chloride was cooled to 0° under an inert atmosphere. To the magnetically stirred solution, 16.7 g (0.088 mol) of triethyloxonium fluoroborate was added, followed by dropwise addition of 10.0 g (0.088 mol) of ethyl diazoacetate. The reaction mixture was maintained at 0° for 3 hr, during which time nitrogen evolved, and then was quenched with 150 ml of saturated sodium bicarbonate solution. After stirring for 0.5 hr at room temperature, the methylene chloride was separated and dried, and the solvent was removed. Distillation of the residue at reduced pressure gave 8.2 g (90%) of 2-carbethoxycycloheptanone, bp 80–82° (0.05 mm).

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Apical Interaction in the Copper(II) Complex of L-Alaninamide with Diethylenetriamine

Sir:

In the previous paper,[1] we reported studies on the poly-L-lysine–copper(II) complex whose circular dichroism (CD) in the ligand-field region was not observed until the peptide amide nitrogen coordinated to the copper(II) ion. In order to clarify the structure of the poly-L-lysine–copper(II) complex, it was necessary to examine amplitudes and wavelengths at CD extrema for the copper(II) complex, in which an amide nitrogen coordinates to the copper(II) ion in the planar or the apical position.

In this communication, we wish to report experimental results which demonstrate that the copper(II) complex of L-alaninamide with diethylenetriamine (dien) has the amide nitrogen coordinated to the copper(II) ion in the apical position, whereas the copper(II) complex of L-alaninamide with ethylenediamine (en) has the amide nitrogen in the planar position.

Wellman, *et al.*,[2] reported detection of apical interaction in copper(II) complexes of potential tridentate α-amino acids by optical rotatory dispersion, and that an α-amino acid substituted with a heteroatom X (*e.g.*, $HOOCCHNH_2(CH_2)_nX$), capable of coordinating with the apical position, might disturb the ring conformational equilibrium ($\lambda \rightleftharpoons \delta$) in favor of an increased λ population with a concomitant shift in the observed Cotton-effect amplitude toward more positive values. However, no study has been reported in relation to the vicinal effects of an asymmetric carbon in a ligand coordinated apically to a copper(II) ion.

The L-alaninamide (L-alaamide) used here as a ligand was derived from L-alanine by a method similar to that described in the literature,[3] which had mp 79–81° (lit.[4] 83–84°) and $[\alpha]_D$ +16.3° (*c* 2.35, H_2O) (lit.[4] +11.1°). All other materials were guaranteed reagents and purified in the usual manner. The pH titrations were carried out by the use of a Hiranuma Model RAT-101 recording pH apparatus. dien and en were protonated by adding HCl in preparing the stock solution. During titration, the solutions were protected from CO_2 by a stream of nitrogen. Both absorption and CD spectra were obtained by a Jasco Model ORD/UV-5 spectrophotometer with a CD attachment. The infrared absorption spectra were recorded on a Hitachi Model G_2 grating infrared spectrophotometer with small bags made of polyethylene films held between NaCl plates.

Potentiometric titrations with base of 1:1:1 molar ratio of copper(II):L-alaninamide:dien or en were performed. The titration curves show a definite inflection at α = 3 or 2 in the case of dien or en, respectively, where α is the number of moles of base added per mole of ligand (L-alaninamide). From the stability constant[5] of dien or en with copper(II) ion, the first 2 or 3 equiv of protons titrated are thought to be due to the ammonium protons in dien or en, respectively.

In the infrared (ir) spectra of the copper(II) complex of L-alaninamide with dien in an aqueous (D_2O) solution, a band around 1633 cm^{-1} is seen at pD below 8.5, which is assigned to an amide carbonyl band. At pD 9.45 a weak band at 1565 cm^{-1} was observed together with the strong band at 1633 cm^{-1}. As the pD value increases over 9.5, the band at 1633 cm^{-1} is replaced by a strong band around 1565 cm^{-1}, which is considered to be due to the carbonyl group of the amide coordinated to the copper(II) ion with displacement of proton.[6] On the other hand, in the case of the copper(II) complex of L-alaninamide with en, the band of the amide carbonyl group coordinating to the copper(II) ion was observed at 1615 cm^{-1} at pD 5.4. At pD 6.60 the weak band around 1565 cm^{-1} appeared beside a strong band at 1615 cm^{-1}. The band at 1565 cm^{-1} became stronger as the acidity of the solution was decreased, whereas the band at 1615 cm^{-1} became weaker. At pD 7.88, the band at 1565 cm^{-1} became stronger than that at 1615 cm^{-1}. As pD increases further, the band at 1615 cm^{-1} is replaced by a strong band at 1565 cm^{-1}.

Table I shows the absorption and CD spectral data of the copper(II) complexes.

Table I. Absorption (AB) and Circular Dichroism (CD) Spectra Data of Copper(II) Complexes

Complex	pH	AB Log ε ($\tilde{\nu}_{max}$, 10^3 cm^{-1})	CD Δε[a] ($\tilde{\nu}_{max}$, 10^3 cm^{-1})
Cu(dien)(L-alaamide)	4.8	1.95 (16.3)	
	7.8	1.99 (16.5)	−0.013 (18.1)
	9.4	1.99 (16.5)	−0.016 (18.2)
	11.8	1.99 (16.5)	−0.019 (18.3)
Cu(en)(L-alaamide)	5.0	1.42 (15.0)	
	6.5	1.68 (16.8)	−0.033 (16.6)
	7.6	1.77 (17.8)	−0.065 (17.7)
	11.7	1.81 (18.5)	−0.108 (18.2)
Cu(dien)(L-alanine)	6.2	1.98 (16.3)	−0.010 (16.5)
	9.3	2.06 (16.2)	−0.032 (17.6)
	11.7	2.00 (16.4)	−0.005 (17.3)

[a] The magnitudes of the deflections observed in comparison to the noise level were less than ±5%.

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(1) M. Hatano, T. Nozawa, and M. Yoneyama, *Bull. Chem. Soc. Jap.*, 43, 295 (1970), and references cited there.

(2) K. M. Wellman, T. G. Mecca, W. Mungall, and C. R. Hare, *J. Amer. Chem. Soc.*, 90, 805 (1968).

(3) P. S. Yang and M. M. Rising, *ibid.*, 53, 3183 (1931); G. Hillmann, *Z. Naturforsch.*, 1, 682 (1946).

(4) T. Komorita, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, 42, 168 (1969).

(5) G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, pp 370 and 472.

(6) K. Nakamoto in "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., Wiley, New York, N. Y., 1968, p 279.

The pH titration curves show that, in the copper(II) complexes of L-alaninamide or L-alanine with dien, the dien–copper(II) complex is formed with an α value <3. The ir spectra and the pH titration curves suggest that the amino group of L-alaninamide or L-alanine coordinated to the copper(II) ion in the region of $\alpha = 3$–4.

The variation in the CD amplitude for the copper(II)–L-alanine–dien complexes implies that L-alanine forms a chelate to the copper(II) ion with a carboxyl group at the apical position, but it coordinates to the copper(II) ion unidentately at pH 11.7. This suggestion was supported by the ir spectra, which had bands at 1607 (pH 6.6), 1588 (pH 9.7), and 1570 cm^{-1} (pH 13.5), assigned to the carboxyl group band coordinated to the copper(II) ion in the planar position, the carboxyl group band coordinated to the Cu(II) ion in the apical position, and the free ionized carboxyl group, respectively. Judging from the fact that the ir spectra of the copper(II) complex of L-alaninamide with dien had no peak at 1565 cm^{-1} at $\alpha < 4$, the amide nitrogen was not thought to coordinate to the copper(II) ion at this point. However, the CD amplitude is as large value as that at $\alpha = 5$, and is similar to that for the copper(II)–L-alanine–dien complex at pH 9.3 ($\alpha = 5$). Thus, the amide carbonyl group is considered to interact with the copper(II) ion in this region ($3 < \alpha < 4$). As the pH increases further (pH >8, $\alpha > 4$), the amide nitrogen starts to coordinate to the copper(II) ion, which is indicated from the occurrence of the ir band at 1565 cm^{-1}, when it was considered to coordinate to the copper(II) ion at the apical position.

In the case of the copper(II) complex of L-alaninamide with en, the copper(II) ion interacts with en at $\alpha < 2$, when the 1615-cm^{-1} band in the ir spectrum indicates that the amide carbonyl group also coordinates to the copper(II) ion. The pH titration curve suggests that the amino nitrogen of L-alaninamide seems to coordinate predominantly to the copper(II) ion from pH 5.5 ($\alpha = 2$) to pH 7.1 ($\alpha = 3$). This is supported by the fact that the ir spectra in this system show little absorption at 1570 cm^{-1}. The ir spectra at pH 7.88 with a band at 1570 cm^{-1} indicate that a donor-atom exchange between the carbonyl group and the amide nitrogen occurs in the pH over 7.

The amide nitrogen in the copper(II) complex of L-alaninamide with en coordinates to copper(II) ion with displacement of a proton at pH *ca.* 7, whereas the amide nitrogen in the copper(II) complex of L-alaninamide with dien coordinates at pH *ca.* 9.5. This result suggests that the coordination position occupied by the amide nitrogen differs between these two complexes.

Moreover, the copper(II) complex of L-alaninamide with en exhibits an absorption maximum in the ligand-field region at a higher wave number by 2 kcm^{-1} than does the copper(II) complex of L-alaninamide with dien (Table I). From these results, it can be confirmed that the amide nitrogen coordinates to the copper(II) ion in the planar position in the former, whereas in the latter it coordinates to the copper(II) ion in the apical position, since the amide nitrogen is higher in the spectrochemical series than the amino nitrogen. The difference in the CD amplitude by one order between these systems may also support this view.

It is also seen that optical activity is apparent over the whole of the visible absorption spectrum in the copper(II) complex of L-alaninamide with en, whereas in the copper(II) complex of L-alaninamide with dien circular dichroism appears mainly in the highest energy component. This indicates that the effective field symmetry is approximately D_{4h} in the latter, whereas the symmetry is highly distorted from D_{4h} in the former,[7] which may be satisfied if we distinguished the amide nitrogen from the amino nitrogen and neglected the groups other than the donor atoms in the main plane.

[7] M. Parris and A. E. Hodges, *Can. J. Chem.*, **48**, 1166 (1970). This paper presents a discussion similar to ours.

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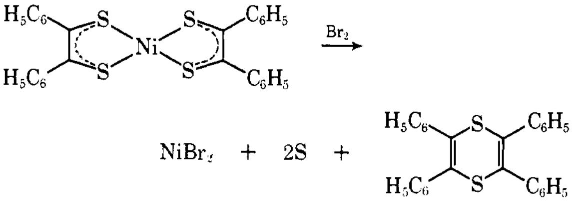
Formation, Properties, and Structure of Cation Radicals of *cis*-1,2-Ethylenedithiols in the Oxidative Solvolysis of Metal Bis- and Trisdithienes

Sir:

Although considerable information is available on radical anions of metal dithienes $M(S_2C_2R_2)_2^-$ or $M(S_2C_2R_2)_3^-$,[1] little is known about cationic species $M(S_2C_2R_2)_2^+$ or $M(S_2C_2R_2)_3^+$ and of metal free ligand radicals derived from *cis*-1,2-ethylenedithiols. To obtain cationic metal dithienes we have previously investigated the oxidation of, *e.g.*, $Ni(S_2C_2(C_6H_5)_2)_2$ with Br_2 but only isolated tetraphenyl-1,4-dithiin, according to[2]



(1)

In subsequent attempts, we have utilized milder methods of oxidation such as H_2SO_4–CH_3NO_2 and $AlCl_3$–CH_3NO_2, which have previously been employed for the oxidation of various sulfur compounds to radical cations.[3,4] All metal bis- and trisdithienes are oxidized under these conditions but undergo simultaneous solvolysis, making it impossible to detect metal dithiene cation radicals presumably formed as initial products. However, the reaction produces two types of radical species characterized by esr signals around $\langle g \rangle = 2.006$ (signal type I) and $\langle g \rangle = 2.014$ (signal type II). By conducting the oxidations in dilute (5–15 wt %) H_2SO_4 in anhydrous CH_3NO_2 signal I could be generated free of signal II and was subsequently identified as due to the cation radicals of 1,4-dithiins (**1**) whose identity was ascertained by comparison with the cation radicals

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[1] See (a) G. N. Schrauzer, *Transition Metal Chem.*, 4, 299 (1968), and references therein; (b) G. N. Schrauzer, *Accounts Chem. Res.*, 2, 72 (1969), and references cited therein; (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1127 (1963); 3, 814 (1964); (d) J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

[2] G. N. Schrauzer and V. P. Mayweg, *Z. Naturforsch. B*, **19**, 192 (1964).

[3] (a) W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, **88**, 2862 (1966); (b) P. D. Sullivan, *ibid.*, **90**, 3618 (1968).

[4] (a) U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 3, 602 (1964); (b) J. H. Hirshon, D. M. Gardner, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **75**, 4115 (1953).