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A Potentiometric Study of the Complex Formation between Cd(II) and *N*-Alkylsubstituted Thiosemicarbazides

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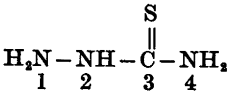
The stability constants between Cd(II) and a series of *N*-alkylsubstituted thiosemicarbazides in 1 M sodium nitrate solution have been determined.

The variation of the two first consecutive stability constants K_1 and K_2 for a number of 4-alkylsubstituted thiosemicarbazides can be rationalized semi-quantitatively in terms of the Hammett linear free energy relationship.

The constants K_3 are identical within the uncertainty of measurements for the whole series of systems investigated regardless of substitution in the thiosemicarbazides. This fact may reflect a change in configuration around the central metal ion when a *bis* thiosemicarbazide complex takes up a third ligand.

The purpose of the present investigation is to elucidate the ligating properties of a series of ligands as a function of various substituents. Thiosemicarbazide



is well suited for this purpose. It is acting as a bidentate ligand, coordinating *via* the N(1) and the S atoms, towards several metal ions [1–10] and this makes it possible to study the influence of substitution on a coordinating atom, N(1), on an atom in a chelate ring, N(2), and on an atom in a side chain, N(4). The choice of the thiosemicarbazide ligand system is moreover based on the fact that most alkylsubstituted thiosemicarbazides are easily prepared, and a vast number of these are described in the literature.[11]

The choice of a suitable central metal ion was less obvious. Potentiometric measurements, using a metal electrode, were considered most promising, since the thiosemicarbazides exhibit only very weak basic properties in aqueous solution.[12] Thus the metals Cu, Zn, Cd, and Hg were considered. The stability constants for the unsubstituted thiosemicarbazide towards zinc,[12] cadmium,[12–15] mercury,[12,16] and silver [13,16] have been determined already. The constants for the cadmium system are of such an order of magnitude as to ensure a good determination of similar systems. The Cu(II)-thiosemicarbazide system cannot be determined, since the Cu^{2+} ion is reduced by the ligand.

EXPERIMENTAL

Chemicals. Demineralized water was distilled twice in an all quartz apparatus with small amounts of sodium permanganate added during the first distillation. The following commercial chemicals were of analytical grade and used without purification: sodium nitrate, cadmium nitrate tetrahydrate, cadmium sulfate 8/3-hydrate, ammonium nitrate, and thiosemicarbazide.

The cadmium metal (Fluka) was an especially pure product, impurities less than 0.0002 %. All mercury used was redistilled.

The ligands except thiosemicarbazide itself were prepared as described by Jensen *et al.*[11]: 4-methylthiosemicarbazide, 4-allylthiosemicarbazide, 4-*tert*-butylthiosemicarbazide, 2,4-dimethylthiosemicarbazide, 1,1,4-trimethylthiosemicarbazide, and 2-isopropyl-4-methylthiosemicarbazide were prepared from hydrazine

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or an alkylsubstituted hydrazine and the appropriate alkylisothiocyanate.[11] 2-Methylthiosemicarbazide was prepared by treating 4-*tert*-butyl 2-methylthiosemicarbazide with hot concentrated hydrochloric acid, a general way of preparing thiosemicarbazides unsubstituted in the 4-position.[11] 1-Methylthiosemicarbazide was prepared from 1-*tert*-butoxycarbonyl-4-*tert*-butyl-1-methyl-thiosemicarbazide.[11]

The crude products were recrystallized from water and ethanol. In case of coloured impurities charcoal was used, until pure products, as shown from the melting points and microanalysis, were obtained. The unsubstituted thiosemicarbazide was treated in the same way.

The cadmium amalgam was prepared in two different ways, which gave equally good products. First a suitable amount of cadmium metal was dissolved in the calculated amount of mercury under nitrogen atmosphere and applying gentle heating (about 60 °C) to give by cooling a two phase system with an overall content of cadmium of 10 % w/w. The second method used was to generate the cadmium metal electrolytically using a mercury cathode and a platinum anode. The electrolyte used was a solution of saturated cadmium sulfate, 0.1 M with respect to sulfuric acid. A current density of 0.125 A/cm² was employed as recommended by Treadwell.[17] With an anode with an active surface of 8 cm² 100 g of amalgam was prepared in *ca* 5 h.

The cadmium amalgams were stored under an oxygen-free atmosphere.

Measurements were made using the following elements:

Hg	Hg_2Cl_2	sat. KCl		sat. NH_4NO_3
10^{-4} M HNO_3 1 M KNO_3 *L* M Ligand *M* M $Cd(NO_3)_2$		Cd,Hg		Hg

Temperature 25 ± 0.1 °C. The total metal ion concentration M was varied between 4×10^{-2} and 10^{-3} M. The total ligand concentration L was varied from 2×10^{-3} M and upwards. The maximal L is limited by the solubility of the individual ligands. Thus a total ligand concentration of 10^{-1} M was obtained for the most soluble ligand 1,1,4-trimethylthiosemicarbazide, whilst 4-*tert*-butylthiosemicarbazide, which is the least soluble ligand investigated, only gave $L_{max} = 6 \times 10^{-3}$ M. Oxygen-free nitrogen was passed through the solution 15 min before and during the measurements to exclude oxygen from the solution and to stir it.

The Nernst equation for this element was shown to be valid in the interval from 10^{-1} to 10^{-4} M Cd^{2+} and $L = 0$.

Fresh solutions were prepared for each measurement from stock solutions of cadmium nitrate and sodium nitrate. The ligand was added as the solid. The stock solutions of cadmium nitrate were standardized against EDTA by potentiometric titrations using the cadmium amalgam electrode and by titration using Eriochrome-T as an indicator.

For 2-isopropyl-4-methylthiosemicarbazide only a very small amount was available (about 0.4 g) and so it was necessary to use another technique. In the element the ammonium nitrate solution was substituted by an agar bridge, containing 1 M sodium nitrate, and a solution of 1 M sodium nitrate, 10^{-4} M nitric acid and 2-isopropyl-4-methylthiosemicarbazide was titrated with a cadmium nitrate solution, adjusted to ionic strength 1 with sodium nitrate.

The EMF of the elements were measured by means of the Radiometer potentiometers PHM25SE or PHM52 and followed until the potential drift was less than 0.1 mV in 15 min. This value was taken as the equilibrium potential.

In the titration experiments a 2.5 ml Radiometer ABU11 automatic burette was used.

Calculations were performed using a least squares minimization computer program outlined in the appendix. Activity coefficients were assumed to be constant and only mononuclear complexes were considered. Moreover it was assumed that the basic properties of the ligands can be neglected. The only ligand, for which the basic properties have been studied is the unsubstituted thiosemicarbazide for which Goddard *et al.* have reported a value of 1.50 for the pK value of the ionization of the protonated ligand.[12] To test the validity of the last assumption the stability constants have been calculated for the Cd^{2+} – thiosemicarbazide system using a modified version of the computer program, performing the required corrections. The results of this calculations were: log $\beta_1 = 2.60(1)$, log $\beta_2 = 4.68(2)$, and log $\beta_3 = 5.85(2)$. These values are indistinguishable from those obtained without corrections (Table 1).

RESULTS AND DISCUSSION

The following thiosemicarbazides were investigated: 1-methyl (*2*), 2-methyl (*3*), 4-methyl (*4*), 4-allyl (*5*), 4-*tert*-butyl (*6*), 2,4-dimethyl (*7*), 1,1,4-trimethyl (*8*), and 2-isopropyl-4-methylthiosemicarbazide (*9*). The ligands have been chosen so that the series includes substitution on all nitrogen atoms and examples on substitution in several positions in the ligand. The number of possible ligands has been limited, however, by the slight solubility of several substituted thiosemicarbazides in aqueous solution.

In addition, the experimental data of Nørlund Christensen and Rasmussen[15] for the

Table 1. The logarithm to the consecutive and cumulative stability constants for the determined Cd^{2+}-alkylsubstituted thiosemicarbazide systems. The standard deviations $\times 10^2$ are given in parentheses. The number of independent experiments (N) for each ligand is given in the last column.

	Thiosemicarbazide	log β_1	log β_2	log β_3	log K_2	log K_3	N
(*1*)	Unsubstituted	2.60(1)	4.68(2)	5.86(2)	2.08(2)	1.18(3)	
(*2*)	1-Methyl	2.34(8)	4.48(11)	5.84(17)	2.14(13)	1.36(20)	12
(*3*)	2-Methyl	2.31(2)	4.22(4)	5.53(5)	1.91(4)	1.31(6)	24
(*4*)	4-Methyl	2.75(2)	5.09(2)	6.30(6)	2.34(3)	1.21(6)	19
(*5*)	4-Allyl	2.60(2)	4.81(3)	5.95(9)	2.21(4)	1.14(9)	18
(*6*)	4-*tert*-Butyl	2.86(6)	5.36(16)		2.50(17)		11
(*7*)	2.4-Dimethyl	2.18(3)	3.88(5)	4.92(10)	1.70(6)	1.04(11)	16
(*8*)	1,1,4-Trimethyl	1.76(4)	3.17(3)		1.41(5)		19
(*9*)	2-Isopropyl-4-methyl	1.51(5)					10

cadmium – thiosemicarbazide (*1*) system were treated by the program described in the appendix.

The results of the calculations are listed in Table 1 as the logarithm to the overall stability constants β_i with the standard deviations in parenthesis. The cadmium(II) ion probably in all cases takes up a maximum of three thiosemicarbazides, but due to limited solubility of the ligands (*6*) and (*8*) it has been possible only to determine the first two stability constants for these systems and only one constant for ligand (*9*).

Substitution in the 4-position. A number of stability constants, involving thiosemicarbazides, substituted in the 4-position only, have been determined and makes it possible to investigate the inductive effect on complex formation from a substituent in this place, since the steric effects from substituents are expected to be of minor importance in this position, away from the reaction sites. Empirical correlations of this type are usually termed linear free energy relationship [18] and owes its name to the fact that, for a series of structurally closely related ligands, a plot of the logarithm of the stability constants (proportional to the free energy of complex formation ΔG°) *versus* a parameter representing the inductive effect of the substituent, usually gives a straight line. This technique, which also holds for, *e.g.*, kinetic data of several organic compounds has been widely used in organic chemistry [18–20] and was used already in 1934 by Larsson [21] for complex formation. It has later been used by several authors [22–25] to correlate the complexing ability of related ligands or metal ions.

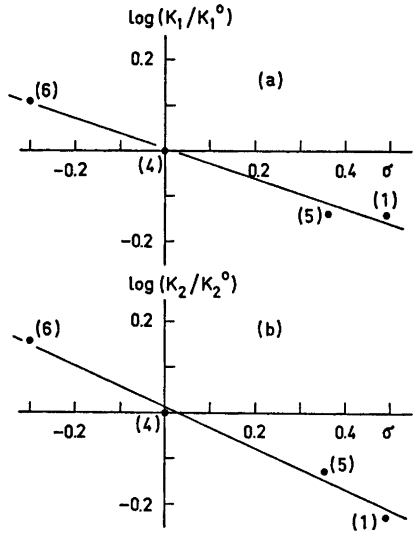

Fig. 1. The Hammet plots for the first (a) and second (b) stability constant for some Cd(II) – 4-alkylsubstituted thiosemicarbazide systems. The ligands are: (*1*) unsubstituted, (*4*) 4-methyl-, (*5*) 4-allyl- and (*6*) 4-*tert*-butyl-thiosemicarbazide.

Using a ligand with acid or basic properties, the best correlations are usually obtained, plotting log K for complex formation *vs.* pK for protonation of the ligand.[21–24] Fair plots are, however, also frequently obtained, using an empirical parameter σ, suggested by Hammet [26] instead of pK.[24,25] This parameter is introduced through the Hammet equation:

$$\log (K/K_0) = \sigma\varrho$$

which relates the equilibrium (or rate) constant K relative to the constant (K_0) for a parent compound to a parameter ϱ, characteristic for the specific reaction and σ, the substituent parameter.

For the Cd^{2+} – 4-alkylthiosemicarbazide systems 4-methylthiosemicarbazide was taken as the reference ligand and σ-values, determined by Taft [19] from kinetic studies of esters of carboxylic acids, were used. The Hammett plots for K_1 and K_2 for these systems are shown in Fig. 1. In both cases fairly good linear relationships are found. The slopes of the lines, found from a least squares fit are $\varrho = -0.35(5)$ and $-0.45(5)$, respectively.

The negative slope of the lines indicates, that the complex formation is promoted by an enhanced negative charge on the ligating sulfur atom adjacent to the substituent. This is what one would intuitively expect and such results are found in many cases. Examples of the opposite behaviour are known, however, and have been interpreted as due to extensive π back donation from the metal ion to the ligand [24,25,27] This interpretation has, however, recently been criticized.[28]

Within the interval of confidence, the slopes of the two lines can be considered identical. Since ϱ is very sensitive to the type and strength of the bonds between donor and acceptor atoms,[23,24] this indicates, that the first and the second ligand is coordinated to the cadmium ion in the same manner, and that only minor steric effects are involved in the series.

The logarithm to the third consecutive stability constants K_3 does not fall in with the scheme mentioned above. The variation of K_3 is discussed later.

Substitution in the 2-position. One might expect the same type of dependence of stability constants on substitution in the 2- and in the 4-position. Reversal behaviours are, however, observed. Introduction of a methyl group in the 4-position increases log K_1 from 2.60 to 2.75. (Only the variations in log K_1 are discussed. The variations in log K_2 are similar). However, a methyl group in the 2-position makes the complex formation less favourable (log $K_1 = 2.31$). When the ligand is substituted in both the 2- and the 4-positions at the same time the complexes are even less stable. This decrease in stability is a function of the bulkiness of the substituents: log $K_1 = 2.18$ for 2,4-dimethylthiosemicarbazide and only 1.51 for 2-isopropyl-4-methylthiosemicarbazide.

This indicates a steric hindrance, presumably because the conformation of the ligand necessary for chelating complex formation is hindered in the case of substitution in the 2-position, this effect being more pronounced in case of a further substitution on the N(4).

This point is illustrated by a study by Jensen *et al.*[29] of the conformation of alkylsubstituted thiosemicarbazides in solution by means of ^1H NMR spectroscopy in $CDCl_3$ and DMSO-d_6. The conclusion is that the C – N bonds of thiosemicarbazide have partly double bond character such that C, N(2), N(4), S and the substituents on these atoms are co-planar, however, with rather low barriers of rotation in these solvents. For N(2)-substituted thiosemicarbazides it was found that the substituent was *s-cis* to the sulfur atom. For 2,4-disubstitution this conformation is even more pronounced. Since chelation demands *s-trans* configuration, the free energy difference between the two conformations may be reflected in the stability constants measured here for the cadmium complexes.

Substitution in the 1-position. Like in the 2-position, introduction of a substituent on N(1) lowers the stability of the complex. log K_1 for 1-methylthiosemicarbazide is 2.34 and for 1,1,4-trimethylthiosemicarbazide log K_1 is only 1.76. Since N(1) is one of the reaction sites in the chelating ligand, this variation is to be expected.

From qualitative judgements of the colour of solutions of Ni^{2+} and a number of 1-substituted thiosemicarbazides, Jensen and Rancke-Madsen have concluded [30] that no complex formation takes place contrary to the behaviour for ligands unsubstituted in this position. Since in case of 1-substitution N(1) is sterically hindered, the difference between the two metal ions towards this type of ligands is mainly due to the difference in the metal-sulfur bond strength. Although Christensen and Rasmussen have argued, that thiosemicarbazide is bound to cadmium mainly through the N(1) atom

and that the S–Cd bond is rather weak [15] this bond is still expected to be stronger than the Ni–S bond.

Variation of K_3. The values of log K_3 together with their estimated standard deviations have been collected in Table 1.

It should be noticed that the values of log K_3 are much smaller than for the two first stepwise stability constants and that their absolute values are surprisingly independent of substitution in the ligands contrary to variations found for K_1 and K_2 (Fig. 1). Within the uncertainty of the measurements log K_3 is constant and identical to the value obtained for the unsubstituted ligand. The great ratio of K_2/K_3 for the cadmium–thiosemicarbazide system ($\log K_2 = 2.08$ and $\log K_3 = 1.18$), led Christensen and Rasmussen to postulate that a change in configuration from a tetrahedral bis complex to an octahedral tris complex takes place with uptake of the third ligand.[15]

From an X-ray structure determination, bis(thiosemicarbazide) cadmium(II) sulfate has recently been shown to contain cadmium ions in an octahedral environment.[31] The unit cell contains two independent complex ions both with octahedral coordination and the two chelating thiosemicarbazides nearly coplanar, in one complex *cis* and in the other *trans* to each other. The two remaining axial coordination sites are occupied by oxygen from the sulfato groups.

One should, however, be careful deducing structures of labile metal complexes in solution from the structure in the solid state and the results of the present investigation support the idea proposed [15] that the bis(thiosemicarbazide) cadmium(II) ion is 4-coordinated in solution.

APPENDIX

Several authors have discussed the use of digital computers in the treatment of complex formation data.[32–36] The program developed for the present study is based on a conventional nonlinear regression technique as described by Demig [37] and Wentworth.[38] In its present state it is designed to treat potentiometric data only. Moreover, it is presumed that only monomeric species are formed.

Notation. For convenience, the most important definitions are collected below:

M, m: total and free metal concentrations, respectively.
L, l: total and free ligand concentrations, respectively.
$\beta_i = [ML_i]/m\,l^i$: the overall stability constant of the i'th mononuclear complex.
E: experimentally measured EMF difference of the cells in which $L=0$ and $L=L$, $E = -k \log m/M$
F = $F(E, M, L, \log \beta_1 ... \log \beta_N)$ function, relating the three variables E, M, and L to the N parameters $\log \beta_n$ $(1 \leq n \leq N)$
σ: Standard deviation.
$k = (RT/zF) \ln 10$

The error square sum to be minimized can be expressed as

$$\sum (E(\log \beta_i)_{calc} - E_{obs})^2 \Big/ \left(\sigma_E^2 + \frac{\delta E}{\delta M} \sigma_M^2 + \frac{\delta E}{\delta L} \sigma_L^2 \right)$$

The required partial derivatives F′ (Demig's nomenclature [37]) are found from the well-known relations:[39]

$$M = m + \sum_{n=1}^{N} \beta_n m l^n$$

$$L = l + \sum_{n=1}^{N} n \beta_n m l^n$$

and from the definitions of E and β_i.

$$F'_M = \frac{\delta E}{\delta M} = -\frac{k}{mM \ln 10} \frac{\delta m}{\delta M} M - m$$

$\frac{\delta m}{\delta M}$ (and $\frac{\delta l}{\delta M}$) is found by solving the two equations:

$$\frac{\delta M}{\delta M} = 1 = \frac{\delta M}{\delta m}\frac{\delta m}{\delta M} + \frac{\delta M}{\delta l}\frac{\delta l}{\delta M}$$

$$\frac{\delta L}{\delta M} = 0 = \frac{\delta L}{\delta m}\frac{\delta m}{\delta M} + \frac{\delta L}{\delta l}\frac{\delta l}{\delta M}$$

$$\left(1 + \sum_{n=1}^{N} \beta_n l^n\right)\frac{\delta m}{\delta M} + \left(\sum_{n=1}^{N} n \beta_n m l^{n-1}\right)\frac{\delta l}{\delta M} = 1$$

$$\left(\sum_{n=1}^{N} n \beta_n l^n\right)\frac{\delta m}{\delta M} + \left(1 + \sum_{n=1}^{N} n^2 \beta_n m l^{n-1}\right)\frac{\delta l}{\delta M} = 0$$

F'_L is found in a similar manner:

$$F'_L = \frac{\delta E}{\delta L} = -\frac{-k}{m \ln 10}\frac{\delta m}{\delta L}$$

$$\frac{\delta M}{\delta L} = 0 = \frac{\delta M}{\delta m}\frac{\delta m}{\delta L} + \frac{\delta M}{\delta l}\frac{\delta l}{\delta L}$$

$$\frac{\delta L}{\delta L} = 1 = \frac{\delta L}{\delta m}\frac{\delta m}{\delta L} + \frac{\delta L}{\delta l}\frac{\delta l}{\delta L}$$

And finally $F'_{\log \beta_n}$ is found thus:

$$F'_{\log \beta_n} = \frac{\delta E}{\delta \log \beta_n} = -\frac{k\beta_n}{m}\frac{\delta m}{\delta \beta_n}$$

$\frac{\delta m}{\delta \beta_n}\left(\text{and } \frac{\delta l}{\delta \beta_n}\right)$ is found in analogy with $\frac{\delta m}{\delta L}$ and $\frac{\delta m}{\delta M}$:

$$\frac{\delta M}{\delta \beta_n} = 0 = \frac{\delta M}{\delta m}\frac{\delta m}{\delta \beta_n} + \frac{\delta M}{\delta l}\frac{\delta l}{\delta \beta_n} + \frac{\delta M}{\delta \beta_n}\frac{\delta \beta_n}{\delta \beta_n}$$

$$\frac{\delta L}{\delta \beta_n} = 0 = \frac{\delta L}{\delta m}\frac{\delta m}{\delta \beta_n} + \frac{\delta L}{\delta l}\frac{\delta l}{\delta \beta_n} + \frac{\delta L}{\delta \beta_n}\frac{\delta \beta_n}{\delta \beta_n}$$

since $\frac{\delta M}{\delta \beta_n} = ml^n$ and $\frac{\delta L}{\delta \beta_n} = nml^n$.

The initial guesses on the parameters $\log \beta_1$ ...$\log \beta_N$ are then corrected with the calculated $\Delta \log \beta_i$ or a fraction of them and the whole calculation is repeated until the limit of the iteration is reached. The sum of squares of the weighted residuals is calculated in each cycle and the iteration is stopped, when the relative difference between two such numbers, arising from two subsequent iterations, is less than 10^{-4}. The standard deviations are assumed to be $\sigma_E = 0.2$ mV and σ_L and $\sigma_M = 1.0$ %.

An ALGOL as well as a FORTRAN version of the program (for the RC4000 from Regnecentralen A/S Copenhagen and the IBM 370/165 computer respectively) has been written.*

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* A punched tape listing or a card deck of the program is available from the author upon request.

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