

On the Reaction of Copper(II) Chloride with 2-Aminoethanol ("Monoethanolamine") in Acetone Solution

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During preparations of different copper(II) complexes of 2-aminoethanol ("monoethanolamine"), the isolation of CuL_2Cl_2 ($\text{L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) reported by Udovenko and Artemenko¹ was attempted. The composition of the product was not in accordance with the given formula, as it was also pointed out in a recent paper by Udovenko *et al.*,² where the product was formulated as $\text{CuCl}_2 \cdot 2(\text{CH}_3)_2\text{C} = \text{NC}_2\text{H}_4\text{OH}$, *i.e.* a complex containing two molecules of a Schiff base derived from acetone and 2-aminoethanol.

When Curtis³ first observed a similar reaction in acetone solutions of nickel(II) ethylenediamine complexes, he formulated the ligands in the isolated products as Schiff bases between ethylenediamine and acetone, but later Curtis and House,⁴ by observing mesityl oxide in the steam distillate of the destructed complexes, reformulated them to contain cyclic tetradentate ligands derived from 4-methyl-3-penten-2-one (mesityl oxide).

In analogy with this, one would expect that $\text{CuCl}_2 \cdot 2(\text{CH}_3)_2\text{C} = \text{NC}_2\text{H}_4\text{OH}$ ought to be reformulated as the isomeric complex (Fig. 1):

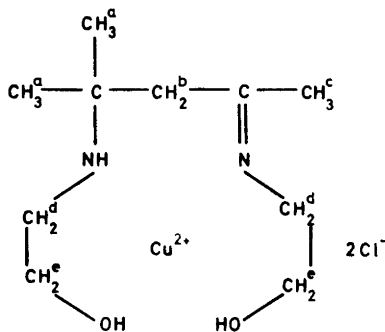


Fig. 1. Expected structure of the compound $\text{CuC}_{10}\text{H}_{22}\text{N}_2\text{O}_2\text{Cl}_2$. Upper indices are used in assignment of peaks in ^1H NMR spectra.

To verify this, the compound was isolated according to Udovenko *et al.*² (Found: C 35.34; H 6.52; N 8.30; Cl 21.10. Calc. for $\text{CuC}_{10}\text{H}_{22}\text{N}_2\text{O}_2\text{Cl}_2$: C 35.67; H 6.55; N 8.32; Cl 21.08.)

The complex was dissolved in water and decomposed by Na_2S ; the filtrate from CuS was acidified with HCl and then evaporated until dryness. The residue was treated with slightly acidified (HCl) methanol, and the methanolic solution was then evaporated yielding an oily product.

^1H NMR spectra (Fig. 2) of the oil dissolved in D_2O show two groups of peaks (Table 1), in the sense that the intensity ratios remain constant within a group from experiment to experiment, whereas the ratio between the intensities of the peaks at, *e.g.*, 1.45 δ and 3.8 δ varies, but is always less than 3/2.

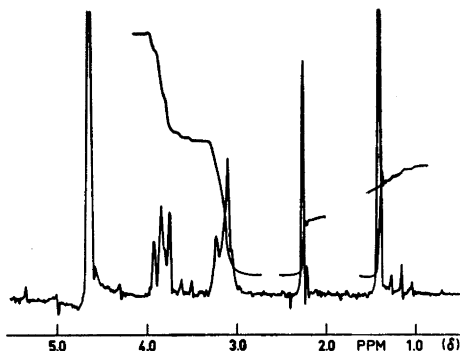


Fig. 2. ^1H NMR spectrum of the residue after destruction of $\text{CuC}_{10}\text{H}_{22}\text{N}_2\text{O}_2\text{Cl}_2$ with Na_2S . Values of integrals: 45(1.45 δ): 23(2.3 δ). 16(3.1 δ) + 43(3.15 δ): 42(3.8 δ).

By many recrystallisations of the oily product using acidified water-containing methanol/ethyl ether, a crystalline white compound was obtained, having a ^1H NMR spectrum consisting of two triplets at 3.15 δ and 3.8 δ with intensity ratio 1:1. This compound was shown by its IR spectrum and by its melting point to be 2-hydroxyethylammonium chloride. It is seen, that ^1H NMR spectra can be interpreted as arising from mixtures of 2-hydroxyethylammonium chloride and hydrogen chlorides of 4,4,6-trimethyl-3,7-diaza-6-en-1,9-nonanediol. As the latter on hydrolysis will produce a β -amino

Table 1. Assignments of peaks in the ^1H NMR spectrum of the residue after destruction of $\text{CuC}_{10}\text{H}_{22}\text{N}_2\text{O}_2\text{Cl}_2$.

PPM (δ)	Degen- eracy	Relative intensities	Assign- ment	
1.45	singlet	6	CH_3^a	Group I
2.3	singlet	3	CH_2^c	
3.1	singlet	2	CH_2^b	
3.15	triplet	1	CH_2^d	Group II
3.8	triplet	1	CH_2^e	

ketone, which would decompose to form the amine and mesityl oxide,⁵ and as mesityl oxide would decompose to acetone in acidic solutions, it seems reasonable to claim the structure given in Fig. 1 as representative for the product obtained by the cited procedure.

The IR spectrum of the compound under discussion contains a band at 3225 cm^{-1} , not explicable in terms of a complex derived from the Schiff base of acetone and 2-aminoethanol, but close to the value observed for secondary amine complexes,⁶ e.g. in triethylenetetramine copper(II) at 3195 and 3225 cm^{-1} , a fact which also lends support to the claimed structure.

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Conformational Spectroscopic Studies of *trans*-1,2-Chloroiodocyclohexane

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Based upon our earlier work we have recently reinvestigated^{2,3} the vibrational spectra of some *trans*-1,2-dihalocyclohexanes as liquids, dissolved in various solvents and as crystalline solids at low temperatures and under high pressures. It appears that the energy difference between the *ee* and *aa* conformation for these molecules is not very large in the liquid state. They crystallize² in the *ee* or *aa* conformations depending upon which halogens are attached to the ring; the dichloro in *ee*, dibromo in *aa*, whereas bromochlorocyclohexane can crystallize in both conformations.^{2,3} We felt it would be of interest to extend these studies to other *trans*-1,2-dihalocyclohexanes to elucidate the steric and polar effects of the halogens upon the conformational stabilities. Moreover, we wanted so far as possible to assign the observed infrared and Raman bands to the *ee* or *aa* conformations and correlate the conformations with the vibrational spectra.

Attempts to prepare the corresponding bromoiodo- and diiodocyclohexane failed, but *trans*-1,2-chloroiodocyclohexane (CIC) could be prepared. To our knowledge this compound has not been studied previously, and the infrared and Raman spectra will be discussed in the present communication.

Experimental. Hypoiodous acid was added to cyclohexene and the formed 2-iodocyclohexanol reacted with phosphorus pentachloride dissolved in benzene. The reaction product was distilled three times under reduced pressure (b.p. 55° at 1 torr).

The infrared and Raman spectrometers have been described, additional infrared bands below 200 cm^{-1} were recorded on a Hitachi Perkin-Elmer FIS 3 spectrometer. A crystalline low temperature solid of CIC was finally achieved after prolonged annealing just below the melting point, but attempts to crystallize the compound under high pressure at room temperature were not successful.