a few tens of milligrams of amino acid. The mixture was taken to dryness under vacuum, solid cupric acetate monohydrate and 40 ml of benzene or ethylene chloride were added, and the mixture was allowed to reflux for several hours. In each case the resulting hot solution was red. The cooled solution of the diethyl-α-alanine derivative remained red; the cool solution of the dibutylglycine derivative turned dark blue, while the cool solution of the diethylglycine derivative deposited blue crystals from the red solution until it became nearly colorless. None of the solutions displayed measurable conductance, and in no case did the infrared spectrum indicate the presence of water in the solutions.

Instrumental Techniques. Visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using matched, glass-stoppered silica cells. Temperature control was maintained by circulating thermostated water through a hollow cell-block attachment.

Infrared spectra were recorded on a Beckman IR 12 spectrophotometer. For solutions, matched sodium chloride cells were used; for solids, KBr pellets were prepared.

Number-average molecular weights of the dibutylglycinatocopper(II) complex in benzene solution were determined by using a Mechrolab Model 301-A vapor-phase osmometer equipped with a nonaqueous probe, and thermostated at 37°. Recrystallized biphenyl was used as a calibration solute.

Single-Crystal X-Ray Investigation of $[(C_2H_5)_2NCHCH_3CO_2]_2Cu$. Red crystals of this compound were grown by very slow evaporation of a solution in ethylene chloride. The crystal which was finally chosen, after 18 specimens were examined and rejected because they were not single, was a fusion of two crystals, but one part gave reflections which were about 20 times more intense than the other,

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[1] A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

[2] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961).

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[4] J. F. Jackovitz, J. A. Durkin, and J. L. Walter, *Spectrochim. Acta*, **A23**, 67 (1967).

[5] A. Rosenberg, *Acta Chem. Scand.*, **10**, 840 (1956).

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[7] R. H. Carlson and T. L. Brown, *Inorg. Chem.*, **5**, 268 (1966).

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[9] H. C. Freeman in "The Biochemistry of Copper," J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N. Y., 1966, p 77.

[10] R. E. Bowman, *J. Chem. Soc.*, 1346 (1950).

and the two diffraction patterns were clearly separated on the Weissenberg photograph. The photographs showed the crystal was triclinic. This crystal was mounted on a Picker four-circle goniometer, carefully centered, and a set of three axes found. The reflections along these axes were identified with those on the photographs and the weak set of reflections was also located. The separation of the two sets seemed to be greater than 4° in ϕ and both sets could be measured independently, so we concluded the weak set would not interfere with our data collection. The χ, ϕ, and 2θ values of ten strong reflections with 2θ greater than 55° were carefully measured for Cu Kα and Kβ radiations and unit-cell dimensions plus diffractometer setting information determined by a least-squares calculation. The unit cell originally chosen had angles $\alpha = 101°$, $\beta = 120°$, $\gamma = 75°$. This cell was transformed by a Delaunay reduction[11] to the reduced cell which revealed no symmetry higher than triclinic. The reflections were all reindexed, and all further work was carried out using the reduced cell. The unit-cell dimensions and other crystal data, including the density as measured by flotation, are given in Table I.

Table I. Crystal Data for Bis(N,N-diethyl-α-alaninato)copper(II), $CuO_4N_2C_{14}H_{28}$

$a = 9.684$ (6) Å $\alpha = 100.57$ (5)°
$b = 7.495$ (6) Å $\beta = 106.85$ (4)°
$c = 8.101$ (7) Å $\gamma = 124.01$ (4)°
Mol wt 351.93; space group $P\bar{1}$, $Z = 1$, $F(000) = 187$
$D_m = 1.40(1)$ g/cm³, $D_x = 1.39$ g/cm³
λCu Kα 1.5418 Å, λCu Kβ 1.3922 Å

Data were collected on an automated Picker diffractometer using Cu Kα radiation, a nickel metal filter, a scintillation detector and pulse-height analyzer, and a θ–2θ scan technique. The scan speed was 1°/min and the scan range included both the Kα_1 and Kα_2 peaks. Because the crystal was very small, no peak required the use of any attenuators. All reflections of the type $\pm h$, $\pm k$, l (or their Friedel equivalents) with 2θ less than 133° were measured; the Weissenberg photographs showed that the diffraction pattern was very weak above $2\theta = 90°$. A single reflection $(\bar{6}11)$ was monitored during the 7 days required to collect the data, and it showed variations not much greater than those expected from counting statistics.

The data were corrected for Lorentz and polarization factors, but no absorption corrections were applied. The crystal measured $0.044 \times 0.067 \times 0.074$ mm and the value of μ for this compound is 14.47 cm^{-1}, so that μr_{max} is about 0.2. Because good crystals were so hard to find, no attempt was made to shape this one into a sphere. The diffractometer surveyed 1459 reflections, of which 1302 were measured more than 3σ above background and were used in the solution and refinement of the structure. Standard deviations were assigned the measured intensities by the formula

$$\sigma^2 I = \sigma_1^{\,2} + (\sigma_2^{\,2} + \sigma_3^{\,2})t^2$$

where

$$\sigma_1 = \sqrt{S} + S/60$$

$$\sigma_2 = \sqrt{BG_1} + BG_1/60$$

$$\sigma_3 = \sqrt{BG_2} + BG_2/60$$

and S = counts in the scan, BG_1 and BG_2 = counts in the background taken at either end of the scan, and t = the ratio of scan time to total background time. The constant, 60, was chosen from a consideration of the variations observed in the measurements of the check reflection.[12]

Results

Spectroscopic Studies. The fact that all the solutions were anhydrous and nonconducting implies that the complex species in solution all have an average ligand: copper ratio of 2. The red forms of all three complexes in benzene or ethylene chloride solution show a visible spectrum having a maximum at 482 mμ (ϵ_{max} 90) with a shoulder at ~590 mμ (ϵ ~55). The ultraviolet spectrum of the diethyl-α-alaninato complex in ethylene chloride shows a broad, unsymmetrical maximum between 260 and 315 mμ having ϵ ~1350.

As the red solutions of the dibutylglycinato complex are made progressively more concentrated, or as they are cooled, they change color until finally they are a dark blue. The visible spectrum of such a solution has its single, fairly broad, absorption maximum at 590 mμ, ϵ_{max} ~100. Number-average molecular weight measurements show that this change in color attends an aggregation in solution which does not stop simply at the dimer. Spectra taken on successive dilutions of a blue solution with corresponding increases in pathlength likewise do not show a convincing isosbestic point. Thus we conclude that the coordination number of copper in the red form of all three complexes is the same, undoubtedly four, while the blue colors which are given in solution by the dibutylglycinato complex and the solid by the diethylglycinato complexes arise from average coordination numbers for copper which are greater than four.

The spectrum of all the red species in solution closely resembles the spectrum reported by Graddon and Munday[13] for bis(1-aminocyclopentanecarboxylato)copper(II) in the solid, namely overlapping peaks at 510 and 590 mμ. The crystal structure of the latter compound has been determined by Barclay and Stephens,[14] who found a centrosymmetric, *trans* "square" planar array of the N and O donor atoms around the metal ion, with the next nearest neighbors of the copper atom being carboxylic oxygen atoms at van der Waals contact distances. The two maxima observed in solution for the red form of the present complexes are similarly identical in position with two of the three bands observed by Ferguson[15] in the polarized crystal spectra of bis(N-methylsalicylaldiminato)copper(II). We fail to find a feature at 670 mμ shown by the latter molecule. This molecule also has a *trans* square-planar array of N and O donors around a central copper atom. Thus, even before the crystal structure of bis(diethyl-α-alaninato)copper(II) was determined, we were confident that the red species would exhibit a *trans* square-planar geometry.

The most unusual result obtained in our spectroscopic survey is the dramatic shift in the COO^- antisymmetric stretching frequency which accompanies the formation of the red complexes. The solid sodium salts of N,N-diethyl-α-alanine and N,N-diethylglycine have absorptions (in KBr pellets) at 1604 and 1612 cm^{-1}, respectively. The red solutions of the copper complexes of these ligands, and of N,N-dibutylglycine as well, all show a single, sharp absorption in benzene or ethylene chloride solution at 1684 cm^{-1}, by far the highest frequency ever reported for copper complexes of amino acids.

Nakamoto, Morimoto, and Martell[2] and Cotton[16] have

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(11) B. Delaunay, *Z. Krist.*, **84**, 132 (1933).

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(13) D. P. Graddon and L. Munday, *J. Inorg. Nucl. Chem.*, **23**, 231 (1961).

(14) G. A. Barclay and F. S. Stephens, *J. Chem. Soc.*, 2027 (1963).

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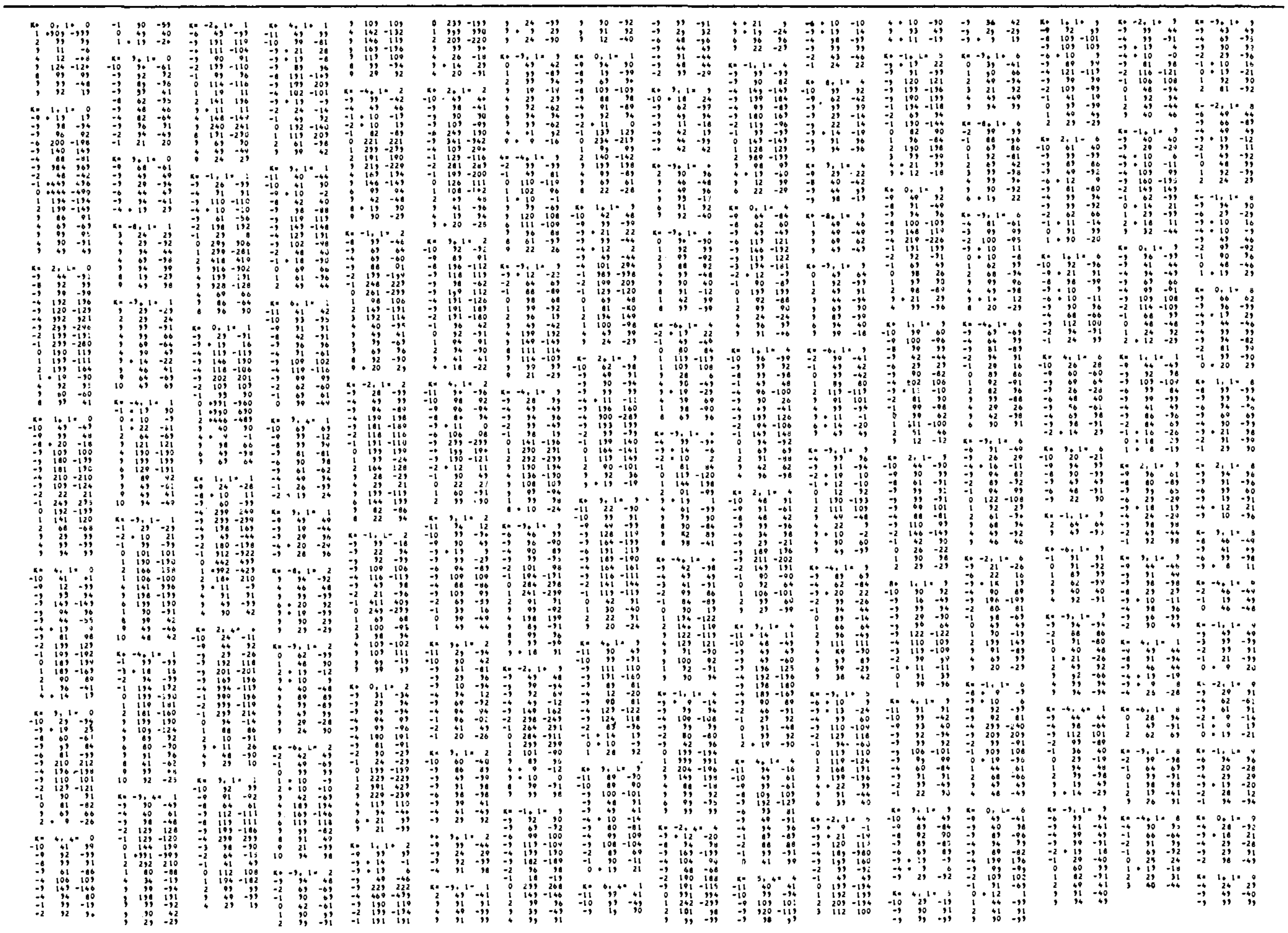
Table II. Observed and Calculated Structure Factors (× 10) (an asterisk indicates the reflection was not used in the refinement)



cautioned that hydrogen bonding could exert a substantial influence on the infrared spectra of amino acid chelates. We have confirmed this effect by obtaining the spectra of bis(N,N-diethyl-α-alaninato)copper(II) in chloroform, where the COO^- antisymmetric stretch is found at 1661 cm^{-1}, and in 50% chloroform-*t*-butyl alcohol, in which the band occurs at 1657 cm^{-1}. This latter solution remains red, and hence copper complexing by the alcohol does not occur.

We have also obtained the infrared spectrum of a blue solution of bis(N,N-dibutylglycinato)copper(II) in benzene in which the number-average molecular weight of the solute was slightly greater than that corresponding to the dimer. The spectrum showed bands at 1684 and 1645 cm^{-1}, the latter being the broader and the more intense. We take this shift in vibration frequency to be confirmatory evidence that the mode of association is *via* carboxylate bridging, since the fully alkylated amine function does not admit the possibility of hydrogen-bond formation between solute molecules.

When the infrared spectrum of the red crystalline diethyl-α-alaninato chelate dispersed in KBr is taken, we find the antisymmetric stretching frequency shifted downward from the solution value of 1684 to 1666 cm^{-1}. It is now also possible to assign the symmetric stretching mode of the COO^- to a triplet at 1360, 1342, and 1328 cm^{-1}. By comparison with the sodium salt, formation of the four-coordinate copper complex increases the antisymmetric carboxylate stretching frequency by 62 cm^{-1}, decreases the symmetric stretching frequency by ~63 cm^{-1}, and produces a separation between these two bands of ~323 *vs.* 199 cm^{-1} in the free anion. These results are indicative of a marked nonequivalence of the two carboxyl oxygens in the ligand molecule which could be produced by an unusually strong metal–oxygen bond. The structural studies were undertaken to confirm the two predictions made on spectroscopic grounds: namely, *trans* four-coordinate geometry around copper and a short metal–oxygen bond. The crystal structure also shows clearly why the diethyl-α-alaninato complex shows only four-coordinate geometry whereas similar complexes lacking the side-chain methyl group readily adopt higher coordination numbers at high concentration.

X-Ray Determination and Refinement of the Structure. Because there was only one copper atom in the unit cell the space group $P\bar{1}$ was assumed and the first calculation was an electron density map phased on the copper atom placed at $^1/_2$, $^1/_2$, $^1/_2$. This revealed the oxygen and nitrogen atoms, but only one carbon atom was well defined. A second map phased on these five atoms showed the rest of the carbon atoms (the structure factor calculation gave an R index, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of

Table III. Positional and Thermal Parameters[a]

Atom	x	y	z	B or b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	5000	5000	5000	17 (0.3)	27 (0.4)	18 (0.3)	31 (0.5)	20 (0.4)	25 (0.5)
O(1)	4331 (6)	2733 (7)	6051 (6)	34 (1)	52 (2)	38 (1)	67 (3)	52 (2)	64 (3)
O(2)	2997 (6)	1387 (7)	7825 (6)	35 (1)	48 (2)	35 (1)	53 (3)	45 (2)	58 (2)
N	3342 (6)	5361 (7)	5817 (6)	21 (1)	35 (2)	22 (1)	39 (2)	23 (2)	27 (2)
C(1)	3496 (7)	2688 (9)	7032 (8)	23 (1)	33 (2)	23 (1)	35 (3)	24 (2)	29 (3)
C(2)	3406 (10)	4646 (12)	7411 (10)	45 (2)	53 (3)	41 (2)	75 (5)	64 (4)	62 (4)
C(3)	1893 (11)	4138 (14)	7991 (11)	52 (3)	64 (3)	51 (2)	87 (5)	84 (5)	73 (5)
C(4)	3837 (10)	7678 (12)	6290 (11)	41 (2)	47 (3)	50 (2)	67 (5)	58 (4)	50 (5)
C(5)	5942 (11)	9749 (11)	7878 (10)	43 (2)	38 (2)	30 (2)	53 (4)	25 (3)	19 (3)
C(6)	1313 (9)	3402 (13)	4167 (10)	28 (2)	61 (3)	34 (2)	50 (4)	29 (3)	28 (4)
C(7)	1095 (10)	3395 (15)	2258 (10)	29 (2)	82 (4)	27 (2)	52 (5)	18 (3)	48 (5)
H(1)	4696	6164	8668	10.7					
H(2)	2932	7691	6747	7.5					
H(3)	3638	7967	5031	10.5					
H(4)	414	3617	4468	10.9					
H(5)	876	1724	4084	10.2					
H(6)	2124	3797	9214	8.5					
H(7)	540	2618	6860	8.9					
H(8)	1988	5629	8302	10.4					
H(9)	6109	9592	9159	11.1					
H(10)	6276	11411	8069	7.0					
H(11)	6898	9711	7478	5.1					
H(12)	1227	4874	2229	10.3					
H(13)	−265	1811	1176	10.9					
H(14)	2098	3474	2020	11.0					

[a] All x, y, and z values have been multiplied by 10^4; b_{ij} values have been multiplied by 10^3. The anisotropic thermal parameters are of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

0.36) and an isotropic least-squares refinement was begun. This converged after four cycles to an R index of 0.115 and a goodness-of-fit ($= [\Sigma w(F_o - F_c)^2/(n - p)]^{1/2}$) of 4.7, where w is $1/(\sigma F_o)^2$ as calculated in the initial data processing, n is the number of data used (1302), and p is the number of parameters refined (100). A difference map showed that most of the atoms were vibrating anisotropically, so first the copper atom and then the light atoms were given ellipsoidal temperature factors. Five hydrogen atoms, those which could be placed from structural considerations, were also included in these structure factor calculations, but their parameters were not refined. The refinement required nine cycles to converge to an R index of 0.078 with a goodness-of-fit of 3.8. A second difference map was calculated and the remaining hydrogen atoms, those around methyl carbon atoms, were located. Six cycles of refinement were carried out allowing the hydrogen positional parameters and temperature factors to vary, but the results were unsatisfactory in that the C–H bond distances and bond angles became quite unreasonable.

The hydrogen atoms were therefore repositioned on the basis of a difference map, and three final cycles of full-matrix least squares varying a scale factor and positional and anisotropic thermal parameters of the 11 heavy atoms converged with a final R index of 0.063 and a goodness-of-fit of 2.94. During the anisotropic refinement, eight strong reflections which appeared to be suffering from secondary extinction (100, $\bar{1}10$, 010, $1\bar{3}1$, 001, 101, 201, and 111) were not included in the least-squares calculations. All calculations were done on an IBM 7044 machine using programs obtained from H. Hope. The refinement was done using the program of Gantzel, Sparks, Long, and Trueblood, which minimizes the function $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors for copper (reduced by 2.15 electrons to correct for the real part of the anomalous dispersion), oxygen, nitrogen, and carbon were taken from the collection of Ibers;[17] the curve for hydrogen was from Stewart, Davidson, and Simpson.[18] The observed and the calculated structure factors are given in Table II. The final atomic parameters are listed in Table III. The B values listed for the hydrogen atoms were taken from the last least-squares cycle during which these parameters were allowed to vary.

The final value of the goodness-of-fit seems high. A difference map was calculated after the final refinement, and it had three peaks between 0.9 and 1.0 e/Å^3; an average hydrogen atom in this map had a peak height of 0.8 e/Å^3. The peaks in the difference map are about 1 Å from carbon atoms C(4), C(5), and C(6), but they cannot be hydrogen atoms. There may well have been an accidental overlap in some regions of reciprocal space of the reflections from the two crystals comprising our specimen, thereby producing a small systematic error in portions of the data set. This systematic error could be responsible for the extra peaks in the difference map and the high value of the goodness of fit. The final agreement between observed and calculated structure factors is good enough, however, to assure that the principal conclusions to be drawn from the investigation are valid.

Discussion

The molecular structure of $[(C_2H_5)_2NCHCH_3CO_2]_2$-Cu is shown in Figure 1 in a projection viewed approximately normal to the plane of atoms N-Cu-O(1). A schematic drawing of the molecule giving bond distances and angles and their standard deviations is given in

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(17) J. A. Ibers, "International Tables of Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202–205.

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

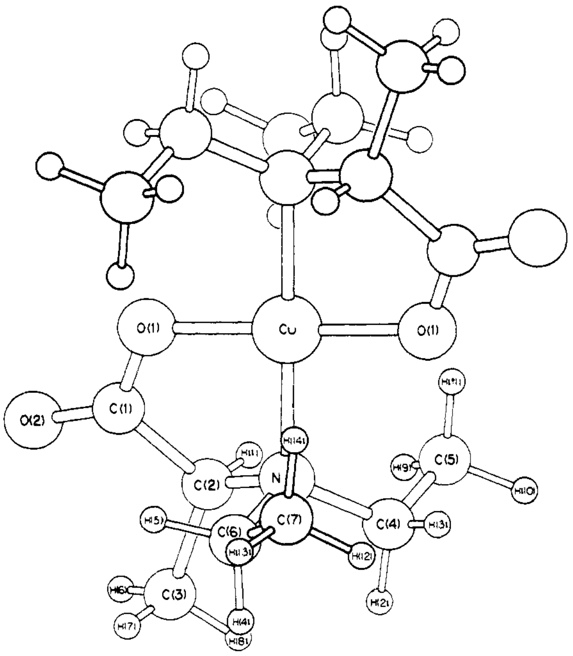

Figure 1. A view of the molecule in a direction roughly perpendicular to the plane of the coordinating ligands.

Figure 2. A list of nonbonded interactions within the molecule and between adjacent molecules is given in Table IV.

It can be seen by studying Figure 1 that the gross configuration shown is the only one accessible to the molecule. van der Waals repulsions between the hydrogen atoms on the C(3) methyl group and those on the C(6) methylene effectively prevent rotation about the N–C(6) bond. Once the orientation about C(6) has been established, hydrogen–hydrogen repulsions also determine the orientation of the ethyl group C(4)–C(5). Rotation about the N–C(4) bond is restricted not only by interference with hydrogen atoms on the C(6)–C(7) ethyl group in the same chelate ring, but equally importantly, with those of the inverse of C(7) in the other half of the molecule. Four-coordinate geometry around copper is maintained by the interlocking network of hydrogen atoms which absolutely eliminates the possibility of further coordination to the metal ion perpendicular to the plane of the ligands. If methyl group C(3) is not present, as in the two glycine derivatives, the alkyl substituents on the nitrogen are no longer constrained to obstruct the apical positions; the metal ion can, and does, adopt higher coordination numbers.

By virtue of the center of symmetry, the copper atom and the four ligand donor atoms are rigorously coplanar. Atoms C(1), O(2), and C(2) lie above the plane by 0.22, 0.27, and 0.62 Å, respectively. Atom C(3) is 0.44 Å above this plane, C(4) is 0.63 Å above, and C(5) is 2.10 Å above while atoms C(6) and C(7) are 1.47 and 2.35 Å, respectively, below it. The bond distances within the chelate ring, apart from the copper–donor distances, are all in excellent agreement with the mean values cited by Freeman,[9] based on his survey of 13 complexes of copper with amino acids and simple peptides.

The metal–oxygen distance in this compound is distinctly abnormal. Freeman cites a mean Cu–O distance of 1.97 ± 0.01 Å based on 12 complexes. For only one other compound, the similarly four-coordinate bis(1-aminocyclopentanecarboxylato)copper(II), has a value of 1.91 Å been reported.[14] While the statistical grounds are less firm, our results suggest also that the Cu–N distance in our molecule is slightly long. Freeman tabulates a mean Cu–NH_2 length of 2.00 ± 0.007 Å *vs.* our Cu–NR_2 = 2.031 ± 0.006 Å. We are unaware of any structural results for tertiary amine complexes which might be used to verify a possible lengthening of the Cu–N bond accompanying alkyl substitution on nitrogen. A wealth of chemical evidence suggests, however, that tertiary

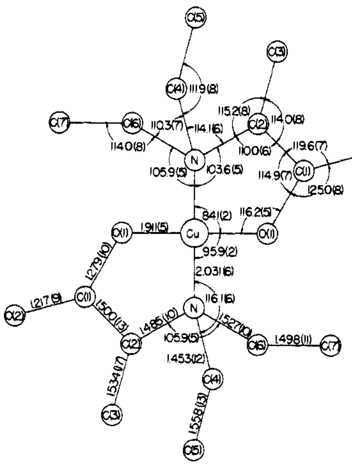

Figure 2. Bond distances and angles in the bis(N,N-diethyl-α-alaninato)copper(II) molecule.

Table IV. Nonbonded Interactions

a. In the Molecule

Atom	Atom	Distance, Å
Cu	C(3)	4.24
	C(4)	2.97
	C(5)	3.32
	C(6)	2.86
	C(7)	3.12
O(1)	C(5)	4.35
O(1)	C(7)	4.03
C(2)	C(7)[a]	4.63
C(3)	C(4)	3.12
C(3)	C(6)	2.87
C(5)	C(7)[a]	4.63

b. To Adjacent Molecules (All distances less than 4 Å are listed)

Atom	to Atom	in Cell	Distance, Å
C(5)	C(7)	1, 1, 1	3.99
O(2)	C(2)[a]	0, 0, 1	3.50
O(2)	C(3)[a]	0, 0, 1	3.84
O(2)	C(5)[a]	0, 0, 1	3.73
C(3)	C(7)	0, 0, 1	3.83
C(1)	C(2)[a]	0, 0, 1	3.93
C(4)	C(1)	0, 1, 0	3.90
O(2)	C(5)	0, −1, 0	3.68
O(2)	C(4)	0, −1, 0	3.43
O(2)	C(7)[a]	−1, −1, 0	3.53
O(2)	C(6)[a]	−1, −1, 0	3.18
O(1)	C(4)	0, −1, 0	3.59
O(1)	C(5)	0, −1, 0	3.66
C(1)	C(6)[a]	−1, −1, 0	3.93

[a] These atoms have coordinates 1 − x, 1 − y, 1 − z, where x, y, and z are as given in Table III.

aliphatic amines are relatively weak ligands.[19]

It is doubtful that the steric effects which restrict the accessible configurations of the ethyl groups in the α-alaninato compound influence the bonding between copper and nitrogen. The visible spectra of all three red complexes in solution are essentially superimposable; thus it is likely that the electronic environments of the copper atoms are virtually identical.

A more subtle steric effect may, however, be operating. Freeman[8] has suggested that α-amino acids are moderately inflexible chelating agents, and our structure is in agreement with this position. The N–Cu–O(1) angle we find is the same as the average of five other copper chelate structures, and the N–O(1) cross-ring distance of 2.64 ± 0.01 Å is substantially the same as the mean value of 2.66 ± 0.01 Å found in 13 structures with various metal ions. Given a fairly rigid chelating agent and a fixed central angle, a shortened Cu–O(1) bond should reflect itself in a lengthened Cu–N bond and a decreased Cu–N–C(2) bond angle. We find an angle of 104°, which may be compared with the mean value of 109 ± 1° found in five similar chelate rings for which the Cu–O(1) bond distances are "normal."

We concur with Freeman's view that the shortened Cu–O(1) distance follows from a lack of ligands in the apical binding sites, leaving the metal ion with bonding capacity which, we suggest, is best satisfied by an interaction with the π system, or possibly the lone pairs, on oxygen. Provided one works only with monomeric solute species in an inert solvent, our spectroscopic results suggest that the antisymmetric stretching frequency of the carboxyl group may be increased markedly by coordinating one oxygen atom to a metal ion. It has been stated that this frequency is insensitive to coordination,[6,7,20] but this conclusion may have been based on systems in which the carbonyl oxygen atom is engaged in either a hydrogen-bonding or a bridging role. Both of these we have shown decrease the stretching frequency by at least 20 cm^{-1}. In the solid, N,N-dimethylglycinatocopper(II) absorbs at 1630 cm^{-1},[2] and N,N-diethylglycinatocopper(II) absorbs at 1640 cm^{-1}. While the color (and hence the coordination type) of the first named compound is not given, the second is blue; most probably both have carbonyl oxygen–copper interactions. In the diethyl-α-alaninato compound the nearest neighbor to the carbonyl oxygen is a hydrogen atom, H(4), in another molecule, 2.71 Å away; this compound absorbs at 1666 cm^{-1} in the solid. The four-coordinated bis(1-aminocyclopentanecarboxylato)copper(II) absorbs at 1620 cm^{-1} in the solid[13] even though the structural evidence indicates an unusually short Cu–O bond.[14] In the solid the carbonyl oxygen is hydrogen bonded to the amino group of a neighboring molecule. Furthermore, there is an irregularity in the reported structure in that the longer of the two carbon–oxygen bonds in the carboxylate function is the one which in our notation would be C(1)–O(2). Indeed, on this basis Freeman[8] has questioned the validity of the data from which the details of the strcture were determined.

The apparent discrepancy in the dimensions of the two ethyl groups bonded to nitrogen in bis(N,N-diethyl-α-alaninato)copper(II) deserves a final comment. While some of the discrepancy may be real, it is most likely that the same systematic errors in the data which produce the three false peaks in the difference map near atom C(6) also are responsible for mispositioning this atom.

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