The cis/trans ratio of the vinylmethylene isomers, as indicated by their signal intensities, can vary between 0.65 and 0.05, depending on the experimental conditions. The lowest ratio is found in the PFK matrix; the highest relative intensity of the cis isomer is observed when vinyldiazomethane is irradiated for short periods (seconds) in an MTHF matrix in the presence of benzophenone. Here continued irradiation increases the intensities of both species but decreases the cis/trans ratio. After reaching an intensity maximum at a ratio of ~0.4, both isomers decay on further illumination. One possible explanation for the change in intensity ratios involves interconversion of 1_c and 1_t. This process is of interest in view of the wide range of inversion rates ($>10^{10}$) reported for the structurally related vinyl radical, depending on matrix and site.[9]

In the dark, the vinylmethylenes are stable between 6 and 15°K and their ratios remain unchanged; at 77°K, both isomers disappear within 1 min. At temperatures between 20 and 35°K, 1_c and 1_t decay with energies of activation <200 cal/mol, the cis isomer at somewhat faster rates than the trans isomer. Accordingly, the vinylmethylenes are considerably more reactive than phenylmethylene[6a] or the naphthylmethylenes[1] in similar environments. At these low temperatures, far below the melting points of the matrices employed, second-order diffusion-controlled processes are not expected. Therefore, we assume an intramolecular conversion of the vinylmethylenes to a more reactive state, probably a singlet, which can then undergo intra- or intermolecular reactions. These transformations are currently under investigation. In several cases substituted vinylmethylenes, presumably in their singlet states, have been invoked as intermediates in the thermal racemization of chiral cyclopropenes and in the photodecomposition of various 3H-pyrazoles leading to cyclopropenes (ring closure) or dienes (hydrogen migration).[10] Closs and coworkers have previously observed esr spectra of several 1,2-benzvinylmethylenes in the photolysis of the corresponding 3H-indazoles.[11,11a]

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(11a) NOTE ADDED IN PROOF. O. L. Chapman, M. Chedekel, J. Pacansky, N. Rosenquist, R. Roth, and R. S. Sheridan have observed the ir and esr of vinylmethylene in matrix-deposited argon and nitrogen. Their experiments and our more limited matrix isolation studies show substantial differences from the frozen solutions discussed above. For example, we find 1_t and 1_c in frozen pentane solutions, whereas vinyldiazomethane and pentane, deposited at 8°K from the vapor phase, give only 1_t. Also, E was 10% lower than observed in solution.
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Synthesis and Structural Characterization of the Nickel(II) and Copper(III) Complexes of the 1,1-Dicarboethoxy-2,2-ethylenedithiolate Ligand

Sir:

The ability of dithiocarbamate ligands to stabilize metal ions in unusually high oxidation states is well documented.[1] A less well-known ligand capable of stabilizing metal ions in high oxidation states is the 1,1-dicarboethoxy-2,2-ethylenedithiolate dianion[2] (DED^{2-}). In our studies of the chemistry of this ligand we have isolated and characterized complexes which formally contain Fe(IV)[3] and Cu(III) ions.

Galactose oxidase, a copper-containing enzyme for which Cu–S coordination has been implicated,[4] catalyzes the oxidation of D-galactose to the corresponding aldehyde. In a recently proposed mechanism for the action of this enzyme, Hamilton, *et al.*, suggested that the two-electron oxidation of the substrate proceeds after the enzyme-bound copper is oxidized to the +3 state.[5] We have undertaken the present study to explore the nature of the Cu–S bonding in oxidized copper complexes and possibly design models for copper-containing metalloenzymes.

The water insoluble $(BzPh_3P)_2Cu(DED)_2$ (I) is precipitated from brown-red dilute aqueous solutions of $K_2Cu(DED)_2$, upon addition of benzyltriphenylphosphonium chloride. This compound is recrystallized from dichloromethane–pentane mixtures, and its physical properties are similar to those reported for other bis-1,1-dithiolate–copper complexes.[6] It is X-ray isomorphous to the $(BzPh_3P)_2Ni(DED)_2$ complex and has similar infrared spectra.

In the presence of a 10–15% excess of Cu(II) ions or H_2O_2, aqueous solutions of $K_2Cu(DED)_2$ afforded a water insoluble[7] green complex of the stoichiometry $KCu(DED)_2$ (II), which can be recrystallized from acetonitrile–chloroform mixtures. Replacement of the potassium ions by $BzPh_3P^+$ is readily accomplished in acetonitrile giving $BzPh_3PCu(DED)_2$ (III). This compound also is obtained by iodine oxidation of the corresponding parent complex, I, in acetonitrile.

Consistent with its chemically determined redox behavior, I undergoes a reversible one-electron electrochemical oxidation at -0.50 V in CH_2Cl_2 vs. Ag|AgI with Bu_4NClO_4 as the supporting electrolyte. The K$^+$ and $BzPh_3P^+$ salts of $[Au^{III}(DED)_2]^-$ were found X-ray isomorphous to II and III, respectively. Furthermore the energies of the bands in the electronic spectra of II and III were similar to those of the corresponding Ni(II) complexes. On the basis of these data it appeared that the anions in II and III could best be described as Cu(III) complexes.

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(7) It is noteworthy that even the sodium salt of this compound is insoluble in water indicating an unusually strong interaction between the complex anion and the alkali metal cation.

In order to differentiate between the two possible formal descriptions for this complex, *i.e.*, a Cu(III)

A

B

C
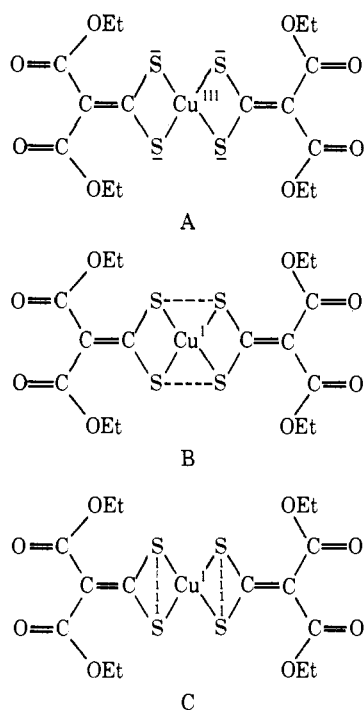
dithiolate *vs.* a Cu(I) disulfide complex, the structures of the isoelectronic $Cu(DED)_2^-$ and $Ni(DED)_2^{2-}$ were determined.

Crystal and refinement data for the two structures are shown in Table I. Intensity data were obtained on a

Table I. Crystal and Refinement Data

	KCu(DED)₂ O(C₂H₅)₂	(PhMe₃N)₂ Ni(DED)₂
Cell dimensions (Å, deg)	$a = 13.781 (3)$	$a = 9.032 (3)$
	$b = 17.527 (3)$	$b = 8.716 (4)$
	$c = 12.903 (3)$	$c = 15.532 (6)$
	$\beta = 107.21 (1)$	$\alpha = 82.04 (2)$
		$\beta = 114.73 (2)$
		$\gamma = 114.48 (2)$
Space group	$C2/c, Z = 4$	$P\bar{1}, Z = 1$
d_{calcd} (g/cm³)	1.44	1.32
$d_{obsd}{}^a$	1.70 (3)	1.26 (3)
Crystal dimensions (mm)	0.1 × 0.2 × 0.2	0.2 × 0.2 × 0.3
2θ(max) (deg)	30	40
Unique reflections	608	1897
Reflections used $F^2 > 3\sigma(F^2)$	451	1569
Parameters	123^b	223^c
$R_1{}^d$	0.060	0.038
$R_2{}^e$	0.068	0.053

^{a} Determined by pycnometry. The discrepancy in the density of the copper complex may be attributed to a difference between the bulk sample and single crystals. ^{b} 23 nonhydrogen atoms were used in the refinement. ^{c} 25 nonhydrogen atoms were used in the refinement, 24 hydrogen atoms were included but not refined. $^d R_1 = \Sigma|\Delta F|/\Sigma|F_o|$. $^e R_2 = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

Picker FACS I automatic diffractometer using a θ–2θ scan technique employing graphite monochromatized Mo Kα radiation (λ 0.7107 Å, $2\theta_m = 12.20°$). The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares calculations (Table I). Structural details for the two complex anions are presented in Table II. The
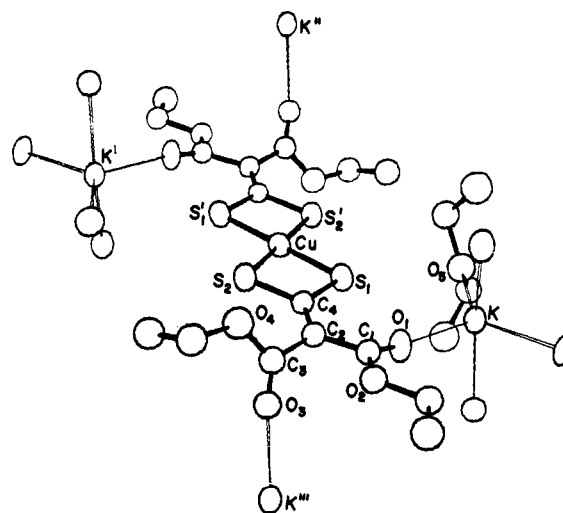
Figure 1. The structure of the $KCu(DED)_2 \cdot O(C_2H_5)_2$ complex. Thermal vibrational ellipsoids are scaled to enclose 50% probability.

Table II. Selected Structural Parameters (Å, deg) in the $Cu(DED)_2^-$ and $Ni(DED)_2^{2-}$ Anions

	$Cu(DED)_2^-$	$Ni(DED)_2^{2-}$
M—S₁	2.199 (5)	2.196 (1)
M—S₂	2.190 (5)	2.193 (1)
S₁···S₂(bite)	2.766 (6)	2.789 (2)
S₁···S₂(other)	3.407 (8)	3.389 (2)
C₄—S₁	1.77 (2)	1.738 (5)
C₄—S₂	1.76 (2)	1.749 (4)
C₄—C₂	1.32 (2)	1.367 (6)
C₂—C₁	1.51 (2)	1.450 (7)
C₂—C₃	1.50 (3)	1.486 (7)
C₁=O₁	1.18 (2)	1.208 (6)
C₃=O₃	1.15 (2)	1.190 (6)
S₁—C₄—S₂	102.9 (7)	106.2 (2)
S₁—M—S₂	78.1 (2)	78.90 (6)
M—S₁—C₄	89.2 (6)	87.1 (2)
M—S₂—C₄	89.6 (7)	87.2 (2)

numbering scheme adopted for the ligand in KCu-$(DED)_2 \cdot O(C_2H_5)_2$ (Figure 1) is also applicable for the structure of $Ni(DED)_2^{2-}$.

The metal ions in both structures are four coordinate, the MS₄ units are rigorously planar and no axial interactions are present in either of the two. Within the accuracy limits of the two determinations there appear to be no significant differences in either the coordination sphere or the structure of the ligand in the two complexes.[8] The S–S intra- and interligand contacts are very similar in both structures and suggest that resonance forms B and C do not contribute to any appreciable extent.

A common feature in both structures is the twist of one of the carboethoxy groups out of the plane of the ligand, thus verifying a prediction made earlier on the basis of infrared data.[9]

The Cu–S bond length in the present structure is similar (within 2σ) to that reported[10] for the only other

(8) Unfortunately, the best crystals that could be obtained for the KCu(DED)₂·O(C₂H₅)₂ complex still were not of sufficient quality to allow for a structural determination of comparable accuracy to that for the nickel complex.
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four-coordinated, S-bonded Cu(III) complex with a 1,1-dithio chelate (2.22 (2) Å in $Cu(Dtc)_2I_3$). A comparison of the Cu–S bond lengths in $Cu(n-Bu_2Dtc)_2I_3$ to those in $Cu(Et_2Dtc)_2$[11] shows that changes in bond lengths within the dithiocarbamate ligand are not significant, and the only real difference is found in the Cu–S bond (shorter by ~ 0.08 Å in the planar, diamagnetic Cu(III) complex). Recent epr studies have indicated[12] that the unpaired electron in $Cu(Dtc)_2$ resides in a σ antibonding orbital which is mainly composed of metal and sulfur orbitals. Removal of this electron would be expected to increase the strength of the Cu–S bond. Similar reasoning, involving a high energy σ antibonding orbital,[13] most probably accounts for the remarkably low oxidation potential of the $Cu(DED)_2^{2-}$ complex.

Acknowledgments. We are grateful to the National Science Foundation and the National Institutes of Health for financial support of this research.

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Conformation and Optical Properties of Poly(L-valine) in Aqueous Solution. "A Single Extended β Chain"[1]

Sir:

The optical properties of the β conformation of polypeptides are not yet well understood due to complexity dependent on the multitude of molecular states determined by the number of associated pleated sheets and their chain length, despite the fact that several detailed theoretical studies[2-5] have been carried out. A major distinction of the β conformation, relative to the α-helical form, is that the molecular state, *i.e.*, the number of associated chains,[2-4] severely influences the optical properties. Thus, all the attempts[6-8] to predict protein conformation based on chiroptical properties are still rather arbitrary, as different sets of standard circular dichroism patterns of helical, β, and random conformations are used. In this paper, we report the optical properties of a species of poly(L-valine) which is probably a single extended chain β structure. To solubilize this polymer in aqueous solution, it was flanked with

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DL-lysyl·HCl blocks on both sides yielding poly(DL-Lys)$_{100}$-poly(L-Val)$_{200}$-poly(DL-Lys)$_{100}$ [(DL-Lys)(L-Val)-(DL-Lys)], a typical sandwich polymer as introduced by Gratzer and Doty.[9] This polymer was synthesized by polymerizing the corresponding amino acid-N-carboxyanhydrides successively in dimethylformamide using n-hexylamine as an initiator.[10] The actual molar ratio of each residue in the copolymer as determined by amino acid analysis was Lys 57.2% and Val 42.8%.

The circular dichroism (CD) spectra and ultraviolet absorption spectra of (DL-Lys)(L-Val)(DL-Lys) in water (pH 7) are shown in Figure 1. These measurements were made respectively with a Cary 60 spectropolarimeter with a CD attachement (No. 6001) and a Cary 14 (under a nitrogen atmosphere).

The CD extrema are seen at 195 nm (peak $[\theta]_{195} = 16,000$) and at 215–216 nm (trough $[\theta]_{215} = -25,000$) where $[\theta]$ is expressed in molar ellipticity (deg cm^2 dmol^{-1}). The uv spectrum showed the maxima at 192 nm with ϵ (molar extinction coefficient) 10,600, after correction for the DL-lysyl block based on absorption spectra of poly(DL-Lys)$_{25}$. As poly(DL-Lys)$_{25}$, in the random conformation at pH 7.0, had ϵ_{max}^{192} 6200, this new form had a 70% relative hyperchromicity. This hyperchromicity can be attributed to the β conformation[11] of the central valyl block. To confirm this conformational assignment, infrared spectroscopy in D_2O solution was carried out as shown in Figure 2.

Poly(DL-Lys·HCl)$_{25}$ shows the amide I' band (D_2O) at 1645 cm^{-1}, characteristic of the random form.[12] (DL-Lys)(L-Val)(DL-Lys) has a sharp amide I' peak (D_2O) at 1636 cm^{-1} and a weak shoulder in the 1650-cm^{-1} region. As the 1650-cm^{-1} shoulder can be attributed to the random lysyl block, the 1636-cm^{-1} band is due to the L-valyl block. The characteristic amide I' of helical synthetic polypeptides is observed at *ca.* 1638 cm^{-1}[12] and thus the 1636-cm^{-1} band would suggest the helical conformation of the valyl block. However, it should be noted that the characteristic amide I' frequency of the β form in proteins differs from that of synthetic polypeptides,[12] and is seen at 1632 cm^{-1} for proteins while found at 1611 cm^{-1} for synthetic polypeptides. It can be expected that the valyl block will be surrounded by hydrocarbon side chains of the charged random DL-lysyl blocks rather than with water because of the strong hydrophobic character of the valyl residue. Therefore, the environment around the valyl block will be similar to that of certain segments in the interior of proteins. Thus, infrared results obtained on proteins will be more applicable for the conformational assignment of the valyl block. Thus from the infrared bands, the CD extrema, and the large hyperchromicity, the β conformation of the valyl block is unequivocally assigned. This conformational assignment was also supported by far-infrared solid state studies which indicated that there were no valyl residues in the helical conformation.[10] It is interesting to note the absence of the band at *ca.* 1680 cm^{-1}, characteristic of the antiparallel β form.[13] This band is absent and not arti-

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