$CHNHCH_2CH_2NH_2$. The meaning of the other symbols follows from these examples.

Use of Terms *cis* and *trans*.—For terdentate groups the words *cis* and *trans* are used in the same manner as they are used to designate the isomers of M 3a 3b; *cis* indicates that the three points of attachment of the polyfunctional ligand are on the same face of the octahedron; *trans*, that they are along a plane which passes through the coördination center. For entities with quadridentate groups, *cis* and *trans* refer to the position of the remaining monodentate ligands.

Probability of Realizing Theoretical Possibilities.—Some quadri-, quinque- and sexadentate groups can be postulated (and even prepared) which are not at all likely to coördinate to a common center. Certainly for $C(CH_2NH_2)_4$, only three of the nitrogens can coördinate to a common center; $(H_2NCH_2)_2CHCH(CH_2NH_2)$ probably will coördinate completely; while *cis*-1,2,3,4-cyclobutanetetramine awaits study to determine whether or not it will coördinate completely. Because of such complications, the classes containing the groups A_4 and A_3B are not considered here. If A_4 were of the type of phthalocyanine, no isomerism is possible for either M A_4 2b or M A_4 b c. Other groups which are difficult of realization or whose coördination to a common center may not be possible are A_5, A_4B, A_3B_2, A_3BC, A_2B_2C, A_6, A_5B, A_4B_2, A_4BC, A_3B_3, A_3B_2C, $A_2B_2C_2$ and A_2B_2CD. These have also been omitted.

TABLE III

ISOMERIC CLASSES AND FORMS FOR AN OCTAHEDRAL CONFIGURATION CONTAINING QUINQUEDENTATE GROUPS

Type	Class symbol	Optically active	Optically inactive	Total
10	A_2BC_2 d	..	1	1
	ABCBA d	8	..	8
	$A_2BC(D)$ e	2	..	2
	A_2BCD e	4	..	4
	A(B)CD(E) f	4	..	4
	A(B)CDE f	8	..	8
	ABCDE f	12	..	12
	Total	38	1	39

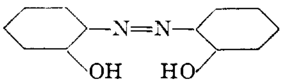
TABLE IV

ISOMERIC CLASSES AND FORMS FOR AN OCTAHEDRAL CONFIGURATION CONTAINING SEXADENTATE GROUPS

Type	Class symbol	Optically active	Optically inactive	Total
11	A_2BBA_2	2	..	2
	ABCCBA[a]	8	..	8
	A(B)CC(B)A	6	..	6
	A_2BCD_2	2	..	2
	$A_2BCD(E)$	4	..	4
	A_2BCDE	4	1	5
	A(B)CDE(F)	8	..	8
	ABCDEF	10	..	10
	Total	44	1	45

[a] An example of this class is being studied by F. P. Dwyer and co-workers, THIS JOURNAL, 69, 2917 (1947); **72**, 1545 (1950); **74**, 4188 (1952).

It seems likely that all groups will not show all the potentialities anticipated for the class to which they belong. Groups may show a preference for certain arrangements because of considerations of steric situations (size, arrangement of atoms, rigidity, etc.). Thus, $H_2NCH_2CH(NH_2)CH_2NH_2$ in contrast to $(H_2NCH_2CH_2)_2NH$ may never be able to coördinate *trans* and



may be sufficiently rigid that it will never coördinate *cis*. The experimental realization of some of the potentialities presented in the tables should not prove too difficult and would contribute greatly to our knowledge of coördination compounds.

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A Polarographic Study of the Zinc Thiocyanate Complexes[1]

BY RICHARD E. FRANK[2] AND DAVID N. HUME

RECEIVED OCTOBER 21, 1952

Although the thiocyanate complexes of cadmium and mercury are well known and have been extensively studied, very little attention has been paid to complex formation between zinc and thiocyanate ions. The existence of such complex ions is suggested by the fact that solids such as $K_2Zn(SCN)_4 \cdot 2H_2O$ have been isolated by Walden.[3] The only published account of an investigation of the ions in solution is the paper by Ferrell, Ridgion and Riley,[4] who obtained potentiometric data which suggested the existence of a $ZnSCN^+$ ion with a formation constant of the order of 50. Some unpublished polarographic measurements by DeFord[5] pointed to the existence of several complexes in solutions between 0.1 and 2.0 *M* thiocyanate ion, but the measurements were, unfortunately, not made at constant ionic strength, and since the shifts in half-wave potential observed were of the same order of magnitude as those sometimes observed due to ionic strength effects alone, no quantitative conclusions could be drawn from them. We have, therefore, measured the half-wave potential of zinc ion in potassium nitrate–potassium thiocyanate mixtures with thiocyanate concentrations ranging from 0.2 to 2.0 *M* at a constant ionic strength of 2.0 *M*.

Experimental

All measurements were made on a Sargent model XXI recording polarograph at a temperature of 30.0 ± 0.1°. The dropping electrode was made of marine barometer tubing and had a value of $m^{2/3}t^{1/6}$ of 1.355 at zero applied volts *vs.* the S.C.E. The working anode and reference potential was a saturated calomel electrode which was connected to the polarograph through a large diameter 2 *M* potassium nitrate agar bridge. All polarograms were started at −0.8 v. and run with a span voltage of 0.4 v. in order to spread out the wave for maximum accuracy of measurement. The initial

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[1] This work was supported in part by the Atomic Energy Commission.

[2] On leave from the University of North Dakota, Grand Forks, North Dakota.

[3] P. Walden, *Z. anorg. Chem.*, **23**, 374 (1900).

[4] E. Ferrell, J. M. Ridgion and H. L. Riley, *J. Chem. Soc.*, 1121 (1936).

[5] D. D. DeFord, M.S. Thesis, University of Kansas, 1947.

and final span voltages were measured to ±0.1 mv. with a Rubicon portable potentiometer. The resistance of the cell system was 143 ohms and the polarograms were recorded with the recorder sensitivity set at 0.04 microampere/mm.

All chemicals were of "analytical reagent" grade. The zinc concentration was 0.001 M and each solution was also 0.0001 M in nitric acid. No maximum suppressor was found necessary; in all probability traces of agar from the salt bridge served in this capacity.

The waves were tested for polarographic reversibility by plotting the quantity log $[i/(i_d - i)]$ against E (corrected for iR drop) at eight or more points along the rising part of the curve. Good straight lines were obtained with slopes between 31.2 and 32.8 mv. per unit log term (average 32.1) and showing no trend in slope with change in thiocyanate concentration.

Half-wave potentials were estimated to the nearest 0.1 mv. using the same technique described in an earlier publication.[6] At least four independent measurements were made on each composition and the average of the concordant values taken. An idea of the precision achieved may be obtained from the eight determinations of the half-wave potential of zinc ion in 2 M potassium nitrate. The mean value was −0.9977 v. with a maximum range of 1.6 mv. and standard deviation of 0.6 mv.

At the same time, an alternative and less laborious method of estimating the half-wave potential was tried. The potential at which the current, corrected for residual current, was equal to one-half of the diffusion current, also corrected for residual current, was very carefully estimated from the polarogram. This, when corrected for iR drop, gave a value each time very close to that obtained by the longer method. Examination of the same eight polarograms of zinc ion in nitrate medium by this method gave again +0.9977 as the average value with a range of 2.1 mv. and a standard deviation of 0.8 mv. When the wave is well spread out by using a small span voltage, as in the present work, it would appear that the shorter method is capable of giving almost as good precision as the more elaborate type of measurement.

Results and Discussion

The resulting data were analyzed mathematically by the method developed by DeFord and Hume[7] and the results are summarized in Table I.

TABLE I

ANALYSIS OF $E^1/_2$ AS A FUNCTION OF THIOCYANATE CONCENTRATION

(SCN⁻), M	$E_{1/2}$, v.	i_d, μa.	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0	−0.9977	6.64	(1.00)	....	..	..	..
.2	1.0066	6.63	1.99	4.95	9.8	..	..
.5	1.0212	6.58	6.12	10.24	14.5	..	..
.8	1.0339	6.58	16.26	19.08	20.1	16.4	19
1.0	1.0430	6.46	33.35	32.35	29.4	22.4	21
1.2	1.0508	6.48	60.4	49.5	38.8	26.5	21
1.5	1.0599	6.51	121.1	80.0	51.4	29.6	19
1.8	1.0693	6.45	252	140	76	38	21
2.0	1.0739	6.44	357	178	88	40	20
				$K_1 = 3$	$K_2 = 7$	$K_3 = 1$	$K_4 = 20$

Figures 1 and 2 show the plots of the F(X) values as a function of thiocyanate concentration. The extrapolated values for the formation constants are $K_1 = 3 \pm 0.5$, $K_2 = 7 \pm 3$, $K_3 = 1 \pm 1$ and $K_4 = 20 \pm 2$. The observed shifts in half-wave potential are small enough to create appreciable uncertainty in the numerical values of the formation constants, as indicated above, but the magnitudes of the values must certainly be correct. It seems clear that no complexes higher than $Zn(SCN)_4^{=}$ are formed in solutions up to 2.0 M in thiocyanate. The zinc complexes, as might be expected from a comparison of other zinc and cadmium complex systems, are much less stable than the corresponding cadmium complexes. It is striking, however,

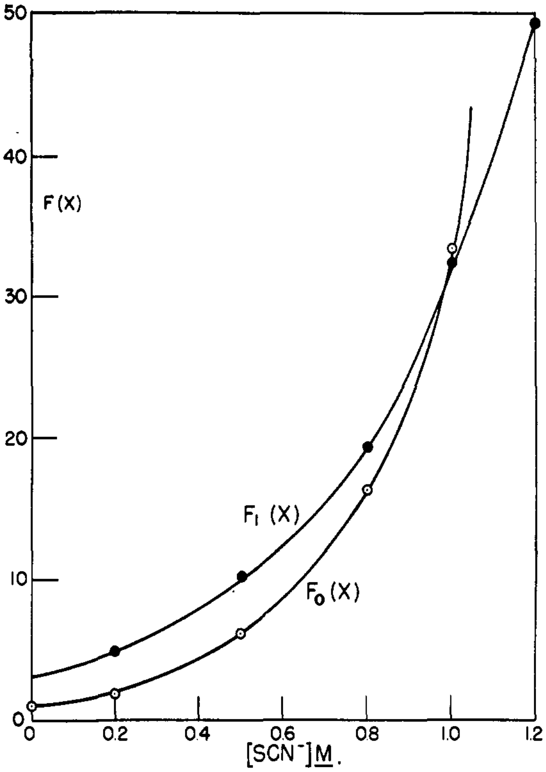

Fig. 1.—Plot of $F_0(X)$ and $F_1(X)$ and a function of thiocyanate concentration.

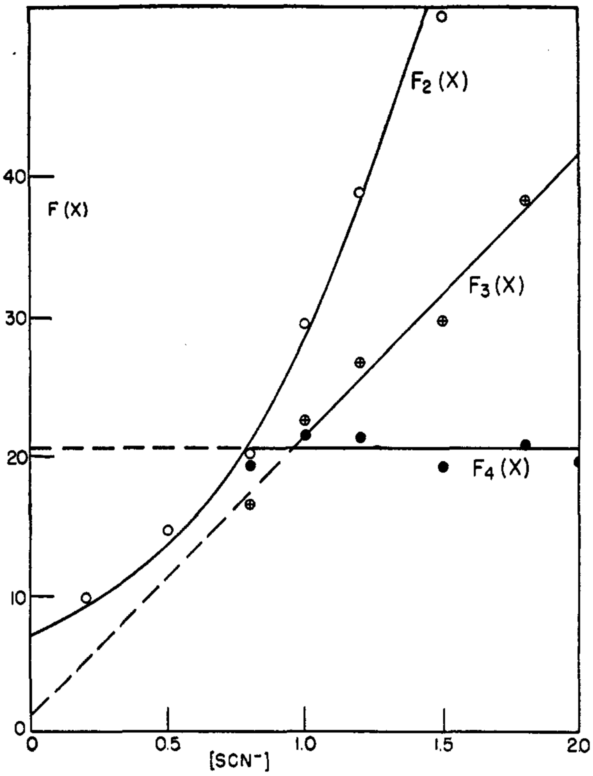

Fig. 2.—Plot of $F_2(X)$, $F_3(X)$ and $F_4(X)$ as a function of thiocyanate concentration.

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[6] D. N. Hume, D. D. DeFord and G. C. B. Cave, THIS JOURNAL, 73, 5323 (1951).

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

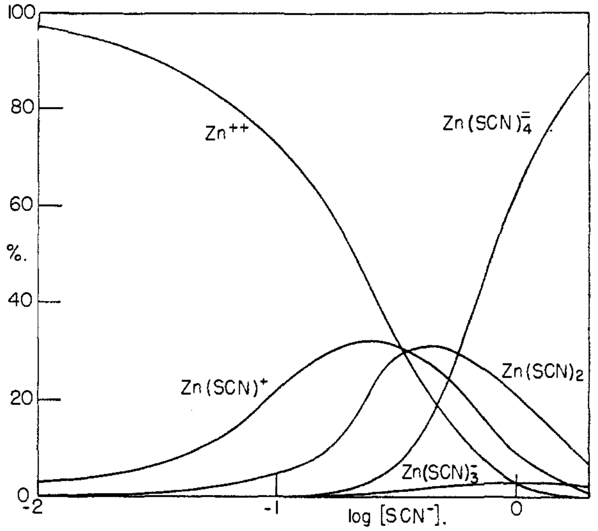

Fig. 3.—Percentage distribution of zinc in various forms as a function of free thiocyanate concentration.

that the relative stabilities of the ions in each series are very similar. The distribution of zinc among the several species as a function of equilibrium thiocyanate ion concentration shown in Fig. 3 is almost identical with the corresponding distribution for cadmium except that the whole family of curves has been displaced toward higher thiocyanate concentrations.

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Synthesis of Isoquinolines by the Use of Acetamidomalonic Ester

By Alexander Galat

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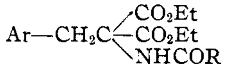
Compounds of the formula



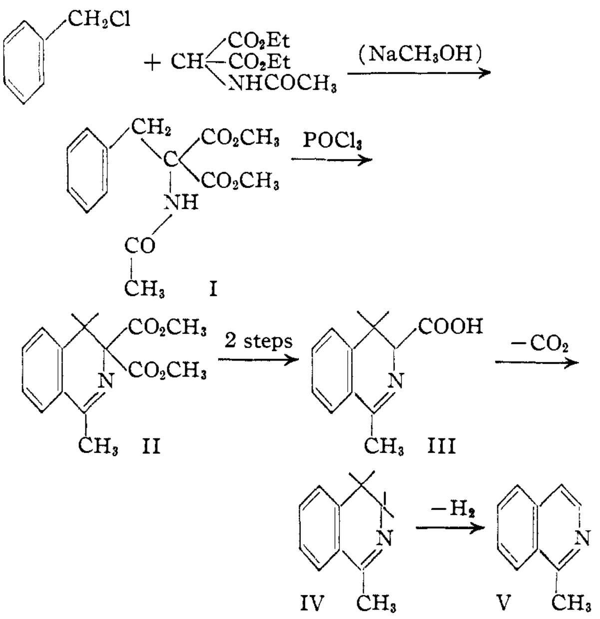
$$\text{Ar—CH}_2\text{C}\begin{cases}\text{CO}_2\text{Et}\\ \text{CO}_2\text{Et}\\ \text{NHCOR}\end{cases}$$

Ar: phenyl, indolyl, naphthyl
R: H, CH_3, phenyl

obtained by the condensation of the appropriate halides or Mannich bases with acylamidomalonic esters, have been used as intermediates in the synthesis of amino acids.[1] Since these compounds are readily accessible, it seemed of interest to investigate their behavior under the conditions of the Bischler–Napieralski reaction.

Methyl 2-acetamido-2-carbomethoxy-3-phenylpropionate (I), obtained by the condensation of benzyl chloride with ethyl acetamidomalonate in methanol, was used as a model substance in this study. It was readily cyclized with phosphorus oxychloride to the dihydroisoquinoline II which was degraded to 1-methylisoquinoline

This synthesis provides a route to a new group of isoquinoline derivatives (compound II) which would be difficult to prepare by any other method, as well as a simple method for the preparation of



some of the known compounds. Since substituted benzyl chlorides are readily available, this synthesis should prove of interest for the preparation of a large variety of isoquinolines.

Experimental

Methyl 2-acetamido-2-carbomethoxy-3-phenylpropionate (I) was prepared from benzyl chloride and commercial ethyl acetamidomalonate by the method of Albertson and Archer[1] except that the reaction was run in methanol.[2] The yield was 85%, m.p. 164–165°.

Anal. Calcd. for $C_{14}H_{17}O_5N$: N, 5.02. Found: N, 5.17.

1-Methyl-3,3'-dicarbomethoxy-3,4-dihydroisoquinoline (II).—Ten grams of I was dissolved in 40 ml. of phosphorus oxychloride and heated under reflux until the evolution of hydrogen chloride ceased (1–1.5 hours). The excess phosphorus oxychloride was removed *in vacuo* in a water-bath and the residue was treated with 100 ml. of cold water. The resulting mixture was stirred with charcoal, filtered and made alkaline with sodium carbonate. The product separated as an oil which soon solidified. The water-washed and air-dried product weighed 6.5 g. (70.5%). It was purified by dissolving in dilute hydrochloric acid, treating with charcoal and precipitating with ammonium hydroxide. It was finally recrystallized from methanol to give an analytically pure material, m.p. 94°.

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 64.4; H, 5.75; N, 5.37. Found: C, 64.8; H, 5.65; N, 5.50.

1-Methyl-3-carboxy-3,4-dihydroisoquinoline (III).—One gram of II was suspended in 10 ml. of boiling water and the mixture treated dropwise with 20% sodium hydroxide until the product went into solution and the alkaline reaction persisted. The hot solution was acidified with hydrochloric acid and kept in a bath of boiling water until the evolution of carbon dioxide ceased. The crystalline product which separated on cooling was filtered, washed with water and purified by recrystallization from water. There was obtained 0.65 g. of a product which melted at 160–165° with evolution of carbon dioxide and water. Analytical figures showed it to be a monohydrate.

Anal. Calcd. for $C_{11}H_{11}O_2N \cdot H_2O$: C, 63.8; H, 6.29; N, 6.77. Found: C, 64.1; H, 6.20; N, 6.90.

1-Methyl-3,4-dihydroisoquinoline (IV).—One-half gram of III was heated in a flask suspended in an oil-bath at 170–180° in an atmosphere of carbon dioxide. When the evolution of gas ceased, there remained a light-colored oil of floral odor. It was dissolved in methanol and treated with

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[1] C. E. Redeman and M. C. Dunn, *J. Biol. Chem.*, **130**, 341 (1939); N. F. Albertson and S. Archer, This Journal, **67**, 308 (1945); E. E. Howe, A. J. Zambito, H. R. Snyder and M. Tishler, *ibid.*, **67**, 38 (1945); A. Galat, *ibid.*, **69**, 965 (1947).

[2] A previous study of similar types of compounds (A. Galat, *ibid.*, **73**, 3654 (1951)) showed that methyl esters give higher yields and purer products on cyclization with phosphorus oxychloride.