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Crystalline Complexes of Allylamine and Propylamine with Copper(I) Chloride and Bromide

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Crystalline 1 : 1 and 1 : 3 complexes of allylamine and propylamine with copper(I) chloride and bromide were synthesized *in vacuo*. Equilibrium vapor pressures of these complexes were measured at several temperatures and the enthalpy of ligation of each amine molecule was determined. Both the thermochemical and infrared absorption data indicate that in the 1 : 1 complexes of allylamine the ligand molecule serves as a bidentate, but in the 1 : 3 complexes the second and third ligand molecules link to the metal only through the amino nitrogen atom.

The ability of simple aliphatic amines to form metal coordination compounds have been examined and found to decrease in the series[1] $NH_3 > RNH_2 > R_2NH > R_3N$. Recently Yoke and his collaborators reported copper(I) chloride complexes of triethylamine,[2] diethylamine[3] and ethylamine.[4] However, the unsaturated amine such as allylamine has not yet been employed as the coordinating ligand. In this paper we report crystalline complexes of copper(I) chloride and bromide with allylamine and propylamine which were synthesized by the same method as that previously adopted in the syntheses of copper(I) chloride complexes of acrolein[5] and allyl alcohol.[6]

Experimental

Materials. Copper(I) chloride and bromide were prepared by the ordinary method[5] and purified by the distillation *in vacuo*. Allylamine (abbreviated as am in this paper), $CH_2{=}CHCH_2NH_2$, and propylamine (abbreviated as pm) were dried with Molecular Sieves Type 3A, Linde Co. and the freshly distilled sample was used in each experiment.

Syntheses of Copper(I) Halide-Amine Complexes with the Mole Ratio of One to Three. Allylamine or propylamine (10—15 g) was distilled into an ampoule containing pulverized copper(I) chloride or bromide (1g). In each case the exothermic reaction occurred and colorless, transparent and bulky crystals grew up on copper(I) halide powder. The reaction

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[1] J. C. Bailar, Jr., and D. H. Busch, "The Chemistry of the Coordination Compounds," ed. by J. C. Bailar, Jr., Reinhold Publishing Co., New York, N. Y. (1956), p. 62; W. E. Hatfield and J. T. Yoke, III, *Inorg. Chem.*, **1**, 463 (1962).

[2] J. T. Yoke, III, J. F. Weiss and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963).

[3] J. R. Clifton and J. T. Yoke, III, *ibid.*, **5**, 1630 (1966).

[4] J. R. Clifton and J. T. Yoke, III, *ibid.*, **6**, 1258 (1967).

[5] S. Kawaguchi and T. Ogura, *ibid.*, **5**, 844 (1966).

[6] T. Ogura, N. Furuno and S. Kawaguchi, This Bulletin, **40**, 1171 (1967).

mixture was kept standing overnight to complete the reaction, and the excess amine was then distilled back to the original ampoule. The copper(I) complex was dried completely without decomposition by keeping the two ampoules at 5 and 0°C respectively for 50 hr. The analytical data of four kinds of complexes thus prepared are as follows:

Found: Cu, 23.2; Cl, 13.1%. Calcd for CuCl$(C_3H_7N)_3$: Cu, 23.5; Cl, 13.1%.

Found: Cu, 20.1; Br, 25.2%. Calcd for CuBr$(C_3H_7N)_3$: Cu, 20.2; Br, 25.4%.

Found: Cu, 22.8; Cl, 13.0%. Calcd for CuCl$(C_3H_9N)_3$: Cu, 23.0; Cl, 12.8%.

Found: Cu, 19.3; Br, 24.5%. Calcd for CuBr$(C_3H_9N)_3$: Cu, 19.8; Br, 24.9%.

Syntheses of Copper(I) Halide - Amine Complexes with the Mole Ratio of One to One. The ampoule containing a copper(I) halide - amine complex with the mole ratio of one to three was kept at room temperature around 20°C and another empty one at 0°C which had been connected with each other and evacuated. The complex decomposed partially and expelled about two moles of amine per mole complex during standing overnight. The amine vessel was cooled with liquid nitrogen for further 24 hr and exactly two moles of amine was recovered. The copper(I) amine complexes prepared in this way showed the following analytical data.

Found: Cu, 40.1; Cl, 22.8% mp around 100°C. Calcd for CuCl(C_3H_7N): Cu, 40.7; Cl, 22.7%.

Found: Cu, 31.8; Br, 39.8%; mp around 100°C. Calcd for CuBr(C_3H_7N): Cu, 31.7; Br, 39.9%.

Found: Cu, 39.3; Cl, 22.6%; mp 22°C. Calcd for CuCl(C_3H_9N): Cu, 40.1; Cl, 22.4%.

Found: Cu, 31.3; Br, 39.7%; mp 75°C. Calcd for CuBr(C_3H_9N): Cu, 31.4; Br, 39.5%.

These copper(I) halide - amine complexes are all stable at room temperature. When they were heated to higher temperatures, 80—90% amine was recovered, but the quantitative dissociation could not be attained.

For comparison, copper(I) chloride complexes of deuterated amines, CuCl$(C_3H_5ND_2)$ and CuCl$(C_3H_7ND_2)$ were also prepared in the following way. Allylamine or propylamine (0.3 g) was distilled into heavy water (5 g) whose deuterium content was 99.8%. The solution was then distilled into an ampoule containing copper(I) chloride (0.2 g) and kept standing overnight. The complex was then dried at a temperature difference of room and dry ice temperatures as described above.

Vapor Pressure Measurement. The dried crystalline complex was prepared in an ampoule connected with a U-type mercury manometer. The equilibrium vapor pressure was measured at various temperatures by keeping the sample tube in appropriate thermostat baths.

Infrared Spectra. The infrared absorption spectra were measured with a Hitachi infrared spectrophotometer, EPI-2. The amine complex with the mole ratio of one to three is unstable and the crystalline specimen was mixed with Nujol and ground down quickly in a nitrogen atmosphere.

Results

Copper(I) halide complexes of allylamine and propylamine with the mole ratio of one to three are all colorless and transparent crystals, showing no difference in appearance. These compounds have appreciable vapor pressures and decompose spontaneously in an open atmosphere resulting in the complexes with the metal-ligand mole ratio of one to one. They are also very sensitive to air and change to deep blue color characteristic of the copper(II) amine complex.

TABLE 1. THE VAPOR PRESSURE DATA OF THE COPPER(I) HALIDE COMPLEXES OF ALLYLAMINE AND PROPYLAMINE WITH THE MOLE RATIO OF ONE TO THREE

CuCl(am)$_3$	t, °C	5.4	9.6	20.7	28.1	
	P, cmHg	1.655	2.405	6.360	11.525	
	t, °C (calc)*	5.4	9.5	20.7	28.1	
	$\log P$ (cmHg)$=11.401-3.115\times10^3/T$					(3)
CuBr(am)$_3$	t, °C	0	5.2	11.0	18.0	24.5
	P, cmHg	1.000	1.599	2.730	5.015	8.804
	t, °C (calc)*	0.1	5.1	10.9	17.9	24.6
	$\log P$ (cmHg)$=11.488-3.140\times10^3/T$					(4)
CuCl(pm)$_3$	t, °C	0	5.2	11.0	19.0	25.2
	P, cmHg	1.956	2.950	4.653	8.853	13.450
	t, °C (calc)*	0.1	5.1	10.8	19.3	25.1
	$\log P$ (cmHg)$=10.292-2.734\times10^3/T$					(5)
CuBr(pm)$_3$	t, °C	0	5.2	10.9	14.4	20.6
	P, cmHg	3.432	4.763	6.978	8.849	12.920
	t, °C (calc)*	0.2	5.0	10.8	14.5	20.6
	$\log P$ (cmHg)$=8.815-2.264\times10^3/T$					(6)
Allylamine	t, °C	0	5.4	9.8	21.2	29.0
	P, cmHg	7.530	9.880	12.240	21.150	29.385
	t, °C (calc)*	−0.1	5.6	9.9	21.3	28.8
	$\log P$ (cmHg)$=7.180-1.725\times10^3/T$					(7)

* Calculated by means of each equation (3)—(7), respectively.

TABLE 2. THE VAPOR PRESSURE DATA OF THE COPPER(I) HALIDE COMPLEXES OF ALLYLAMINE AND PROPYLAMINE WITH THE MOLE RATIO OF ONE TO ONE

CuCl(am)	t, °C	107.0	112.9	119.3	124.5		
	P, cmHg	0.228	0.315	0.636	0.939		
	t, °C	107.8	111.5	119.8	124.7		
	$\log P$ (cmHg)$=13.838-5.517\times10^3/T$						(8)
CuBr(am)	t, °C	95.1	104.8	114.6	124.6		
	P, cmHg	0.117	0.235	0.639	1.507		
	t, °C*	95.9	103.4	114.7	124.9		
	$\log P$ (cmHg)$=14.281-5.615\times10^3/T$						(9)
CuCl(pm)	t, °C	84.9	95.1	104.8	114.6	124.6	
	P, cmHg	0.624	0.988	1.661	2.772	4.554	
	t, °C*	85.9	94.2	104.2	114.2	125.0	
	$\log P$ (cmHg)$=8.134-3.154\times10^3/T$						(10)
CuBr(pm)	t, °C	82.3	90.8	101.0	109.6	119.6	125.0
	P, cmHg	0.734	1.192	2.048	3.142	4.953	6.200
	t, °C*	82.1	90.9	100.9	110.0	119.7	124.7
	$\log P$ (cmHg)$=8.530-3.079\times10^3/T$						(11)

* Calculated by means of each equation (8)—(11), respectively.

On the other hand copper(I) halide complexes of these amines with the mole ratio of one to one are fairly stable against air or heat just as the monoammine adduct of copper(I) chloride is.

The Vapor Pressure Data. The equilibrium vapor pressure of the copper(I) halide-amine system was determined at various compositions and the following two equilibria were found to exist:

$$\mathrm{CuX} + \mathrm{RNH_2} = \mathrm{CuX(RNH_2)} \qquad (1)$$

$$\tfrac{1}{2}\mathrm{CuX(RNH_2)} + \mathrm{RNH_2} = \tfrac{1}{2}\mathrm{CuX(RNH_2)_3} \qquad (2)$$

where X represents Cl or Br, and R stands for C_3H_5 or C_3H_7. However, the copper(I) complex of the composition, $CuX(RNH_2)_2$ or $CuX(RNH_2)_{1.5}$ was not identified.

The equilibrium dissociation pressure of the copper(I) halide complexes of allylamine and propylamine with the mole ratio of one to three was determined at various temperatures. The results obtained are shown in Table 1 and represented by Eqs. (3) through (6).

The vapor pressure of the copper(I) halide-amine complexes with the 1 : 1 composition was lower and determined at temperatures higher than 100°C. The results are listed in Table 2 and reproduced by Eqs. (8) through (11). However, data for allylamine complexes might be less reliable than those for the above 1 : 3 complexes, since some kind of chemical change of the ligated allylamine (possibly disproportionation to ammonia and diallylamine or triallylamine) was noticed to occur when the complex was maintained at temperatures higher than 130°C for several days.

From Eqs. (3) through (11) the heat of formation of each complex referring to Eqs. (1) and (2) was calculated and listed in Table 3. The vapor pressure data of allylamine were not available in literature and determined for the specimen which had been specially purified by formation and decomposition of copper(I) chloride complex with the mole ratio of one to three. The results obtained are represented by Eq. (7) in Table 2. The boiling point of allylamine calculated by means of Eq. (7) is 54.8°C which coincides fairly well with the literature value[7] of 55—58°C. As the heat of vaporization of propylamine the value of 7.3 kcal·mol⁻¹ due to Stull[8] was used for calculation in Table 3.

TABLE 3. THE CONSECUTIVE ENTHALPY OF FORMATION OF COPPER(I) HALIDE COMPLEXES OF ALLYLAMINE AND PROPYLAMINE CALCULATED FOR ONE MOLE OF GASEOUS AMINE*

Compound	ΔH kcal·mol^{-1}	Compound	ΔH kcal·mol^{-1}
CuCl(am)	−25.2 (−17.3)	CuCl(am)$_3$	−13.9 (−6.0)
CuBr(am)	−25.7 (−17.8)	CuBr(am)$_3$	−14.3 (−6.4)
CuCl(pm)	−14.4 (−7.1)	CuCl(pm)$_3$	−12.5 (−5.2)
CuBr(pm)	−14.1 (−6.8)	CuBr(pm)$_3$	−10.4 (−3.1)

* The value in a bracket refers to the enthalpy of formation from the liquid amine.

Infrared Spectra. The infrared spectra of these complexes are very complicated in comparison with those of free amines. Several characteristic absorption bands due to NH_2 group were assigned on the observation of their shifts by the deuteration. They are listed in Table 4 together with the stretching frequency of the double bond of allylamine.

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[7] "The Merck Index of Chemicals and Drugs," 7th ed., Merck Co., Inc., Rahway, New Jersey (1960), p. 36.

[8] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

TABLE 4. THE INFRARED ABSORPTION BANDS (cm^{-1}) DUE TO THE AMINE GROUP AND DOUBLE BOND IN THE COPPER(I) HALIDE COMPLEXES OF ALLYLAMINE AND PROPYLAMINE

Compound	$\nu(NH_2)$		$\delta(NH_2)$		$\nu(C=C)$
$C_3H_5NH_2$	3400	3310	1615	820	1645
$CuCl(C_3H_5NH_2)$	3240	3160	1605	630	1535
$CuCl(C_3H_5ND_2)$	2440	2380	1175		1535
$CuBr(C_3H_5NH_2)$	3260	3150	1580	610	1535
$CuCl(C_3H_5NH_2)_3$	3240	3160	1590	660	1645, 1535
$CuBr(C_3H_5NH_2)_3$	3240	3130	1590	610, 675	1645, 1535
$C_3H_7NH_2$	3390	3310	1615	810	
$CuCl(C_3H_7NH_2)$	3215	3135	1585	635	
$CuCl(C_3H_7ND_2)$	2430	2380	1180		
$CuBr(C_3H_7NH_2)$	3220	3140	1570	620	
$CuCl(C_3H_7NH_2)_3$	3220	3120	1585	625, 665	
$CuBr(C_3H_7NH_2)_3$	3220	3140	1570	620	

Propylamine has no way of coordination to the metal other than *via* nitrogen atom, and the remarkable shifts of the stretching and deformation frequencies of the NH_2 group by ligation indicate that this is the case. Allylamine, on the other hand, may be linked to copper(I) either by nitrogen atom or by the double bond. As shown in Table 4 coordinated allylamine shows similar shifts of $\nu(NH_2)$ and $\delta(NH_2)$ to the lower frequency side as propylamine does. This suggests that nitrogen atom of every allylamine molecule is used in bonding to copper(I). The stretching frequency of the double bond of allylamine in the 1 : 1 complex is lower by 110 cm^{-1} than that of the free amine. However, two peaks are observed at 1645 and 1535 cm^{-1} for the 1 : 3 complex, corresponding to the free and ligated double bond, respectively.

These results indicate that in the 1 : 1 complex every allylamine molecule is coordinated to copper(I) by both double bond and amine group, while in the 1 : 3 complex two kinds of allylamine molecules are contained, one acting as a bidentate and the other as a unidentate ligand which is linked solely by the amine group.

Discussion

Wilkins and Burkin9) investigated the reactions of copper(I) halides with long-chain aliphatic amines such as *n*-octyl-, *n*-dodecyl- with *n*-octadecylamines, and identified $[CuBr(RNH_2)_2]_2$ and $[CuX(RNH_2)]_4$ where X is Cl, Br or I. Triethylamine was reported to form 1 : 1 complexes with copper(I) halides,2) and diethylamine to form both 1 : 1 (tetrameric) and 1 : 2 (dimeric) complexes with copper(I) chloride. In the system of copper(I) chloride - ethylamine 1 : 1 and 1 : 2 complexes were isolated and 1 : 3 complex was noticed in the isothermal phase study at 0°C. In the present case 1 : 1 and 1 : 3 complexes were obtained for the copper(I) halides and allylamine or propylamine systems, but no indication of 1 : 2 complexes was observed.

As shown in Table 3 the enthalpy of formation of the 1 : 1 complex from solid copper(I) halide and liquid propylamine was determined as -7.1 kcal·mol^{-1} for the chloride complex and -6.8 kcal·mol^{-1} for the bromide complex, but the enthalpy of ligation of the second and third molecule of propylamine is -5.2 and -3.1 kcal·mol^{-1}, respectively. It is quite reasonable that the first ligand molecule coordinates to the metal atom more exothermically than the second or third one since more or less negative charge is brought in around the central metal by the ligand molecule. The fact is noticed that the heat evolved by ligation of propylamine to copper(I) bromide is a little less than that for copper(I) chloride. Bromine may make a more covalent bond and bring larger negative charge around the central metal than chlorine does, reducing the bond strength between copper(I) and the hard amine ligand.

The enthalpy of formation of $CuI(NEt_3)$ from CuI(s) and triethylamine(*l*) was reported2) as -8.21 kcal·mol^{-1}, and ΔH for the second molecule of diethylamine(*l*)3) and ethylamine(*l*)4) ligating to each 1 : 1 copper(I) chloride complex was estimated as -7.8 and -6.65 kcal·mol^{-1}, respectively. These data together with our present ones indicate the possible region of values for the enthalpy of ligation of aliphatic amines to copper(I) halide. The observed values of ΔH for the second and third molecule of allylamine ligating to copper(I) chloride and bromide lie in this probable region suggesting that the ligand molecule in question coordinates to copper(I) through the amine group.

However, ΔH for the ligation of the first molecule of allylamine to copper(I) chloride or bromide is much more negative, and even more negative than those for other vinyl complexes as summarized in Table 5. This clearly indicates that the first

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9) R. G. Wilkins and A. R. Burkin, *J. Chem. Soc.*, **1950**, 127.

molecule of allylamine coordinates to copper(I) atom with both the amino nitrogen atom and π-electrons of the double bond. In the case of allylamine ΔH's for copper(I) bromide are a little more negative than those for the chloride in contrast to the case of propylamine complexes. The softness of bromine in comparison with chlorine may enhance the bonding between copper(I) and the C=C double bond in which the contribution of back donation from metal to ligand is significant.

TABLE 5. THE ENTHALPY OF FORMATION OF 1:1 COPPER(I) CHLORIDE COMPLEX WITH SEVERAL VINYL COMPOUNDS AND THB SHIFT OF C=C STRETCHING FREQUENCY

Compound	$-\Delta H$ kcal·mol^{-1}	$\Delta\nu$(C=C) cm^{-1}	Ref.
CH_2=CH-CHO	11.8	90	5
CH_2=CH-CH_2OH	12.0	95	6
CH_2=CH-CN	14.9	100	10
CH_2=CH-CH_2NH_2	25.2	110	this study

The conclusion that in the tris(allylamine)-copper(I) complexes one ligand molecule coordinates to the metal with both nitrogen atom and the double bond but the second and third molecules only with nitrogen, is also supported by the infrared absorption data as mentioned already. Copper(I) usually prefers the coordination number four. If one of three molecules of allylamine is serving as a bidentate ligand, the 1 : 3 copper(I) halide complexes must be salts keeping the halide as outer-sphere anions. Some extensive studies such as the conductivity measurement of copper(I) halides in allylamine are desired but have not yet been performed.

There are summarized in Table 5 the enthalpy of formation of 1 : 1 copper(I) chloride complexes with several vinyl compounds together with the associated shift of C=C stretching frequency. A remarkable correspondence is noticed between these two properties. The X-ray analysis of the copper(I) chloride complex of acrolein revealed that each acrolein molecule is assuming the s-trans configuration and acting as a bridging ligand between two copper atoms.11) On the other hand the allyl alcohol complex seems to exist as a dimer12) with the chloride double bridge, the alcohol molecule acting as a chelating agent. In the present case the molecular weight of the 1 : 1 complex of copper halide with allylamine has not been determined owing to the lack of any suitable solvents, but it might be presumed by analogy with the allyl alcohol complex to exist as a dimer. Further information concerning the real structure must be offered by the X-ray analysis of this compound.

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10) G. N. Schrauzer, *Chem. Ber.,* **94**, 1891 (1961).

11) Y. Kushi, T. Ogura, S. Kawaguchi and H. Kuroya, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

12) In a previous paper (Ref. 6) copper(I) chloride was reported to exist as a monomer in boiling allyl alcohol, but further detailed measurements revealed that this rather preliminary observation was wrong. Copper(I) chloride exists as a dimer in allyl alcohol even at the boiling point just as at lower temperature.