

SHORT COMMUNICATIONS

Ethylenediamine Conjugates of Bis-*O*-carboxymethylsalicylaldehyde-alkylenediimine-copper*

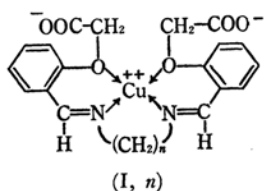
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The isolation and the structures of the penta-coordinate addition compounds of bis-salicylaldehyde-ethylenediimine-copper with acids and phenols have previously been reported.¹⁾ Therefore, it now seems of interest to synthesize some side-chain acid bis-salicylaldehyde-ethylenediimine-copper substances and examine their chemical behavior.

Yellow-green bis-*O*-carboxymethylsalicylaldehyde-ethylenediimine-copper (I, $n=2$)- $2\text{H}_2\text{O}$, (Found: C, 49.80; H, 4.83; N, 5.71; Cu 13.36. Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_6\text{Cu}\cdot 2\text{H}_2\text{O}$: C, 49.84; H, 4.60; N, 5.68; Cu, 13.19%) was synthesized through copper salt of *O*-carboxymethylsalicylaldehyde. Found: C, 47.13; H, 4.13, Cu, 13.86. Calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_8\text{Cu}\cdot 2\text{H}_2\text{O}$: C, 47.20; H, 3.69; Cu, 13.88%.



The 1660 cm^{-1} peak in its infrared spectra as well as the $830\text{ m}\mu$ absorption maximum in its visible spectra support a partially-polarized²⁾ ionic structure.³⁾

Ethylenediamine conjugate (II, $n=2$) was obtained by the reaction of (I, $n=2$) with two moles of ethylenediamine in an alcoholic solution.

The analytical results (Found: C, 46.72; H, 6.49; N, 13.95; Cu, 10.34. Calcd. for $\text{C}_{24}\text{H}_{36}\text{N}_6\text{O}_7\text{Cu}\cdot 3\text{H}_2\text{O}$: C, 45.16; H, 6.63; N, 13.17; Cu, 9.96%) and the titration curve (Fig. 1) substantiate the formula, [(I, $n=2$)- $2\text{C}_2\text{H}_4(\text{NH}_2)_2$ -

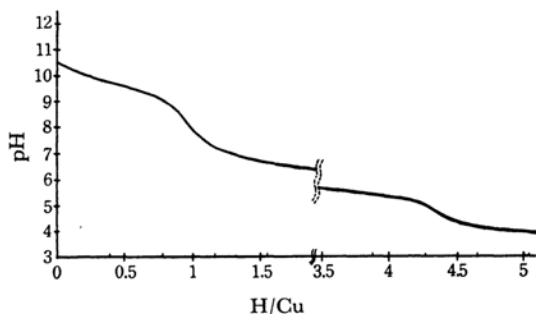


Fig. 1. Titration of (II, $n=2$), 186.67 mg. in 50 ml. H_2O , titrated with 1.0 N HCl ($f=1.135$).

$\text{H}^+(\text{OH})\cdot 3\text{H}_2\text{O}$, of the ethylenediamine conjugate (II, $n=2$). The 1578 cm^{-1} peak of the perfectly-ionized carboxylate ion⁴⁾ in the infrared spectra and the $570\text{ m}\mu$ absorption maximum in the visible region, unlike those of the chelate (I, $n=2$), reveal the structural difference between (I, $n=2$) and (II, $n=2$). By dehydration (II, $n=2$) changes, by way of a blue modification (weight decrease; Found: 8.35%. Calcd. for $3\text{H}_2\text{O}$: 8.47%), into a green compound (weight decrease: Found; 11.1%; Calcd. for $4\text{H}_2\text{O}$: 11.3%), which, in dry air or in an oxygen atmosphere, changes into a gray modification (III, $n=2$) (weight increase: 2.56–2.96% and, slowly, 3.6–4.0%).

Several bis-*O*-carboxymethylsalicylaldehyde-alkylenediimine-copper (II, $n=2$ –6)- $2\text{H}_2\text{O}$ substances and their ethylenediamine conjugates (II, $n=2$ –6) are given in Table I.

TABLE I. BIS-*O*-CARBOXYMETHYLSALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER (I, n)- $2\text{H}_2\text{O}$ AND THEIR ETHYLENEDIAMINE CONJUGATE (II, n)

$n=$	(I, n) Color	(II, n) Color
2	yellow-green	purple
3	green	purple
4	green-blue	purple
6	pale-blue	purple

* Part VIII of "Some Addition Compounds of Salicylaldehyde-ethylenediimine-copper." Partly reported in the Proceedings of the IX I. C. C. C., St. Moritz, 1966.

** Eisai Pharmaceutical Company.

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