Spectrochemical Investigations of the Interaction between Simple Salt Anions and Transition Metal Cations. II. Association between Bisethylenediamine Cupric Complex and Several Anions

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Introduction

In the previous report[1] the author studied the absorption due to association between hexammine complexes of cobalt(III) and chromium(III) and anions of simple salts and concluded from the estimation of the degrees of association that the particular deforming power of the transition metal ions plays an important role in association.

In the present investigation, the author studied the absorption due to association between $[Cu\ en_2]^{2+}$ complex cation and several anions which had reducing power against cupric aquo ion. As the result, marked absorption due to association was found in the cases of iodide, sulphite and thiosulphate ions. At the same time, the author devised a new method to determine the equilibrium constant of association from the analysis of absorption data.

1) This Bulletin, 28, 125 (1955).

Experimental

Bisethylenediamine cupric complex was prepared from cupric perchlorate and an equivalent amount of ethylenediamine, and was recrystallized once from hot water.

Optical densities were measured by means of the Shimadzu spectrophotometer using tungsten and hydrogen lamps and 1 cm. quartz cells. All measurement was made at room temperature 18°C.

Results

In the preliminary experiment, the following measurement was made. The salts used were KNCS, KBr, KI, Na_2SO_3 and $Na_2S_2O_3$. Each sa was dissolved to make a solution of 1 mol./l. concentration. In each solution $[Cu\ en_2](ClO_4)_2$ was dis-

solved to 0.01 mol./l. concentration. Such solutions of the complex were measured in relation to their optical densities. In order to cancel the absorption due to the unassociated free anions, the corresponding salt solution was used as a standard. The results are shown in Fig. 1. The inspection of these curves reveals the following facts.

1) In every case the characteristic absorption band proper to the complex remained constant in its maximum position ($\nu_{max.}$: 54.8×10^{13} sec^{-1}) and height (log $\varepsilon_{max.}$: 1.82).

2) In the cases of NCS^- and Br^-, only slight enhancement of the end absorption was observed, while in the cases of I^-, SO_3^{2-} and $S_2O_3^{2-}$, marked absorption due to association was observed in the near ultraviolet. Accordingly, it was expected that we could determine the equilibrium constants of association in the latter cases by using such absorption.

In order to determine the equilibrium constant, the author made the following measurement. At first the method of continuous variations devised by Shibata[2] and Tsuchida[3] was applied to determine the composition of the association product. In the cases of $SO_3^{2-}$and I^-, 1/10 g.ion/l. solutions of the complex and the anion, and in the case of $S_2O_3^{2-}$, 1/40 g.ion/l. solutions were prepared respectively. Next such solutions of the complex and the anion were mixed with each other in the volume ratios (equal to the mole ratios) of 3:1, 2:1, 1:1, 1:2 and 1:3. The mixed solutions thus obtained were measured in their optical densities. As the result it was found that the absorption of the 1:1 association product was predominent under the present experimental conditions. Some parts of the results are listed in Table I. These results were used in the determination of the equilibrium constants.

TABLE I

OBSERVED OPTICAL DENSITIES

Wave-lengths / Mole ratios	350 mμ	345 mμ	340 mμ	335 mμ	330 mμ	325 mμ
[Cu en_2]$^{2+}$: SO_3^{2-}						
1:1	0.271	0.298	0.316	0.334	0.360	0.395
2:1	.255	.272	.294	.311	.335	.371
3:1	.220	.238	.254	.271	.295	.331
[Cu en_2]$^{2+}$: I^-						
1:1	0.167	0.205	0.255	0.312	0.385	0.479
2:1	.163	.197	.240	.294	.359	.449
3:1	.137	.166	.201	.245	.302	.380
[Cu en_2]$^{2+}$: $S_2O_3^{2-}$						
1:1	0.170	0.217	0.259	0.305	0.358	0.411
2:1	.153	.199	.239	.280	.325	.373
3:1	.124	.163	.191	.227	.266	.305
[Cu en_2]$^{2+}$ only (c=1/10 g.ion/l.)	0.062	0.065	0.070	0.080	0.098	0.132

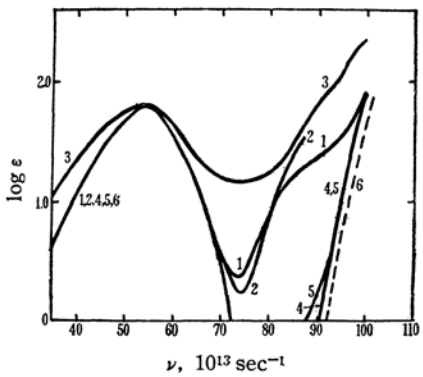

Fig. 1. Absorption Spectra of [Cu en_2] $(ClO_4)_2$
1. in Na_2SO_3 solution.
2. in KI solution.
3. in $Na_2S_2O_3$ solution.
4. in KBr solution.
5. in KNCS solution.
6. in distilled water.

(Under these mole ratios of the complex and the anion, the possibility of producing the 1:2 and 1:3 complex-anion association pairs is practically negligible. One has only to consider the 1:1 product.)

Determination of the Equilibrium Constant.— In order to determine the equilibrium constant by using the above listed values, the following method was devised.

Consider the case where [Cu en_2]$^{2+}$ and SO_3^{2-} associate in aqueous solution to form the following equilibrium

$$Cu\ en_2^{2+} + SO_3^{2-} \rightleftarrows Cu\ en_2\text{-}SO_3$$

The equilibrium constant of association is represented by

$$K = \frac{[Cu\ en_2\text{-}SO_3]}{[Cu\ en_2^{2+}][SO_3^{2-}]}$$

If we represent the total concentrations of the complex and the anion with xc and c respectively,

2) Y. Shibata, T. Inoue and Y. Nakatsuka, *J. Chem. Soc. Japan*, **42**, 983 (1921).
3) R. Tsuchida, This Bulletin, **10**, 27 (1935).

and the concentration of the association product in equilibrium with u, then the concentrations of the complex and the anion in equilibrium are represented by $xc-u$ and $c-u$ respectively. Accordingly, the equilibrium constant is represented by

$$K=\frac{u}{(xc-u)(c-u)} \tag{1}$$

Here we consider the degree of association α with the anion,

$$\alpha=\frac{u}{c} \tag{2}$$

Introducing the relation (2) into the equation (1), we obtain

$$K=\frac{x}{c(x-\alpha)(1-\alpha)} \tag{3}$$

On the other hand, the observed optical density D is represented by

$$D=\varepsilon_{\text{comp.}}(xc-u)+\varepsilon_{\text{ass.}}u \tag{4}$$

where $\varepsilon_{\text{comp.}}$ and $\varepsilon_{\text{ass.}}$ mean the extinction coefficients of the complex and the association product respectively. (In the present cases the absorption of the anion is negligible.)

Substituting the relation (2) into the equation (4), we obtain

$$\frac{D-\varepsilon_{\text{comp.}}xc}{c}=(\varepsilon_{\text{ass.}}-\varepsilon_{\text{comp.}})\alpha=\Delta\varepsilon\cdot\alpha \tag{5}$$

The left side of the equation (5) can be calculated from the observed optical density and is represented by y. The values of y are listed in Table II. The equation (5) is abbreviated to

$$y=\Delta\varepsilon\cdot\alpha \tag{6}$$

From the equation (3) and (6), we obtain

$$y^2-ya\Delta\varepsilon-xy\Delta\varepsilon-(\Delta\varepsilon)^2x=0 \tag{7}$$

where $$a=1+\frac{1}{ck} \tag{8}$$

The numerical values of x and y are introduced into this equation (7), then the equation of the second order about a and $\Delta\varepsilon$ is obtained. At one wave-length three such equations are obtained. From these equations we can find the most probable values of a and $\Delta\varepsilon$ by using the method of least squares. When the values of a is known, we can determine the value of K by using the relation (8). The results thus obtained are listed in Table III.

TABLE II

CALCULATED VALUES OF y

Wave-lengths / Mole ratios	350 mμ	345 mμ	340 mμ	335 mμ	330 mμ	325 mμ
$[Cu\ en_2]^{2+}:SO_3^{2-}$						
1:1	4.80	5.30	5.63	5.89	6.22	6.58
2:1	6.42	6.88	7.41	7.76	8.10	8.49
3:1	6.92	7.58	8.08	8.44	8.84	9.30
$[Cu\ en_2]^{2+}:I^-$						
1:1		3.44	4.40	5.44	6.72	8.26
2:1		4.62	5.79	7.26	8.82	10.83
3:1		4.70	5.92	7.40	9.16	11.24
$[Cu\ en_2]^{2+}:S_2O_3^{2-}$						
1:1	12.96	16.72	20.016	23.60	27.82	31.56
2:1	17.16	22.58	27.276	32.04	37.04	42.12
3:1	17.92	24.23	28.48	33.92	39.70	44.80

TABLE III

MOST PROBABLE VALUES OF a, $\Delta\varepsilon$ AND K

Wave-lengths / Ion-pairs		350 mμ	345 mμ	340 mμ	335 mμ	330 mμ	325 mμ
$[Cu\ en_2]^{2+}$-SO_3^{2-}							
	a	1.401	1.401	1.410	1.402	1.384	1.333
	$\Delta\varepsilon$	12.07	12.85	13.70	14.11	14.42	14.55
		the mean value of $a=1.40$ $K=25$					
$[Cu\ en_2]^{2+}$-I^-							
	a		1.094	1.098	1.095	1.100	1.107
	$\Delta\varepsilon$		5.53	7.02	8.70	10.83	13.42
			the mean value of $a=1.10$ $K=100$				
$[Cu\ en_2]^{2+}$-$S_2O_3^{2-}$							
	a	1.160	1.180	1.217	1.118	1.298	1.244
	$\Delta\varepsilon$	23.11	32.00	39.25	44.32	59.63	63.76
		the mean value of $a=1.21$ $K=190$					

Discussion

As the preliminary experiment indicated, the characteristic absorption band proper to the complex remained constant in association. This fact suggests that the association is not a kind of partial substitution of the ligand by the anion, and that the association product is not a penta-coordinated complex [Cu en_2 x] like [Cu $(NH_3)_5$]$^{2+}$ [4]. In such cases the characteristic absorption band proper to [Cu en_2]$^{2+}$ must change its maximum position and height. Accordingly, the association is presumed to occur without any essential change of the structure of [Cu en_2]$^{2+}$. According to the results of the determination of the equilibrium constants of association, the stability of the association product increases in the order of $SO_3^{2-} < I^- < S_2O_3^{2-}$. The univalent anion I^- forms a more stable product than the bivalent anion SO_3^{2-}, and the more voluminous anion $S_2O_3^{2-}$ forms a more stable product than the less voluminous anion SO_3^{2-}. This fact indicates that the association is not caused merely by the electrostatic attraction between the complex and anion. Rather, it must be considered that, although the detailed mechanism of binding is not known, the specific polarising power of the central cupric ion acts upon the extremely polarisable anion to form the association product.

4) J. Bjerrum and C.G. Lamm, *Acta chimica Scandinavica* **4**, 997 (1950).

Conclusion

Marked absorption due to association was found between bisethylenediamine cupric complex and anions SO_3^{2-}, I^- and $S_2O_3^{2-}$ which have a strong reducing power against cupric aquo ion, and the equilibrium constants of association were determined by the newly devised method. The values of K's were 25 for SO_3^{2-}, 100 for I^- and 190 for $S_2O_3^{2-}$. This results indicates that the cause of association is not always the mere electrostatic attraction between cation and anion, rather it suggests that the association can be caused by the strong polarising effect of the central cupric ion upon the extremely polarisable anion.

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