rines we cannot assign the peaks to particular fluorines on the basis of intensities.

We have not yet analyzed the data for the other two compounds in such detail. The ClF_3 spectrum shows two resolved peaks in a ratio of about 2:1. The larger peak, due to the axial fluorines, is at the lower binding energy, in agreement with the idea that the axial fluorines are more negative than the equatorial ones. The PF_5 spectrum is not clearly resolved, but consists of one asymmetric peak, whose shape is consistent with the two axial fluorines being more negatively charged than the three equatorial ones.

In addition to the results reported above, we have observed evidence for the nonequivalent fluorines in BrF_3, BrF_5, and IF_5. We are preparing a more complete analysis of all these results.

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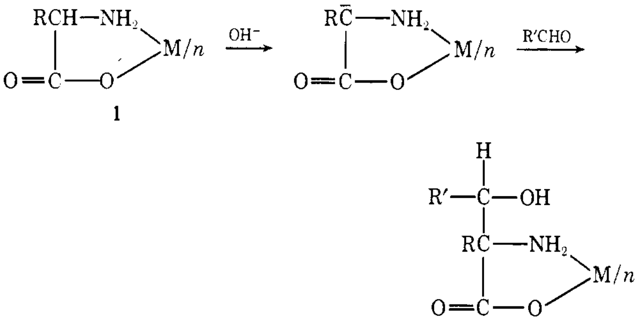
Robert W. Shaw, Jr., Thomas X. Carroll, T. Darrah Thomas*
Department of Chemistry and Radiation Center
Oregon State University
Corvallis, Oregon 97331
Received December 18, 1972

Nature of the Copper(II) Complex Formed in the Reaction of Formaldehyde with Bis((*S*)-serinato)copper(II)

Sir:

The reaction of (α-amino acidato)metal complexes, **1**, with aldehydes under alkaline conditions has been considered to occur as follows (n = oxidation state of metal; R = H, CH_3, etc.).[1–8]



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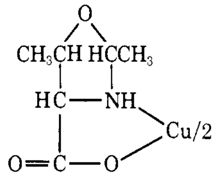
The metal-containing product of the reaction has rarely been isolated[7,8] since the reaction mixtures are normally treated under acid conditions, *e.g.*, with H_2S, to give the corresponding metal-free α-hydroxymethyl-substituted amino acid. Recently,[9] it has been shown that reaction of glycine with acetaldehyde in alkaline solution in the presence of basic copper(II) carbonate gives the bis(oxazolidine)copper(II) complex shown schematically as **2**. Threonine is obtained when **2** is treated with H_2S. Formation of **2** indicates that the amino group is attacked by the aldehyde to form the *N*-hydroxymethyl derivative. Attack by the aldehyde on the carbanion species formed under the basic conditions also occurs and the oxazolidine is subsequently formed by cyclization. The ready formation of the carbanion is indicated by proton magnetic resonance studies on glycinato–Co(III) complexes in D_2O. The exchange of the hydrogens on the α carbon with deuterium is extremely rapid.[10] Rate studies in the presence of hydroxide ion of the exchange of the α-carbon hydrogen in several other coordinated α-amino acids also indicate carbanion formation.[11] We wish to report a novel metal ion-assisted reaction of bis((*S*)-serinato)copper(II) (**1**, R = $-CH_2OH$, M = Cu, n = 2) with excess formaldehyde at pH 7–9 which results in the formation of the bis(amino acidato)copper(II) complex of **3**.[12] The results of an X-ray structure analysis of the deep blue crystals are also reported. The complex, isolated in 80% yield, is optically inactive, but an intermediate[13] corresponding to **4** which can be isolated in the initial stages of the reaction is optically active. The intermediate slowly loses activity at 40° in the presence of formaldehyde at pH 7–9. This behavior supports the formation of the mono-*N*-hydroxymethyl species as the first step in the reaction rather than the removal of the hydrogen on the α-carbon atom to form a carbanion. Cyclization of the hydroxymethyl groups occurs followed by addition of hydroxymethyl groups on the α-carbon atom (this step leads to loss of optical activity) and the secondary nitrogen. Cyclization again occurs to give the copper(II) complex of **3**. The importance of the copper(II) ion in this reaction is shown by the fact that no detectable reaction occurs in the absence of metal ion over a period of at least 1 week. Catalytic hydrogenation of the copper(II) complex in water or treatment with H_2S gives high yields of α-hydroxymethylserine, indicating that the cyclic structure is readily ruptured under such conditions. Treatment of the complex with sodium borohydride in aqueous solution, however, followed by esterification gives the ester, **5** (R = CH_3, C_2H_5). The latter method appears to have general application as a method for the synthesis of analogs of **3** having a variety of substituents in both rings. This aspect will be reported in detail at a later date.



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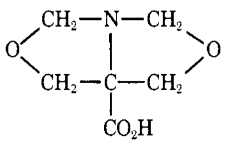

3

Tabular crystals of the deep blue reaction product are monoclinic and have space group $P2_1/c$. The unit-

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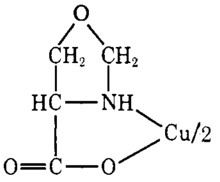
(12) The systematic name for **3** is dihydro-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazole-7a-carboxylic acid.

(13) All new compounds gave satisfactory analyses.



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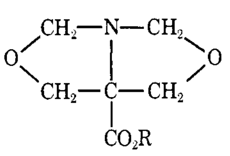

5

cell constants obtained (from the setting angles of 12 high-angle reflections on a Picker diffractometer) with monochromatic Cu Kα radiation (λ_1 1.5405 Å) are a = 18.559 (1), b = 10.142 (1), and c = 7.345 (1) Å and β = 101.60 (1)°. The measured density is 1.86 g/cm^3 (by flotation). The formula $C_{12}H_{16}CuN_2O_8$ (mol wt = 379.8 g-atoms) corresponds to the asymmetric unit, and for $Z = 4$ the calculated density is 1.863 g/cm^3. A total of 2035 diffractometer data with $I > 3\sigma(I)$ were collected. Absorption corrections (μ(Cu Kα) = 28.00 cm^{-1}) were not applied. Structure analysis by the heavy-atom method established the molecular formula, and full-matrix, least-squares refinement converged with a R factor on F of 0.041.

The chelate molecules (Figure 1) are linked into chains in the crystal by a glide-related O(4) atom to Cu interaction of length 2.35 (1) Å. This interaction results in a square-pyramidal coordination of the copper ion. While the O(1)-Cu-O(3) atoms are linear (angle, 177.5°) the N(1)-Cu-N(2) atoms are bent (161.6°) so that the highly substituted nitrogen atoms are moved away from the fifth coordination site. This bending must have a steric origin and some close interchelate contacts exist in the chain. Thus the glide-related O(3) atom associated with the fifth ligand (O(4′)) imposes a close contact with a C(8) hydrogen atom. The C(8)···O(3′) distance is 3.28 Å and this repulsive contact leads to an opening of the Cu-N(1)-C(8) angle (117.0 (5)°) compared to the other chemically equivalent angles (av 113.0 (10)°). Steric effect considerations also explain why the copper is only five coordinate and not six as in many other bis(amino acid) complexes.[9,14] Five coordination however need not arise solely for this reason; *cis*-Cu((*S*)-α-alanine)$_2$ for instance is similarly five coordinate[14] and six coordination is not sterically blocked. The averaged molecular geometry (Table I) agrees well with that for copper-α-amino acid complexes.[14] All four oxazolidine rings are closely similar and adopt envelope conformation with the oxygen as the envelope tip.

Table I. Averaged Molecular Geometry[a]

Bond	Distance, Å	Atoms	Angle, deg
Cu-O(3)	1.925 (7)	O(3)-Cu-N(2)	85.5 (10)
Cu-N(2)	2.025 (2)	Cu-N(2)-C(4)	107.1 (10)
O(3)-C(3)	1.267 (3)	N(2)-C(4)-C(3)	110.9 (20)
O(4)-C(3)	1.236 (1)	C(4)-C(3)-O(3)	117.8 (10)
C(3)-C(4)	1.527 (4)	C(4)-C(3)-O(4)	116.9 (10)
N(2)-C(4)	1.515 (4)	Cu-O(3)-C(3)	114.5 (20)
N(2)-C(12)	1.492 (4)	O(3)-C(3)-O(4)	125.4 (10)
C(4)-C(10)	1.536 (10)	C(4)-N(2)-C(12)	104.1 (5)
C(10)-O(9)	1.416 (4)	C(10)-O(9)-C(12)	104.4 (10)
		C(10)-C(4)-N(2)	103.3 (5)
		N(2)-C(12)-O(9)	106.4 (5)
		C(4)-C(10)-O(9)	104.4 (5)

[a] Atom numbers refer to one chelate, but the values are averages for both chelates. Standard deviations in the mean values are given in parentheses.

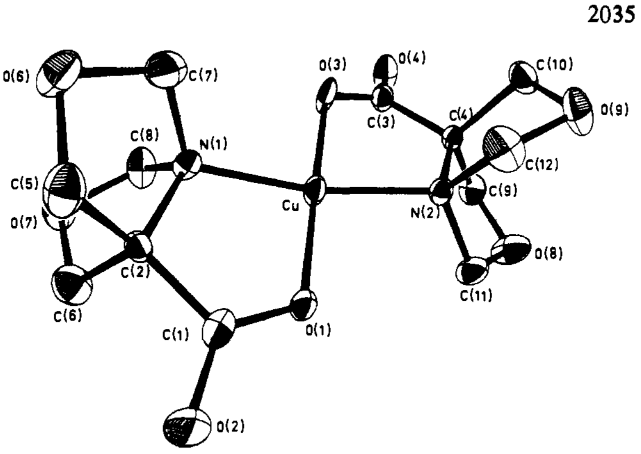

Figure 1. The molecular structure of bis(dioxazolecarboxylate)-copper(II). The copper is five coordinate in the crystal. Atoms are shown as 50% probability ellipsoids and methylene hydrogens are omitted for clarity.

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J. R. Brush, R. J. Magee, M. J. O'Connor,* S. B. Teo
Department of Inorganic and Analytical Chemistry
La Trobe University
Bundoora, Victoria 3083, Australia

R. J. Geue, M. R. Snow
Department of Physical and Inorganic Chemistry
University of Adelaide
Adelaide, South Australia 5001, Australia

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Photochemical Generation of Electronically Excited Organic Products in Adiabatic Pericyclic Photoreactions. An Unexpected Propensity toward Spin Inversion in a Retrocycloaddition and in a Valence Isomerization[1]

Sir:

Careful scrutiny of the photochemical literature reveals[2,3] that the overwhelming majority of organic photochemical reactions leads directly from an initial electronically excited state to a product in its ground state (eq 1). The intuitively acceptable conversion of an *electronically excited state of a reactant into an electronically excited product molecule* (eq 2) is exceedingly rare for molecules possessing a high number of vibrational modes.[4] The best known examples of these electronically excited product-forming reactions are photoinduced acid-base reactions[5] and excimer (or

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