CHEMISTRY LETTERS, pp. 671-674, 1986.

ETHYLENE ABSORPTION BY SOLUTIONS OF COPPER(I) CHLORIDE AND AMINES IN METHANOL

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N,N,N',N'-Tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine, and N,N,N'-trimethylethylenediamine are stirred with copper(I) chloride in methanol at a charged molar ratio of unity, resulting in homogeneous solutions of the copper(I) chloride-diamine complexes. The solutions, respectively, absorb 11.0, 4.8, and 11.3 mmol of ethylene at 20 °C under 1 atm.

Ethylene and propylene are usually obtained as gas mixtures with methane, ethane, nitrogen, and hydrogen.1) Thus separation of these olefins from gas mixtures is an important process in industry.

Previously,2) the authors have reported that adsorbents composed of copper(I) chloride and a polystyrene resin having amino groups effectively and selectively adsorb ethylene. The adsorption has been attributed to coordination of ethylene to the copper(I) ions which are complexing with the amino groups.

There have been considerable number of crystallographic studies on copper(I) ion-amine complexes.3,4) However, informations either on the complex formations between copper(I) ion and amines in solutions or on the complex formations between copper(I) ion-amine complexes and olefins have been scanty.

This paper reports on the complex formation between copper(I) chloride (CuCl) and various amines in methanol. Effects of the structures of amines on homogeneity of CuCl-amine-methanol mixtures and on the ethylene absorbing abilities of the mixtures are shown.

The mixtures are prepared by stirring CuCl and amine at a charged molar ratio of unity in methanol under nitrogen. Absorption of ethylene by the mixtures, vigorously stirred with a magnetic stirrer, was achieved at 20 °C under 1 atm. Uptake of ethylene was measured by use of a gas burette.

Table 1 shows the states of the mixtures of CuCl and ethylenediamines having various numbers of methyl substituents on the nitrogen atoms in methanol as well as the ethylene absorbing capacities of the mixtures. Homogeneous and transparent solution was obtained by mixing 10.0 mmol of N,N,N',N'-tetramethylethylenediamine (I) with 10.0 mmol of CuCl in methanol. This was attributable to formation of complex between CuCl and I, since CuCl did not effectively dissolve in methanol in the absence of I. The solution remained homogeneous even after storage for 2 days under nitrogen. Similarly, methanol solutions of the complexes of CuCl with N,N,N'-trimethylethylenediamine (II) and N,N,N',N'-tetraethylethylenediamine (VII) were prepared as homogeneous solutions of bluish green and pale pink colors, respectively.

When CuCl was mixed in methanol with N,N-dimethylethylenediamine (III), N,N'-dimethylethylenediamine (IV), N-methylethylenediamine (V), and ethylenediamine (VI), which have two to zero methyl groups on the two nitrogen atoms, disproportionation of copper(I) ions took place significantly and promptly, and heterogeneous mixtures containing precipitates of metallic copper were obtained immediately. The colors of the supernatants were blue due to copper(II) ions. Thus, the methyl and ethyl groups on the nitrogen atoms in I, II, and VII were definitely required for the formation of homogeneous solutions without

Table 1. States and ethylene absorbing capacities of CuCl-ethylenediamine-methanol mixtures[a,b]

Ethylenediamine		State of mixture	Ethylene absorbing capacity/mmol
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	(I)	Homogeneous	11.0
$(CH_3)_2N(CH_2)_2NH(CH_3)$	(II)		11.3
$(CH_3)_2N(CH_2)_2NH_2$	(III)	Heterogeneous	3.6
$CH_3NH(CH_2)_2NH(CH_3)$	(IV)		5.0
$CH_3NH(CH_2)_2NH_2$	(V)		2.3
$H_2N(CH_2)_2NH_2$	(VI)		3.1
$(C_2H_5)_2N(CH_2)_2(C_2H_5)_2$	(VII)	Homogeneous	4.8
None		Heterogeneous	2.8

a) CuCl, 10.0 mmol; ethylenediamine, 10.0 mmol; methanol, 30 cm^3.

b) Absorption of ethylene was carried out at 20 °C under 1 atm.

disproportionation of copper(I) ions in methanol.

All the CuCl-ethylenediamine-methanol mixtures absorbed ethylene at 20 °C under 1 atm. The equilibria were attained within 30-40 min. The absorbing capacities (11.0 and 11.3 mmol) of the homogeneous solutions of the CuCl-I and the CuCl-II complexes were slightly larger than the value (10.0 mmol) equivalent to the charged CuCl. The heterogeneous mixtures of CuCl and the diamines III-VI in methanol exhibited small absorbing capacities. The capacity (4.8 mmol) of the methanol solution of the CuCl-VII complex was smaller than half of that (11.0 mmol) of the methanol solution of CuCl-I complex. This is probably ascribed to the fact that steric repulsion between the ethyl groups and ethylene on the coordination of ethylene to the copper(I) ion in the CuCl-VII complex is more significant than that between the methyl groups and ethylene for the case of the CuCl-I complex.

Both a mixture of 10.0 mmol of CuCl and 20.0 mmol of triethylamine in 30 cm^3 of methanol and a mixture of 10.0 mmol of CuCl and 30.0 mmol of ammonia in 50 cm^3 of water were heterogeneous. No dissolution of CuCl was perceived.

As shown in Table 2, chain lengths between the two nitrogen atoms in diamines having four methyl groups on the nitrogen atoms exhibited large effects on the states of CuCl-diamine-methanol mixtures as well as on the ethylene absorbing capacities of the mixtures. A homogeneous solution was obtained by use of the diamine I, which has two methylene carbon atoms between the two nitrogen atoms, as described above. With the use of N,N,N',N'-tetramethyldiaminomethane (VIII) and

Table 2. States and ethylene absorbing abilities of mixtures of CuCl and tetramethylated diamines with various chain lengths between the two nitrogen atoms in methanol[a,b)]

Diamine		State of mixture	Ethylene absorbing capacity/mmol
$(CH_3)_2N(CH_2)N(CH_3)_2$	(VIII)	Heterogeneous	5.4
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	(I)	Homogeneous	11.0
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	(IX)	c)	11.2
$(CH_3)_2N(CH_2)_4N(CH_3)_2$	(X)	Heterogeneous	4.5

a) CuCl, 10.0 mmol; tetramethylated diamine, 10.0 mmol; methanol, 30 cm^3.

b) Absorption of ethylene was carried out at 20 °C under 1 atm.

c) The mixture, which was heterogeneous under nitrogen, gradually became homogeneous on the absorption of ethylene (see text in detail).

N,N,N',N'-tetramethyldiaminobutane (X), however, yellowish green precipitates were formed under pale green solutions.

On stirring of CuCl under nitrogen with N,N,N',N'-tetramethyldiaminopropane (IX), which has three methylene carbon atoms, heterogeneous mixture composed of yellow precipitates and pale green supernatant was formed. The precipitates, however, gradually dissolved on the contact of the mixture with ethylene. After absorption of 11.2 mmol of ethylene, the mixture became entirely homogeneous, and a bluish green solution was obtained. For all the solutions containing I and VIII-X, the equilibria in absorptions were achieved in 30-40 min.

These significant effects of number of methylene carbon atoms are associated with difference in the stability of chelate-type coordination of the diamines to copper(I) ion. The diamine I with two methylene carbon atoms favorably forms a chelate-type complex with copper(I) ion, since stable five-membered ring is produced there. For the diamines VIII, IX, and X, formations of chelate-type complexes with CuCl are less favorable, resulting in heterogeneous mixtures. Dissolution of the precipitates of the CuCl-IX complexes on the contact with ethylene is ascribed to enhancements of solubilities of the complexes by coordinations of ethylene to the copper(I) ions. The absorbing capacities of the mixtures are probably governed both by the amounts of copper(I)-diamine complexes in the liquid phase and by the absorbing abilities of the complexes.

In conclusion, homogeneous methanol solutions of copper(I) chloride-amine complexes were obtained by use of ethylenediamines having three or four alkyl substituents on the two nitrogen atoms. The ethylene absorbing abilities of CuCl-amine-methanol mixtures were highly dependent on the structures of the amines.

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(Received February 13, 1986)