Table I. Molecular Amplitudes [ϕ] (in Degrees) of 2:1 and 1:1:1 Square-Planar Copper(II) Complexes[a] (*ca.* 10^{-3} *M*, pH ~8)

Amino acid of parent 2:1 Cu(II) complex	$[\phi] \times 10^{-2}$						
	Parent 2:1 complex	Mixing ligands[b] (%)					
		Gly	DL-Ala	DMG	en	DL-pn	Oxalate
L-α-Alanine	−3.40	−1.70 (50)	−1.80 (53)	−1.90 (56)	−1.43 (42)	−1.48 (43)	−1.90 (56)
L-α-Aminobutyric acid	−7.4	−3.60 (49)	−3.80 (52)	−4.20 (57)	−2.99 (41)	−3.10 (42)	−3.60 (49)
L-Norvaline	−7.8	−3.85 (49)	−4.10 (53)	−4.50 (58)	−3.43 (44)	−3.45 (44)	
L-Leucine	−6.3[c]	−3.15 (50)		−3.15 (50)			
L-Valine	−13.1	−6.40 (49)	−6.65 (51)	−7.35 (57)	−5.52 (42)	−5.68 (43)	−6.20 (47)
L-Isoleucine	−15.0	−7.41 (49)	−7.60 (51)	−7.95 (53)	−6.90 (46)	−6.91 (46)	−7.90 (53)
L-Phenylglycine[d]	−25.0	−12.5 (50)	−13.0 (52)	−13.4 (54)	−11.8 (47)	−11.8 (47)	−11.7 (47)

[a] A Cary Model 60 spectropolarimeter was used for all measurements. Reproducibility varied from *ca.* ±3% in the L-α-alanine series to ±1% in the L-phenylglycine series. Because the mixed diamine complexes were in a more accessible spectral region, the precision is better; the reverse is true for the mixed oxalate complexes. [b] Values in parentheses are $[\phi]_{1:1}/[\phi]_{2:1} \times 100$. [c] This value was estimated from the value for the 1:1:1 mixed glycine complex since the parent 2:1 complex was insoluble. [d] The material used was D-phenylglycine, which was generously furnished by Kay-Fries, Chemicals, Inc.

random shifts were observed when the mixing ligand was an amino acid. A fivefold excess of inactive mixing ligand as the bis complex gave essentially a completely mixed 1:1:1 complex since larger excesses gave identical results.

An interesting feature of the data in Table I is that, whereas there is a sevenfold variation in the amplitude of the metal band Cotton effects, the diminution in amplitude in the bis(amino acid) complexes *vs.* the 1:1:1 mixed complex is approximately 50% in all cases (see values in parentheses in Table I). This is particularly evident with the glycine mixing ligand whose 1:1:1 complexes exhibit precisely a 50% diminution within experimental error. The mixed complexes with DL-Ala show only a slightly higher amplitude (*ca.* 2%) than the glycine complexes even though the mixed DL-Ala complexes are most certainly a composite of diastereomers. The trend to higher amplitudes for the mixed complexes with α substitution in the mixing ligand is amplified with DMG, the increase over the glycine complexes being an average of *ca.* 5%. On the basis of these results, where the ligand field about the metal is changing negligibly, it can be concluded that changing steric requirements of the mixing ligand has a negligible or small effect on the Cotton effect amplitude of the d-d transition. The lack of a cross-plane steric effect as a factor in the magnitude of the metal band rotational strength is further evidenced by the Cotton effects of the mixed ethylenediamine and DL-propylenediamine complexes. Again, the mixed DL-propylenediamine-amino acid complexes are undoubtedly diastereomeric mixtures; nevertheless, the Cotton effects for the mixed en and DL-pn complexes are identical within experimental error.

On the other hand, changes in the ligand field strength as a result of changing from 2:1 amino acid complexes to 1:1:1 mixed complexes involving either a diamine or oxalate ligand also exert only a small effect upon the d-d Cotton effect. Thus, the ethylenediamine mixed complexes show a diminution to 41-47% of that for the parent 2:1 amino acid complex, whereas the mixed oxalate complexes give Cotton effect amplitudes on the order of 48-56% of the amplitudes of the 2:1 complexes.[4]

It is evident from these results that *cross-plane, steric, and electronic interactions between ligands and ligand field changes have small or negligible effects on the Cotton effect amplitudes of a d-d transition in an amino acid-copper(II) complex.*

Acknowledgment. We wish to thank the U. S. Public Health Service (1 R01 GM 13,962-01) and the Research Foundation of the State University of New York for partial support of this work.

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Relationship of Ring Conformation to Rotational Strengths of d-d Transitions in Amino Acid-Copper(II) Complexes

Sir:

In the preceding communication[1] data are presented which demonstrate negligible vicinal interactions on the visible optical rotatory dispersion (ORD) curves of a variety of amino acid-copper(II) complexes. On the other hand, the rotational strengths, as measured by the Cotton effect amplitudes, were found to be very sensitive to the substituted glycine ($RCHNH_2COOH$). Thus, the d-d transition amplitudes for the 2:1 or 1:1:1 complexes show a sevenfold variation with the effect of the R group being in the order $CH_3 < CH_2CH_3 < CH_2CH_2CH_3 < CH(CH_3) < CH_2Ph \not< Ph$.

In order to gain further insight into the nature of substituent effects on the ORD spectra of copper(II) chelate systems, we have measured the spectra of several amino acid-copper(II) complexes with special emphasis placed on those amino acids which could act as tridentates. The Cotton effect amplitudes for the d-d transition are given in Table I. The visible region ORD curves of several 1:1:1 amino acid-glycine-copper(II) complexes are presented in Figure 1 for comparison.

Recently, Mason and Norman have argued that the optical activity of trigonal complexes is due in a large measure to mixing of d-d with charge-transfer transitions involving both the chelate ligand and metal.[2] Hence, the optical activity can be expected to be sensi-

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(4) In the case of mixed oxalate complexes, preliminary CD data indicate the diminution is actually 43-49%.

(1) K. M. Wellman, T. G. Mecca, W. Mungall, and C. R. Hare, *J. Am. Chem. Soc.*, **89**, 3646 (1967).

(2) S. F. Mason and B. J. Norman, *Chem. Commun.*, 48 (1965).

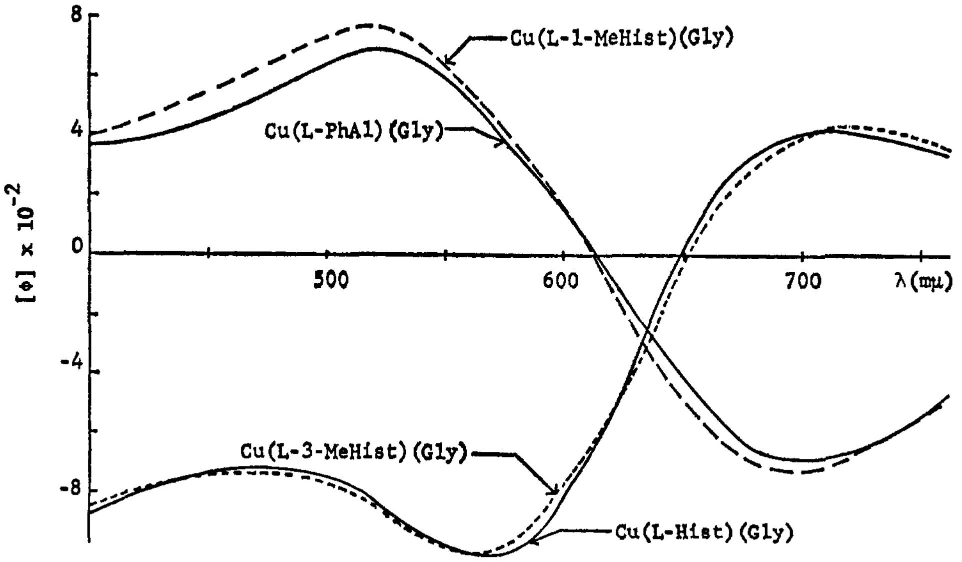
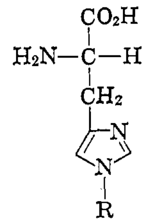
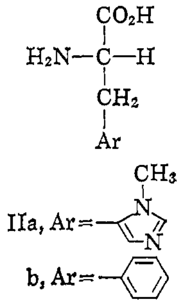


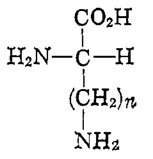
Figure 1. Visible region optical rotatory dispersion spectra of 10^{-3} *M* solutions of L-1-methylhistidinatoglycinatocopper(II), L-phenylalaninatoglycinatocopper(II), L-3-methylhistidinatoglycinatocopper(II), and L-histidinatoglycinatocopper(II).

tive to the conformation of the chelate ring. Woldbye still earlier pointed out the possibility that ring conformations can influence optical activity of complexes.[3]



Ia, R=H
b, R=CH_3





$$H_2N-\overset{\overset{\displaystyle CO_2H}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{\underset{\displaystyle (CH_2)_n}{\underset{|}{C}}}}-H$$

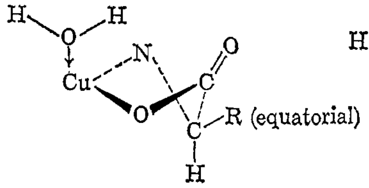
IIIa, $n = 2$
b, $n = 4$

X-Ray evidence has shown that the amino acid–copper(II) chelate ring is puckered;[4] hence, the ligand can take up the two extreme conformations, IV and V, corresponding to k′ and k conformations, respectively. The important point to note here is that the ring conformations k′ and k are of opposite chirality, *i.e.*, they bear a mirror image relationship to one another. Therefore, the d–d Cotton effect amplitudes of the two chelate conformers k′ and k will be equal and opposite in sign. The direct contribution of the R groups in IV and V will be predictably small because of their relatively long distance from the absorbing chromophore. Indirectly, however, the R groups can be all-important since they determine the conformational equilibrium IV ⇄ V.

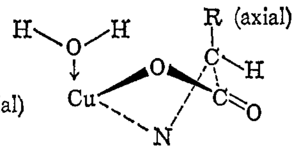
Table I. Molecular Amplitudes [ϕ] of Some α-Amino Acid–Glycine–Copper(II) Complexes[a]

α-Amino acid	$[\phi]_{1:1:1} \times 10^{-2}$, degrees
L-Histidine (Ia)	+14.2
L-3-Methylhistidine (Ib)	+14.1
L-1-Methylhistidine (IIa)	−14.6
L-Phenylalanine (IIb)	−12.5
L-2,4-Diaminobutyric acid (IIIa)	+24.4
L-2,6-Diaminohexanoic acid (IIIb)	−3.2

[a] Spectra were measured with a Cary 60 spectropolarimeter using 10^{-3} *M* aqueous solutions at pH ~8. For methods see ref 1.



IV (k′)



V (k)

Assuming that nonbonded interactions between water coordinated along an axis normal to the molecular plane[5] and the axial R group destabilize V relative to IV, then the R group "size" effect in the above sequence represents a shift in the equilibrium (IV ⇄ V) as the R group is varied. When R is phenyl, the equilibrium will be displaced strongly in favor of IV and a correspondingly large Cotton effect amplitude representative of the k′ conformation will be observed. Small groups such as methyl permit the presence of increasing amounts of V with a concomitant decrease in the observed amplitudes.

The ligands Ia, Ib, and IIIa present a new situation since in each case a second nitrogen atom is present which allows the amino acid to act as a tridentate. In the case of the bis(histidino)copper(II) complex, potentiometric and ion-exchange techniques indicate that histidine acts as a tridentate ligand.[6] A consequence of these ligands acting as tridentates will be to force the amino acid–copper(II) chelate ring into the k configuration. Hence, a positive Cotton effect is predicted and observed (see Table I) for the complexes Ia, Ib, and IIIa. In contrast, L-1-methylhistidine (IIa) has an N-methyl group which prevents the imidazole group from coordinating into the axial position.

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(4) H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Cryst.*, 71, 1463 (1964).

(5) J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, 8, 1277 (1954).

(6) J. Z. Hearon, D. Burk, and A. L. Schade, *J. Natl. Cancer Inst.*, 9, 337 (1949); N. C. Li, E. Doody, and J. M. White, *J. Am. Chem. Soc.*, 79, 5859 (1957); R. Leberman and B. R. Rabin, *Trans. Faraday Soc.*, 55, 1660 (1959).

As anticipated, IIa gives a Cotton effect amplitude opposite to Ia and Ib but similar in sign and magnitude to its carbocyclic analog, phenylalanine. In the case of the acid IIIb, unfavorable ring size requirements will prevent the ligand from acting as **a** tridentate. Thus, IIIb behaves as a simple amino acid (compare with L-2-aminobutyric acid and L-norvaline complexes in ref 1).

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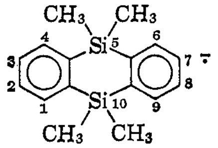
Line Broadening in Electron Spin Resonance Spectra of 5,10-Dihydrosilanthrene Radical Ion Pairs[1]

Sir:

Previous electron spin resonance studies of organosilane anion radicals have provided evidence for spin delocalization into silicon 3d orbitals.[2,3] A radical anion with the unpaired electron entirely delocalized in overlapping silicon d orbitals has been made by alkali metal reduction of dodecamethylcyclohexasilane in ether solvents.[4]

We have made an esr study of the radical anions of certain 5,10-dihydrosilanthrene, dibenzasilole, and silacyclopentadiene derivatives. Spin densities obtained from Hückel-McLachlan MO calculations correlate well with experimentally obtained coupling constants.[5] In this communication we report on the effect of solvent and metal ion on the esr spectrum of 5,5,10,10-tetramethyl-5,10-dihydrosilanthrene radical anion (I).



I

Radical anion I is readily obtained by sodium or potassium reduction in 1,2-dimethoxyethane (DME) at room temperature. The esr spectrum at low resolution consists of five lines due to four equivalent hydrogens, A_H = 2.2 gauss. From MO calculations[5] and by analogy to similar radicals[6] the hyperfine coupling is assigned to hydrogens in the 2, 3, 7, and 8 positions. Under better resolution more lines with 0.18-gauss spacing due to methyl hydrogens are obtained (Figure 1). This radical is probably the free ion since identical spectra are obtained using either sodium or potassium as gegenion. The spectrum does not change at lower temperature (−52°) except that the lines sharpen. In tetrahydrofuran (THF) potassium reduction gives the same spectrum at room temperature, but at lower temperatures (−87°) marked line-width alternation is observed (Figure 1).[7] At −115° broadening has progressed to the point that the observed intensity sequence of the multiplet is approximately 1:0.5:4:0.5:1, as compared to the normal 1:4:6:4:1 expected for four equivalent hydrogens. In diethyl ether (DEE) similar results are obtained within the same temperature range. At lower temperatures the intensity sequence becomes 1:0.1:1.4:0.1:1 at −125° and 1:0:1:0:1 at −141°.

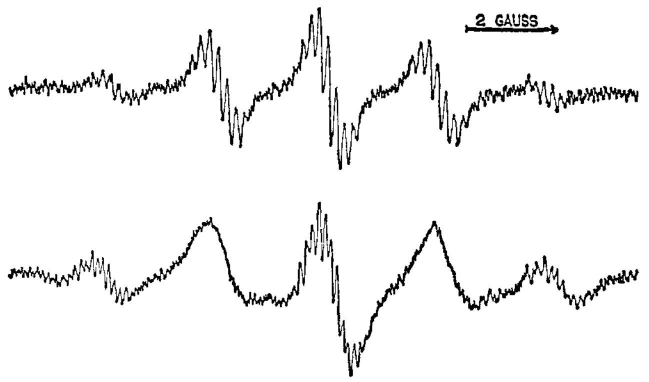
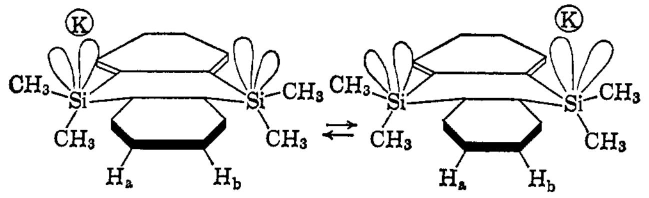


Figure 1. Esr spectrum of tetramethyl-5,10-dihydrosilanthrene radical anion in dimethoxyethane at room temperature (top) and in tetrahydrofuran at −87° (bottom). Gegenion is potassium in both cases.

The line-broadening process observed in THF and DEE (to −115°) comes from rapid interchange of two slightly different coupling constants in the molecule. Since in these solvents ion pairing usually takes place, the line broadening could be caused by rapid interchange of the location of potassium ion in the molecule. A choice location would seem to be a silicon 3d orbital since MO calculations place the largest spin density (and hence charge) on this atom (almost 20% per silicon atom). We suggest that the following equilibrium exists in solutions of I in THF or DEE.[8]



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[1] Organometallic Radicals. I. This work is supported by a grant from Dow Corning Corp. Grateful acknowledgment is hereby made.

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[5] Presented at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 27–29, 1966, Paper No. 119.

[6] *E.g.*, thianthrene S,S,S′-tetroxide: R. Gerdil and E. A. C. Lucken, *Mol. Phys.*, **9**, 529 (1965); E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963).

[7] For a review and discussion of line-width alternation and broadening processes in anion radical ion pairs see M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967).

[8] No definitive information regarding the structure of 5,10-disilanthrenes or the radical anions is available at this time. The line width of the methyl proton nmr peak is not temperature dependent at temperatures down to −75° (private communication from Dr. W. H. Atwell). Models show small barriers to bond inversion about the silicon atom but considerable steric interaction between one pair of methyl groups in a nonplanar structure. In the contact radical ion pair a small deviation from planarity would seem to provide better d-orbital bonding facilities for the metal ion than a completely planar structure. Our data for the free radical anion are consistent with either a planar or rapidly inverting structure while for the contact ion pair a structure deviating slightly from planarity is suggested. An analogous sulfur compound, 5,10-thianthrene dioxide, exhibits an inversion rate of greater than 100 sec^{-1}: K. F. Purcell and J. R. Berschied, Jr., *J. Am. Chem. Soc.*, **89**, 1579 (1967).