It would appear to the authors that trisethylenediaminecopper(II) sulfate is hexacoördinated in both solid state and in aqueous solutions which are sufficiently concentrated in ethylenediamine to stabilize the tris complex.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Coördinating Tendencies of Alkyl Substituted Thioureas in Solvents of Varying Dielectric Constant[1]

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Polarographic studies of copper(I) and cadmium(II) complexes of thiourea and its methyl-, 1,3-dimethyl-, trimethyl-ethyl- and 1,3-diethyl- homologs were carried out in solvent mixtures of different dielectric constant. Values for the formation constants of copper(I) complexes in aqueous, 50% dioxane–water and 70% dioxane–water mixtures were considered on a relative basis. Formation constants for cadmium complexes in aqueous, 50% ethanol–water and 50% dioxane–water mixtures were determined by the DeFord–Hume method. The order of decreasing stability for the substituted thiourea complexes was: ethyl > diethyl > methyl > dimethyl > trimethyl. The nature of the solvent system affected only the complexes of unsubstituted thiourea.

In a previous paper,[2] polarographic studies of thiourea complexes with cadmium(II) and lead(II) ions in aqueous media were reported, and the method[3] of DeFord and Hume was applied in the calculation of consecutive formation constants for the respective species existing in solution. As an extension of this work the relative stabilities of various alkyl substituted thiourea complexes with cadmium(II) ion and with copper(I) ion have been determined and a correlation between the nature of the alkyl group on the thiourea ligand and the stability of the resulting complex has been established. Since solvent effects are of interest in coördination processes, an attempt has been made to determine the effects of four solvent systems of varying dielectric constant on the coördinating tendencies of the various ligands.

Experimental

Materials, Apparatus and Solutions.—1-Methyl-2-thiourea, 1-ethyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,3-diethyl-2-thiourea and 1,1,3-trimethyl-2-thiourea were prepared by the method of Moore and Crossley.[4] Thiourea (Eastman Kodak) was recrystallized from 95% ethanol and dried *in vacuo* over sulfuric acid. Reagent grade cadmium nitrate was used without further purification. Other materials and apparatus used are described in a previous paper.[2]

Stability constants for cadmium complexes of the thioureas were measured in three different solvent systems: aqueous, 50% v./v. dioxane–water and 50% v./v. ethanol–water. Each system was 0.1 M in potassium nitrate, 10^{-3} M in cadmium nitrate and 0.004% (% by weight) in Triton X-100.

Three separate solvent systems: aqueous, 50% v./v. dioxane–water and 70% v./v. dioxane–water also were used in the studies of the copper(I) complexes. The aqueous and 50% dioxane systems were 0.1 M in potassium nitrate, 10^{-3} M in crystalline copper(I) complex[5] and 0.004% Triton. The 70% dioxane system was 1.67 M in acetic acid, 0.1 M in sodium acetate, 10^{-3} M in copper(I) complex and 0.004% in Triton. The acetate buffer was used in 70% dioxane solutions since use of potassium nitrate as supporting electrolyte in this solvent system yielded distorted polarographic curves.

The following procedure was used in polarographic analysis of the complexes in each solvent system. Each of the above solvent systems was made 1.0 M with respect to each ligand under study. A 30-ml. aliquot of the 1.0 M ligand solution was transferred to the polarographic cell, deaerated, brought to temperature, and the current voltage curve was recorded. A measured amount of diluent, containing all components of the appropriate solvent system except the ligand itself, was then added to the solution, bringing about a decrease in ligand concentration while the concentrations of metal ion, supporting electrolyte and maximum suppressor remained constant. The diluted solution was deaerated and the current–voltage curve recorded. By repeated application of this method of dilution and subsequent current–voltage measurement, a series of half-wave values and diffusion currents for each metal complex in solutions containing successively smaller known amounts of ligand was obtained. Three separate series of polarographic determinations were made for each ligand with cadmium ion in the solution and for each ligand with copper ion in the solution. Each series differed only with respect to the solvent system employed.

All polarographic measurements were made with a Sargent cell (S-29438). The dioxane used as a solvent component was purified according to the method of Vogel.[6]

Treatment of Data.—The method of DeFord and Hume[3] was used to determine consecutive formation constants when its application was possible. Since the values of the half-wave potential and of the diffusion current for simple cadmium ion in 50% dioxane had to be known for calculation of formation constants, a graphical procedure was employed in their determination. The diffusion currents of the cadmium complexes were plotted against concentration of excess ligand and the curve was extrapolated to zero concentration of ligand. This value for the diffusion current of the simple ion was used in the DeFord–Hume equation for $F_0(X)$, with an arbitrarily assumed value for the half-wave potential of the simple ion. The function $F_0(X)$ was plotted against concentration of ligand and extrapolated to zero concentration of ligand. At ligand concentration equal to zero, $F_0(X)$ must equal unity. The arbitrary value for the half-wave potential was corrected by the amount necessary to fulfill this condition, and the resulting value, −0.564 volt, was used as the half-wave potential of simple cadmium ion. The procedure is sufficiently accurate to give comparative values for formation constants in 50% dioxane, although comparison of these constants with those observed in other solvent systems may not be warranted.

Results

Polarographic data for the copper(I) thiourea complex in 70% dioxane and for 1,3-dimethyl-2-

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[1] Presented before the Physical and Inorganic Division of the 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] T. J. Lane, C.S.C., J. A. Ryan and E. F. Britten, THIS JOURNAL, **80**, 315 (1958).

[3] D. D. DeFord and D. N. Hume, *ibid.*, **73**, 5321 (1951).

[4] M. Horning, "Organic Syntheses," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 617.

[5] Thomas J. Lane, C.S.C., J. V. Quagliano and Ernest Bertin, S.J., *Anal. Chem.*, **29**, 481 (1957).

[6] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1956, p. 177.

TABLE I

ANALYSIS OF CADMIUM–METHYLTHIOUREA COMPLEX IN AQUEOUS MEDIUM

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.574	9.00	....	...	...	...	...
.0065	.576	8.68	1.1212	...	...	...	...
.0100	.578	8.40	1.463	46	...	...	...
.0498	.588	8.20	3.268	45	...	...	...
.0829	.597	7.88	6.855	70	333	1122	...
.1381	.607	7.60	15.46	104	446	1499	...
.2072	.622	7.40	51.19	242	961	3485	...
.2486	.626	7.20	71.90	285	974	2952	...
.3552	.640	6.99	220.40	617	1617	3877	...
.4144	.652	6.72	583.80	1406	3289	7358	16368
.4973	.661	6.48	1221	2453	4846	9262	17468
.6216	.672	6.30	2952	4747	7568	11789	18044
.7104	.676	6.06	4203	5914	8265	11298	15094
.8288	.687	6.00	10000	12064	14504	17210	20071
.9946	.693	5.96	16070	16156	16200	16048	15557
1.0000	.694	5.90	17820	17820	17777	17537	16962
			$K_0 = 1$	$K_1 = 43$	$K_2 = 240$	$K_3 = 575$	$K_1 = 1.7 \times 10^4$

TABLE II

ANALYSIS OF CADMIUM–DIMETHYLTHIOUREA COMPLEX IN AQUEOUS MEDIUM

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.574	8.76	....	...	...	...	...
.0704	.592	8.20	4.242	47	...	...	...
.0911	.596	8.08	6.019	55	50	...	...
.1290	.601	7.64	9.404	65	113	...	...
.2211	.622	7.04	52.34	232	818	...	...
.2714	.627	6.80	80.15	291	888	3088	...
.3512	.641	6.60	245.4	695	1837	5103	..
.4975	.654	6.28	710.6	1426	2763	5461	9971
.5970	.662	6.12	1360	2276	3728	6160	9480
.7463	.672	5.72	3172	4248	5625	7470	9339
.9950	.686	5.24	9530	9574	9572	9570	9568
1.0000	.685	5.18	10420	10419	10368	10318	9818
			$K_0 = 1$	$K_1 = 50$	$K_2 = 50$	$K_3 = 500$	$K_4 = 9.7 \times 10^3$

TABLE III

ANALYSIS OF CADMIUM–ETHYLTHIOUREA COMPLEX IN AQUEOUS MEDIUM

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.574	8.76	....	...	...	...	...
.0375	.580	7.26	1.986	26	34	...	...
.0500	.581	7.20	2.114	22	74	...	...
.0667	.585	7.08	3.008	30	76	...	...
.1000	.591	6.87	4.721	37	122	220	...
.1500	.616	6.15	35.57	243	1453	9020	...
.2000	.626	6.00	85.94	425	2124	10120	...
.2500	.635	5.85	180	717	2869	11080	...
.3000	.644	5.79	358	1193	3977	12923	...
.3750	.655	5.79	819	2183	5821	15256	...
.4286	.660	5.58	1317	3070	7163	16479	...
.5000	.668	5.46	2433	4864	9728	17107	...
.6000	.676	5.35	4742	7902	13130	21716	34526
.7000	.683	5.30	8676	12393	17668	25097	34445
.8000	.689	5.20	13049	16310	20356	25320	30400
.9000	.694	5.15	20249	22497	24968	27631	29590
1.0000	.699	5.10	29039	29034	29014	28914	27914
			$K_0 = 1$	$K_1 = 25$	$K_2 = 100$	$K_3 = 1000$	$K_4 = 3.1 \times 10^4$

thiourea complex with cadmium(II) ion in 50% dioxane were unsatisfactory, but qualitatively the stability constants for these complexes followed the general trend observed in this study.

The average value of the slopes of log $(i_d - i)/i$ *versus* $E_{d.e.}$ for copper(I) complexes and for cadmium(II) complexes was 0.0594 (±0.002) and 0.030 (±0.001), respectively. However, the greater slope of the simple cadmium ion in 50% dioxane indicated the irreversibility of the reaction.

Polarographic data for cadmium complexes are presented in Tables I through XIII. Consecutive

TABLE IV

ANALYSIS OF CADMIUM–THIOUREA IN 50% ETHANOL

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	0.516	1.00	...	...	...	...
.0250	.573	.512	2.03	41.4	334	9380	20800
.0500	.582	.494	4.25	64.9	638	10800	38200
.0714	.590	.496	7.89	96.5	889	11000	30800
.1000	.600	.491	17.4	164	1310	12100	32200
.1666	.618	.487	71.2	421	2230	13400	27200
.2000	.625	.483	123.7	614	2900	14000	25800
.2500	.633	.474	235	934	3600	14000	20600
.3333	.647	.473	702	2100	6280	18500	29000
.4286	.658	.472	1660	3870	8950	20600	27500
.5000	.667	.472	3350	6690	13300	26400	35200
.625	.680	.469	9270	14800	23700	37700	46200
.7143	.687	.469	16000	22400	31300	43700	48800
.833	.695	.465	30800	37000	44300	53100	53100
1.000	.704	.460	61300	61300	61200	61100	52300
			$K_0 = 1$	$K_1 = 33$	$K_2 = 100$	$K_3 = 9 \times 10^3$	$K_4 = 4 \times 10^4$

TABLE V

ANALYSIS OF CADMIUM–METHYLTHIOUREA COMPLEX IN 50% ETHANOL

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.568	5.28	....	....	....	....	....
.0067	.570	5.06	1.219	32.6	....	..	....
.0100	.571	5.03	1.324	32.4	....	....	....
.0143	.572	4.98	1.446	31.2	....	....	....
.0333	.580	4.80	2.802	54.1	664	7920	....
.0556	.589	4.70	5.768	85.7	968	10215	....
.0714	.595	4.60	9.404	117.7	1200	11204	....
.1000	.606	4.50	22.66	216.6	1846	14460	....
.1250	.616	4.42	50.27	394.1	2897	19976	126208
.1667	.628	4.36	129.8	772.6	4442	24247	120258
.2000	.636	4.23	249.6	1248	6080	28400	121000
.2500	.647	4.21	591.5	2362	9320	35680	125920
.3333	.660	4.18	1637	4908	14628	42684	115452
.4167	.670	4.14	3605	8648	20676	48658	106690
.5000	.680	4.11	7925	15884	31704	62608	116816
.6250	.692	4.05	20470	32750	52348	83117	126256
.7143	.698	4.04	32750	45847	64111	89193	118987
.8333	.706	3.95	62510	75014	89980	107500	124009
1.0000	.716	3.94	136600	136599	136567	136167	131967
			$K_0 = 1$	$K_1 = 32$	$K_2 = 400$	$K_3 = 4.2 \times 10^3$	$K_4 = 1.2 \times 10^5$

TABLE VI

ANALYSIS OF CADMIUM–DIMETHYLTHIOUREA COMPLEX IN 50% ETHANOL

Ligand, M	$-E_{1/}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	5.28	....	....	...	...	...
.0112	.566	5.19	1.188	16.78	...	...	...
.0225	.568	5.09	1.416	18.49	...	...	...
.0482	.575	4.86	2.561	32.39	340	...	...
.0750	.583	4.69	4.946	52.61	488	...	...
.0965	.588	4.58	7.481	67.16	530	...	...
.1350	.597	4.42	15.64	108.4	684	...	...
.1875	.613	4.22	56.99	298.6	1507	6277	27077
.2250	.619	4.12	93.06	409.1	1747	6298	22657
.2500	.626	4.06	163.1	648.4	2530	8800	30400
.3125	.636	3.94	366.1	1168	3686	10739	30524
.3750	.642	3.86	596.5	1588	4192	10298	24261
.4166	.648	3.81	964.6	2313	5514	12443	26987
.4682	.656	3.76	1822	3889	8272	16962	33665
.5356	.662	3.68	2972	5547	10324	18659	32597
.6250	.669	3.58	5272	8434	13468	21021	31713
.7500	.679	3.45	11930	15905	21185	27807	35476
			$K_0 = 1$	$K_1 = 16$	$K_2 = 330$	$K_3 = 1.2 \times 10^3$	$K_4 = 2.9 \times 10^4$

TABLE VII

ANALYSIS OF CADMIUM–ETHYLTHIOUREA COMPLEX IN 50% ETHANOL

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	5.16	....	......	....	....	....
.0133	.580	4.96	3.618	196.8	....	....	....
.0200	.584	4.88	5.022	201.1	....	....	....
.0250	.586	4.85	5.901	196.0	....	....	....
.0333	.590	4.76	8.219	216.6	....	....	....
.0400	.592	4.71	9.702	217.5	487	....	....
.0588	.600	4.60	18.54	298.2	1700	22108	....
.0833	.611	4.46	45.06	528.9	3973	42893	440492
.1000	.618	4.38	79.17	781.7	5840	54400	482000
.1250	.627	4.27	163.7	1301	8824	67392	489536
.1667	.639	4.15	429.0	2567	14211	82849	459802
.2000	.644	4.04	651.1	3250	15260	74300	340500
.3330	.672	3.82	6101	18300	54306	161718	466554
.4167	.684	3.74	15870	38082	90914	217216	506398
.5000	.692	3.61	30680	61358	122320	243840	475280
.6250	.705	3.40	89620	143390	229107	365920	575552
.7143	.713	3.30	172400	241355	337613	472088	652230
.8333	.719	3.11	291100	350290	420127	503692	597200
			$K_0 = 1$	$K_1 = 198$	$K_2 = 400$	$K_3 = 6.2 \times 10^3$	$K_4 = 4.8 \times 10^5$

TABLE VIII

ANALYSIS OF CADMIUM–DIETHYLTHIOUREA COMPLEX IN 50% ETHANOL

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	5.16	....	....	....	....	....
.0100	.570	5.01	1.642	64.20	....	....	....
.0200	.574	4.98	2.258	62.90	645	7250	....
.0417	.584	4.64	5.284	102.7	1263	18297	306880
.0500	.587	4.53	6.836	116.7	1334	16680	223600
.0714	.596	4.23	14.75	192.5	1995	20938	216200
.1000	.607	4.00	36.75	357.5	3075	25750	202500
.1250	.613	3.86	61.10	480.8	3446	23568	144544
.1562	.622	3.74	126.5	803.2	4822	27669	141300
.2083	.638	3.58	460.4	2207	10355	47311	200725
.2500	.644	3.42	768.3	3069	12076	46304	163216
.3125	.658	3.24	2417	7731	24579	77052	228900
.3571	.664	3.02	4137	11582	32293	89031	233900
.4167	.672	2.86	8145	19544	46782	111067	253340
.5000	.681	2.46	19540	39078	78056	155112	299224
.6250	.693	2.06	58100	92958	148652	237043	370468
.7143	.701	1.71	130600	182834	255892	357541	492800
			$K_0 = 1$	$K_1 = 50$	$K_2 = 500$	$K_3 = 5.5 \times 10^3$	$K_4 = 2.2 \times 10^5$

TABLE IX

ANALYSIS OF CADMIUM–TRIMETHYLTHIOUREA COMPLEX IN 50% ETHANOL

Ligand, M	$-E_{1/2}$	i_d (μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	5.16	....	......	.....	...	...
.0357	.572	5.07	1.897	25.13	.....	...	...
.0500	.573	4.95	2.101	22.02	.....	...	....
.0735	.576	4.84	2.710	23.26	.....	...	...
.1042	.583	4.81	4.717	35.67	.....	...	...
.1389	.590	4.54	8.605	54.75	264.6	1041	...
.1786	.597	4.46	15.14	79.17	342.5	1245	...
.2631	.616	4.31	68.83	257.8	911.4	3008	...
.3571	.631	4.18	228.0	635.6	1729	4505	10655
.4167	.640	4.13	465.5	1114	2630	6023	14906
.5000	.648	4.06	884.6	1767	3498	6756	12112
.6250	.660	3.96	2308	3691	5876	9209	13614
.7143	.666	3.86	3780	5290	7381	10165	13250
.8333	.674	3.80	7156	8586	10282	12194	13793
1.0000	.682	3.69	13750	13749	13731	13611	12911
			$K_0 = 1$	$K_1 = 18$	$K_2 = 120$	$K_3 = 700$	$K_4 = 1.3 \times 10^4$

TABLE X

ANALYSIS OF CADMIUM–THIOUREA COMPLEX IN 50% DIOXANE

Ligand, M	$-E_{1/2}$	$i_d(\mu a.)$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	3.82	....	......	.....	...	...
.0415	.574	3.75	2.221	29.42	323.3	...	...
.0464	.575	3.74	2.405	30.28	307.7	...	...
.0675	.582	3.65	4.256	48.23	477.4	...	...
.0789	.585	3.60	5.449	56.38	511.8	...	...
.0986	.590	3.56	8.135	72.36	571.6	...	...
.1315	.598	3.44	15.73	112.0	730.0	...	...
.2625	.628	3.12	179.6	680.4	2531	8363	23141
.2952	.633	3.06	269.9	910.9	3031	9122	23120
.3634	.641	3.03	508.6	1396	3797	9523	19900
.4295	.650	3.00	1035	2407	5566	12182	23035
.5249	.658	2.97	1953	3718	7052	12784	19968
.5905	.664	2.92	3164	5356	9050	14750	21100
.7874	.677	2.86	8906	11309	14349	17800	19600
.9860	.690	2.80	25060	25414	25758	25778	23810
1.0242	.692	2.58	31790	31037	30293	29251	27400
			$K_0 = 1$	$K_1 = 16$	$K_2 = 340$	$K_3 = 2.3 \times 10^3$	$K_4 = 2.2 \times 10^4$

TABLE XI

ANALYSIS OF CADMIUM–METHYLTHIOUREA COMPLEX IN 50% DIOXANE

Ligand, M	$-E_{1/2}$	$i_d(\mu a.)$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	3.82	....	......	.....	...	...
.0317	.568	3.64	1.433	13.50	.....	...	...
.0476	.574	3.50	2.380	28.73	.....	...	...
.0571	.577	3.44	3.059	36.06	421.3	1948	...
.0635	.579	3.42	3.594	40.85	454.3	2267	...
.0714	.581	3.38	4.250	45.52	469.4	2227	...
.0816	.584	3.34	5.430	54.28	518.1	2549	...
.0952	.588	3.28	7.555	68.85	597.1	3014	...
.1588	.609	3.22	39.53	242.7	1453	7188	...
.2041	.620	3.18	94.30	457.3	2182	9176	...
.2381	.628	3.14	178.1	744.1	3075	11618	40830
.3572	.646	3.00	758.0	2119	5898	15653	38500
.4088	.653	2.94	1335	3263	7952	18684	41020
.4770	.662	2.93	2699	5656	11832	24155	46600
.5724	.670	2.89	5107	8920	15573	26683	43300
.6360	.676	2.86	8233	12943	20347	31504	46500
.8177	.689	2.77	23400	28378	34689	42026	49040
			$K_0 = 1$	$K_1 = 12$	$K_2 = 310$	$K_3 = 1.9 \times 10^3$	$K_4 = 4.3 \times 10^4$

TABLE XII

ANALYSIS OF CADMIUM–ETHYLTHIOUREA COMPLEX IN 50% DIOXANE

Ligand, M	$-E_{1/2}$	$i_d(\mu a.)$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.564	3.82	....	......	.....	....	....
.0345	.571	3.36	1.963	27.89	228.9	....	....
.0518	.579	3.19	3.834	54.71	863.1	....	....
.0622	.583	3.08	5.455	71.62	990.6	....	....
.0777	.588	3.00	8.260	93.45	1074	5586	....
.0888	.591	2.93	10.68	109.0	1114	5337	....
.1036	.596	2.88	16.06	145.3	1306	6403	....
.1726	.622	2.72	128.8	738.7	4208	20624	89156
.2589	.641	2.58	597.7	2305	8861	31857	102922
.3107	.651	2.49	1348	4335	13906	42656	120430
.3884	.660	2.37	2858	7356	18933	47147	108110
.5179	.674	2.15	9378	18106	34934	66204	117700
.5611	.681	2.09	16650	29679	52903	93160	156800
.6412	.687	1.96	28320	44181	68909	106500	158030
			$K_0 = 1$	$K_1 = 10$	$K_2 = 640$	$K_3 = 5.2 \times 10^3$	$K_4 = 1.2 \times 10^5$

formation constants, obtained by plotting $F_j(X)$ values against ligand concentration, are listed in each table. In Table XIV, K_4 values for complexes of cadmium in the three solvent mixtures are compared. In Table XV, values of the half-wave potential for copper complexes at 1.0 M

TABLE XIII

ANALYSIS OF CADMIUM[a]–DIETHYLTHIOUREA COMPLEX IN 50% DIOXANE

Ligand, M	$-E_{1/2}$	i_d(μa.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.574	2.56	......	......	.....	...	...
.0627	.575	2.25	1.258	4.115	.....	.....	...
.0731	.577	2.19	1.477	6.525	.....	...	...
.0878	.582	2.14	2.231	14.02	113.8	...	...
.1097	.587	2.07	3.403	21.90	162.7	...	...
.1268	.592	2.03	5.126	32.54	225.0	1459	...
.1463	.595	1.99	6.604	38.30	234.4	1329	...
.2743	.626	1.88	78.30	281.8	1012	3543	...
.3657	.642	1.82	281.3	766.4	2084	5585	15150
.4388	.650	1.79	533.5	1213	2755	6184	...
.4876	.655	1.73	814.7	1668	3409	6903	14060
.5486	.662	1.70	1432	2608	4743	8566	15530
.6269	.677	1.66	4717	7521	11988	19055	30300
.7314	.682	1.60	7225	9876	13497	18398	25100
			$K_0 = 1$	$K_1 = 14$	$K_2 = 40$	$K_3 = 40$	$K_4 = 2 \times 10^4$

[a] Concentration of cadmium was reduced for this series.

TABLE XIV

K_4 VALUES FOR SUBSTITUTED THIOUREAS IN VARIOUS SOLVENT MIXTURES

Complexing agent	Cd(II) complex in water	Cd(II) complex in 50% ethanol	Cd(II) complex in 50% dioxane
Ethylthiourea	3.1×10^4	4.8×10^5	1.2×10^5
sym-Diethylthiourea	....	2.2×10^5	2.0×10^4
Methylthiourea	1.7×10^4	1.2×10^5	4.3×10^4
sym-Dimethylthiourea	9.7×10^3	2.9×10^4	.....
Trimethylthiourea	....	1.3×10^3	.....
Thiourea[a]	3.6×10^3	4.0×10^4	2.2×10^4

[a] Value in water from previous paper[2].

TABLE XV

VALUES OF $-E_{1/2}$ *vs.* S.C.E. FOR COMPLEXES OF COPPER(I) WITH VARIOUS LIGANDS AT 1.0 M CONCENTRATION OF LIGAND

Complexing agent	Cu(I) complex in water	Cu(I) complex in 50% dioxane	Cu(I) complex in 70% dioxane
Thiourea	0.773	0.800	0.845
Ethylthiourea	.808	.819	.850
sym-Diethylthiourea	...	.799	.845
Methylthiourea	.773	.788	.808
sym-Dimethylthiourea	.714	.749	.753
Trimethylthiourea	...	.667	.683

concentration of complexing agent are presented. Copper(I) complexes were studied at concentrations of ligand ranging from 0.01 to 1.0 M, but only those data pertinent to the discussion have been tabulated.

Discussion

Data from the tables indicate the presence of species of coördination number four and lower for complexes of cadmium(II) ion in each solvent mixture. Interpretation of curves from the graphs of $-E_{1/2}$ *vs.* log C for copper(I) shows that the four coördinated species is the only form present over a wide range of ligand concentration. Since no value for the half-wave potential of the simple copper(I) ion in ethanol or dioxane mixtures is known, calculation of formation constants for the complexes of copper(I) is not possible. However, it may be shown that for complexes with the same univalent metal ion in the same solvent

$$\frac{K_a}{K_b} = \text{antilog}\left\{16.92\left[(E_{1/2})_{c_a} - (E_{1/2})_{c_b}\right]\right\}$$

in which K_a and K_b are formation constants involving different complexing agents and the $E_{1/2}$ values are the respective half-wave potentials for the complexes in solutions 1.0 M with respect to complexing agent. The data of Table XV were substituted into this equation to obtain the relative values presented in Table XVI. The equation is valid if the diffusion currents of the two complexes, a and b, are not greatly different under the specified conditions of concentration.

TABLE XVI

RELATIVE STABILITIES OF Cu(I) COMPLEXES WITH VARIOUS THIOUREAS[a]

	Water	50% Dioxane	70% Dioxane
Thiourea	9.9	7.3	36
Ethylthiourea	39	15	44
sym-Diethylthiourea	..	7.0	36
Methylthiourea	9.9	4.6	8.5
sym-Dimethylthiourea	1	1	1
Trimethylthiourea	..	0.04	0.06

[a] Relative to *sym*-dimethylthiourea in each solvent mixture.

Examination of data presented in Tables XIV and XVI leads to three conclusions: (1) ethylthiourea shows the strongest coördinating tendency with cadmium(II) and copper(I) ions; (2) ethyl homologs form more stable complexes than methyl homologs under the conditions described; (3) the effect of increasing the number of alkyl groups substituted in the thiourea molecule is quite pronounced.

The first and second conclusion may be partially explained by the greater electron releasing power of the ethyl group. According to Riley,[7] any factor which increases the localization of negative charge in the coördinating ligand increases the ability of the ligand to coördinate. This observation has been confirmed by several other studies.[8,9]

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(7) H. L. Riley, *J. Chem. Soc.*, 2985 (1928).

(8) R. J. Bruehlman and F. H. Verhoek, THIS JOURNAL, **70**, 1401 (1948).

(9) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

A possible explanation for the third conclusion is the effect of steric factors, which are of great importance in complex stability. From their consideration one would expect the following order of increasing stability in the alkyl thiourea complexes: tri-alkyl < di-alkyl < mono-alkyl. The results given in Tables XIV and XVI show this to be the case. Steric factors, however, do not account for the fact that ethylthiourea complexes are more stable than those of methylthiourea.

An alternative explanation for the three conclusions listed above might be advanced by taking into consideration the peculiar symmetry of the thiourea molecule, which is, to some degree, similar to the guanidine molecule. Davis and Elderfield[10] noted that mono-alkyl and N,N'-dialkylguanidines are less basic than the parent molecule. Furthermore, they found that the ethyl group has a smaller effect than the methyl in decreasing the basicity. Pauling[11] explained the decreased basicity of the substituted guanidines as an effect of the alkyl group on the resonance energy of the unusually symmetric parent molecule. If, in agreement with Pauling's explanation, it is assumed that the methyl homologs of thiourea have a lower resonance stabilization than the corresponding ethyl homologs, one would expect the energetics of coördination to favor greater stability of the ethylated complexes, provided the resonance energy is not lost in complex formation, but is able to contribute to the stability of the complex, presumably by resonance involving the metal ion. The fact that diethylthiourea forms less stable complexes than ethylthiourea and that the complexes of di- and tri-methylthiourea show less stability than those of methylthiourea supports this assumption. A recent study[12] of the kinetics of decomposition of thiourea and several homologs of thiourea also suggests that alkylation of the parent thiourea molecule decreases its resonance stabilization.

In many cases of complex formation involving ligands of similar structure, differences in energies of coördination are relatively large when compared to differences in energies of solvation. Since the data presented in this paper clearly show that the order of increasing stability for the complexes of the alkyl-substituted thioureas is the same in four solvent systems of different dielectric constant and that the order is preserved for both metal ions studied, it is apparent that the observed differences in stability are due primarily to the structure of the ligand and not to the nature of the solvent or of the metal ion.

It seems probable, however, from the data in the tables that solvation does play an important role in determining the stability of the complexes of the parent molecule, thiourea. These complexes do not occupy a fixed position in the order of increasing stabilities (Tables XIV, XVI) but tend to be among the least stable in aqueous solution, of intermediate stability in the 50% mixtures and of stability comparable to the ethylthiourea complexes in 70% dioxane. This solvent effect was not unexpected. While the dipole moments for the other ligands differ by small amounts, thiourea has a dipole moment which is considerably larger.[13] Consequently, thiourea complexes would tend to dissociate more readily in a solution of high dielectric constant, such as water, whereas their dissociation would be repressed in a low dielectric medium such as 70% dioxane.

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Synthesis and Properties of Bis-(trifluoromethylthio)-mercury

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Bis-(trifluoromethylthio)-mercury, $Hg(SCF_3)_2$, was obtained in 72% yields from carbon disulfide and mercury(II) fluoride at 250°. Physical and chemical properties of this mercurial are described.

A simple and direct synthesis of bis-(trifluoromethylthio)-mercury, $Hg(SCF_3)_2$, has been found in the reaction of mercury(II) fluoride and carbon disulfide.[1,2] The reaction, effected either in a sealed reactor or by passing the disulfide over heated HgF_2 at 250°, has given the mercurial in yields averaging 72%. Small amounts of CF_3SCF_3 and CF_3SSCF_3 are formed under these conditions. Above 300°, CF_3SSCF_3 becomes the major product. Source of the sulfides is probably the pyrolysis of

$$3HgF_2 + 2CS_2 \longrightarrow 2HgS + Hg(SCF_3)_2$$

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[1] E. L. Muetterties, U. S. Patent 2,729,663 (Jan. 3, 1956).

[2] This mercurial was first prepared by Brandt, Emeleus and Haszeldine (*J. Chem. Soc.*, 2198 (1952)) by irradiating a mixture of bis-(trifluoromethyl)-disulfide and mercury for 4 days in a sealed tube.