Contribution from the Istituto di Chimica Generale della Università di Parma, 43100 Parma, Italy

Complexes of Thiocarbohydrazide with Divalent Metals: Stability Constants in Aqueous Solutions

A. Braibanti, F. Dallavalle, and E. Leporati

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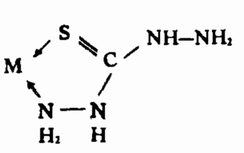
The association equilibria of thiocarbohydrazide, $S{=}C(NH{-}NH_2)_2$, with divalent ions Co^{2+}, Ni^{2+}, Zn^{2+} have been determined potentiometrically at 25.0±0.1 °C in 0.5 M KCl solution. The following stability constants have been obtained: for Co^{2+}, $\log K_1 = 2.969(18)$, $\log K_2 = 2.689(18)$; for Ni^{2+}, $\log K_1 = 4.404(8)$, $\log K_2 = 3.700(8)$, $\log K_3 = 3.113(8)$; for Zn^{2+}, $\log K_1 = 2.526(23)$. A method for the calculation of the estimated standard deviations is given. The stability constants obtained are comparable, for number of steps as well as values, with the stability constants of carbohydrazide, $O{=}C(NH{-}NH_2)_2$, with the same metals. For both ligands, complexes with five-membered ring chelates can be postulated, the donor atoms being N,S and N,O respectively. The constants for thiocarbohydrazide are slightly higher than the corresponding constants of the oxygenated analog, except for zinc where the reverse occurs. Therefore, in agreement with the classification of Ahrland, Zn^{II} confirms to be an (A)-acceptor, and Ni^{II} a (B)-acceptor.

Introduction

On prosecution of researches on protonation equilibria[1] and on crystal structure[2] of thiocarbohydrazide, the association constants of this ligand with divalent metals in acidic solutions have now been determined. Burns[3] studied complexes of this ligand with Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II} in the solid state. He concluded, on the basis of their infrared spectra, that they contain rings of the thio-ketonic form



The study of the crystal structure of the pure ligand[2] has shown how the two $-NH-NH_2$ groups are in fact disposed as in the formula above, thus supporting the interpretation given by Burns. On the other hand, Campi, Ostacoli, Vanni and Casorati,[9] studying the association equilibria of the analogous ligand carbohydrazide, $O{=}C(NH{-}NH_2)_2$, with divalent metals, suggest that this ligand chelates through N,N, thus forming six-membered rings.

The study of the protonation equilibria[1] of thiocarbohydrazide has shown that in acidic media the compound can associate two protons, one for each hydrazinic group, thus maintaining the thioketonic form. On the other hand, in alkaline media the molecule, probably changed into a thioenolic form, is deprotonated twice. We have now determined the association equilibria of this ligand with divalent metals in acidic media. In alkaline media precipitation of solid substances makes it impossible to study equilibria with potentiometric or spectrophotometric methods.

Experimental Section

Materials. Thiocarbohydrazide has been prepared and purified as described in a preceding paper.[1] All the other materials employed were of reagent grade purity. Bidistilled, boiled water has been used to prepare the solutions.

Solutions. One stock solution of hydrogen chloride was prepared and its concentration (1.4525 *M*) determined titrimetrically both with potassium hydrogencarbonate and THAM. Stock solutions of potassium hydroxide were stored in neutral Jena glass vessels and their concentrations periodically checked against the standard solution of hydrochloric acid. The concentrations of the stock solutions of divalent metal chlorides (0.05-0.08 *M*) were determined by conventional analytical methods. Each solution to be titrated was prepared by subsequent addition of a weighed amount of thiocrabohydrazide, exact volumes of metal chloride and hydrochloric acid, as much solid potassium chloride as required to keep the ionic strenght at the chosen value (0.5 *M*) and water. The initial volume of the aqueous solution was 99.965±0.013 ml in each titration. The total volumes of the titrant KOH solution were 3-4 ml, subdivided by a microburette into 12-18 steps, measured with precision ±0.005 ml.

Potentiometric measurements. Potentiometric measurements were performed by a Metrohm E 388 potentiometer with Metrohm EA 107 UX glass elec-

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[1] A. Braibanti, E. Leporati, F. Dallavalle, and M. A. Pellinghelli, *Inorg. Chim. Acta*, *2*, 449 (1968).
[2] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, in press.
[3] G. R. Burns, *Inorg. Chem.*, *7*, 277 (1968).

trode. The glass electrode was calibrated with respect to $[H^+]$ with the standard hydrochloric acid added to a KCl solution 0.5 *M*. Calomel electrode (KCl sat.) was used as reference. The titrant solution flask, the burette and the reaction vessel were connected in such a way as to avoid contamination from the air. The reaction vessel and the calomel electrode were maintained at 25.0±0.1°C by circulation of thermostated water.

The concentration ranges for each titration are quoted in Table I.

Table I. Summary of potentiometric determinations

Ion	Initial concn, m*M*			Range	
	MCl_2	tcaz	HCl	$-\log[H^+]$	$\bar{n}$
Co^{2+}	0.7153	2.8627	5.7257	1.70—3.10	0.5—1.5
	0.7979	2.3936	4.7874	1.77—3.09	0.4—1.5
	0.8789	2.1967	4.4068	1.77—2.88	0.4—1.3
	0.8634	1.2943	2.5898	1.97—3.00	0.4—1.0
Ni^{2+}	1.7485	1.7484	6.0888	1.42—3.00	0.7—1.0
	0.7632	3.0540	3.6312	1.80—4.50	2.1—2.8
	0.6097	3.0502	6.1033	1.56—4.60	1.8—2.9
	1.0162	2.0328	2.4256	1.85—3.00	1.4—1.8
Zn^{2+}	0.7416	1.5308	5.5645	1.58—2.48	0.1—0.4
	1.4832	1.4281	5.6182	1.50—2.44	0.1—0.3
	0.5931	1.4139	5.5528	1.50—2.71	0.2—0.4

Spectrophotometric measurements. A Beckman DK 2 spectrophotometer has been employed. Solutions containing nickel chloride and thiocarbohydrazide in variable amounts have been examined.

Results

Titrations with metals Cu^{II} and Cd^{II} failed because of precipitation of solid compounds even in acidic media; Mn^{II} does not show detectable association. The formation functions according to Bjerrum[4] for Co^{2+}, Ni^{2+}, Zn^{2+} complexes are drawn in Figure 1. The calculations of the formation constants have been carried out following Sillén's method,[5] using programs prepared by Vacca, Arenare, and Paoletti.[6]

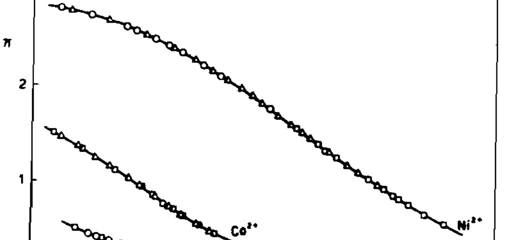


Figure 1. Formation functions of complexes of thiocarbohydrazide with divalent metals. Points along each line (graphically adjusted) with different symbols, correspond to different titrations.

The concentration of the complexed species are given by the expression:

$$[H_pM_qL_r] = \beta_{pqr}[H]^p[M]^q[L]^r \tag{1}$$

where β_{pqr} are the formation constants, [H], [M] and [L] are the equilibrium concentrations of hydrogen ion, metal ion and free ligand, respectively. Values of $\log \beta_{1,0,1} = 3.159(30)$,[1(*)] $\log \beta_{2,0,1} = 3.968(18)$,[1] $\log K_w = \log \beta_{\bar{1},0,0} = -13.79$[5] have been used in the calculations. The other constants were chosen tentatively and improved values of them are introduced during the calculations. The program calculates by successive approximations

$$T_H = [H] + \Sigma p\beta_{pqr}[H]^p[M]^q[L]^r \tag{2}$$

$$T_M = [M] + \Sigma q\beta_{pqr}[H]^p[M]^q[L]^r \tag{3}$$

$$T_L = [L] + \Sigma r\beta_{pqr}[H]^p[M]^q[L]^r \tag{4}$$

where T_H, T_M, T_L are the total concentrations of acid, metal and ligand, respectively. For all the *n* points, the quantity

$$U = \sum_n (p[H_o]_n - p[H_c]_n)^2 \tag{5}$$

was calculated. In (5), $p[H_o] \equiv -\log[H_o]$ was obtained from the potentiometric determination and $p[H_c] \equiv -\log[H_c]$ was the value obtained from the solution of the system formed by the expressions (2), (3) and (4). Successive calculations were performed with new values of β_{pqr} until *U* was minimum. The final β_{pqr} are those corresponding to *U* minimum and to a normal distribution of $p[H_o]_n - p[H_c]_n$ as function of $p[H_o]_n$ or of some other variable as shown in the next paragraph.

Calculation of errors. The estimated standard deviations of $\log \beta_{pqr}$ and $\log K_r$, where K_r are stepwise constants, have been obtained as follows. If one writes in logarithmic form (for $p=0$, $q=1$ and a protonated ligand $H_{p'}L$)

$$\log \beta_{01r} = r \log \beta_{p'01} - p'r\,p[H] - r \log[H_{p'}L] + \log[ML_r] - \log[M] = -p'r\,p[H] + \log R \tag{6}$$

where p[H] depends on the potentiometric determination $p[H_o]$, $\log[H_{p'}L]$ mainly on $\log T_H$, $\log[ML_r]$ mainly on $\log T_L$ and $\log[M]$ mainly on $\log T_M$. The variance of $\log \beta_{01r}$, by considering independent variables and disregarding covariances, is therefore[7]

$$\sigma^2(\log \beta_{01r}) = r^2\sigma^2(\log \beta_{p'01}) + p'^2r^2\sigma^2(p[H_o]) + r^2\sigma^2(\log T_H) + \sigma^2(\log T_L) + \sigma^2(\log T_M) \tag{7}$$

(*) The value in parenthesis indicated the estimated standard deviation x 10^3.

(4) J. Bjerrum: Metal Ammine Formation in Aqueous Solution, P. Haase & S., Copenhagen, 1941.

(5) L. G. Sillén, *Acta Chem. Scand.*, *16*, 159 (1962); *18*, 1085 (1965); N. Ingri and L. G. Sillén, *Arkiv. Kemi*, *23*, 97 (1964).

(6) A. Vacca, D. Arenare, P. Paoletti, *Inorg. Chem.*, *5*, 1384 (1966).

(7) W. C. Hamilton, Statistics in Physical Science, New York: Ronald Press. 1964 p. 31.

The variances of the right hand side are significant only if $\log T_L$ and $\log T_M$ have been measured several times, in other words only if several titrations for each metal have been performed.

The single variances do not need, however, to be calculated separately. In fact, the calculated quantity $p[H_c]$· is related, according to the calculation procedure followed, to the constant $\log \beta_{01r}$ by

$$\log \beta_{01r} = p'r p[H_c] + \log R \tag{8}$$

Being $\log \beta_{01r}$ constant, then the variance of $p'r$ $p[H_c]$ is the same as the variance of $\log R$, i.e.

$$p'^2 r^2 \sigma^2(p[H_c]) = \sigma^2(\log R) \tag{9}$$

If one calculates, disregarding covariances,

$$\sigma^2(p[H_o]-p[H_c]) \approx \sigma^2(p[H_o]) + \sigma^2(p[H_c]) \tag{10}$$

by substitution in (7), one gets for n points

$$\sigma^2(\log \beta_{01r}) = p'^2 r^2 \sigma^2(p[H_o]-p[H_c]) = p'^2 r^2 \frac{U}{n(n-1)} \tag{11}$$

and with the same arguments as above one gets

$$\sigma^2(\log K_r) = p'^2 \sigma^2(p[H_o]-p[H_c]) = p'^2 \frac{U}{n(n-1)} \tag{12}$$

$\frac{U}{n(n-1)}$ is an unbiased estimate of variance only if $\Delta p[H] = p[H_o]-p[H_c]$ has a normal distribution around the mean $\bar{m} = 0$.

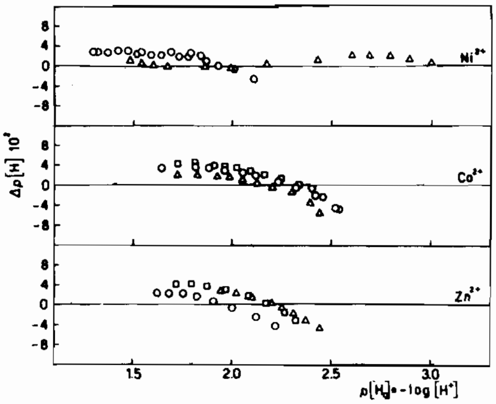


Figure 2. Scatter diagram of final $\Delta p[H]$ with respect to $p[H_o] \equiv -\log[H_o]$.

In order to assess that the actual distribution is normal, $\Delta p[H]_n$ for n points is plotted against $p[H_o]_n$ (Figure 2) or other parameter of the titration and the distribution analysed according to statistical criteria. Any regression between $\Delta p[H]$ and the chosen parameter is sought for. For the three distributions of Figure 2 the linear regression of type

$$\Delta p[H]_n = \overline{\Delta p[H]} + b(p[H]_n - \overline{p[H]})$$

has been calculated, where

$$b = \sum_n (p[H_o]_n - \overline{p[H_o]})(\Delta p[H]_n - \overline{\Delta p[H]}) / \sum_n (p[H_o]_n - \overline{p[H_o]})^2 \tag{14}$$

Then the hypothesis that the regression coefficient b is significantly different from zero is tested by calculating $F = M_1/M_2$, where

$$M_1 = \frac{[\sum_n (p[H_o]_n - \overline{p[H_o]})(\Delta p[H]_n - \overline{\Delta p[H]})]^2}{\sum_n (p[H_o]_n - \overline{p[H_o]})^2}$$

and

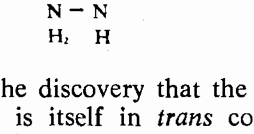
$$M_2 = \sum_n (\Delta p[H]_n - \overline{\Delta p[H]})^2 - M_1 \tag{16}$$

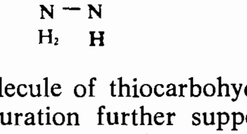
and comparing it in the F-distribution table for $n-2$ degrees of freedom at 90% significance level. The statistical analysis of the distributions is quoted in Table II. In case that the regression is significant then the data are affected by some systematic error, which might be either an experimental error, for example the p[H] scale is not correct, or a calculated error, for example further equilibria have been disregarded or partial $\log K_r$ has not been correctly chosen. It is worth noting that the error so calculated substantiates the common sense observation that it is unthinkable to achieve accuracy in $\log \beta_r$ higher than the accuracy obtainable in the experimental measurements of $p[H_o]$ and of other experimental concentrations on logarithmic scale.

The cumulative stability constants with their standard deviations are quoted in Table III.

Discussion

The equilibrium constants of thiocarbohydrazide (abbrev. tcaz) with divalent metals are closely related to the equilibrium constants presented by carbohydrazide (abbrev. caz).[4] The equilibrium constants of these ligands (Table IV) show how they probably belong to a common family. For these ligands five-membered ring chelates can be postulated.





The discovery that the molecule of thiocarbohydrazide is itself in *trans* configuration further supports this hypothesis. The formation of analogous rings in complexes of thiocarbohydrazide (S,N) donor) and in complexes of carbohydrazide (O,N donor) is confirmed also by the small, but significant, difference between the constants for the two ligands. In fact

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(8) C. J. Brookes, I. G. Betteley, and S. M. Loxston, Mathematics and Statistics, J. Wiley & S., New York, 1966 p. 346.

(9) E. Campi, G. Ostacoli, A. Vanni, and E. Casorati, *Ric. Sci.*, *34*, (II-A), 341 (1964).

Table II. Regression analysis of $\Delta p[H]$ on $p[H_o]$

M	b	M_1	M_2	$\overline{m}\times 10^3$	$F=\frac{M_1}{M_2}$	$n-2$	$F_{1,\ n-2,0.10}$	Significance of $b\neq 0$
Co^{2+}	–0.110	0.03131	0.04368	1.135	0.72	39	2.87	not signif.
Ni^{2+}	–0.013	0.00132	0.00556	0.499	0.24	47	2.84	not signif.
Zn^{2+}	–0.095	0.01140	0.00520	0.702	2.19	22	2.96	not signif.

Table III. Cumulative equilibrium constants $\beta_{01r}\equiv\beta_r$ for the ligand thiocarbohydrazide

M	log β_1 (σ)	log β_2 (σ)	log β_3 (σ)
Co^{2+}	2.969(18)	5.658(36)	—
Ni^{2+}	4.404(8)	8.104(16)	11.217(24)
Zn^{2+}	2.526(23)	—	—

Table IV. Step-wise equilibrium constants for complexes of thiocarbohydrazide (25°C) and carbohydrazide (20°C)

Complex	Thiocarbohydrazide [a]		Complex	Carbohydrazide [b]	
$Htcaz^+$	log K_1	3.159(30)	$Hcaz^+$	log K_1	4.143
H_2tcaz^{2+}	log K_2	0.809(48)	H_2caz^{2+}	log K_2	2.09
$Co(tcaz)^{2+}$	log K_1	2.969(18)	$Co(caz)^{2+}$	log K_1	2.827
$Co(tcaz)_2^{2+}$	log K_2	2.689(18)	$Co(caz)_2^{2+}$	log K_2	2.548
$Ni(tcaz)^{2+}$	log K_1	4.404(8)	$Ni(caz)^{2+}$	log K_1	3.438
$Ni(tcaz)_2^{2+}$	log K_2	3.700(8)	$Ni(caz)_2^{2+}$	log K_2	3.184
$Ni(tcaz)_3^{2+}$	log K_3	3.113(8)	$Ni(caz)_3^{2+}$	log K_3	2.019
$Zn(tcaz)^{2+}$	log K_1	2.526(23)	$Zn(caz)^{2+}$	log K_1	2.770

[a] Medium 0.5 M KCl, present work;
[b] Medium 0.1 M $NaClO_4$, Reference 9.

for zinc, $K_1(caz)>K_1(tcaz)$ whereas for the other metals the reverse is true. This is in accordance with the conclusions of Ahrland, Chatt and Davies,[10] Ahrland[11] and Suzuki and Yamasaki[12] who affirm that affinity of zinc for uncharged sulphur is smaller than that for oxygen, while affinity of nickel is larger for sulphur than for oxygen.

Other features can be mentioned. Successive constants for thiocarbohydrazide with nickel present ratios nearly constants[13] (log $K_1/K_2=0.704$, log $K_2/K_3=0.587$). In nickel solutions at low hydrogen ion concentration and with excess of ligand the predominant species is $Ni(tcaz)_3^{2+}$. As a matter of fact the visible spectrum of the nickel complex in concentrated solution of thiocarbohydrazide agrees well with the spectrum of $Ni(tscaz)_3^{2+}$ (tscaz = thiosemicarbazide) to which a octahedral coordination S_3N_3, with five-membered ring chelates, has been attributed.[14] The spectrum of $Ni(tcaz)_3^{2+}$ shows maxima at 955, 580, 363 mμ while the reflectance spectrum of $Ni(tscaz)_3I_2$[14] shows maxima at (1000?), 900, 580, 370 mμ.

Conclusion

The study of the association equilibria between thiocarbohydrazide and divalent metals Co^{II}, Ni^{II}, Zn^{II} has confirmed that the complexes very likely contain pentatomic chelates with N and S as donor atoms. The same rings are very likely formed with the same metals also by carbohydrazide, with N and O as donor atoms. The two ligands form complexes of comparable stabilities. The stability constants of complexes with thiocarbohydrazide (S, N), however are slightly higher than those of the corresponding complexes with carbohydrazide (O, N), except for zinc. This metal according to the classification of Ahrland[11] has to be considered as an (A)-acceptor and therefore it should be bound more strongly to O rather than to S; while Ni^{II}, a (B)-acceptor, should be preferably bound to S rather than to O. Therefore the results of this research agree with the classification of Ahrland. Also Co^{II} can be classified as a (B)-acceptor.

Acknowledgements. We wish to thank Prof. Paoletti and Prof. Vacca of the University of Florence for supplying computer programs. Consiglio Nazionale delle Ricerche, Rome, is thanked for the financial aid.

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(10) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, *12*, 265 (1958).
(11) S. Ahrland, *Structure and Bonding*, *1*, 207 (1966).
(12) K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, *24*, 1093 (1962).
(13) F. J. C. Rossotti in Modern Coordination Chemistry, ed. Lewis & Wilkins, Interscience, New York, 1960.
(14) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, *24*, 1571 (1962).