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Equilibria in Aqueous Solutions. The Systems Cadmium Nitrate — Thiosemicarbazide, and Cadmium Nitrate — Ethylenethiourea

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The systems: Cd^{2+} — thiosemicarbazide and Cd^{2+} — ethylenethiourea were investigated using e.m.f. methods.
The following equilibria were found at 25°C in 1 M $NaNO_3$:
$Cd^{2+} + n$ thiosemicarbazide = $Cd^{2+}(thio)_n$; $\beta_1 = 370 \pm 15$; $\beta_2 = 50\,000 \pm 1500$; $\beta_3 = 725\,000 \pm 25\,000$.
$Cd^{2+} + n$ ethylenethiourea = $Cd^{2+}(etu)_n$; $\beta_1 = 20.4 + 0.8$; $\beta_2 = 137 \pm 25$; $\beta_3 = 466 \pm 175$; $\beta_4 = 2240 \pm 470$.

In the literature information is available on complex compounds of thiourea and metal ions. Little else is known about the affinity between metal ions and compounds containing =C=S groups. Complexes containing ethylenethiourea (etu) were prepared by Morgan and Burstall [1]. Jensen and Rancke-Madsen [2] prepared several complexes containing thiosemicarbazide (thio). They proved by chemical methods that thiosemicarbazide is a chelate, which forms bonds through the hydrazine nitrogen and the sulphur atom to metal ions of the transition groups.

X-Ray investigations have confirmed the qualitative stereochemical conclusions, and have added new quantitative details. Cavalca, Nardelli, and Fava [3] solved the crystal structure of $Cd(etu)_2(NCS)_2$. They found that sulphur of etu is bonded to Cd with a Cd—S distance of 2.60 Å. Cavalca, Nardelli, and Branchi [4] found the distances: Zn—N = 2.11 Å, Zn—S = 2.29 Å in $Zn(thio)Cl_2$. Grønbæk and Rasmussen [5] found the bond lengths: Ni—S = 2.16 Å, Ni—N = 1.90 Å in trans-$Ni(thio)_2SO_4 \cdot 3H_2O$.

The X-ray investigations prove that a classical valence description of carbon-sulphur double bonds is inadequate. A bond order of 1.3 is reported [5] for the C—S bond of thiosemicarbazide. The short nickel-ligand distances in nickel-thiosemicarbazide indicate a considerable affinity for the complex formation. A direct measurement of the complexity constants of the nickel-thiosemicarbazide system is difficult. Thiosemicarbazide has practically no acid-base

properties, and nickel electrodes are notorious for irreversibility. According to Leden [6] cadmiumamalgamelectrodes behave reversibly in aqueous solutions. The Cd^{2+}-thio system was therefore chosen for obtaining some quantitative information about the complexing power of thiosemicarbazide. For comparison the Cd^{2+}-etu system was investigated also.

Electrochemical measurements were made using the cell:

$$\mathrm{Cd,Hg} \left\| \begin{array}{l} 1\ \mathrm{M\ NaNO_3} \\ 0.01\ \mathrm{M\ Cd^{2+}} \\ 0.0001\ \mathrm{M\ HNO_3} \end{array} \right\| 1\ \mathrm{M\ NaNO_3} \left\| \begin{array}{l} 1\ \mathrm{M\ NaNO_3} \\ x\ \mathrm{M\ Cd^{2+}}, y\ \mathrm{M\ thio\ or}\ y\ \mathrm{M\ etu} \\ 0.0001\ \mathrm{M\ HNO_3} \end{array} \right\| \mathrm{Cd,Hg}$$

Complexity constants were calculated from these measurements.

EXPERIMENTAL

Deionised water was distilled in an all glass apparatus. Small amounts of $KMnO_4$ and NaOH were added before distillation. Sodium nitrate was an analytical grade from E. Merck and used without purification.

Cadmium nitrate tetrahydrate from The British Drug House was a laboratory reagent. It too was used without purification. The mercury was a redistilled Merck product.

Merck cadmium metal powder (99.9 % Cd) was distilled at 10^{-3} mm Hg at 350 – 400°C.

Cd-amalgams were prepared and kept in a nitrogen atmosphere. Nitrogen from a cylinder was purified by passing a copper catalyst. The amalgams contained about 10 % Cd. They remained bright and clean for weeks when kept under nitrogen.

Merck thiosemicarbazide was recrystallized once from water.

Ethylenethiourea was prepared from ethylenediamine (Fluka, pure) and redistilled carbondisulfide using the method described by Adkins [7]. The melting point of the product was 197° – 199°C. Adkins found the melting point 197° – 198°C.

The half cells of the elements were made according to descriptions by Pedersen [8]. Purified nitrogen passed through the half cells during measurements. It was saturated with water vapour by passing a washbottle containing the same solution as the half cell.

Two quinhydrone electrodes and one Cd – Hg electrode were used for reference electrodes. Bright Pt electrodes were used for the quinhydrone electrodes. Quinhydrone was prepared according to Biilmann and Lund [9]. The solutions were of the composition: 1 M $NaNO_3$, 0.01 M HNO_3. Fresh quinhydrone electrodes were used for each run.

The Cd – Hg reference electrode contained 1 M $NaNO_3$ and 0.01 M $Cd(NO_3)_2$. Solutions of the composition: 1 M $NaNO_3$, x M Cd^{2+}, y M thio or etu were prepared from stock solutions except that the ligand was added as the solid. All possible galvanic elements were made of the four half cells. Their potentials were measured on a Radiometer PHM 4 valve potentiometer. The cells were kept in a water thermostat at 25 ± 0.02°C. The constancy of the potentials were controlled for 1 – 2 h for each run. The electric potential measurements within one run were consistent with each other within 0.2 mV. The Nernst equation:

$E = \frac{RT}{2F} \log \frac{[Cd_1^{2+}]}{[Cd_2^{2+}]}$ was found valid for the concentration interval $0.001 < Cd^{+2} < 0.01$ M.

TREATMENT OF DATA

The e.m.f. measurements determine the concentration of free cadmium ion. The treatment of the data was based upon the assumption that only mononuclear complexes were formed. The mass law and the stoichiometry give the two independent equations:

$$\mathrm{M} = \mathrm{m} + \beta_1 \mathrm{m}\alpha + \beta_2 \mathrm{m}\alpha^2 + \ldots\ldots \beta_N \mathrm{m}\alpha^N$$
$$\mathrm{A} = \alpha + \beta_1 \mathrm{m}\alpha + 2\beta_2 \mathrm{m}\alpha^2 + \ldots\ldots \mathrm{N}\beta_N \mathrm{m}\alpha^N$$

M denotes total concentration of metal ion, m, free metal ion concentration; $[MA_n]$, concentration of nth complex; A, total ligand and α, free ligand concentration. β_n is a mass law constant:

$$\beta_n = \frac{[MA_n]}{m \cdot \alpha^n}$$

Iterative procedures must be used for calculating the constants as these and α are interdependent. Leden [6] has described numerical and graphical methods for evaluation of equilibrium constants. The methods of computation are different for weak and for strong complexes. Cadmium thiosemicarbazide complexes are of intermediate strength and the iterative solutions of the equations converged rather slowly.

The experimental data for the Cd^{2+}-thio system are given in Table 1. The ratio A/M was varied within the limits: $0.2 < A/M < 110$. The higher limit was determined by the solubility of thio in 1 M $NaNO_3$. For high values of A/M the modified Bodländer formula:

$$\frac{dE}{d\ln\alpha} = -\bar{n}\frac{RT}{zF} \text{ (Bjerrum [10]) is approximated by}$$

$$\frac{dE}{d\ln A} = -\bar{n}\frac{RT}{zF}; \; \bar{n} \text{ is defined by } \bar{n} = \frac{(A-\alpha)}{M}.$$

Table 1. Data for the Cd^{2+}-thio system.

A mole/l	M mole/l	ΔE mV	A mole/l	M mole/l	ΔE mV
0.002217	0.01001	2.3	0.0513	0.010013	55.4
0.004339	0.01001	4.6	0.1011	0.010013	82.0
0.006233	0.01001	6.8	0.02002	0.010001	23.5
0.007446	0.01001	8.3	0.10000	0.010001	81.1
0.000485	0.003243	1.0	0.02001	0.01000	23.4
0.000902	0.003243	1.9	0.02028	0.009890	24.6
0.001373	0.003243	2.8	0.03034	0.009890	37.2
0.001794	0.003243	3.9	0.04046	0.009890	47.7
0.002955	0.003243	6.0	0.05073	0.009890	56.1
0.002026	0.003244	4.3	0.07508	0.009890	71.1
0.003036	0.003244	6.7	0.1004	0.009890	82.1
0.003440	0.003244	7.7	0.09915	0.003285	89.3
0.004067	0.003244	9.1	0.1317	0.003285	98.0
0.004840	0.003244	10.9	0.1654	0.003285	108.7
0.005919	0.003244	13.2	0.03309	0.003285	53.0
0.007442	0.003244	16.5	0.06618	0.003285	74.2
0.000924	0.003241	1.9	0.1652	0.003285	105.1
0.001644	0.003249	3.4	0.08100	0.001623	83.8
0.002330	0.003249	4.75	0.1131	0.001623	94.4
0.0202	0.010013	25.2	0.1460	0.001623	103.2
0.0301	0.010013	35.9	0.1767	0.001623	110.0

The Bjerrum-Bodländer formula assumes that M is constant. For the Cd^{2+}-thio system $\bar{n}$ was about 2.7 for A/M = 100 thus suggesting that three thio molecules may coordinate to Cd^{2+}. $\bar{n}$ was calculated by numerical differentiation. Calculation of $\bar{n}$ by this method proved to be impracticable for A/M < 50.

For A/M ratios between 0.2 and 1, β_1 was estimated using the approximation that only the first complex $Cd(thio)^{2+}$ was formed. For the high A/M ratios α was determined by $\alpha = A - \bar{n} \cdot M$.

As $\frac{M-m-\beta_1 \cdot m\alpha}{m \cdot \alpha^2} = \beta_2 + \beta_3\alpha$, the plot $\frac{M-m-\beta_1 \cdot m\alpha}{m \cdot \alpha^2}$ *versus* α

gave approximate values of β_2 and β_3.

With approximate beta values α could be approximated for all the solutions measured. The plot $\frac{M-m}{m \cdot \alpha}$ *versus* α gave improved value for β_1 and β_2 for A/M < 50.

After 3 iterations the following values were found:

$$\beta_1 = 385$$
$$\beta_2 = 52\,500$$
$$\beta_3 = 700\,000$$

The equations: $M = m + \sum_1^N \beta_n m\alpha^n$ (1) and $A = \alpha + \sum_1^N n\beta_n m\alpha^n$ (2) are independent of each other. The ratio $\frac{A}{M-m}$ is determined by the available experimental data. From the equations we derive:

$$\frac{A}{M-m} = \frac{1/m + \beta_1 + 2\beta_2\alpha + 3\beta_3\alpha^2}{\beta_1 + \beta_2\alpha + \beta_3\alpha^2} \qquad (3)$$

The right hand side of the expression contains the experimental value m, the "parameters" β and the derived value α.

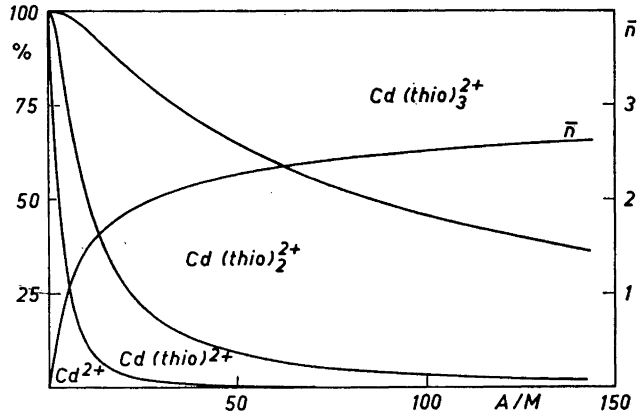


Fig. 1. The distribution of Cd^{2+}-thiosemicarbazide complexes, and the variation of $\bar{n}$ as functions of A/M at $M = 10^{-3}$ mole/l.

Table 2. Data for the Cd^{2+}-etu system.

A mole/l	M mole/l	ΔE mV
0.09730	0.003243	19.8
0.19740	0.003243	35.8
0.011733	0.003241	2.5
0.016843	0.003241	3.8
0.025417	0.003241	5.6
0.039006	0.003241	8.4
0.057167	0.003248	12.0
0.085160	0.003248	17.4
0.131061	0.003248	25.1
0.197342	0.003248	35.7
0.040314	0.0010492	9.7
0.068845	0.0010492	14.8
0.098364	0.0010492	20.7
0.127181	0.0010492	25.2
0.157455	0.0010492	30.2
0.197785	0.0010492	36.4

Small variations of β cause small changes in α. When changing systematically from one set of β-values to another set new α-values are calculated very accurately from previous α-values using the expression $\alpha = A - \bar{n} \cdot M$ or

$$\alpha = A - M \frac{\beta_1\alpha_1 + 2\beta_2\alpha_1^2 + 3\beta_3\alpha_1^3}{1 + \beta_1\alpha_1 + \beta_2\alpha_1^2 + \beta_3\alpha_1^3} \quad (4)$$

where α_1 is the α-value belonging to a previous set of β-values. (4) is independent of (3).

We define the best set of constants β_n as the one for which

$$V = \left(\frac{A}{M-m} - \frac{1/m + \beta_1 + 2\beta_2\alpha + 3\beta_3\alpha^2}{\beta_1 + \beta_2\alpha + \beta_3\alpha^2} \right)^2$$

is a minimum. The computation of V for varying values of β_n was carried out on the computer GIER of Regnecentralen, Aarhus. A programme was written in Algol for evaluating V for sets of values of the β_n, varying the β_n in the intervals:

$$365 = \beta_1 = 405 \text{ in steps of } 5$$
$$45\,000 = \beta_2 = 62\,500 \text{ in steps of } 2\,500$$
$$650\,000 = \beta_3 = 850\,000 \text{ in steps of } 25\,000$$

The set of constants: $\beta_1 = 370$, $\beta_2 = 50\,000$, $\beta_3 = 725\,000$ yielded the lowest value of V. This set is close to the set of constants obtained by graphical methods.

Fig. 1 shows the distribution of the complexes as a function of A/M. The data of the Cd^{2+}-etu system could be treated by more straightforward methods

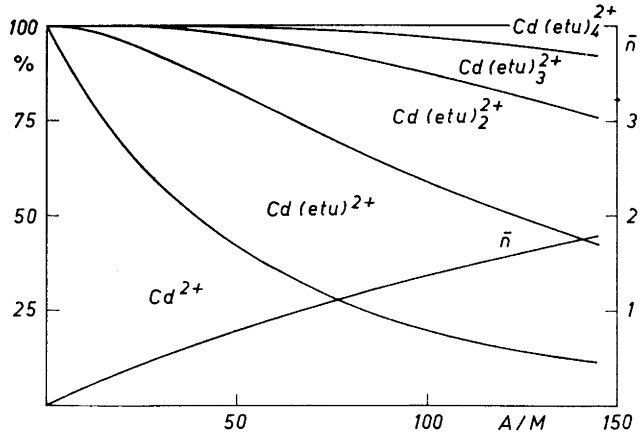


Fig. 2. The distribution of Cd^{2+}-ethylenethiourea complexes, and the variation of n as functions of A/M at M = 10^{-3} mole/l.

than those of the Cd^{2+}-thio system. The complexing power of etu is weak and the approximation $\alpha = A$ is very accurate even at low A/M ratios. Therefore $\bar{n}$ may be calculated from the Bjerrum-Bodländer formula and α is corrected as $\alpha = A - \bar{n} \cdot M$. Even with $\bar{n}$ values of moderate accuracy, α is determined quite accurately. When α is known the β_n values can be found directly using α, A, and M as shown by Bjerrum [10].

Graphical methods indicated that a maximum of 4 etu molecules could coordinate to Cd^{2+}. Sixteen runs were available for the determination of four constants. With α known accurately the equations for the β_n are linear, and the classical least squares method is applicable for obtaining a set of constants. Calculations with a desk calculator gave:

$$\begin{aligned} \beta_1 &= 20.4 \pm 0.8 \\ \beta_2 &= 137 \pm 25 \\ \beta_3 &= 466 \pm 175 \\ \beta_4 &= 2240 \pm 470 \end{aligned}$$

Graphical methods gave:

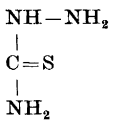
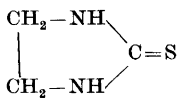
$$\begin{aligned} \beta_1 &= 19 \\ \beta_2 &= 150 \\ \beta_3 &= 600 \\ \beta_4 &= 1400 \end{aligned}$$

Fig. 2 shows the distribution of the complexes as a function of A/M.

DISCUSSION

In Table 3, complexity constants are given for reactions between Cd^{2+} and some compounds containing hydrazine groups or sulphur groups.

Table 3. Complexity constants of Cd complexes.

	β_1	β_2	β_3	β_4	β_5	Ref.
	370 ± 15	50 000 ± 1500	725 000 ± 25 000			
	20.4 ± 0.8	137 ± 25	466 ± 175	2240 ± 470		
NH_2-NH_2	178	253	607	7830		Rebertus [11]
NH_3	350 ± 50	$(6 \pm 1) \times 10^4$	$(1.5 \pm 0.4) \times 10^6$	$(1.9 \pm 0.2) \times 10^7$	$(1.5 \pm 0.2) \times 10^7$	Leden [6]
$NH_2-CH_2-CH_2-SH$	9.3×10^{10}	5.6×10^{19}	3.1×10^{39}			Li and Manning [12]

Inspection of the table shows that thiosemicarbazide is not bound to Cd^{2+} much stronger than is pure hydrazine. This is in agreement with the low affinity between Cd^{2+} and etu. The C=S group is evidently a weak complexing agent compared to the $-C-S^-$ group. The first and the second thiosemicarbazide molecule coordinate to the Cd^{2+} ion with approximately equal afinities, whereas the affinity for the uptake of the third molecule is comparatively low.

This is consistent with previous results of Bjerrum [10]. Cd^{2+} ion has the characteristic coordination number four and the maximum coordination number six. We postulate that $Cd(thio)_2^{2+}$ has tetrahedral configuration and that $Cd(thio)_3^{2+}$ has octahedral configuration. At present no theory explains, why Cd^{2+} favours tetrahedral configuration for octahedral.

We propose that the $Cd(etu)_4^{2+}$ complex has a tetrahedral configuration, and that the complexing power of etu is too low for octahedral complexes to be formed. It is probable that hexa-aquacadmium ions are present in aqueous solutions, and possibly the lower Cd-etu complexes have octahedral configuration.

Our results are not in agreement with the polarographic investigation of Toropova and Naimushina [13].

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