

On the (Methylthio)acetate and (*tert*-Butylthio)acetate Complexes of Copper(II)

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The formation of (methylthio)acetate and (*tert*-butylthio)acetate complexes with copper(II) in aqueous solution at 25.0°C has been studied by determination of the concentration of free ligand in the complex solutions.

In both systems the formation of three mononuclear complexes was indicated. The following stability constants were obtained:

$$\begin{array}{l} \text{Cu}^{2+}/(\text{methylthio})\text{acetate:} \\ \beta_1 = (254 \pm 2) \text{ M}^{-1}, \\ \beta_2 = (2.23 \pm 0.02) \times 10^4 \text{ M}^{-2}, \\ \beta_3 = (3.1 \pm 0.3) \times 10^4 \text{ M}^{-3}. \\ \text{Cu}^{2+}/(\textit{tert}\text{-butylthio})\text{acetate:} \\ \beta_1 = (319 \pm 3) \text{ M}^{-1}, \\ \beta_2 = (8.27 \pm 0.06) \times 10^4 \text{ M}^{-2}, \\ \beta_3 = (6.6 \pm 0.9) \times 10^4 \text{ M}^{-3}. \end{array}$$

The acid constant of (methylthio)acetic acid was determined to $(2.48 \pm 0.05) \times 10^{-4}$ M and of (*tert*-butylthio)acetic acid to $(2.27 \pm 0.05) \times 10^{-4}$ M.

The constants refer to the ionic strength 1.00 M (NaClO₄).

The results indicate that the ligands act bidentately in forming the complexes ML and ML₂. With R=methyl, isopropyl, and *tert*-butyl the stability of the first and second complexes with R·S·CH₂·COO⁻ is found to increase with the size of R.

The formation of copper(II) complexes with ligands of the type R·X·CH₂·COO⁻, where X stands for O or S, has been studied earlier for R=C₂H₅ (Ref. 1) and for R=i-C₃H₇ (Ref. 2). The results indicate that the (alkylthio)acetates act bidentately to a much higher extent than the alkoxyacetates in forming complexes with the copper(II) ion. Since the measurements were made at 20.0°C with the C₂H₅-compounds and at 25.0°C with the i-C₃H₇-compounds, it could not be concluded, with any certainty, if the nature of R affects the stability of the complexes. The present investigation has been made to find out if such a dependence exists with the thio-compounds. Thus the formation of (methylthio)acetate and (*tert*-butylthio)acetate complexes of copper(II) has been studied at the same temperature and ionic strength and using the same experimental technique as in the investigation

of the copper(II) complexes of (isopropylthio) acetate.² As far as possible the same apparatus and stock solutions have been used as in that investigation.

An attempt to include a comparison of the corresponding oxy-compounds in the investigation had to be abandoned owing to the difficulties encountered in preparing pure *tert*-butoxyacetic acid (*vide infra*).

NOTATIONS AND CALCULATIONS

In the present paper the following symbols are used.

C_M	= total concentration of Cu^{2+} -ion.
$[M]$	= concentration of free Cu^{2+} -ion.
α	= proportionality factor. The excess of acid in the copper(II) perchlorate stock solution is αC_M .
C_L'	= stoichiometric total concentration of ligand L.
C_L	= corrected total concentration of ligand L.
δ	= buffer quotient in a ligand buffer. The stoichiometric concentration of the acid HL is $\delta C_L'$.
$[L]$	= concentration of free ligand.
K_a	= $[\text{H}_3\text{O}^+][L]/[\text{HL}]$.
N	= maximum coordination number.
β_n	= $[\text{ML}_n]/([\text{M}][L]^n)$ = gross stability constant.
K_n	= $[\text{ML}_n]/([\text{ML}_{n-1}][L])$ = stepwise stability constant.
X	= $1 + \sum_{n=1}^N \beta_n [L]^n$.
\bar{n}	= $(C_L - [L])/C_M$ = the ligand number.
X_i	= $(X_{i-1} - \beta_{i-1})/[L]$; ($1 \leq i \leq N$; $X_0 = X$; $\beta_0 = 1$).
h_M and h_0	= $[\text{H}_3\text{O}^+]$ in solutions with the same C_L' -value, h_0 referring to a solution with $C_M = 0$.
h_R	= $[\text{H}_3\text{O}^+]$ in a reference solution.
E_M and E_0	= $59.16 \log (h_M/h_R)$ mV and $59.16 \log (h_0/h_R)$ mV.
E_L	= $E_M - E_0 = 59.16 \log (h_M/h_0)$ mV.

Since the concentration of protolytic impurities in the sodium perchlorate was negligible, the equations earlier presented³ for the calculation of $[L]$ and \bar{n} from the experimental data could be simplified.

$$[L] = (h_0/h_M)(C_L' + h_0)(\delta C_L' + \alpha C_M - h_M)/(\delta C_L' - h_0) \quad (1)$$

$$\bar{n} = (C_L' - \alpha C_M + h_M - [L])/C_M \quad (2)$$

The stability constants were calculated both graphically and numerically as earlier described.³ The limits of error ascribed to the graphically calculated stability constants are obtained by integration of limiting curves to the $\bar{n}/[L]$ -plots. The limits of error given in the present paper with numerically calculated constants are computed estimates of 99 % confidence limits.

EXPERIMENTAL

Chemicals

The same *copper(II) perchlorate* stock solution was used as in an earlier investigation.² The value of α was -1.7×10^{-3} .

Sodium perchlorate was prepared as described before.⁴ The concentration of protolytic impurities, found to be less than about 3×10^{-6} M in a 1.00 M solution of the salt, was neglected in the buffer calculations.

(*Methylthio*)acetic acid was prepared from methyl iodide and freshly distilled mercaptoacetic acid.⁵ The (*tert-butylthio*)acetic acid was easily prepared from *tert*-butyl alcohol and mercaptoacetic acid according to Hellström and Lauritzson.⁶ In the latter synthesis the remaining traces of mercaptoacetic acid were destroyed by FeCl_3 before the extraction with ether. Both acids were rectified by repeated vacuum distillation. Buffer solutions were prepared from carbonate-free sodium hydroxide and the constant-boiling fraction of the acid in question. The (*methylthio*)acetic acid boiled at 109°C at 1.0 kPa (equiv. w. 106.0, calc. 106.1) and the (*tert-butylthio*)acetic acid at 130°C at 1.5 kPa (equiv. w. 148.1, calc. 148.2). The buffer solutions were analysed with the aid of a cation exchange resin.

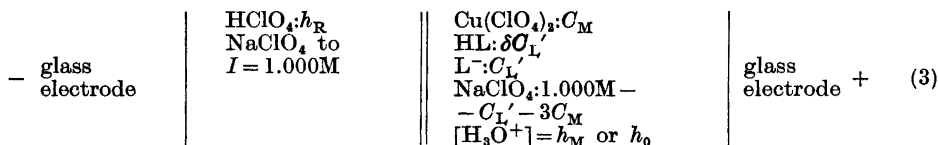
Nitrogen was passed through the buffers and the other stock solutions in order to remove oxygen.

An attempt was made to prepare *tert*-butoxyacetic acid from *tert*-butyl alcohol and chloroacetic acid according to a method given for the synthesis of ethoxyacetic acid.⁷ Potassium metal was used instead of sodium. The crude product, however, could not be vacuum distilled without decomposing.

Method

The same method and the same experimental equipment was used as in an earlier investigation.²

The emf of cell (3) is represented by E_0 if $C_M = 0$, otherwise by E_M . The double lines represent a salt bridge with 1.000 M NaClO_4 .



The glass electrode was a Jena Type U, found to have the theoretical slope. All emf-values were reproducible within the limits set by the possibility to read off the Radiometer PHM 4 potentiometer, *viz.* 0.1 or 0.2 mV.

The cells were thoroughly thermostated at $(25.00 \pm 0.05)^\circ\text{C}$.

During most titrations the complex solutions were kept free from oxygen. The same potentials were obtained, however, when this precaution was omitted.

MEASUREMENTS AND RESULTS

The copper(II) (methylthio)acetate system. Measurements were made at three different C_M -values in a ligand buffer with $\delta = 0.253$, and at one C_M -value in a buffer with $\delta = 0.614$. The results are collected in Tables 1 and 2. As illustrated in Fig. 1, the $\bar{n}/[\text{L}]$ -values were independent of both C_M and δ . Thus it is indicated that the hydrolysis of the hydrated copper(II) ion is negligible in the complex solutions (pH = 4 to 5). Also it is likely that only

Table 1. Determination of [L] and $\bar{n}/[L]$ in the copper(II) (methylthio)acetate system. Ligand buffer with $\delta=0.253$. The values of E_0 refer to $h_R=3.88 \times 10^{-3}$ M.

C_L' (mM)	$-E_0$ (mV)	$C_M=50.0$ mM			$C_M=40.0$ mM			$C_M=30.0$ mM		
		E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M^{-1})	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M^{-1})	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M^{-1})
3.75	108.3	47.9	0.327	237	45.5	0.395	238	42.0	0.503	238
4.72	107.9	50.8	0.401	241	48.0	0.486	240	44.0	0.623	239
5.78	107.5	52.9	0.485	241	49.7	0.592	239	45.2	0.765	236
7.06	107.3	54.7	0.589	240	51.2	0.720	238	46.3	0.934	233
8.86	107.1	56.5	0.732	239	52.7	0.897	237	47.3	1.176	230
11.09	107.0	57.9	0.916	237	53.8	1.125	234	47.9	1.489	225
13.61	106.9	58.9	1.126	234	54.4	1.397	229	48.2	1.856	219
16.73	106.8	59.5	1.403	228	54.6	1.757	221	48.1	2.34	211
20.53	106.8	59.7	1.763	221	54.6	2.21	214	47.5	3.00	199
25.38	106.8	59.7	2.24	213	54.3	2.83	204	46.5	3.93	186
31.2	106.8	59.0	2.90	200	53.1	3.72	189	44.8	5.24	168
37.0	106.9	58.0	3.63	188	51.6	4.73	173	42.7	6.80	150
42.7	106.9	56.9	4.42	176	49.8	5.91	158	40.5	8.61	133
48.2	107.0	55.8	5.25	166	48.1	7.18	144	38.1	10.72	118
53.6	107.0	54.3	6.23	154	46.3	8.61	132	35.8	13.09	104
58.8	107.1	53.1	7.20	145	44.5	10.17	121	33.7	15.63	93
64.0	107.2	51.5	8.38	134	42.6	11.96	110	31.6	18.50	82
73.9	107.2	48.2	11.08	114	38.5	16.28	89	27.6	25.0	65
83.3	107.4	45.1	14.15	98	35.1	21.0	74	24.5	31.9	54
96.8	107.7	40.3	19.93	78	30.5	29.3	58	21.1	42.4	43
109.4	107.9	35.8	26.9	62	26.8	38.3	46	18.5	53.1	36
121.2	108.1	32.1	34.5	50	23.9	47.6	39	16.5	63.6	30
139.4	108.3	27.2	48.1	38	20.2	63.3	30	14.2	80.0	25
159.1	108.7	23.3	64.0	30	17.5	80.3	25	12.4	98.0	21
179.5	109.1	20.1	81.8	24	15.3	98.7	20	11.0	116.8	18
202.4	109.4	17.4	102.6	20	13.4	119.9	17	9.5	139.7	15
230.2	110.0	15.1	127.6	16	11.8	145.2	15	8.6	164.5	13
258.1	110.3	13.2	154.2	14	10.2	173.3	12	7.4	193.3	11
285.7	110.9	11.8	180.2	12	9.3	198.7	11	7.0	217	10
333	111.6	9.9	226	9.4	7.9	245	9.0	5.9	264	8.6

Table 2. Determination of [L] and $\bar{n}/[L]$ in the copper(II) (methylthio)acetate system. $C_M=40.0$ mM. Ligand buffer with $\delta=0.614$. The E_0 -values refer to $h_R=3.88 \times 10^{-3}$ M.

C_L' (mM)	$-E_0$ (mV)	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M^{-1})	C_L' (mM)	$-E_0$ (mV)	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M^{-1})
3.56	85.9	45.2	0.411	244	47.1	84.1	48.3	6.99	147
4.63	85.2	47.4	0.526	241	51.2	84.2	47.1	7.99	138
5.65	85.0	49.3	0.622	244	59.1	84.2	44.2	10.39	119
7.09	84.7	50.8	0.773	240	66.7	84.4	41.5	13.08	104
8.87	84.4	52.1	0.957	237	77.4	84.6	37.5	17.81	85
10.89	84.2	53.0	1.172	233	87.5	84.8	33.8	23.3	69
13.38	84.1	53.7	1.443	229	97.0	84.9	30.5	29.4	58
16.42	84.1	54.0	1.796	221	111.5	85.1	26.2	40.1	45
20.31	84.0	54.0	2.27	212	127.3	85.4	22.7	52.5	36
25.00	84.0	53.6	2.89	202	143.6	85.7	19.8	66.3	29
29.63	84.0	52.8	3.59	190	161.9	86.0	17.2	82.8	24
34.2	84.0	51.9	4.33	179	184.2	86.4	14.9	103.1	20
38.6	84.0	50.8	5.14	168	206.5	86.9	13.2	123.5	17
42.9	84.0	49.6	6.02	158	228.6	87.3	11.9	143.8	15

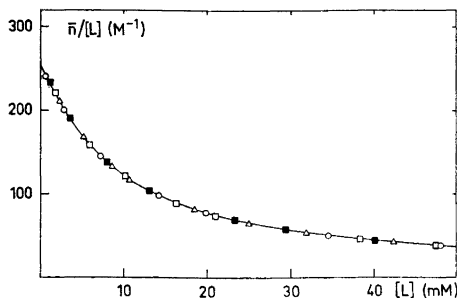


Fig. 1. Some $\bar{n}/[L]$ -values for $[L] < 50$ mM in the copper(II) (methylthio)acetate system. Buffer with $\delta = 0.253$: $C_M = 50$ mM (○), $C_M = 40$ mM (□), $C_M = 30$ mM (△). Buffer with $\delta = 0.614$ and $C_M = 40$ mM (■). The full-drawn curve is calculated from the stability constants listed in Table 6.

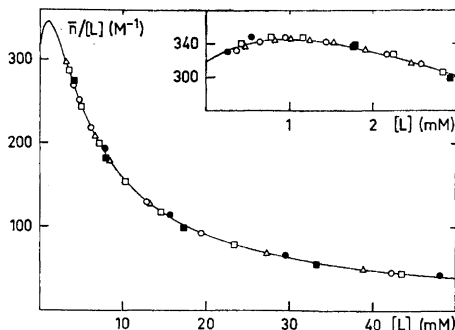


Fig. 2. Some $\bar{n}/[L]$ -values for $[L] < 50$ mM in the copper(II) (*tert*-butylthio)acetate system. Buffer with $\delta = 0.1916$: $C_M = 50$ mM (○), $C_M = 40$ mM (□), $C_M = 30$ mM (△). Buffer with $\delta = 0.0961$: $C_M = 30$ mM (■), $C_M = 20$ mM (●). The full-drawn curve is calculated from the stability constants listed in Table 6.

mononuclear complexes are formed³ and that the free acid HL does not act as a ligand.

The following estimates of the gross stability constants were obtained.

	Graphically	Numerically	
β_1	255 ± 6	254 ± 2	M^{-1}
β_2	$(2.28 \pm 0.05) \times 10^4$	$(2.23 \pm 0.02) \times 10^4$	M^{-2}
β_3	$(2.9 \pm 0.2) \times 10^4$	$(3.1 \pm 0.3) \times 10^4$	M^{-3}

Table 3. Representative values from the graphical determination of the stability constants in the copper(II) (methylthio)acetate system.

[L] (mM)	X_1 (M^{-1})	$X_2 \times 10^{-4}$ (M^{-2})	[L] (mM)	X_1 (M^{-1})	$X_2 \times 10^{-4}$ (M^{-2})	$X_3 \times 10^{-4}$ (M^{-3})
0	255	2.28				
0.50	265		18.00	668	2.29	
1.00	276		20.0	715	2.30	
1.50	288		24.0	809	2.31	
2.00	300		28.0	906	2.33	
2.50	312		32.0	1005	2.34	
3.00	324		36.0	1100	2.35	
3.50	336		40.0	1200	2.37	
4.00	347		45.0	1330	2.39	
4.50	358		50.0	1460	2.40	
5.00	370		60.0	1720	2.44	
6.00	392	2.28	70.0	2000	2.49	3.0
7.00	415	2.29	80.0	2270	2.51	2.9
8.00	438	2.29	100.0	2820	2.57	2.9
9.00	461	2.29	120.0	3410	2.63	2.9
10.00	483	2.28	140.0	4020	2.69	2.9
12.00	529	2.28	160.0	4660	2.75	3.0
14.00	575	2.29	180.0	5320	2.81	3.0
16.00	621	2.29	200	5970	2.86	2.9

Table 4. Determination of [L] and $\bar{n}/[L]$ in the copper(II) (*t*-butylthio)acetate system. Ligand buffer with $\delta=0.1916$. The values of E_0 refer to $h_R=3.88 \times 10^{-3}$ M.

C_L' (mM)	$-E_0$ (mV)	$C_M=50.0$ mM			$C_M=40.0$ mM			$C_M=30.0$ mM		
		E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M ⁻¹)	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M ⁻¹)	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M ⁻¹)
3.75	117.2	51.9	0.243	321	50.0	0.293	325	46.9	0.375	327
4.72	117.0	55.5	0.296	329	53.3	0.354	336	49.7	0.455	337
5.78	116.8	58.2	0.355	333	55.7	0.424	341	51.8	0.543	343
7.06	116.6	60.7	0.422	340	57.7	0.512	342	53.4	0.657	344
8.86	116.4	62.9	0.525	339	59.7	0.633	344	55.0	0.816	345
11.09	116.4	65.0	0.645	343	61.6	0.776	349	56.4	1.010	347
13.61	116.3	66.6	0.781	345	62.8	0.949	348	57.3	1.239	345
16.73	116.3	68.1	0.946	348	63.9	1.161	348	58.0	1.527	342
20.53	116.3	69.1	1.160	346	64.7	1.425	346	58.2	1.909	333
25.38	116.4	69.9	1.438	343	65.1	1.786	339	57.8	2.46	317
31.2	116.6	70.4	1.787	338	65.1	2.25	328	56.9	3.19	297
37.0	116.7	70.3	2.17	328	64.0	2.84	306	55.1	4.12	270
42.7	116.8	69.9	2.58	316	62.9	3.47	287	52.9	5.23	241
48.2	116.9	69.1	3.04	301	61.4	4.19	266	50.0	6.67	209
53.6	117.0	68.2	3.54	286	59.7	5.02	244	46.9	8.42	180
58.8	117.1	67.0	4.11	270	57.7	6.00	222	43.4	10.64	152
64.0	117.3	65.6	4.75	252	55.5	7.16	200	40.0	13.28	128
73.9	117.6	62.6	6.24	219	50.1	10.29	155	33.7	19.69	92
83.3	117.8	58.5	8.32	181	44.3	14.63	118	28.5	27.3	69
96.8	118.1	51.3	12.91	130	36.2	23.4	79	23.3	38.9	50
109.4	118.6	44.1	19.42	93	30.4	33.3	57	19.8	50.4	39
121.2	118.9	37.9	27.5	68	26.2	43.5	45	17.3	61.6	32
139.4	119.5	30.5	42.3	46	21.6	59.9	33	14.7	78.5	26
159.1	119.9	25.0	59.9	33	18.0	78.7	26	12.3	98.4	21
179.5	120.5	20.9	79.3	25	15.4	98.3	21	10.7	118.1	17
202.4	121.2	17.9	100.5	20	13.3	120.4	17	9.4	140.2	15
230.2	121.9	15.0	128.1	16	11.2	148.6	14	8.0	168.4	12
258.1	122.7	12.8	156.5	13	9.8	176.0	12	6.9	197.1	10
285.7	123.6	11.6	181.6	12	8.8	203	10	6.2	224	9

The copper(II) (*tert*-butylthio)acetate system. The solubility of (*tert*-butylthio)acetic acid in water was found to be 0.24 M at 24°C. A ligand buffer with $\delta=0.1916$ was used in the main investigation. The experimental results are collected in Table 4.

In Fig. 2 are plotted $\bar{n}/[L]$ -values (at different C_M) from the main investigation and from a preliminary investigation, in which a buffer with $\delta=0.0961$ was used. The plot shows that $\bar{n}/[L]$ is independent of both C_M and δ . This indicates that only mononuclear complexes are formed and that complexes between Cu^{2+} and HL are not formed in noticeable concentrations under the experimental conditions of the present investigation. (The copper(II) perchlorate and the (*tert*-butylthio)acetic acid used in the preliminary investigation were not prepared in the same way as those used in the main investigation.)

The following stability constants were calculated.

	Graphically	Numerically
β_1	315 ± 5	319 ± 3 M ⁻¹
β_2	$(8.3 \pm 0.2) \times 10^4$	$(8.27 \pm 0.06) \times 10^4$ M ⁻²
β_3	$(5 \pm 2) \times 10^4$	$(6.6 \pm 0.9) \times 10^4$ M ⁻³

The acid constants were estimated by the extrapolation method earlier presented.² The C_L' - and E_0 -data in Tables 1, 2, and 4 were used. With the three buffers the plots of E_0 (at sufficiently high C_L') and pK_a as functions of C_L' were all linear. For (methylthio)acetic acid the K_a -values obtained in the buffer with $\delta=0.253$ were $(2.471 \pm 0.005) \times 10^{-4}$ M from the E_0 -plot and $(2.472 \pm 0.006) \times 10^{-4}$ M from the pK_a -plot. In the buffer with $\delta=0.614$ the corresponding K_a -values were $(2.492 \pm 0.005) \times 10^{-4}$ M and $(2.488 \pm 0.005) \times 10^{-4}$ M.

For (*tert*-butylthio)acetic acid $K_a = (2.267 \pm 0.004) \times 10^{-4}$ M was obtained both from the E_0 - and from the pK_a -plot. The data from the preliminary investigation of the (*tert*-butylthio)acetate system only permitted K_a to be estimated at $(2.3 \pm 0.1) \times 10^{-4}$ M.

Considering the sources of error mentioned in Ref. 2, the following K_a -values should be valid in the medium in question, *viz.* for (methylthio)acetic acid $(2.48 \pm 0.05) \times 10^{-4}$ M and for (*tert*-butylthio)acetic acid $(2.27 \pm 0.05) \times 10^{-4}$ M.

DISCUSSION

The investigation has shown that only mononuclear complexes are formed between the copper(II) ion and the (alkylthio)acetate ions in question. No complex formation between Cu^{2+} and the free ligand acid, HL, was observed in either of the two systems.

For both systems the complex formation curves have similar shapes (Figs. 3 and 4). In both cases \bar{n} reaches a value slightly above 2. In the vicinity of $\bar{n}=2$ the curves are almost horizontal, which indicates that the tendency to form complexes with more than two ligands is small in the two

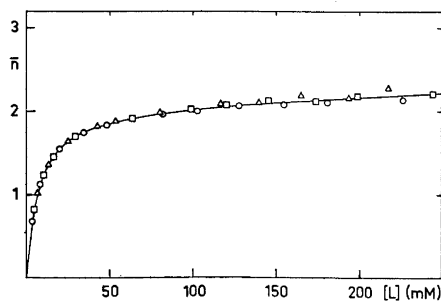


Fig. 3. Some \bar{n} -values in the copper(II) (methylthio)acetate system. Buffer with $\delta=0.253$: $C_M=50$ mM (O), $C_M=40$ mM (\square), $C_M=30$ mM (Δ). The curve is calculated from the stability constants listed in Table 6.

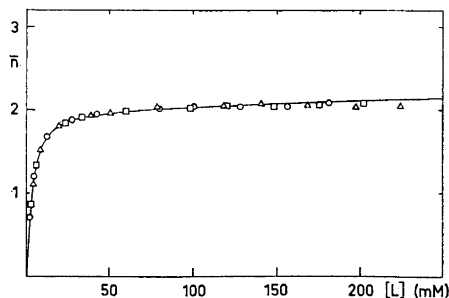


Fig. 4. Some \bar{n} -values in the copper(II) (*tert*-butylthio)acetate system. Buffer with $\delta=0.1916$: $C_M=50$ mM (O), $C_M=40$ mM (\square), $C_M=30$ mM (Δ). The curve is obtained by means of the stability constants listed in Table 6.

Table 5. Representative values from the graphical determination of the stability constants in the copper(II) (*t*-butylthio)acetate system.

[L] (mM)	X ₁ (M ⁻¹)	X ₂ × 10 ⁻⁴ (M ⁻²)	[L] (mM)	X ₁ (M ⁻¹)	X ₂ × 10 ⁻⁴ (M ⁻²)	X ₃ × 10 ⁻⁴ (M ⁻³)
0	316	8.36				
0.50	353		16.00	1650	8.36	
1.00	397		18.00	1820	8.36	
1.50	440		20.0	1990	8.38	
2.00	483		24.0	2330	8.40	
2.50	525		28.0	2680	8.44	
3.00	568		32.0	3020	8.47	
3.50	609		36.0	3370	8.49	
4.00	651		40.0	3720	8.52	
4.50	692		45.0	4170	8.56	
5.00	733		50.0	4620	8.62	5.2
6.00	817		60.0	5530	8.69	5.5
7.00	901	8.36	70.0	6420	8.72	5.1
8.00	985	8.36	80.0	7310	8.74	4.8
9.00	1070	8.36	100.0	9220	8.90	5.4
10.00	1150	8.36	120.0	11100	9.01	5.4
12.00	1320	8.37	140.0	13100	9.16	5.7
14.00	1490	8.36	180.0	17200	9.37	5.6

Table 6. Stability constants for some copper(II) (alkylthio)acetate systems at ionic strength 1.0 M (NaClO₄).

System	Temp. (°C)	β ₁ =K ₁ (M ⁻¹)	β ₂ × 10 ⁻⁴ (M ⁻²)	β ₃ × 10 ⁻⁴ (M ⁻³)	K ₂ (M ⁻¹)	K ₃ (M ⁻¹)	$\frac{K_1}{K_2}$	$\frac{K_2}{K_3}$
Cu ²⁺ / CH ₃ ·S·CH ₂ ·COO ⁻	25.0	254	2.23	3.1	88	1.4	2.9	60
Cu ²⁺ / C ₂ H ₅ ·S·CH ₂ ·COO ⁻ ^a	20.0	365	5.8	7.0	160	1.2	2.3	130
Cu ²⁺ / <i>i</i> -C ₃ H ₇ ·S·CH ₂ ·COO ⁻ ^b	25.0	307	5.91	13	192	2.2	1.6	90
Cu ²⁺ / <i>t</i> -C ₄ H ₉ ·S·CH ₂ ·COO ⁻	25.0	319	8.27	6.6	259	0.8	1.2	320

^a See Ref. 1. ^b See Ref. 2.

systems. The steep form of the curves at $\bar{n} \approx 1$ is consistent with the large value of the second stepwise stability constant, K_2 , in both systems.

In the graphical treatment the first two stability constants, β_1 and β_2 , could be calculated from the X₁-plot, which in both systems was perfectly linear for [L] < 20 mM (corresponding to $\bar{n} < 1.6$ in the (methylthio)acetate system and $\bar{n} < 1.8$ in the (*tert*-butylthio)acetate system). The β_3 -values were obtained from the slope of the X₂-plots in the region 50 mM < [L] < 200 mM. As earlier pointed out,² the β_3 -values may be influenced by systematic errors.

In Table 6 are collected the stability constants obtained in the present investigation, together with the stability constants of some related systems which have been investigated earlier. A comparison of the different sets of constants shows that the complex formation follows the same scheme in all the copper(II) (alkylthio)acetate systems in question.

The high stability of the first and second complexes indicates that the ligands act mainly bidentately in forming these complexes. This interpretation is strengthened by the large values of the quotient K_2/K_3 , indicating that the coordination square of the Cu^{2+} -ion is largely occupied by the two ligands in the complex ML_2 . The small K_3 -values indicate that the ligands in the third complex ML_3 are not all forming chelates. The present investigation, however, gives no information whether the third ligand occupies a fifth coordination site or if the three ligands, in one way or another, share the four positions of the coordination square.

A comparison of the stability constants of the three systems investigated at 25°C shows that both K_1 and K_2 increase with the size of the R-group in the ligand $\text{R}\cdot\text{S}\cdot\text{CH}_2\cdot\text{COO}^-$. It seems not possible, however, to give a closer interpretation of this trend on the basis of the present equilibrium studies at only one temperature.

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REFERENCES

1. Sandell, A. *Acta Chem. Scand.* **15** (1961) 190.
2. Sandell, A. *Acta Chem. Scand.* **25** (1971) 2609.
3. Sandell, A. *Acta Chem. Scand.* **24** (1970) 1561.
4. Sandell, A. *Acta Chem. Scand.* **24** (1970) 3391.
5. Larsson, E. *Ber.* **B 63** (1930) 1347.
6. Hellström, N. and Lauritzson, T. *Ber.* **B 69** (1936) 2003.
7. Blatt, A. H. *Org. Syn. Coll. Vol.* **2** (1946) 260.

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