

## Protonated Forms and Metal Complexes in Aqueous Solutions of S-methylisothiocarbohydrazide

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

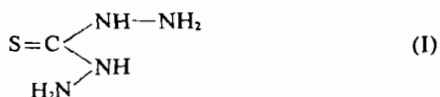
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Equilibria in aqueous solutions of S-methylisothiocarbohydrazide (S-tcaz) with protons and divalent metals have been studied by potentiometric method. The dissociation constants of the acids formed by S-tcaz and the formation constants of its complexes with divalent metals have been calculated by means of computer programs. The dissociation constants of the cation acids formed with protons are  $pK_1 = 7.708(2)$  and  $pK_2 = 1.364(7)$  at 25°C and ionic strength  $\mu = 0.5$  M KCl. Dependence of dissociation constants upon temperature between 5° and 35°C has been determined and the thermodynamic functions  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  calculated. The dependence upon ionic strength between  $\mu = 0.01$  and  $\mu = 2.0$  M KCl shows the trend typical for cation acids. The determination of the formation constants of complexes formed by S-tcaz with divalent metals  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , and  $Cd^{2+}$  has demonstrated that there are in solution the species:  $Mn(S-tcaz)_2^{2+}$ ;  $Co(S-tcaz)_2^{2+}$ ;  $Co(S-tcaz)_2^{2+}$ ;  $Ni(S-tcaz)_2^{2+}$ ,  $Ni(S-tcaz)_2^{2+}$ ,  $Ni(S-tcaz)_2^{2+}$ ;  $Zn(S-tcaz)_2^{2+}$ ,  $Zn(S-tcaz)_2^{2+}$ ;  $Cd(S-tcaz)_2^{2+}$ ,  $Cd(S-tcaz)_2^{2+}$ . The complexes follow the same pattern as those formed by the parent compound thiocarbohydrazide, but complexes of S-tcaz are stronger than the latter. Structures with pentatomic chelate rings with N, S as donor atoms are suggested for these complexes.

## Introduction

Thiocarbohydrazide and carbohydrazide and their derivatives have been reviewed recently by Kurzer and Wilkinson<sup>1</sup> who show how the interest about these compounds is ever growing.

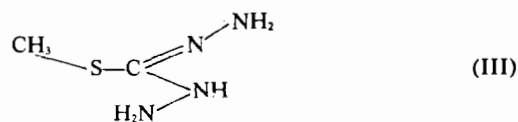
In our researches concerning thiocarbohydrazide and its complexes with divalent metals both in solution<sup>2,3</sup> and in the solid state<sup>4,5,6,7</sup> we have found that the molecule can assume form *cis*, *trans* (I)



with  $-\text{NH}-\text{NH}_2$  rotated around C-N in opposite ways with respect to  $\text{S}=\text{C}$ : (i) in neutral molecule,<sup>4</sup> (ii) in complexes<sup>3,5</sup> and (iii) in monoprotonated cation,<sup>7</sup> with  $\text{H}^+$  added to  $-\text{NH}_2$  in *cis* position. The molecule can assume form *cis,cis* (II) in the biprotonated cation:<sup>6</sup>



We have now undertaken the study of the behaviour in solution of the thiouronium compound (III), S-methylisothiocarbohydrazide,



## Experimental Section

**Reagents.** S-methylisothiocarbohydrazide hydroiodide has been prepared following Scott and Audrieth.<sup>8</sup>

The analysis of the compound (m.p. 145°C) gives for  $\text{C}_2\text{H}_9\text{N}_4\text{SI}$ : calcd %: C, 9.81; H, 3.63; N, 22.61; found %: C, 9.68, H, 3.66; N, 22.58. All the solutions for potentiometric measurements have been prepared using bidistilled freshly boiled water. Hydrochloric acid solutions (0.1-0.15 M) have been standardized against tris-hydroxymethylaminomethane (THAM); KOH solutions (0.3-0.4 M) have been prepared by diluting BDH solutions and their titres checked against potassium hydrogenphthalate. Equivalence point has been determined potentiometrically by Gran's method.<sup>9,10</sup> The concentrations of the stock solutions of divalent metal chlorides were determined by conventional analytical methods. Solutions to be titrated have been obtained by adding successively a weighed amount of ligand, a known volume of hydrochloric acid, a known volume of metal chloride, and then potassium chloride and water. The total volume was  $99.70 \pm 0.01$  ml. The titrant was added by a

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(1) F. Kurzer and M. Wilkinson, *Chem. Rev.*, **70**, 111 (1970).

(2) A. Braibanti, E. Leporati, F. Dallavalle, and M.A. Pellinghelli, *Inorg. Chim. Acta*, **2**, 449 (1968).

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(4) A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, **B25**, 2286 (1969).

(5) F. Bigoli, A. Braibanti, A.M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, **5**, 392 (1971).

(6) A. Braibanti, M.A. Pellinghelli, A. Tiripicchio, and M. Tiri-

**Table I.** Acid dissociation constant determinationsInitial concentrations (*mM*),  $-\log[\text{H}^+]$  and  $\bar{n}$  ranges for the titrations.

N.	Ionic strength	Temperature	S-tcaz	$T_H$	$-\log[\text{H}^+]$	$\bar{n}$
1	0.010	25°	0.355015	0.810243	2.329-10.029	0.97-0.01
2			0.355499	0.810727	2.375-10.343	1.10-0.01
3			0.345221	0.800449	2.337-9.958	1.00-0.01
4			0.376216	0.831444	2.361-9.963	1.06-0.02
5	0.034	25°	0.307540	0.762775	2.353-10.358	1.01-0.03
6			0.325650	0.780883	2.366-10.612	1.05-0.01
7			0.357440	0.812672	2.378-10.088	1.08-0.01
8			0.321070	0.776296	2.388-10.101	1.11-0.00
9	0.050	25°	0.359738	0.814970	2.373-10.546	1.09-0.00
10			0.481499	0.936730	2.353-9.807	1.03-0.01
11			0.399936	0.855170	2.368-9.831	1.07-0.01
12			0.403203	0.908870	2.324-10.700	1.08-0.02
13	0.10	25°	0.241594	0.517391	2.579-9.970	1.06-0.00
14			0.284077	0.570928	2.542-10.127	1.00-0.00
15			0.318296	0.649253	2.532-10.392	1.06-0.00
16			0.230994	0.561951	2.493-10.931	1.05-0.00
17			0.301247	0.604679	2.532-11.124	1.04-0.00
18			0.538488	1.659442	2.009-11.136	1.27-0.00
19			0.845619	1.795172	2.075-11.121	1.13-0.00
20	0.25	25°	0.258966	0.589920	2.500-10.674	1.06-0.00
21			0.319667	0.694730	2.442-9.689	1.05-0.01
22			0.258805	0.920715	2.182-7.968	1.03-0.30
23			0.311646	0.725397	2.402-10.909	1.06-0.02
24	0.50	25°	0.305036	0.713260	2.412-10.592	1.07-0.02
25			0.331720	0.772994	2.385-10.399	1.09-0.01
26			0.415474	0.911909	2.339-10.502	1.09-0.01
27			0.382988	0.879423	2.324-10.614	1.06-0.02
28	1.00	25°	0.314185	0.700301	2.383-10.338	1.02-0.02
29			0.428614	0.925049	2.327-10.761	1.06-0.01
30			0.313863	0.733141	2.442-10.472	1.08-0.01
31			0.310276	0.696392	2.439-10.156	1.08-0.02
32	1.50	25°	0.316039	0.718736	2.432-10.446	1.11-0.03
33			0.280449	0.666565	2.437-10.240	1.08-0.04
34			0.354854	0.796131	2.383-9.856	1.08-0.02
35			0.342198	0.761476	2.420-10.343	1.12-0.03
36	2.00	25°	0.314911	0.723135	2.430-10.524	1.12-0.05
37			0.324060	0.765336	2.383-10.414	1.09-0.05
38			0.270574	0.634693	2.451-10.855	1.04-0.03
39			0.343810	0.774032	2.413-10.769	1.13-0.00
40	0,10	35°	0.269687	0.539957	2.577-9.937	1.02-0.00
41			0.279159	0.560481	2.567-9.626	1.04-0.01
42			0.269607	0.539877	2.579-9.834	1.03-0.01
43			0.260981	0.525724	2.602-10.367	1.06-0.01
44	0,10	30°	0.339296	0.678543	2.477-9.951	1.02-0.00
45			0.295685	0.593590	2.533-9.981	1.02-0.00
46			0.262755	0.572379	2.548-9.765	0.85-0.00
47			0.285529	0.505501	2.636-9.805	1.20-0.16
48	0,10	20°	0.253444	0.507244	2.628-10.079	1.08-0.00
49			0.261667	0.526410	2.582-10.599	1.01-0.00
50			0.327809	0.658766	2.486-9.681	1.02-0.01
51			0.329824	0.660781	2.496-10.009	1.04-0.01
52	0,10	15°	0.444454	0.889046	2.392-10.039	1.09-0.01
53			0.367954	0.743016	2.443-9.866	1.04-0.01
54			0.275290	0.551087	2.600-10.634	1.09-0.00
55			0.367830	0.734820	2.450-10.636	1.04-0.01
56	0,10	10°	0.271220	0.547020	2.607-10.688	1.11-0.00
57			0.239500	0.482240	2.623-10.854	1.02-0.00
58			0.300240	0.631196	2.500-9.707	1.05-0.02
59			0.271620	0.569530	2.559-9.188	1.08-0.06
60	0,10	5°	0.328170	0.714290	2.464-10.907	1.13-0.00
61			0.293870	0.735147	2.375-10.574	1.07-0.01
62			0.293430	0.734700	2.364-9.733	1.03-0.01
63			0.268841	0.610850	2.558-11.168	1.25-0.00

**Table II.** Complex formation constant determinationsInitial concentrations (*mM*),  $-\log[H^+]$  and  $\bar{n}$  ranges for the titrations.

N.	Ion	$T_M$	$T_L$	$T_H$	$-\log[H^+]$	$\bar{n}$
1	Mn <sup>2+</sup>	0.153215	0.455417	0.989801	4.800-7.814	0.00-0.18
2		0.326287	0.827808	0.743559	3.671-8.083	0.00-0.14
3		0.123552	0.500116	1.058179	4.129-7.868	0.00-0.21
4		0.202685	0.402777	0.877904	4.344-7.926	0.00-0.17
5	Co <sup>2+</sup>	0.515119	0.514103	1.159273	4.303-6.574	0.01-0.81
6		0.293609	0.582865	1.295377	3.580-6.721	0.10-1.71
7		0.226723	0.683710	1.515212	3.860-6.041	0.15-1.54
8		0.106626	0.419706	1.013466	3.372-6.418	0.12-1.81
9	Ni <sup>2+</sup>	0.079180	0.302456	0.694410	3.345-5.143	0.16-2.70
10		0.198002	0.406082	0.881209	3.311-6.000	0.19-1.89
11		0.087121	0.445703	0.920830	3.122-4.976	0.18-2.76
12		0.102932	0.414829	0.889837	3.183-5.132	0.21-2.85
13		0.158400	0.390323	0.865450	3.027-5.463	0.11-2.46
14	Zn <sup>2+</sup>	0.116628	0.465937	1.047436	4.527-7.588	0.03-1.71
15		0.148111	0.443849	0.923901	4.078-8.206	0.00-1.76
16		0.356033	0.355499	1.223999	4.117-8.059	0.01-1.58
17		0.216407	0.433007	0.960907	4.067-8.239	0.00-1.63
18	Cd <sup>2+</sup>	0.393400	0.396127	1.025811	4.332-9.109	0.01-0.92
19		0.203519	0.404752	0.959819	4.141-8.548	0.01-1.13
20		0.149241	0.438811	0.972571	4.603-8.778	0.02-1.19
21		0.113992	0.456586	0.976480	3.742-8.592	0.03-1.20

Metrohm piston burette, with precision 0.005 ml. The initial concentrations, pH and  $\bar{n}$  intervals of the solutions employed are quoted in Tables I-II.

**Potentiometric measurements.** The potentiometric measurements have been performed by a digital potentiometer Radiometer PHM52, with precision 0.1 mV, using glass electrodes Radiometer G 2025B in the field 25-35°C, G 202 C in the field 15-20°C and G2027C in the field 5-10°C. Reference electrode was a saturated calomel electrode. The titration cell was maintained at  $t \pm 0.1^\circ\text{C}$  by circulation of thermostated water. A nitrogen atmosphere, presaturated by bubbling it throughout an appropriate KCl solution, was maintained in the cell by a continuous slow stream of gas. The glass electrode has been standardized by titrating HCl solution of known concentration with KOH solution whose concentration was also known, at the requested ionic strength. About 20 equally spaced points both in acidic and alkaline media were measured. The equivalence point was determined according to Gran's method<sup>9,10</sup> by plotting  $(V_o + \nu)e^{E/b}$  in the acidic field and  $(V_o + \nu)e^{-E/b}$  in alkaline field, against  $\nu$ , where  $b = RT/F$ ,  $V_o$  is the initial volume and  $\nu$  the volume of the KOH added. Intercepts for  $\nu = \nu_e$  ( $\nu_e =$  equivalence point) are calculated by least squares; the differences between the intercepts in acidic and alkaline fields do not exceed the experimental error. The standard electrode potential,  $E^\circ$ , is then obtained from:

$$E^\circ = E - b \ln[H^+] \quad (1)$$

$$[H^+] = \frac{1}{2} \frac{(\nu_e - \nu)N}{(V_o + \nu)} + \sqrt{\frac{1}{4} \frac{(\nu_e - \nu)^2}{(V_o + \nu)^2} N^2 + K_w} \quad (2)$$

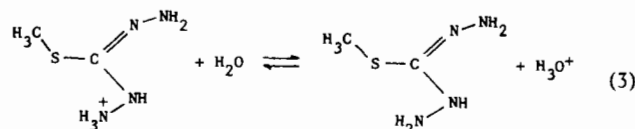
where  $N$  is the titre of KOH and  $K_w$  is the ionic product of water.  $E^\circ$  comprehends both effects of ionic strength and junction potential. The experimental

points very close to the equivalence point are not used in the calculation of  $E^\circ$ ; this was checked before and after each titration; the observed difference did not exceed 0.3 mV. The ionic product  $K_w$  for each ionic strength and each temperature was obtained by varying its value until the average  $E^\circ$  in alkaline field equals that in acidic field. Values of  $K_w$  were found to be in agreement with those quoted in literature.<sup>11</sup>

**Calculations.** The trial values of the stepwise constants to be introduced into the refinement process have been calculated following Albert.<sup>12</sup> The equilibrium constants have been refined by the program GAUSS Z prepared by Tobias<sup>13</sup>. The function to be minimized in the refinement procedure is  $\sum (\bar{n}_c - \bar{n}_o)^2$ , where  $n$  is the formation function; the program has been completed with a statistical analysis of the distribution of the residuals.<sup>14</sup> The calculations have been performed on the computer CDC 6600 of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna.

## Result

**Dissociation of the ligand.** The dissociation constants of the ligand are at 25°C and at  $\mu = 0.5 M$  KCl:  $pK_1 = 7.708(2)$  for the equilibrium



(11) H.S. Harned and B.B. Owen « The Physical Chemistry of Electrolytic Solutions », 3rd Ed., Reinhold Publishing, Corp. New York 1964, p. 638.

(12) A. Albert, *Biochem., J.*, 47, 531 (1950).

(13) R.S. Tobias and M. Yasuda, *Inorg. Chem.*, 2, 1307 (1963).

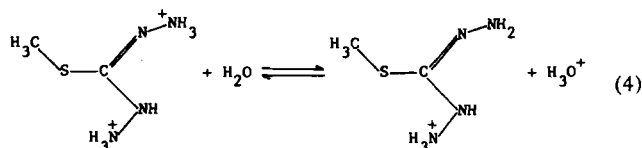
(14) A. Braibanti, E. Leporati, F. Dallavalle, and G. Mori, *Inorg. Chim. Acta*, accepted for publication.

**Table III.** Dependence of the ionisation constants of S-methylisothiocarbohydrazide upon temperature. Ionic strength,  $\mu = 0.1 M$  KCl.

Temperature		$pK_1(\sigma)$	$p(K_1 \cdot K_{12})(\sigma)$	$pK_{12}(\sigma)$	N.	$F_{95\%}$
5°	obs	8.070(9)	9.481(26)	1.411(28)	209	0.74
	calc*	8.091		1.375		
10°	obs	7.937(3)	9.295(12)	1.358(12)	177	2.96
	calc*	7.944		1.333		
15°	obs	7.808(3)	9.036(11)	1.228(11)	209	2.76
	calc*	7.805		1.295		
20°	obs	7.674(3)	8.745(14)	1.071(14)	181	2.94
	calc*	7.673		1.262		
25°	obs	7.563(3)	8.888(8)	1.325(9)	305	3.76
	calc*	7.548		1.231		
30°	obs	7.430(2)	8.281(17)	0.851(17)	157	2.56
	calc*	7.429		1.205		
35°	obs	7.312(2)	8.526(9)	1.214(9)	164	1.74
	calc*	7.318		1.181		

(\*) Values calculated from the equations:  $pK_1 = \frac{4753.8}{T} - 57.885 + 20 \log T$   $pK_{12} = \frac{3094.7}{T} - 58.637 + 20 \log T$

and  $pK_{12} = 1.364(7)$  for the equilibrium



The assignment of this conformation to the cation acids and the assignment of the proton, and of the corresponding constants, to the sites in the molecule can be done on the basis of the following arguments. The crystals structure determinations have shown that the monoprotonated<sup>7</sup> and biprotonated<sup>6</sup> cations of thiocarbonylhydrazide present the  $-\text{NH}-\text{NH}_3^+$  group or groups always bent in *cis* position: on the other hand the hydrazone residue is very weakly basic. However S-tcazH<sup>+</sup> ( $pK_1 = 7.708(2)$ ) is a much weaker acid than the cation tcazH<sup>+</sup> ( $pK_1 = 3.159(30)$ ) due to the changing of carbon-sulphur bond from  $\text{S}=\text{C}<$  to  $\text{CH}_3-\text{S}-\text{C}<$ . This is a general behaviour as shown also by the difference between the acid strengths of urea ( $pK_1 = 0.18$ )<sup>15</sup> and O-methylurea ( $pK_1 = 9.72$ )<sup>16</sup> and between those of thiourea ( $pK_1 = -1.0$ )<sup>17</sup> and S-methylthiourea ( $pK_1 = 9.78$ )<sup>18</sup>. The increase of  $pK_1$  in S-tcazH<sup>+</sup> is lower than in thiourea derivative due to the fact that the basic site in  $-\text{NH}-\text{NH}_2$  is further from S-C than in S-methylthiourea.

The influence of the temperature on the dissociation constants of the protonated forms of S-tcaz (Fig. 1) between 5° and 35° C is indicated by the data reported in Table III. The empirical relation of Pitzer<sup>19</sup>

$$pK(T) = A/T - B + 20 \log T \quad (5)$$

can be applied to the data and the following coefficients are obtained for  $pK_1$  and  $pK_{12}$  respectively:

(15) G. Brube and G. Motz, *Z. Physik. Chem.*, **118**, 145 (1925).

(16) M. Zief and J.T. Edsall, *J. Am. Chem. Soc.*, **59**, 2245 (1937).

$A_1 = 4753.8$ ,  $B_1 = 57.895$ ;  $A_{12} = 3094.7$ ,  $B_{12} = 58.637$ . From the difference between observed and calculated values one obtains  $\sigma(pK_1) = 0.004$  and  $\sigma(pK_{12}) = 0.065$ . By differentiating the Pitzer relation with respect to temperature the thermodynamic functions at 25° C, with e.s.d.'s in parenthesis in units of the last significant digit, are obtained:  $\Delta G_1 = 10.3(1)$  kcal · mole<sup>-1</sup>,  $\Delta H_1 = 9.9(1)$  kcal · mole<sup>-1</sup>,  $\Delta S_1 = -1.4(3)$  cal · degree<sup>-1</sup> mole<sup>-1</sup> and  $\Delta G_{12} = 1.7(51)$  cal · degree<sup>-1</sup> mole<sup>-1</sup>.

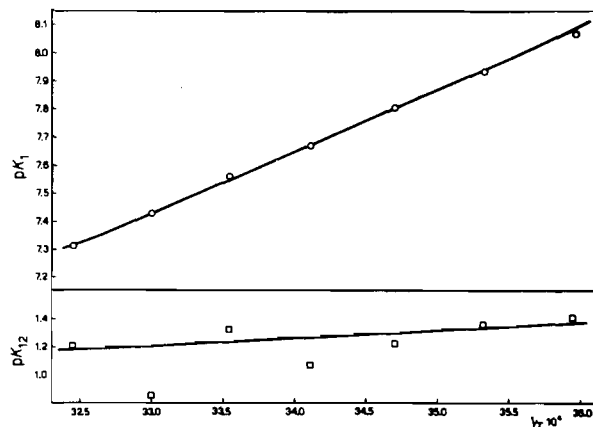


Figure 1. Dependence of the ionisation constants of S-tcazH<sup>+</sup> and S-tcazH<sub>2</sub><sup>2+</sup> upon temperature at  $\mu = 0.1 M$  KCl. Curves have been calculated from equation (5) by weighted least squares method.

The dissociation constants at different ionic strengths  $\mu(0.01-2.0 M$  KCl) at 25° C have been also determined. The variation of  $pK$  with  $\sqrt{\mu}$  is that typical for a cation acid and it can be expressed by

(17) J. Walker, *Z. Physik. Chem.*, **4**, 319 (1889).

(18) A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948).

(19) K.S. Pitzer, *J. Am. Chem. Soc.*, **56**, 2365 (1937).

**Table IV.** Ionisation constants of S-tcaz at different ionic strengths at 25°C.

Ionic strength		$pK_1(\sigma)$	$p(K_1 \cdot K_{12})(\sigma)$	$pK_{12}(\sigma)$	N.	$F_{95\%}$
0.010	obs	7.402(4)	8.394(20)	0.992(20)	125	0.53
	calc*	7.420				
0.034	obs	7.488(3)	8.698(10)	1.210(10)	125	0.95
	calc*	7.482				
0.050	obs	7.515(3)	8.643(9)	1.128(9)	186	3.54
	calc*	7.507				
0.10	obs	7.563(3)	8.888(8)	1.325(9)	305	1.54
	calc*	7.560				
0.25	obs	7.640(13)	8.943(20)	1.303(22)	216	2.63
	calc*	7.642				
0.50	obs	7.708(2)	9.072(7)	1.364(7)	183	2.27
	calc*	7.714				
1.00	obs	7.832(4)	9.254(12)	1.422(13)	152	1.19
	calc*	7.823				
1.50	obs	7.970(6)	9.561(14)	1.591(15)	156	0.93
	calc*	7.950				
2.00	obs	8.096(6)	9.762(15)	1.666(16)	155	1.55
	calc*	8.110				

(\*) Values calculated from the equations (6), (7).

empirical relations:

$$pK_1 = 7.332 + 0.9644\mu^{-1} - 0.9106\mu + 0.4367\mu^{3/2} \quad (6)$$

$$pK_{12} = 0.906 + 1.7301\mu^{-1} - 2.1630\mu + 0.9476\mu^{3/2} \quad (7)$$

whose coefficients have been calculated by least squares. Experimental and calculated values are reported in Table IV. The trend of the curves (Fig. 2) is the same as that of the protonated forms of thiocarbonylhydrazide.<sup>2</sup>

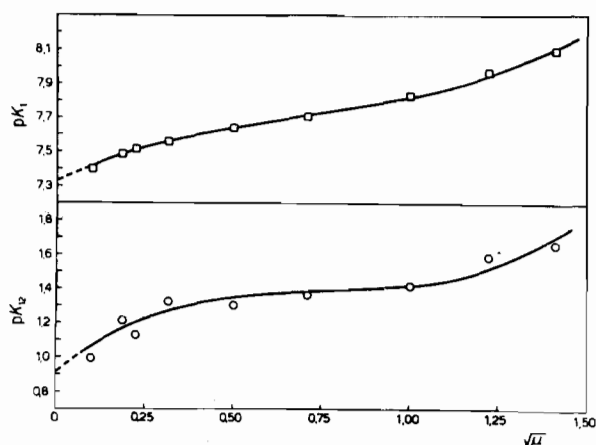


Figure 2. Dependence of the ionisation constants of S-tcazH<sup>+</sup> and S-tcazH<sub>2</sub><sup>2+</sup> upon ionic strength at 25°C. Curves have been calculated from equations (6) and (7) by weighted least squares method.

**Complexes with divalent metals.** Equilibria in aqueous solution at 25°C at  $\mu = 0.5 M$  KCl between S-tcaz and the divalent cations Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> have been determined. Equilibria with Cu<sup>2+</sup> cannot be studied because of the oxydation-re-

duction processes in the solutions. The behaviour of the ligand with these cations shows that association takes place, in variable amounts, except in strongly acidic regions. The absence of mixed or polynuclear complexes has been demonstrated by titrations with varied ratios metal to ligand, 1/1, 1/2, 1/3, 1/4, 1/5; the formation functions  $\bar{n} = f(pL)$ , where  $L$  = free ligand concentration (Figure 3), overlap one another independently of metal/ligand ratio.

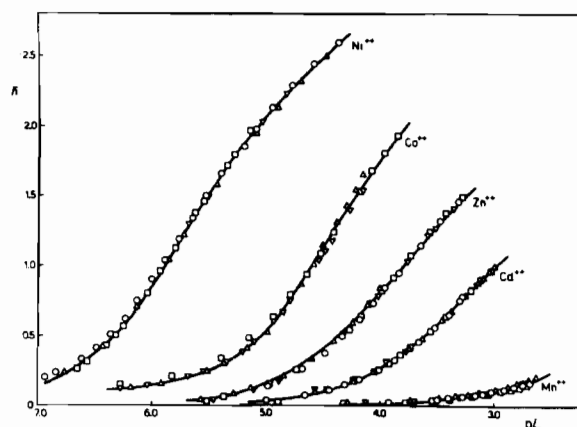
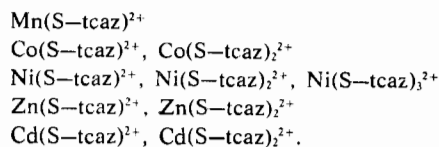


Figure 3. Formation curves for metal complexes of S-tcaz. Full lines: values calculated from the equilibrium constants reported in Table V.

The stoichiometric compositions of the species in solutions of different cations are:



**Table V.** Formation constants of S-methylisothiocarbohydrazide complexes with divalent metals.  $t = 25^\circ\text{C}$  and  $\mu = 0.5 \text{ M KCl}$ .

Metal	$\log \beta_1(\sigma)$	$\log \beta_2(\sigma)$	$\log K_2(\sigma)$	$\log \beta_3(\sigma)$	$\log K_3(\sigma)$	N.	$F_{95}\%$
Mn <sup>2+</sup>	2.022(7)	—	—	—	—	67	2.54
Co <sup>2+</sup>	4.813(27)	9.249(15)	4.436(31)	—	—	51	0.12
Ni <sup>2+</sup>	6.160(6)	11.787(4)	5.627(7)	16.395(7)	4.608(8)	84	0.08
Zn <sup>2+</sup>	4.271(22)	7.619(20)	3.348(30)	—	—	107	1.75
Cd <sup>2+</sup>	3.553(11)	5.971(14)	2.418(18)	—	—	99	0.89

**Table VI.** Formation constants of S-methylisothiocarbohydrazide complexes with divalent metals compared with those of thiocarbohydrazide.  $t = 25^\circ\text{C}$  and  $\mu = 0.5 \text{ M KCl}$ .

Complex	S-methylisothiocarbohydrazide	Complex	Thiocarbohydrazide
Co(S-tcaz) <sup>2+</sup>	$\log K_1$ 4.813(27)	Co(tcaz) <sup>2+</sup>	$\log K_1$ 2.969(18)
Co(S-tcaz) <sub>2</sub> <sup>2+</sup>	$\log K_2$ 4.436(31)	Co(tcaz) <sub>2</sub> <sup>2+</sup>	$\log K_2$ 2.689(18)
Ni(S-tcaz) <sup>2+</sup>	$\log K_1$ 6.160(6)	Ni(tcaz) <sup>2+</sup>	$\log K_1$ 4.404(8)
Ni(S-tcaz) <sub>2</sub> <sup>2+</sup>	$\log K_2$ 5.627(7)	Ni(tcaz) <sub>2</sub> <sup>2+</sup>	$\log K_2$ 3.700(8)
Ni(S-tcaz) <sub>3</sub> <sup>2+</sup>	$\log K_3$ 4.608(8)	Ni(tcaz) <sub>3</sub> <sup>2+</sup>	$\log K_3$ 3.113(8)
Zn(S-tcaz) <sup>2+</sup>	$\log K_1$ 4.271(22)	Zn(tcaz) <sup>2+</sup>	$\log K_1$ 2.526(23)
Zn(S-tcaz) <sub>2</sub> <sup>2+</sup>	$\log K_2$ 3.348(30)		
Cd(S-tcaz) <sup>2+</sup>	$\log K_1$ 3.553(11)		
Cd(S-tcaz) <sub>2</sub> <sup>2+</sup>	$\log K_2$ 2.418(18)		

The assessment of the composition of the species is given by the agreement between observed ( $\bar{n}_o$ ) and calculated ( $\bar{n}_c$ ) values of the formation function. The stability constants obtained for the various complexes are reported in Table V. Representative distribution diagrams are presented for Co<sup>2+</sup> (Figure 4) and for Ni<sup>2+</sup> (Figure 5).

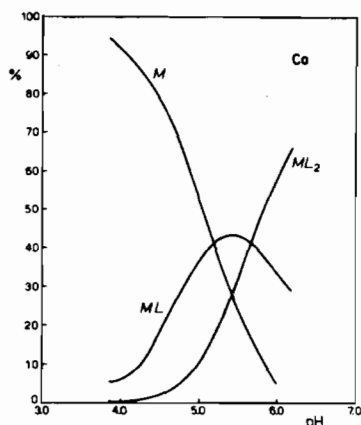


Figure 4. Representative distribution diagram for Co/S-tcaz system. The percentages have been calculated from the data of curve 7 in Table II.

The stoichiometry and the stability constants of the complexes  $M(S-tcaz)_n^{2+}$  parallel those formed by thiocarbohydrazide with the same metal, except that the former complexes are more strongly associated than the latter (Table VI). The increase of the stability constant values explains also some discrepancies between S-tcaz and tcaz complexes as the absence of complexes  $Mn(tcaz)_2^{2+}$  and  $Zn(tcaz)_2^{2+}$  which are so weak that they cannot be detected. The successive stepwise constants  $\log K_n$  decrease with increasing  $n$ ; the decrease however is not exactly con-

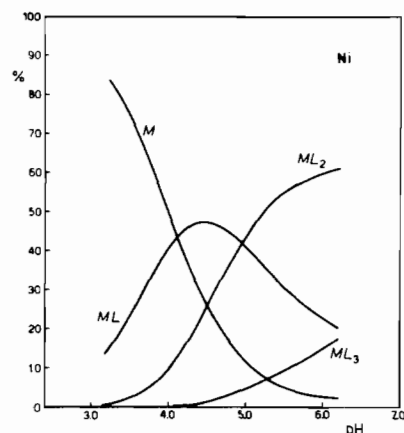
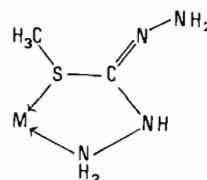


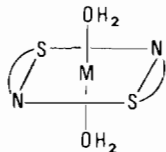
Figure 5. Representative distribution diagram for Ni/S-tcaz system. The percentages have been calculated from the data of curve 10 in Table II.

stant for corresponding complexes of different cations (for Co<sup>2+</sup>,  $\log K_1/K_2 = 0.38$ ; for Ni<sup>2+</sup>,  $\log K_1/K_2 = 0.53$ ; for Zn<sup>2+</sup>,  $\log K_1/K_2 = 0.92$ ; for Cd<sup>2+</sup>,  $\log K_1/K_2 = 1.14$ ) but the differences are not so high as to alter the fact that both  $\log K_1$  and  $\log K_2$  follow the Irving-Williams order:  $Mn < Co < Ni > Zn > (Cd)$ . It can be concluded therefore that the complexes are of the same type for every metal considered. Very likely these complexes form pentatomic chelate rings



with N,S as donor atoms, analogous to those formed by tcaz.<sup>3,5</sup> For complexes  $M(S-tcaz)_2^{2+}$  the *trans*(N),

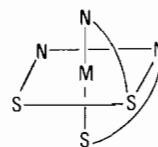
*trans(S)*, *trans(OH<sub>2</sub>)* structure



is the most probable, for its analogy with the complex  $\text{Cd}(\text{tc}az)_2\text{Cl}_2$ , whose structure has been determined by X-rays;<sup>5</sup> although a *cis(N)*, *cis(S)*, *cis(OH<sub>2</sub>)* structure, as that formed by hydrazinecarboxylato anion,<sup>20</sup>  $\text{H}_2\text{N}-\text{NH}-\text{COO}^-$ , with N,O as donor atoms, cannot be excluded *a priori*.

The nickel complex  $\text{Ni}(\text{S}-\text{tc}az)_3^{2+}$  can be assigned the structure

(20) A. Braibanti, A. Tiripicchio, A.M. Manotti Lanfredi, and M. Camellini, *Acta Cryst.*, 23, 248 (1967).



analogous to that formed by hydrazinecarboxylato anion.<sup>21</sup> The difference between  $\log K_1/K_2 = 0.53$  and  $\log K_2/K_3 = 1.02$  could account for the previous rearrangement of  $\text{Ni}(\text{S}-\text{tc}az)_2(\text{OH}_2)^{2+}$  from *trans(N)*, *trans(S)*, *trans(OH<sub>2</sub>)* to the *cis(N)*, *cis(S)*, *cis(OH<sub>2</sub>)* structure.

*Acknowledgments.* We wish to thank the Consiglio Nazionale delle Ricerche, Rome for financial aid.

(21) A. Braibanti, A.M. Manotti Lanfredi, and A. Tiripicchio, *Z. Kristallogr.*, 124, 335 (1967).