The Complex Formation between Copper(II) Ion and Methoxyacetate, Ethoxyacetate, (Ethylthio)acetate, and Thiodiacetate Ions

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The complexity constants of the mononuclear complexes formed by copper(II) ion in water solution with methoxyacetate, ethoxyacetate, (ethylthio)acetate, and thiodiacetate ions have been determined by potentiometric methods at 20.0°C. The investigations have been carried out in a perchlorate medium at ionic strength $I = 1.0$ M. The constants obtained are collected in Tables 11 and 12.

The complex formation between copper(II) ions and both acetate and glycolate ions in water solution is well known^{1,2}, showing a considerably greater stability of the glycolate complexes than of the acetate complexes. For the copper(II) alkoxyacetate systems, however, no determination of stability constants seems to have been published so far.

In recent years a number of investigations have been published permitting a comparison of the complex formation tendency between metal central ions and ligands containing oxygen or bivalent sulphur, as donor atoms. Copper(II) systems have been investigated in respect to comparatively complicated polydentate ligands (*e.g.*, $\text{Me}\cdot\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\cdot\text{COOH})_2$ and $\text{X}[\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\cdot\text{COOH})_2]_2$ where $\text{X} = \text{oxygen or sulphur}$)¹. The investigation reported here, including the copper(II) (ethylthio)acetate and the copper(II) thiodiacetate systems, makes such a comparison possible on simpler types of ligands.

The measurements have been performed potentiometrically, thus acquiring high accuracy, which permits a determination of the stability constants of even the third and fourth complexes. The copper(II) (ethylthio)acetate system has been investigated by measuring the free ligand concentration and the other three systems by measuring the free central ion concentration.

SUMMARY OF THE PRINCIPLES FOR CALCULATION OF THE COMPLEXITY CONSTANTS

The methods of calculation are elaborated by Bjerrum³, Leden⁴ and Fronæus². Only a short summary is given here.

1. Calculation from the measurements of the free ligand concentration

Assuming formation in solution of only mononuclear complexes MA_1 , MA_2 , . . . MA_N between the central ion M (total concentration C_M) and the ligand A (total concentration C_A), the complexity constant β_n is defined by

$$\beta_n = \frac{[MA_n]}{[M][A]^n}$$

corresponding to the equilibrium

which is valid for the formation of the complex MA_n .

Using β_n , we obtain

$$C_M = [M] \cdot X \quad (1)$$

$$C_A = [A] + [M] \cdot [A] \cdot X' \quad (2)$$

where $X = X([A])$ and $X' = X'([A])$, are defined by

$$X = 1 + \sum_{n=1}^N \beta_n \cdot [A]^n$$

and

$$X' = \frac{d X([A])}{d[A]}$$

The ligand number $\bar{n}$ is defined by Bjerrum³ as

$$\bar{n} = \frac{C_A - [A]}{C_M} \quad (3)$$

The curve obtained by plotting $\bar{n}$ as a function of $[A]$ is known as the complex formation curve.

From eqns. (1), (2), and (3), we get

$$\frac{X'}{X} = \frac{\bar{n}}{[A]} \quad (4)$$

which on integration leads to

$$\ln X([A]_j) = \int_0^{[A]_j} \frac{\bar{n}}{[A]} \cdot d[A] \quad (5)$$

Evaluating this integral, which has to be done graphically, leads to a set of corresponding values of X and $[A]$ for the system under investigation, thus enabling the determination of the different complexity constants. In the present paper this determination is carried out by successive extrapolation to $[A] = 0$ of the following functions

$$\begin{aligned} X_1 &= \frac{X-1}{[A]} = \beta_1 + \beta_2[A] + \beta_3[A]^2 + \dots \\ X_2 &= \frac{X_1 - \beta_1}{[A]} = \beta_2 + \beta_3[A] + \dots \end{aligned} \quad (6)$$

and so forth.

If the formation of polynuclear complexes is not negligible, $\frac{\bar{n}}{[A]}$ will not be a function only of $[A]$.

Assuming formation of mono- and dinuclear complexes and introducing (*cf.* Fronæus²)

$$\beta'_n = \frac{[M_2A_n]}{[M]^2[A]^n}$$

and
$$Y([A]) = \sum_{n=1}^L \beta'_n [A]^n$$

the total concentrations of central ion and ligand will be

$$\begin{aligned} C_M &= [M] \cdot X + 2[M]^2 \cdot Y \\ C_A &= [A] + [M] \cdot X' \cdot [A] + [M]^2 \cdot Y' \cdot [A] \end{aligned}$$

From these equations we arrive at

$$\frac{\bar{n}}{[A]} = \frac{X' + [M] \cdot Y'}{X + 2[M] \cdot Y} \quad (7)$$

Thus $\frac{\bar{n}}{[A]}$ is found to be a function of both $[A]$ and $[M]$. However, it is still possible to compute the constants, β_n , of the mononuclear complexes by arranging the investigation to include measurements at different values of C_M and using the fact that

$$\lim_{C_M \rightarrow 0} \frac{\bar{n}}{[A]} = \frac{X'}{X} \quad (8)$$

The calculation can then be performed as described above.

If $C_A \rightarrow 0$, then $[M] \rightarrow C_M$. Applying this to eqn. (8) we arrive at

$$\lim_{C_A \rightarrow 0} \frac{\bar{n}}{[A]} = \beta_1 + C_M \cdot \beta_1' \quad (8')$$

Hence it follows that an increase of C_M at low $[A]$ must cause an increase of $\frac{\bar{n}}{[A]}$, if both mono- and dinuclear complexes are formed.

2. Calculation from the measurements of the free central ion concentration

Assuming only mononuclear complexes to be formed and using the same symbols as above, we can write eqn. (1)

$$\frac{C_M}{[M]} = X[A] \quad (1')$$

In emf measurements of the free central ion concentration, E_M is determined

$$E_M = \frac{RT}{\nu F} \ln \frac{C_M}{[M]} \quad (9)$$

Keeping C_M constant (or a known function of C_A) and varying C_A within a measurement gives us C_A as a function of E_M . Repeating this operation with other C_M -values results in a set of curves on plotting C_A against E_M .

From these curves we obtain a set of corresponding values $(C_M, C_A)_i$ for every arbitrarily chosen value of $E_M = E_{M_j}$. As E_{M_j} is constant within a set, it follows from eqns. (9), (1'), and (4) that X_j , $[A]_j$, and $\bar{n}_j$, are also constant. For every E_{M_j} , eqn. (3) is the equation of a straight line

$$C_A = \bar{n}_j C_M + [A]_j \quad (3')$$

from which $[A]_j$ can be determined by extrapolation to $C_M = 0$. Thus, corresponding values of $[A]$ and $X[A]$ have been obtained and the complexity constants can be determined from eqns. (6). The ligand number, $\bar{n}$, can be calculated by the aid of these constants and compared with the slope, $\bar{n}_j$, of eqn. (3').

If both mono- and dinuclear complexes are present in the solution, we obtain

$$\frac{C_M}{[M]} = X + 2[M] \cdot Y \quad (1'')$$

and

$$E_M = \frac{RT}{\nu F} \ln(X + 2[M]Y) \quad (9')$$

If we put $E_M = E_{M_j}$, we obtain a set of corresponding values $(C_M, C_A)_i$ as before. Keeping E_M constant will not cause $[A]$, $X([A])$, and $Y([A])$ to be constant, and plotting $(C_M, C_A)_i$ will not result in a straight line. However, extrapolation to $C_M = [M] = 0$ will lead to

$$E_{M_j} = \frac{RT}{\nu F} \ln X([A]_j) \quad (9'')$$

and

$$C_A = [A]_j$$

resulting in corresponding values of $[A]$ and $X([A])$.

If the complex formation is very strong, the values of $[A]_j$ will be too small to be determined with sufficient accuracy for small C_A . However, if only mononuclear complexes are formed, $\bar{n}_j$ can be determined from eqn. (3') for every X_j , and corresponding values of $[A]$ and $X([A])$ can be calculated by the aid of

$$\log \frac{[A]_j}{[A]_0} = \int \frac{X([A]_j)}{X([A]_0)} \cdot \frac{1}{\bar{n}} \cdot d \log X \quad (10)$$

obtained by integration of eqn. (4).

$[A]_0$ has to be determined from eqn. (3') by extrapolation at a comparatively high value of C_A .

THE GRAPHICAL REPRESENTATION OF THE COMPLEX SYSTEMS

At any value of $[A]$ the composition of a complex system can be computed by means of the determined complexity constants. If only mononuclear complexes are formed the following equations are valid

$$\alpha_0 = \frac{[M]}{C_M} = \frac{1}{X} \quad (11)$$

$$\alpha_n = \frac{[MA_n]}{C_M} = \frac{\beta_n [A]^n}{X}; n \geq 1 \quad (12)$$

The ligand number, $\bar{n}_1$, for the mononuclear complexes can be calculated at any $[A]$ according to

$$\bar{n}_1 = \sum_{n=1}^N \frac{n \beta_n [A]^n}{1 + \beta_n [A]^n} \quad (13)$$

In the systems investigated by measurements of the free central ion concentration, values of the ligand number for the mononuclear complexes can be calculated according to the approximate equation

$$\bar{n}_1 = \frac{\Delta E_M}{\frac{RT}{\nu F} \Delta \ln [A]} \quad (14)$$

obtained from eqns. (1), (4), and (9). This equation is applied to every two consecutive points of the titration curve and the calculated $\bar{n}_1$ is ascribed to the geometrical mean of the $[A]$ values in question.

CALCULATIONS FROM EXPERIMENTAL DATA

1. *Ligand measurements.* With C'_A and C'_{HA} denoting the stoichiometric concentrations of the ligand ion and its corresponding acid, and $[H^+]'$ the hydrogen ion concentration in the buffer solution, we have

$$K_c = \frac{[H^+]'(C'_A + [H^+]')}{C'_{HA} - [H^+]'} \quad (15)$$

if the central ion concentration is zero.

In a solution with the same C'_A and C'_{HA} but with the total central ion concentration C_M , we denote the concentrations of hydrogen ion by $[H^+]$, of free ligand ions by $[A]$, and of unprotolysed acid by $[HA]$. If the concentration $C_H = \alpha \cdot C_M$ of free perchloric acid in the stock solution of central ion is taken into consideration, we get the equation

$$K_c = \frac{[H^+][A]}{C'_{HA} + C_H - [H^+]} \quad (16)$$

Putting $C'_{HA} = \delta \cdot C'_A$, we obtain from eqns. (15) and (16)

$$[A] = \frac{[H^+]'}{[H^+]} \cdot \frac{(C'_A + [H^+]')(\delta C'_A + C_H - [H^+])}{\delta C'_A - [H^+]'} \quad (17)$$

The ligand number, $\bar{n}$, is obtained from

$$\bar{n} = \frac{C'_A + [H^+] - C_H - [A]}{C_M} \quad (18)$$

The determination of $[H^+]$ and $[H^+]'$ was carried out with the aid of the element (25), the emf of which is denoted by E and E' , respectively. The slope of the glass electrode was found to be 57.3 mV. Hence,

$$E' - E = E_A = 57.3 \log \frac{[H^+]}{[H^+]'} \quad (19)$$

2. *Central ion measurements.* Using the same symbols as above, we obtain the total ligand concentration in the solution

$$C_A = C'_A + [H^+] - C_H$$

E denotes the emf of an element of the type (21), and E_o the emf of the same element, if $C_M = 0$. The difference between E and E_o is denoted by E_M .

$$E_M = 29.08 \log \frac{C_M}{[M]} \quad (20)$$

EXPERIMENTAL

Chemicals

Copper(II) perchlorate was prepared in the following manner. Copper(II) oxide was precipitated from a hot solution of copper(II) sulphate (Merck's p.a.) by sodium carbonate (Merck's p.a.), washed, and dissolved in perchloric acid (Baker's analysed). The precipitation was repeated four times and the copper(II) perchlorate was recrystallized several times. An approximately 1/3 M stock solution was prepared and the copper(II) concentration determined by electrolysis after addition of sulphuric acid. No foreign ions could be detected in the stock solution.

Copper amalgam, 2.01 % by weight, was prepared by electrolysing a solution of copper(II) sulphate, with pure mercury as cathode. The amalgam was stored under dilute perchloric acid in a closed bottle.

Sodium perchlorate was prepared from perchloric acid (Baker's analysed), sodium carbonate (Merck's p.a.), and carbonate-free sodium hydroxide.

Ethoxyacetic acid was prepared from freshly distilled monochloroacetic acid and sodium ethoxide⁶. Purification was by repeated vacuum distillation, dry nitrogen being led through the distillation apparatus. The fraction boiling at 8 torr at $96.5 \pm 0.2^\circ\text{C}$ was collected. The equivalent weight was determined by titration with NaOH to 104.1 (calc. 104.1).

A buffer was prepared by adding a calculated amount of carbonate-free sodium hydroxide solution to a weighed portion of the free acid. The buffer was analysed with the aid of a cation exchange resin in the hydrogen form.

In an analogous manner *methoxyacetic acid* was prepared. The portion collected boiled at $98.0 \pm 0.2^\circ\text{C}$ at 9 torr, and was a colourless, hygroscopic liquid, which crystallised on cooling (m.p. $+9^\circ\text{C}$).

A buffer was prepared from 68.69 g of freshly distilled acid, care being taken to prevent humidity from the air being absorbed during weighing. The buffer was then analysed with the aid of a cation exchange resin. Result: $[\text{HA}] + [\text{A}^-] = 1.526 \text{ M}$ (calc. 1.525 M with equiv. wt. 90.1).

(Ethylthio)acetic acid was prepared from freshly distilled mercaptoacetic acid and ethyl bromide by a method described for similar substances by Larsson⁶. Synthesis and purification were carried out in absence of oxygen. The collected portion, a colourless liquid, boiled at 117.3°C at 10 torr. The equivalent weight was determined to 120.1 (calc. 120.2). A buffer was made and analysed in the same way as with ethoxyacetic acid.

Thiodiacetic acid was prepared and purified according to the method of Lovén⁷ and had a melting point of 129°C , and an equivalent weight of 75.0 (calc. 75.1). A stock solution of the disodium salt was prepared by neutralizing the acid with carbonate-free sodium hydroxide.

Quinhydrone was Merck's p.a.

Method

The methoxy- and ethoxyacetate systems were investigated by central ion measurements. The emf, E (mV), of elements of the following composition was measured.

-Cu(Hg)	C_M mM $\text{Cu}(\text{ClO}_4)_2$	1.00 M NaClO_4	10.00 mM HClO_4 990 mM NaClO_4 Quinhydrone	* Au + (21)
	C'_A mM NaA			
	$\delta \cdot C'_A$ mM HA			
	NaClO_4 to $I = 1.00 \text{ M}$			

* The right hand half-cell is in this paper denoted by RE.

The solutions in the left hand half-cell were prepared by adding increasing volumes of solution S_2 to a known volume of a solution S_1 .

	S_1	S_2	
$\text{Cu}(\text{ClO}_4)_2$	C_M	C_M	mM
NaA	0	C_A°	mM
HA	0	C_{HA}°	mM
NaClO_4	$1\,000 - 3\,C_M$	$1\,000 - 3\,C_M - C_A^\circ$	mM

(22)

The thiodiacetate system was investigated by the same method with the exception that no buffer solution was used. The elements had here the composition:

$-\text{Cu}(\text{Hg})$	$\left \begin{array}{l} C_M \text{ mM } \text{Cu}(\text{ClO}_4)_2 \\ C_A' \text{ mM } \text{Na}_2\text{A} \\ \text{NaClO}_4 \text{ to } I = 1.00 \text{ M} \end{array} \right $	$\left \begin{array}{l} \text{NaClO}_4 \\ 1.00 \text{ M} \end{array} \right $	$\text{RE} +$
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(23)

and the solutions S_1 and S_2 had the composition:

	S_1	S_2	
$\text{Cu}(\text{ClO}_4)_2$	C_M	C_M	mM
Na_2A	0	C_A°	mM
NaClO_4	$1\,000 - 3\,C_M$	$1\,000 - 3\,C_M - 3\,C_A^\circ$	mM

(24)

A stream of oxygen-free nitrogen was led through the solution in the left half-cell before the amalgam was put into the electrode vessel. Good mixing of the solutions during the titration was brought about by the nitrogen stream and by stirring the amalgam with a glass rod. Before entering the electrode vessel, the nitrogen had bubbled through a 1.00 M NaClO_4 solution to attain the correct vapour pressure. Within one minute the potentials reached stable values and could with very few exceptions, be reproduced within 0.1 mV (in the thiodiacetate system 0.3 mV). Every titration series was repeated at least once.

For the measurements, a Wulff's potentiometer was used, in connection with a Cambridge Light Spot Galvanometer used as a zero instrument.

The investigation of the (ethylthio)acetate system was performed by the ligand measurement method, a glass electrode being used to determine the hydronium ion concentration in the complex solution.

The emf of the following cell

$-\text{Glass-electrode}$	$\left \begin{array}{l} C_M \text{ mM } \text{Cu}(\text{ClO}_4)_2 \\ C_A' \text{ mM } \text{NaA} \\ C_{\text{HA}}' = \delta \, C_A' \text{ mM } \text{HA} \\ \text{NaClO}_4 \text{ to } I = 1.00 \text{ M} \end{array} \right $	$\left \begin{array}{l} \text{NaClO}_4 \\ 1.00 \text{ M} \end{array} \right $	$\text{RE} +$
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(25)

was determined by means of a Radiometer PHM3 valve potentiometer.

During a titration series C_M was kept constant and C_A' was varied by mixing solutions analogous to S_1 and S_2 in (22). As before, a stream of nitrogen was used for mixing the solutions and keeping them free from oxygen. The titration series were repeated at least once and the potentials were stable and reproducible in general within 0.2 mV.

MEASUREMENTS

The copper(II) perchlorate. In order to determine the concentration of free perchloric acid in the stock solution, $[\text{H}^+]$ was measured by a glass electrode ($I = 1.00 \text{ M}$), at different copper(II) perchlorate concentrations, C_M . The results are collected in Table 1. The values in the fourth column are those found by Pedersen⁸ in solutions of pure copper(II) nitrate. Thus the figures

Table 1. The hydronium ion concentration in the copper(II) perchlorate solution at different C_M .

$C_M \times 10^3 \text{ M}$	$[\text{H}^+] \times 10^5 \text{ M}$	$([\text{H}^+]/C_M) \times 10^4$	$([\text{H}^+]/C_M)_P \times 10^4$
10.00	0.48	48	16
20.00	13.7	68	12
50.00	41.9	84	8.8

in the third column indicate an excess of free perchloric acid in the stock solution.

From these measurements, the excess of perchloric acid cannot be calculated, owing to the influence of hydrolysis. To eliminate this the following method was employed.

The emf was measured for the cell

This emf (E mV) can be written

$$E = E_1 + \frac{RT}{F} \ln \frac{c+h}{c} = E_1 + \frac{RT}{F} \ln \left(1 + \frac{h}{c} \right)$$

For small values of $\frac{h}{c}$ we arrive at

$$E = E_1 + \frac{RT}{F} \cdot \frac{h}{c} = E_1 + k \cdot h \cdot \frac{1}{c}$$

If c is sufficiently increased the hydrolysis will be totally depressed and h will attain a limit value h_o , corresponding to the concentration of free perchloric acid in the copper(II) perchlorate solution.

Plotting E against c^{-1} will give a curve which, for small values of c^{-1} , will be approximately a straight line, from the slope S of which we will obtain

$$h_o = \lim_{c^{-1} \rightarrow 0} h = \frac{S}{k}$$

where $k = 25.26 \text{ mV}$.

h_o was found to be $2.0 \times 10^{-3} \text{ M}$ and $E_1 = 1.6 \text{ mV}$. Thus $\frac{h_o}{C_M} = a = 1.0 \times 10^{-2}$.

The copper (II) methoxyacetate system. This system was investigated by central ion measurements as described above. In order to suppress the hydrolysis of the copper(II) ions the measurements were carried out in a buffer (element 21).

It was concluded that the complex solutions were not reduced by the amalgam, since the potentials were well reproducible and remained constant for several hours.

To find out if complex formation occurred between the free acid and the central ion, the emf of the following elements was measured:

When C_{HA} was increased from 0 to 300 mM the potential decreased 0.7 mV. Obviously no complex formation occurred since this should have caused an increase of the potential.

The dissociation constant, K_c , of the methoxyacetic acid at $I = 1.00 \text{ M}$ was determined from the emf of the following element:

where $\delta = 0.515$.

In the range $0.005 \text{ M} \leq C'_A \leq 0.670 \text{ M}$, the constant was found to be

$$K_c = (4.3 \pm 0.1) \times 10^{-4} \text{ M}$$

Table 2. Determination of corresponding values of C_A and E_M for the copper(II) methoxyacetate system.

$C_M = 10.0 \text{ mM}$ $E_o = 300.2 \text{ mV}$		$C_M = 20.0 \text{ mM}$ $E_o = 291.4 \text{ mV}$		$C_M = 33.3 \text{ mM}$ $E_o = 285.0 \text{ mV}$	
$C_A \text{ mM}$	$E_M \text{ mV}$	$C_A \text{ mM}$	$E_M \text{ mV}$	$C_A \text{ mM}$	$E_M \text{ mV}$
20.5	9.5	27.1	9.6	34.8	9.5
30.3	13.3	36.4	12.6	51.2	14.1
39.2	16.4	53.6	17.8	67.0	18.2
51.4	20.1	70.2	22.2	82.3	21.8
67.2	24.5	86.1	26.1	97.0	25.2
82.5	28.2	101.5	29.5	118.1	29.5
97.2	31.5	123.5	33.8	151	35.5
118.3	35.5	158	39.7	181	40.3
151	41.0	189	44.3	263	51.0
220	50.2	275	54.6	310	55.8
263	55.1	383	64.5	367	61.1
373	65.0	474	71.3	429	66.3
453	71.0	518	74.2	495	71.1
566	78.3	592	78.9	566	75.9
647	82.9	676	83.7	647	80.8
725	87.0	758	87.8	725	85.1

Table 3. Determination of $[A]$ and X_1 for the copper(II) methoxyacetate system.

E_M mV	C_A mM for				X	X_1 M ⁻¹	$\bar{n}$ cf. eqn. (3')
	$C_M = 33.3$ mM	$C_M = 20.0$ mM	$C_M = 10.0$ mM	$C_M = 0$ mM			
10.0	35.9	28.2	21.6	15.7	2.21	76.9	0.62
11.0	39.5	31.2	24.2	17.8	2.39	78.1	0.67
13.0	46.7	37.5	29.4	22.2	2.80	81.0	0.76
15.0	54.6	44.0	35.1	27.0	3.28	84.4	0.84
18.0	66.4	54.4	44.3	35.2	4.16	89.7	0.95
20.0	74.6	61.7	51.1	41.3	4.87	93.8	1.01
30.0	120.8	104.0	90.4	77.5	10.77	126	1.31
35.0	148.1	130.2	115.5	102	16.00	147	1.40
40.0	179	160	145	130	23.77	175	1.47
45.0	215	194	179	163	35.2	210	1.57
55.0	302	279	263	245	77.8	314	
65.0	413	390	373	356	171.8	480	
70.0	479	456	440	423	255.3	601	1.7
75.0	552	530	512	495	379	764	
80.0	634	612	596	580	564	970	1.6
85.0	724	702	687	671	838	1 247	

The experimental results from the complex measurements are collected in Tables 2 and 3.

By graphical extrapolation of the functions X_1 , X_2 , and X_3 , to $[A] = 0$, the complexity constants were determined:

$$\begin{aligned}\beta_1 &= (66 \pm 3) \text{ M}^{-1} \\ \beta_2 &= (640 \pm 50) \text{ M}^{-2} \\ \beta_3 &= (1\,300 \pm 300) \text{ M}^{-3} \\ \beta_4 &= (600 \pm 300) \text{ M}^{-4}\end{aligned}$$

β_4 was obtained from the slope of the function $X_3([A])$.

The copper (II) ethoxyacetate system. The measurements were performed in the same way as in the methoxyacetate system.

No complex formation could be found between the free acid and the copper(II) ion and the potentials were stable and well reproducible.

For the buffer solution used, δ had the value 0.500, and the dissociation constant K_c at $I = 1.00$ M was found to be

$$K_c = (3.5 \pm 0.1) \times 10^{-4} \text{ M}$$

The experimental results are collected in Tables 4 and 5.

Graphical extrapolation gave the constants:

$$\begin{aligned}\beta_1 &= (62 \pm 3) \text{ M}^{-1} \\ \beta_2 &= (740 \pm 50) \text{ M}^{-2} \\ \beta_3 &= (1\,600 \pm 300) \text{ M}^{-3} \\ \beta_4 &= (600 \pm 300) \text{ M}^{-4}\end{aligned}$$

β_4 was obtained from the slope of $X_3([A])$.

Table 4. Determination of corresponding values of C_A and E_M for the copper(II) ethoxyacetate system.

$C_M = 5.00$ mM $E_o = 308.9$ mV		$C_M = 10.0$ mM $E_o = 300.2$ mV		$C_M = 20.0$ mM $E_o = 291.4$ mV		$C_M = 33.3$ mM $E_o = 285.0$ mV	
C_A mM	E_M mV	C_A mM	E_M mV	C_A mM	E_M mV	C_A mM	E_M mV
9.6	5.6	16.5	7.7	17.1	6.2	16.9	4.6
18.3	9.7	23.6	10.5	27.4	9.6	36.7	10.1
30.6	14.7	30.1	12.9	36.2	12.5	59.9	16.2
46.3	20.1	41.6	16.9	46.7	15.5	80.9	21.4
65.0	25.4	60.1	22.4	65.1	20.8	98.6	25.4
81.9	30.0	74.2	26.1	83.6	25.6	121.3	30.1
100.1	33.6	96.5	31.4	94.0	28.0	150.0	35.4
110.6	35.8	117.5	35.8	108.1	31.0	450	69.4
137.4	40.7	150.1	41.5	136.6	36.5	492	72.5
168.4	45.5	180.1	45.8	199.8	46.3	563	77.5
243.2	55.0	261.8	55.9	273.3	55.3	643	82.7
287.8	59.8	371	66.3	381	65.5		
341	64.8	450	72.5	470	72.6		
400	69.8	563	80.3	588	80.7		
450	73.7	643	85.2	671	85.8		

The copper (II) (ethylthio)acetate system. For this system, two formation constants in 50 % dioxane at 30°C are reported by Irving and Fernelius⁹.

The system could not be investigated by means of copper amalgam or quinhydrone since the potentials did not attain stable values and obviously

Table 5. Determination of $[A]$ and X_1 for the copper(II) ethoxyacetate system.

E_M mV	C_A mM for					X	X_1 M ⁻¹	$\bar{n}$ cf. eqn. (3')
	$C_M = 33.3$ mM	$C_M = 20.0$ mM	$C_M = 10.0$ mM	$C_M = 5.0$ mM	$C_M = 0$ mM			
10.0	36.2	28.6	22.3	19.2	16.2	2.208	74.6	0.61
12.0	43.9	34.9	27.7	23.9	20.4	2.586	77.7	0.72
16.0	59.2	48.3	38.9	34.1	29.8	3.55	85.5	0.90
20.0	75.2	62.2	51.7	45.9	41.1	4.87	94.2	1.05
24.0	92.4	77.2	66.1	59.8	54.2	6.69	104.9	1.16
35.0	148	128.5	114	107	99	16.00	151.2	1.46
40.0		157	141	133	125	23.77	182	1.6
45.0		190.5	174	165	156	35.2	220	1.7
50.0		228	211.5	202	193	52.4	266	1.8
55.0		271	254	243	234	77.8	328	1.9
60.0		321	301	290	280	115.6	409	2.1
65.0		378	355	344	333	171.8	513	2.2
70.0	458	436	417	403	396	255.3	642	
75.0	526	504	485		468	379	808	
80.0	600	578	560		543	564	1 036	

some reaction occurred between the complex solution and the electrode material. Thus a yellow precipitate is formed if the complex solution is shaken with metallic copper or copper amalgam.

Using a glass electrode instead of quinhydrone to determine the hydronium ion concentration of the complex solutions gave stable potentials reproducible in general within 0.2 mV.

The present investigation was carried out by measuring the emf of the element (25) as described above.

By measurements in buffer solutions of known pH the slope of the glass electrode was found to be 57.3 mV.

Immediately before and after each titration series the asymmetry potential of the glass electrode was controlled in a reference methoxyacetate buffer of approximately the same pH as the complex solutions. A determination of $[H^+]$ in this buffer by quinhydrone gave the value 2.228×10^{-4} M and the mean value of the emf of the cell

was, in a series of determinations, 390.8 mV. All potential readings were corrected to this reference potential, thus avoiding the influence of slow variations in the asymmetry potential of the glass electrode.

For the buffer used δ had the value 0.510.

In the range $4 \text{ mM} \leq C'_A \leq 50 \text{ mM}$, the mean value of the dissociation constant, K_c , of the acid is

$$K_c = (2.43 \pm 0.03) \times 10^{-4} \text{ M}$$

A spectrophotometrical examination of the solutions A—F below showed that, within experimental error, the concentration of unprotolysed (ethylthio)-acetic acid had no influence on the shape of the light absorption curve. Thus it was assumed that any complex formation between copper(II) ion and the unprotolysed acid could be neglected.

	A	B	C	D	E	F	
$\text{Cu}(\text{ClO}_4)_2$	10	—	10	10	10	10	mM
$\text{Et-S-CH}_2\text{-COOH}$	—	15	15	15	150	15	mM
$\text{Et-S-CH}_2\text{-COO}^-$	—	—	—	—	—	30	mM
HClO_4	880	880	880	10	100	—	mM
NaClO_4 to $I = 1.00 \text{ M}$							

The complex formation caused a considerable alteration of the absorption spectrum curve, especially in the ultraviolet range. Even in solution C, the C_{A^-} of which was calculated to be 4×10^{-6} M, this effect was noticeable as a slight increase of the absorption with its maximum value at the wave length $330 \text{ m}\mu$. The absorption curves of the two solutions D and E, with C_{A^-} calculated to 3.4×10^{-4} M and 3.6×10^{-4} M, were almost identical and showed a strong absorption in the ultraviolet range.

Table 6. Determination of corresponding values of $[A^-]$ and $\frac{\bar{n}}{[A]}$ for $C'_A < 50$ mM in the copper (II) (ethylthio)acetate system.

C'_A mM	$C_M = 10.0$ mM			$C_M = 20.0$ mM			$C_M = 50.0$ mM			$C_M = 80.0$ mM		
	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹
	—	0	374	—	0	382	—	0	399	—	0	418
3.83	32.6	0.95	338	44.5	0.53	356						
5.64	32.8	1.42	320	45.7	0.78	346	62.5	0.33	379			
9.05	32.1	2.41	290	46.4	1.28	326	65.0	0.52	370			
12.23	30.5	3.51	257	46.2	1.79	308	66.1	0.71	359			
15.19	28.6	4.75	226	45.5	2.32	290	66.7	0.89	351	76.3	0.555	371
19.92	25.6	7.08	185	44.1	3.27	263	67.2	1.19	338	77.3	0.737	358
25.8	21.7	10.79	141	41.3	4.81	223	67.2	1.58	323	77.9	0.97	346
30.9	18.8	14.5	114	38.4	6.52	190	66.7	1.97	307	78.0	1.19	335
37.4	15.8	19.85	88.8	34.6	9.25	154	65.8	2.51	288	78.0	1.47	323
49.8	12.0	30.9	61.8	27.3	16.6	100	63.5	3.75	252	77.3	2.08	299

For $C'_A \leq 50$ mM, measurements with the cell (25) were carried out with four different C_M . The results are collected in Table 6.

For every C_M -value, $\frac{\bar{n}}{[A]}$ was plotted against $[A]$ and the curve extrapolated to $[A] = 0$.

Table 7. Determination of corresponding values of $[A]$ and $\frac{\bar{n}}{[A]}$ for $C'_A > 50$ mM in the copper(II) (ethylthio)acetate system.

C'_A mM	$C_M = 26.7$ mM			$C_M = 53.3$ mM			$C_M = 80.0$ mM			$C_M = 100.0$ mM		
	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹	E_A mV	$[A]$ mM	$\frac{\bar{n}}{[A]}$ M ⁻¹
63.4	30.9	18.33	92.5	62.1	5.10	217.5	75.9	2.86	273	83.3	2.07	308
85.6	21.9	35.7	52.6	54.5	9.50	151.2	72.6	4.50	229	81.2	3.13	270
106.4	16.9	54.2	36.1	45.3	17.23	97.3	68.0	6.81	184.7	78.4	4.42	235
139.4	12.4	85.0	24.0	32.1	38.5	49.1	57.7	13.67	115.3	72.1	7.59	175.1
180.8	9.5	123.8	17.2	22.5	73.6	27.3	42.3	33.2	55.6	60.8	15.68	105.5
216	7.7	159.3	13.4	17.8	106.3	19.4	32.3	59.4	33.0	48.9	30.4	61.1
287	5.7	229	9.5	12.6	173.6	12.2	21.8	120.2	17.3	32.4	78.5	26.5
349	4.8	288	7.9	10.0	234.0	9.2	16.9	177.5	12.0	24.6	130.3	16.7
498				7.2	374	6.2	11.5	315	7.2	14.4	280	7.7
596				6.3	464	5.3	9.5	408	5.7	12.0	369	6.1
697				5.3	564	4.4	8.1	505	4.8	10.2	464	5.0

Table 8. X-functions obtained by graphical integration of the $\frac{\bar{n}}{[A]}$ -function for the copper(II) (ethylthio)acetate system.

[A] mM	X([A])	X_1 M ⁻¹	X_2 M ⁻²	X_3 M ⁻³
0	1	365	56 000	76 000
1.00	1.420	420		
2.00	1.948	474		
4.00	3.343	586		
6.00	5.19	698		
8.00	7.49	811		
12.00	13.45	1 038		
16.00	21.26	1 266		
20.00	31.0	1 500		
100.0	676	6 750	63 800	
150.0	1 593	10 610	68 300	
200.0	2 950	14 730	71 800	
300	7 220	24 100	79 000	77 000
400	13 900	34 700	86 000	75 000
500	23 600	47 200	94 000	76 000

These curves did not quite coincide for small [A], which could indicate a very slight formation of polynuclear complexes.

If the values of $\lim_{C_A \rightarrow 0} \frac{\bar{n}}{[A]}$ were plotted against C_M a straight line was obtained.

This is in accordance with the theory if mono- and dinuclear complexes are formed.

From eqn. (8') β_1 was found to be $(370 \pm 5) \text{ M}^{-1}$.

If the change in activity coefficients can be neglected in this concentration range ($[A] < 3 \text{ mM}$), β'_1 can be estimated to $(600 \pm 200) \text{ M}^{-2}$.

A similar titration series was performed where C'_A was increased to 700 mM. These results are collected in Tables 7 and 8.

The $\frac{\bar{n}}{[A]}$ functions for the different C_M -values all coincide well, especially for $4 \text{ mM} < [A] < 300 \text{ mM}$. Thus, for $[A] > 4 \text{ mM}$, the mean values of $\frac{\bar{n}}{[A]}$ have been plotted against corresponding [A]. On this curve the graphical integration has been carried out.

Graphical extrapolation gave the constants:

$$\begin{aligned}\beta_1 &= (365 \pm 10) \text{ M}^{-1} \\ \beta_2 &= (58\,000 \pm 2\,000) \text{ M}^{-2} \\ \beta_3 &= (70\,000 \pm 5\,000) \text{ M}^{-3}\end{aligned}$$

The copper(II) thiodiacetate system. Tichane and Bennet¹⁰, who have investigated this system in 0.1 M KCl at 30.0°, report two stability constants, $\log K_1 = 4.5$ and $\log K_2 = 2.8$, but they do not mention any higher complexes.

Fig. 1. The complex formation curve of the copper(II) ethoxyacetate system. The full-drawn curve represents $\bar{n}_1$ computed by means of eqn. (13). $\bar{n}_1$ from eqn. (14) is denoted by (O).

Fig. 2. The complex formation curve of the copper(II) (ethylthio)acetate system. The full-drawn curve represents $\bar{n}_1$ computed by means of eqn. (13). The sign (O) refers to $\bar{n}_1$ obtained from Tables 6 and 7.

To find out if there is any formation of higher complexes, an investigation has been carried out by emf measurements of the concentration of free central ion in the same way as for the copper(II) methoxyacetate system (element 23).

Fig. 3. The complex formation curve of the copper(II) thiodiacetate system. The full-drawn curve represents $\bar{n}_1$ computed by means of eqn. (13), and the sign (O) refers to $\bar{n}_1$ obtained from eqn. (14).

However, a buffer solution of the ligand could not be used owing to the formation of the ion HA^- . Therefore the complex solutions were prepared from a stock solution of 1/3 M disodium thiodiacetate. The systematic error caused by the hydrolysis of the copper ions was supposed to be negligible owing to the relatively strong complexity of the system under investigation.

Some reaction occurs between the complex solutions and the copper amalgam as in the (ethylthio)acetate system. However, the reaction rate is slow and the potentials measured in some sample solutions showed good constancy during as long a time as required for a titration series.

The titrations were repeated several times and the reproducibility of the potentials was in general 0.3 mV.

At higher C_M a bluish white precipitate was easily formed which was supposed to be the neutral complex. (Found: Cu 30.0 %. Calc. for $\text{CuS}(\text{CH}_2 \cdot \text{COO})_2$: Cu 30.0 %).

This tendency of the neutral complex to precipitate from the complex solution made it necessary to use $C_M \leq 5$ mM. If Cu^+ is formed in noticeable amounts in the complex solutions in contact with copper amalgam during the titration, this could give rise to considerable errors in the calculated complexity constants, especially at these small C_M (cf. Frønaeus²). However, checking by measuring in freshly mixed complex solutions, the compositions of which were chosen to cover the titration series, gave the same potential readings as in the titrations (within the same limits of error).

A separate control was made in a solution with $C_M = 5$ mM and $C_A = 20$ mM through which nitrogen was bubbled for several hours. Amalgam was put in the oxygen-free solution and samples taken from this solution after 10 and 45 min. The samples were analysed by means of EDTA according to Schwarzenbach¹¹, and showed an increase in the consumption of titrator of about 2 %.

A similar experiment with CuSO_4 -solution showed no increase in the metal ion concentration in the solution.

Table 9. Determination of corresponding values of C_A and E_M for the copper(II) thiodiacetate system.

$C_M = 5.00$ mM		$C_M = 2.00$ mM		$C_M = 1.00$ mM		$C_M = 0.50$ mM	
C_A mM	E_M mV	C_A mM	E_M mV	C_A mM	E_M mV	C_A mM	E_M mV
2.97	10.6	1.06	8.3	0.59	9.1	0.388	9.3
5.88	26.8	2.09	20.7	1.15	20.2	0.51	12.9
8.74	42.6	3.11	32.5	1.70	29.3	0.87	22.8
11.54	55.6	4.10	42.2	2.48	40.2	1.32	32.4
14.29	66.1	5.08	50.2	3.21	48.6	1.94	42.9
19.63	84.5	6.04	57.6	4.14	58.1	2.83	55.1
27.3	105.3	7.44	66.8	5.41	68.4	3.67	64.7
34.5	120.2	8.81	75.4	6.74	78.2	4.44	72.3
		12.3	92.2	8.42	88.9	5.49	81.1
		15.2	104.3	10.00	97.6	6.67	89.4
				12.4	107.6		

Table 10. Determination of [A] and X-functions for the copper(II) thiodiacetate system.

E_M mV	$\bar{n}$	$\frac{X([A])}{\int \frac{1}{\bar{n}} d \log X}$ $X([A]_0)$	[A] mM	X([A])	$X_1 \times 10^{-3}$ M ⁻¹	$X_2 \times 10^{-7}$ M ⁻²	$X_3 \times 10^{-9}$ M ⁻³	$X_4 \times 10^{-11}$ M ⁻⁴
15	0.73	1.7058	0	1	15.0	1.2	0.4	8
20	0.90	1.4974	0.138	3.279	16.5			
25	1.03	1.3216	0.22	4.873	17.6	1.18		
30	1.17	1.1664	0.33	7.239	18.9	1.18		
35	1.30	1.0284	0.48	10.77	20.4	1.13		
40	1.44	0.8974	0.66	16.00	22.7	1.17		
45	1.58	0.7854	0.89	23.77	25.6	1.19		
70	2.43	0.3476	1.15	35.24	29.8	1.29		
75	2.62	0.2805	3.14	255.3	81.0	2.10	2.87	7.9
80	2.80	0.2176	3.67	379	103	2.40	3.27	7.8
90	3.19	0.1003	4.24	564	133	2.78	3.77	7.9
100	3.59	0	5.56	1245	224	3.76	4.68	7.7
			7.00	2748	392	5.39	6.0	8.0

This minute effect on the composition of the complex solutions caused by reaction with the amalgam was not considered to influence seriously the possibility of a fairly accurate determination of the complexity constants for the system under investigation, particularly as the amalgam was not allowed to be in contact with a complex solution for more than 10 to 15 min in the measurements.

If only mononuclear complexes are formed, C_A will be a linear function of C_M if E_M is constant (eqn. 3'). This was the case with this system.

Owing to the strong complexity, the values of [A] had to be determined by numerical integration according to eqn. (10).

The value of $[A]_0$ had to be determined by extrapolation. In this case the value at the highest E_M obtained (100 mV, corresponding to $X([A]_0)=2\ 750$) was chosen. Extrapolation gave $[A]_0 = 7.00$ mM.

The results are collected in Tables 9 and 10.

The following constants were obtained by graphical extrapolation:

$$\begin{aligned}\beta_1 &= (1.5 \pm 0.1) \times 10^4 \text{ M}^{-1} \\ \beta_2 &= (1.2 \pm 0.2) \times 10^7 \text{ M}^{-2} \\ \beta_3 &= (4 \pm 2) \times 10^8 \text{ M}^{-3} \\ \beta_4 &= (8 \pm 3) \times 10^{11} \text{ M}^{-4}\end{aligned}$$

β_4 was obtained from the slope of the function $X_3([A])$.

DISCUSSION

The complex formation curves for the methoxyacetate and the ethoxyacetate systems are almost identical and one of them is reproduced in Fig. 1. The ligand number $\bar{n}$ attains here a highest value of 2.5. The steep form of the curve indicates the presence of a fourth complex. These curves coincide

Table 11. The logarithms of the complexity constants determined at 20.0°C and ionic strength 1.00 M.

Systems	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
$\text{Cu}^{2+} - \text{Me} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COO}^-$	1.82	2.81	3.11	2.8
$\text{Cu}^{2+} - \text{Et} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COO}^-$	1.79	2.87	3.20	2.8
$\text{Cu}^{2+} - \text{Et} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO}^-$	2.56	4.76	4.85	—
$\text{Cu}^{2+} - \text{S}(\text{CH}_2 \cdot \text{COO}^-)_2$	4.18	7.08	8.6	11.9

well in their general shape with the corresponding curve for the copper(II) acetate system according to Fronæus². This might indicate that the complex formation should occur mainly in the same way as in the acetate system.

For the (ethylthio)acetate system the complex formation curve is of a somewhat different form (Fig. 2). With increasing $[\text{A}]$, the value of the ligand number rapidly increases to $\bar{n} \simeq 1.6$. Then the curve becomes flatter, indicating a wide range of existence of the second complex. The ligand number reaches approximately the same value as in the ethoxyacetate system but on account of the flat course of the curve, there seems to be no reason to take more than three complexes into consideration.

The complex formation curve for the thiodiacetate system as presented in Fig. 3, indicates a relatively wide range of existence of the first complex, since the slope of the curve is comparatively small within the range $0.5 < \bar{n} < 1.5$. The ligand number reaches a value of 3.7, indicating the for-

Fig. 4. The distribution of the central ion between the mononuclear complexes with varying $[\text{A}]$ according to eqns. (11) and (12) in: A, the copper(II) ethoxyacetate system; B, the copper(II) (ethylthio)acetate system.

Fig. 5. The distribution of the copper(II) ion between the mononuclear complexes in the thiodiacetate system according to eqns. (11) and (12).

mation of at least four complexes. The steep form of the curve at $\bar{n} > 2$ points to a narrow range of existence of the third complex.

From the complexity constants, β_n , the stability constants, b_n ,

$$b_n = \frac{[MA_n]}{[MA_{n-1}][A]}$$

have been calculated and brought together in Table 12. For the sake of survey the constants of the copper(II) acetate system according to Fronæus² have been included.

A comparison between the constants for the acetate system on one hand and for the methoxyacetate and ethoxyacetate on the other hand, strengthens the assumption made above that the formation of the complexes within these systems follows mainly the same scheme. Except for the slightly higher values of b_1 in the alkoxyacetate systems, there is no evidence for chelate formation.

For the (ethylthio)acetate system the situation is quite different. The high values of b_1 and b_2 indicate that the first two complexes are mainly chelates with the sulphur atom strongly bound to the central atom. With regard to the small value of b_3 , the third ligand can be considered to co-ordinate monodentately. The high value of the quotient $\frac{b_2}{b_3}$ expresses the predominance of the second complex.

An interpretation of the data obtained in the investigation of the thiodiacetate system is far more difficult. On account of the experiences from the

Table 12. The stability constants calculated from the determined complexity constants.

Systems	b_1 M ⁻¹	b_2 M ⁻¹	b_3 M ⁻¹	b_4 M ⁻¹	$\frac{b_1}{b_2}$	$\frac{b_2}{b_3}$	$\frac{b_3}{b_4}$
Cu ²⁺ — Me·O·CH ₂ ·COO ⁻	66	9.7	2.0	0.46	6.8	4.9	4.3
Cu ²⁺ — Et·O·CH ₂ ·COO ⁻	62	11.9	2.2	0.38	5.2	5.4	5.8
Cu ²⁺ — Et·S·CH ₂ ·COO ⁻	365	160	1.2		2.3	130	
Cu ²⁺ — S(CH ₂ ·COO ⁻) ₂	15 000	800	33	2 000	19	24	0.02
Cu ²⁺ — CH ₃ ·COO ⁻ (according to Fronæus ²)	47	9.6	2.6	0.65	4.9	3.7	4.0

(ethylthio)acetate system, however, it may be reasonable to regard the ligand ion as tridentate, capable of filling two or three of the planarly disposed co-ordination positions of the four-co-ordinated copper(II) ion. The great stability of the first two complexes may therefore be attributed to chelating. The value of the constant b_4 , obtained in this investigation, is largely influenced by any imperfections in the applied methods. The unexpectedly high value of b_4 can be due to this. However, it may be mentioned that Fronæus² observed a similar effect in the copper(II) tartrate system.

Finally, I wish to express my gratitude to my teachers, Professor S. Bodforss and Professor S. Fronæus, who interested me in complex chemistry, put the best working facilities at my disposal, and stimulated this work by many valuable discussions.

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Received July 22, 1960.