with a mole ratio of one to one may be because the tetrahydropyran molecule cannot act as a bidentate group and form such a bicyclic structure with dinitrogen tetroxide. The fact that neither a stable dinitrogen tetroxide·2(1,4-dioxane) nor a stable ternary compound is formed may be due to the high stability of such a bicyclic structure for the compound $N_2O_4 \cdot$1,4-dioxane. In such a structure there are no bonding orbitals on the nitrogen atoms available for coördinating a second ether molecule.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Equilibrium Constants for the Formation of Complexes between Metal Ions and Amines Containing Sulfur[1,2]

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RECEIVED OCTOBER 13, 1953

The complexes of copper, nickel, cobalt(II) and zinc with methyl 2-aminoethyl sulfide, bis-(2-aminoethyl) sulfide, 1,8-diamino-3,6-dithiaoctane and bis-(2-aminoethyl) disulfide have been studied. Formation constants were calculated for the complexes of nickel and copper with methyl 2-aminoethyl sulfide, those of nickel and cobalt(II) with bis-(2-aminoethyl) sulfide, and those of nickel, copper and cobalt(II) with 1,8-diamino-3,6-dithiaoctane at 30°. Formation constants were also obtained at 0 and 50° for complexes of nickel with each of the ligands for which constants were obtained at 30° and for the complex of cobalt(II) with bis-(2-aminoethyl) sulfide. From the data at different temperatures ΔH and ΔS values were calculated for the reactions involved. In all cases the sulfur-containing amines give less stable complexes than the analogous polyamines containing no sulfur.

Bjerrum[4] has shown that the formation of complexes between metal cations and ammonia or amines is a stepwise process. Further, he has shown how measurements of the hydrogen ion concentrations of solutions containing amines and salts of complex-forming metals may be used to determine the successive formation constants and the composition of the coördinatively saturated complex ion.[5] There are presently available data on ammonia,[4] monoamines,[6] ethylenediamine,[4,5] propylenediamine,[5] diethylenetriamine,[7-9] triethylenetetramine,[8,10] 1,2,3-propanetriamine,[11] tris-(2-aminoethyl)-amine,[12] and N-alkylethylenediamines.[13,14]

This paper reports the results of a study of the formation constants of complexes of copper, nickel, cobalt and zinc ions with methyl 2-aminoethyl sulfide, bis-(2-aminoethyl) sulfide and 1,8-diamino-3,6-dithiaoctane.

Experimental

Bis-(2-aminoethyl) sulfide, bis-(2-aminoethyl) disulfide,[15] methyl 2-aminoethyl sulfide and 1,8-diamino-3,6-dithiaoctane[16] were prepared according to published methods and carefully purified.

The general procedure involved the titration of 100 ml. of solution, 1 M in neutral electrolyte (either KCl or KNO_3) and containing known concentrations of metal salt and mineral acid. The titrant was either pure amine or a standardized aqueous solution of amine. In the case where the amine was in the form of the acid salt, a weighed amount of the salt was placed in the solution to be titrated and a standardized solution of sodium hydroxide was the titrant.

The pH measurements were made with the Beckman Model G pH meter using a glass electrode with a saturated calomel electrode as the reference electrode. A nitrogen atmosphere was maintained over all the solutions titrated and the titrant was protected from atmospheric carbon dioxide by means of a soda lime tube. Measurements were made at 0 ± 0.1°, 30 ± 0.1° and 50 ± 0.1°. The 30 and 50° baths were regulated by means of thermoregulators controlled by mercury switches. The 0° bath was obtained by means of a stirred water–ice mixture.

Aqueous solutions of the acids and metal salts used were prepared and analyzed by means of generally accepted methods. The pH meter was standardized both before and after the titrations against buffer solutions prepared from National Bureau of Standards buffer salts. In the titrations it was found that equilibrium was obtained in most cases as rapidly as the solution could be stirred and the heat of reaction dissipated to the bath. From twenty to forty pH readings were taken in each titration.

The acid dissociation constants of the amines were determined in similar titrations substituting barium ion, a noncoördinating ion, for the coördinating metal ions.

Data and Results

Dissociation Constants of the Amines.—The results are given in Table I.

Complexes of Sulfur-containing Amines.—The measurements of pH and calculation of $\bar{n}$ and A yield the results which are recorded as formation curves in Figs. 1–3. From these curves the formation constants given in Table II were calculated.

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[1] This investigation was carried out under contract N6-onr 26913 between The Pennsylvania State University and The Office of Naval Research.

[2] A portion of a thesis presented by Ely Gonick in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

[3] University of Pittsburgh, Pittsburgh 13, Pennsylvania.

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Table I

Acid Dissociation Constants of Sulfur-containing Amines in 1 *M* KNO_3 Solutions (Solutions Containing HCl Were 1 *M* in KCl)

Barium salt concentration 0.020 *M* except in solutions marked by an asterisk which contain 0.004 *M* barium ion.

Amine		Acid	Salt	0°	30°	50°
$CH_3SCH_2CH_2NH_2$	pK_{AH}	0.07412 *N* HNO_3	1.00 *M* KNO_3	10.43	9.45	8.85
$S(CH_2CH_2NH_2)_2$	pK_{AH_2}	.0295 *N* HNO_3	1.00 *M* KNO_3	9.84	8.84	8.26
	pK_{AH}			10.60	9.64	9.11
$S(CH_2CH_2NH_2)_2$	pK_{AH_2}	.07372 *N* HNO_3	1.00 *M* KNO_3*	9.81	8.84	8.28
	pK_{AH}			10.65	9.64	9.10
$(-CH_2SCH_2CH_2NH_2)_2$	pK_{AH_2}	.1419 *N* HNO_3	1.00 *M* KNO_3		8.89	
	pK_{AH}				9.73	
$(-CH_2SCH_2CH_2NH_2)_2$	pK_{AH_2}	.2286 *N* HCl	1.00 *M* KCl	9.97	9.00	8.45
	pK_{AH}			10.59	9.61	9.07
$(-SCH_2CH_2NH_2)_2$	pK_{AH_2}	.0827 *N* HCl	1.00 *M* KCl*		8.82	
	pK_{AH}				9.58	

For certain combinations of amine and cation it is not possible to determine the formation curve because precipitates form before appreciable coördination takes place in solution. This situation obtains for methyl 2-aminoethyl sulfide with zinc and cobalt(II), for 1,8-diamino-3,6-dithiaoctane with zinc, and for bis-(2-aminoethyl) disulfide with all of the metal ions investigated except barium. No constants were calculated for the complexes of copper and zinc with bis-(2-aminoethyl) sulfide because of irregularities in the formation curves, particularly after $\bar{n} = 1$.

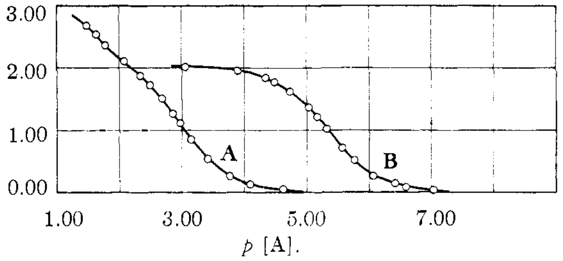

Fig. 1.—Formation curves for complexes of methyl 2-aminoethyl sulfide at 30°: A, Ni; B, Cu.

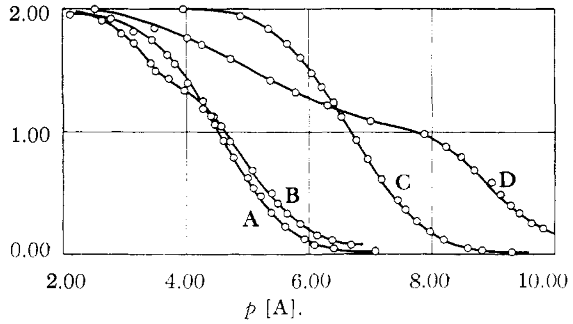

Fig. 2.—Formation curves for complexes of bis-(2-aminoethyl) sulfide at 30°: A, Co(II); B, Zn; C, Ni; D, Cu.

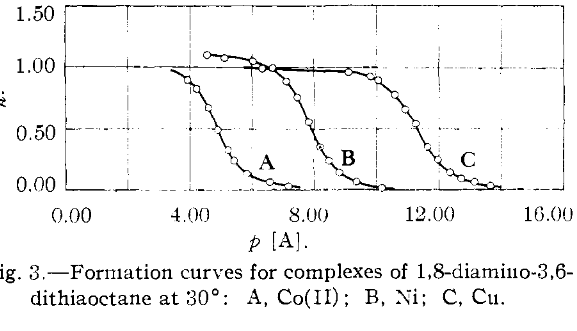

Fig. 3.—Formation curves for complexes of 1,8-diamino-3,6-dithiaoctane at 30°: A, Co(II); B, Ni; C, Cu.

The plots of log K_N *vs.* $1/T$ for the various complexes are shown in Fig. 4. The thermodynamic quantities calculated from these data are presented in Table III. The ΔF values were calculated from the constants determined at 30°. The ΔH values are the average of the values calculated for the intervals 0–30 and 30–50°. The ΔS values were calculated using the ΔF and ΔH values in the tables. The *p*H readings at 0 and 50° were corrected using the formula supplied by the Beckman Instrument Company: any error arising from the use of this formula would be reflected in the ΔH and ΔS values.

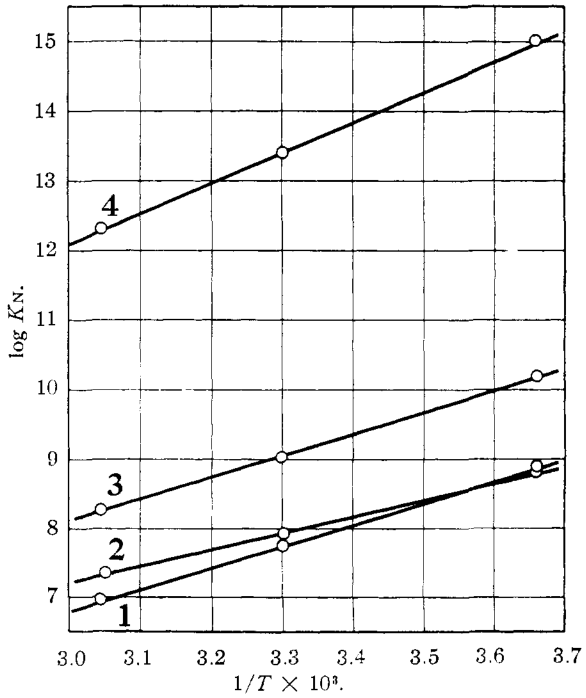

Fig. 4.—Plots of log K_N as a function of the reciprocal of the absolute temperature for the following complexes: 1, 2 and 4 nickel complexes with $CH_3SCH_2CH_2NH_2$, $(-CH_2SCH_2CH_2NH_2)_2$ and $S(CH_2CH_2NH_2)_2$, respectively; 3, cobalt complex with $S(CH_2CH_2NH_2)_2$.

TABLE II

FORMATION CONSTANTS OF VARIOUS COMPLEXES OF SULFUR-CONTAINING AMINES

The formation constants for corresponding polyamines without sulfur are given in parentheses for comparison.

		0°	30°		50°	20°
Ni^{++} with $CH_3SCH_2CH_2NH_2$ and ($H_2NCH_2CH_2NH_2$)[5]	log k_1	3.64	3.23	(7.52)	2.98	
	log k_2	3.26	2.79	(6.28)	2.50	
	log k_3	*2.00*	*1.73*	(*4.26*)	*1.48*	
	log K_n	8.90	7.75	(18.06)	6.96	
Cu^{++} with $CH_3SCH_2CH_2NH_2$ and ($H_2NCH_2CH_2NH_2$)[5]	log k_1		5.58	(10.55)		
	log K_2		*5.10*	(*9.05*)		
	log K_n		10.68	(19.60)		
Co^{++} with $S(CH_2CH_2NH_2)_2$ and ($HN(CH_2CH_2NH_2)_2$)[9]	log k_1	5.56	5.09		4.70	(8.1)
	log k_2	*4.63*	*3.92*		*3.58*	(*6.0*)
	log K_n	10.19	9.01		8.28	(14.1)
Ni^{++} with $S(CH_2CH_2NH_2)_2$ and $HN(CH_2CH_2NH_2)_2)$[9]	log k_1	8.05	7.27		6.81	(10.7)
	log k_2	*6.96*	*6.10*		*5.53*	(*8.25*)
	log K_n	15.01	13.37		12.34	(18.95)
Co^{++} with $(-CH_2SCH_2CH_2NH_2)_2$ and ($(-CH_2NHCH_2CH_2NH_2)_2$)[10]	log k		4.89			(11.0)
Ni^{++} with $(-CH_2SCH_2CH_2NH_2)_2$ and ($(-CH_2NHCH_2CH_2NH_2)_2$)[10]	log k	8.86	7.90		7.38	(14.0)
Cu^{++} with $(-CH_2SCH_2CH_2NH_2)_2$ and ($(-CH_2NHCH_2CH_2NH_2)_2$)[10]	log k		11.32			(20.4)

TABLE III

THERMODYNAMIC QUANTITIES FOR THE STEPWISE FORMATION OF VARIOUS COMPLEXES AT 30°

The values in parentheses are for the complexes of corresponding polyamines without sulfur.

	n value	$-\Delta F$, kcal./mole	$-\Delta H$, kcal./mole	ΔS, cal./degree mole
Ni^{++} with $CH_3SCH_2CH_2NH_2$	1	4.5	5	−3
	2	3.9	6	−8
	3	2.4	4	−7
	Total	10.7	15	−17
Ni^{++} with ($NH_2CH_2CH_2NH_2$)[17] and ($CH_3NHCH_2CH_2NH_2$)[17]	1	(10.1)(9.7)	(8.8)(8.5)	(+4)(+4)
	2	(8.5)(7.5)	(7.5)(8.5)	(+3)(−3)
	3	(5.8)(3.3)	(8.9)(7.1)	(−10)(−13)
	Total	(24.4)(20.5)	(25.2)(24.1)	(−3)(−12)
Ni^{++} with $S(CH_2CH_2NH_2)_2$ and ($NH(CH_2CH_2NH_2)_2$)	1	10.1 (15.0)	10 (12)	0 (+10)
	2	8.4 (11.2)	12 (13)	−11 (− 6)
	Total	18.5 (26.2)	22 (25)	−11 (+ 4)
Ni^{++} with $(-CH_2SC_2H_4NH_2)_2$ and ($(-CH_2NHC_2H_4NH_2)_2$)	1	10.9 (19.8)	12 (13)	− 3 (+23)
Co^{++} with $S(CH_2CH_2NH_2)_2$ and ($NH(CH_2CH_2NH_2)_2$)	1	7.0 (11.8)	7 (9)	0 (+9)
	2	5.4 (8.4)	8 (10)	−9 (−5)
	Total	12.4 (20.2)	15 (19)	−9 (+4)

Discussion

The complete parallel between the values of N (the characteristic coördination number) for $CH_3SCH_2CH_2NH_2$ and $H_2NCH_2CH_2NH_2$, for $S(CH_2CH_2NH_2)_2$ and $HN(CH_2CH_2NH_2)_2$, and for $(-CH_2SCH_2CH_2NH_2)_2$ and $(-CH_2NHCH_2CH_2NH_2)_2$ indicates that the sulfur atom is active in coördination. A comparison of the actual values for the formation constants for each of the pairs listed above shows clearly that coördination through sulfur for the systems studied is not as strong as through nitrogen. This is further indicated by the failure to obtain complexes with the sulfide amines in certain instances, whereas the corresponding imine compounds form readily. The colors of the complexes formed between the various metal ions and the amines containing sulfur as a sulfide linkage are much the same as those formed with amines containing a secondary amino group in place of the sulfur atom.

The constants reported here are considered to be reliable to at least 0.1 log unit as *concentration* constants for the conditions specified. The data obtained at different temperatures were used to calculate the thermodynamic quantities presented in Table III. The ΔF values should be reliable to *ca.* ±0.2 kcal., since the only uncertainty is that in the log K values. The error in the ΔF values would be slightly greater if the values of the concentration constants differ from those of the activity constants to a greater extent than is anticipated. The average error in ΔH is probably of the order of ±2 kcal. The ΔS values are probably valid to within *ca.* ± 7 cal./degree.

The results of McIntyre[17] indicate that the activity constants in general are slightly lower than the concentration constants determined under con-

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[17] G. McIntyre, Jr., Ph.D. Thesis, Pennsylvania State University, 1953.

ditions similar to those used in this study. The slope of the plots of log K *vs.* $1/T$ seem to be slightly greater for the activity constants. If this relationship is assumed to be general, the ΔF values can be interpreted as maximum values and the ΔH values as minimum values. This interpretation of the limits of the ΔH and ΔF values would indicate that the correct ΔS values are probably no more positive than those given in Table III.

There are rather large differences in the thermodynamic quantities reported by various workers[13,14,17] for nickel with ethylenediamine. The conditions used by Hares[18] in this Laboratory are very nearly the same as those used in this investigation and the constants obtained by Hares are in closer agreement with the activity constants obtained by McIntyre[17] than any other values which have been reported. The thermodynamic data of McIntyre are used for comparisons rather than those of Basolo[13] because of the close agreement between the results of Hares and McIntyre and the wide discrepancies between the results of Basolo and McIntyre. Basolo[19] has since reported that the ΔH values obtained by calorimetric measurement are in much closer agreement with those of McIntyre.

The lower ΔF values indicate clearly that the sulfur-containing amines give much less stable complexes than the corresponding polyamines without sulfur. However, the decreased stability is not due entirely to a decrease in bond strength, although the ΔH values are generally lower for the complexes of the sulfur-containing amines. The stability is decreased appreciably by the less favorable entropy changes accompanying the formation of the complexes of the sulfur-containing amines.

The irregularities in the formation curves of zinc and copper with bis-(2-aminoethyl) sulfide are probably due to other equilibria which apparently are not important in the formation of the cobalt and nickel complexes. In the case of zinc there might be an intermediate complex with a ratio of three ligands to two zinc ions, or perhaps the second molecule of amine is not coördinated through all three points of attachment initially. In the adjustment from a tetrahedral to an octahedral arrangement accompanying the change in the coördination number some alteration in the shape of the formation curve might be more likely in the case of the sulfur-containing amines because of the greater variety in the means of attachment of a second molecule of amine to the zinc ion with a tetrahedral configuration. The formation curve for copper might be drawn out because not all of the sulfur and nitrogen atoms are active in coördination and perhaps there is a change in the ratio of the number of copper–nitrogen to copper–sulfur bonds. No formation constants are given for zinc or copper with bis-(2-aminoethyl) sulfide because of the irregularities. More information is needed for an understanding of these cases.

The slope of the formation curve of copper with 1,8-diamino-3,6-dithiaoctane differs from the expected theoretical slope. However, the deviation is slight and the formation constant presented in Table II is probably not appreciably less reliable than the other constants given. The slope of the formation curve of nickel with 1,8-diamino-3,6-dithiaoctane shows no appreciable deviation from the theoretical slope for a one to one complex. However, the curve is somewhat unusual in that it levels off slightly above an $\bar{n}$ value of 1. In each of these cases the slight irregularities are probably due to equilibria of minor importance as compared to the simple addition reaction to form the one to one complex.

PITTSBURGH, PENNA.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

An Investigation of the Low Pressure Photolysis of Acetone by Means of the Mass Spectrometer

BY THOR RUBIN AND ROBERT O. LEACH

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The photolysis of acetone in the wave length region 2800 to 3100 Å. has been studied by means of mass spectrometric technique. The pressure includes those in the range from 5 to 100 μ. Additional steps in the mechanism proposed by Dorfman and Noyes and Herr and Noyes appear to be demanded by the data.

In the photolysis of acetone, the formation of ethane, methane, carbon monoxide and biacetyl as major products has been substantiated by many authors.[1–7] The quantum yields of carbon monoxide and ethane under varying conditions of light intensity and pressure have been studied in great detail.[4–7] However, the direct measurement of the quantum yield for biacetyl has been made infrequently and the measured quantum yield of acetone decomposition has been determined only from the total amounts of the major products.[4]

Indirect estimates of the number of molecules of acetone decomposed per quantum and yield of biacetyl per quantum have been in general based upon the two net reactions[5,7]

$$(CH_3)_2CO \longrightarrow C_2H_6 + CO$$

$$2(CH_3)_2CO \longrightarrow (CH_3CO)_2 + C_2H_6$$

It has been found[5,6] too in the most successful mechanism explaining the results that both a het-

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