determined by the resistance thermometer, *viz.*, the freezing points of pure thiophene and of a 50–50 mixture of thiophene and benzene. Undercooling was observed in all cases and the curves except for the pure compounds were concave downward. The pure compounds froze into rigid masses adhering to the walls of the freezing tube, while their mixtures always froze into a soft, mushy slurry. As previously observed,[25] these data show the existence of solid solutions; no eutectic was observed, the addition of benzene always raising the freezing point of thiophene even at concentrations of about 1 mole per cent. The freezing point data are given in Table IV and Fig. 3.

Acknowledgment.—The authors wish to express their appreciation for the assistance given by Mr. David Christison of this Laboratory who worked out the procedure for and ran the mass spectrometer analyses.

Summary

1. A sample of thiophene large enough to assure good working quantities has been purified by distillation and crystallization to give a product which froze at a temperature constant to 0.01°.

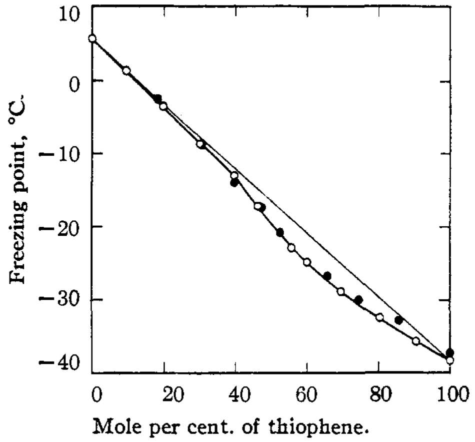

Fig. 3.—Freezing point-composition diagram for thiophene-benzene: O, this investigation; ●, literature data (25b).

2. The following properties have been determined for the purified sample: f. p., b. p. over the range 500–900 mm., n_D, d_4 and η at 20, 25 and 30°, specific dispersion at 20° and some derived constants.

3. For the system thiophene–benzene the following properties have been determined as a function of composition: $n^{20}{}_D$, $d^{20}{}_4$, η_{20} and f. p.

PAULSBORO, NEW JERSEY RECEIVED JUNE 25, 1945

[25] (a) Beckmann, *Z. physik. Chem.*, **22**, 609 (1897); (b) Tsakalotos and Guye, *J. chim. phys.*, **8**, 340–357 (1910); *B. C. A.*, **98**, II, 826 (1910).

[CONTRIBUTION FROM RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Polyethyleneammonium Chlorocuproates[1]

BY HANS B. JONASSEN,[2] THOMAS B. CRUMPLER AND THOMAS D. O'BRIEN

Grossman and Schueck[3] have previously reported the preparation of the chlorocuproate of ethylenediamine ("en"). This paper reports the repetition of the preparation of this substance and also the attempt to prepare and study the corresponding chlorocuproates of diethylenetriamine ("dien"), triethylenetetramine ("trien"), and tetraethylenepentamine ("tetren").

Experimental

Materials.—The tetraethylenepentamine was generously provided by the Carbide and Carbon Chemicals Corporation. The other polyethyleneamines were obtained from the Eastman Kodak Company. The ethylenediamine in 60% aqueous solution was used without further treatment. The others were refluxed for several hours over metallic sodium and were then distilled *in vacuo* over sodium. The fractions collected had the boiling ranges: dien, 78–79° at 3 mm.; trien, 128–131° at 3 mm.; and tetren, 152–154° at 1 mm.

Procedure.—One-tenth mole of cupric chloride ($CuCl_2 \cdot 2H_2O$) was dissolved at room temperature in about 50 ml. of absolute methanol and the amine was added in small portions until 0.1 mole had been added or until a thick paste was produced. The reaction mixture was cooled in an ice-bath before being filtered by suction, following which the precipitate was washed with absolute methanol until the washings were colorless. The precipitate, which contained yellow, green, and blue particles, was washed at room temperature first with a few small portions of acetone and then with ether and finally dried for about three minutes at 100°.

The dry solid was mixed with sufficient concentrated hydrochloric acid to convert it to a homogeneous yellow residue and then a few milliliters in excess was added. The yellow residue was filtered by suction and washed with ethyl alcohol until the washings were free of acid. This residue was dissolved in the minimum volume of water at room temperature and upon addition of an equal volume of concentrated hydrochloric acid a distinctly crystalline, yellow precipitate formed. At least four such reprecipitations were effected in each instance. The physical properties, freezing-point depressions, and analyses of these compounds are given in Table I.

Discussion

In color these compounds resemble the solid chlorocuproate salts of various monoamines reported previously[4] and of ethylenediamine.[3] To

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[1] Based on M.S. thesis of H. B. Jonassen, 1944.

[2] Present address: Graduate School, University of Illinois.

[3] H. Grossman and B. Schueck, *Z. anorg. Chem.*, **50**, 1 (1906).

[4] H. Topsoe, *Dansk. Videns.*, 17 (1882); W. M. Dehn, THIS JOURNAL, **48**, 275 (1926); Y. Michaelenko, *J. Russ. Phys.-Chem. Soc.*, **61**, 2253 (1929); H. Remy and G. Laves, *Ber.*, **66B**, 401 (1933);, J. Amiel, *Compt. rend.*, **201**, 964 (1935); **201**, 1383 (1935).

TABLE I

Chlorocuproate	Yellow color	Time pptn., min.[a]	Crystal habit[a]	Extin.	Biref[b]	Mol. wt.[c] Calcd.	Mol. wt.[c] Found
En	Brownish y.	0	Plates	Incl.	+	267.5	270
Dien	Yellow	5	Laths	Para	++	...	...
Trien	Light y.	15	Rect. pl.	Para	+	426.6	430
Tetren	Pale y.	30	Clusters	...	++	...	...

Formula	Analyses,[d] % HCl Calcd.	HCl Found	Cl Calcd.	Cl Found	Cu Calcd.	Cu Found	N Calcd.	N Found
$(En{\cdot}H_2)CuCl_4$	27.27	...	53.01	52.95	23.76	23.70	10.47	10.47
$(Dien{\cdot}H_3)CuCl_5$	31.52	31.49	51.08	51.00	18.31	18.29	12.10	12.10
$(Trien{\cdot}H_4)CuCl_6$	34.19	34.17	49.87	49.83	14.90	14.77	13.13	13.06
....	36.02	33.3	49.04	47.5	12.56	10.9	13.80	16.2

[a] The crystalline characterizations were determined by placing a drop of saturated solution of the chlorocuproate on a microscope slide and adding a drop of concentrated hydrochloric acid. Crystallization rates and crystal forms were observed under a polarizing microscope. [b] ++ = high; + = moderate. [c] The molecular weights were determined by the freezing point method. Calculated values are based on the assumption of the dissociation of the en compound into 6 and the trien compound into 8 ions in the 0.093 molal solutions employed. [d] The hydrochloric acid was determined by electrometric titration with standard sodium hydroxide using a glass electrode. It was observed that the chloride precipitated completely as silver chloride without boiling. Copper was determined by iodometric titration, nitrogen by the micro Dumas method.

TABLE II

Amine	1	2	3
Ethylenediamine	$(En{\cdot}H_2)_4Cu_4Cl_{16}$; 8Cl bridges	$(En{\cdot}H_2)CuCl_4$	$(En{\cdot}H_2)CuCl_4$
Diethylenetriamine	$(Dien{\cdot}H_3)_2Cu_2Cl_{10}$; 2Cl bridges	$(Dien{\cdot}H_2{\cdot}HCl)CuCl_4$	$(Dien{\cdot}H_3)CuCl_5$
Triethylenetetramine	$(Trien{\cdot}H_4)CuCl_6$; no Cl bridges	$(Trien{\cdot}H_2{\cdot}2HCl)CuCl_4$	$(Trien{\cdot}H_4)CuCl_6$
Tetraethylenepentamine	No reasonable empirical formula obtainable from analysis.		

all these previously reported compounds, the various authors assigned structures involving only mononuclear tri-, tetra- and pentachlorocuproate complex ions.

The data obtained in several studies of absorption spectra of solutions of copper chloride with varying chloride-ion concentrations[5] indicate that $CuCl^+$, $CuCl_3^-$, and $CuCl_4^=$ are present in such solutions and that the tri- and tetrachloro ions are yellow.

In 1937 Dubsky and Wagenhofer[6] postulated a uniform coördination number of six for the central copper ion in all chlorocuproate complexes wherein the copper ions are linked by chloride bridges. They prepared several chlorocuproates of aromatic amines to which they assigned polynuclear structures with a coördination number of six for the central copper ions.

In 1938 Amiel[7] reported that the magnetic properties of several substituted ammonium chlorocuproates were the same as for the hydrated cupric ion both in solution and in the solid state. It was observed that the chlorocuproates reported herein gave aqueous solutions which were pale blue and which matched cupric chloride solutions of equivalent concentration both in hue and in intensity. This fact, coupled with the observed freezing point data and the additional fact that the total chloride ion content was precipitated as silver chloride immediately without the necessity of boiling, indicates that these complexes are completely dissociated in aqueous solution. It would appear also that they would be completely dissociated only if the chlorocuproate ions were held together in the solid state by simple electrostatic attraction. The above data and the assumptions based upon them seem to accord with the findings of Amiel.

The analytical data permit the assignment of at least four types of structures. The three most worthy of consideration are given in Table II.

It could hardly be agreed that the polyethyleneamines are directly coördinated with the copper because (1) a blue color would be expected, and (2) such a compound could hardly be expected to dissociate completely in aqueous solution.

The postulate of Dubsky and Wagenhofer[6] would require the structures given in column 1 of Table II. It would appear that such polynuclear ions with chloride bridges would require bonding that is predominantly covalent. The arguments against these structures with chloride bridges are (1) the previously adduced conclusion that the compounds are completely dissociated in solution, and (2) the difficulty in believing that cupric ions bound together by chloride bridges could have the same magnetic susceptibility as "free" cupric ions.

The structures given in column 2 of Table II result from the assumption of a constant coördination number of four. The arguments against these structures for the diethylenetriamine and triethylenetetramine compounds are: (1) the gradation in color is difficult to explain because the hydrochlorides of all the polyethyleneamines are colorless, and (2) the tetraethylenepentamine

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[5] F. H. Getman, *J. Phys. Chem.*, **26**, 217 (1922); G. Spacu and I. G. Murgulescu, *Z. physik. Chem.*, **A170**, 70 (1934); A. K. Babko, *Univ. état de Kiev. Bull. Sci., Recueil. chim.*, **4**, 81 (1939); W. V. Bhagwat, *J. Indian Chem. Soc., Ind. and News Ed.*, **17**, 53 (1940); T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944).

[6] J. V. Dubsky and E. Wagenhofer, *Z. anorg. allgem. Chem.*, **230**, 112 (1937).

[7] J. Amiel, *Compt. rend.*, **206**, 1113 (1938).

complex having the formula (tetren·H_2·3HCl)Cu-Cl_4 should have been formed with equal ease.

Consequently the structures given in column 3 of Table II are tentatively assigned.

Further investigation of the properties of these crystalline compounds by both X-ray and microscopic methods is under way.

Acknowledgment.—The generous assistance of Mr. Merril E. Jefferson, Physicist at the Southern Regional Research Laboratory, New Orleans, in the microscopic investigation is gratefully acknowledged.

Summary

This paper reports the repetition of the preparation of (1) ethylenediammonium tetrachlorocuproate, and the preparation of (2) diethylenetriammonium pentachlorocuproate, and (3) triethylenetetrammonium hexachlorocuproate.

These compounds appear to be completely dissociated in aqueous solution.

Tentative structures have been assigned in which coördination numbers for the copper of four, five and six, respectively, are assumed.

NEW ORLEANS, LA. RECEIVED APRIL 23, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY, MEAD JOHNSON AND CO.]

Pyrazine Chemistry. I. Derivatives of 3-Aminopyrazinoic Acid

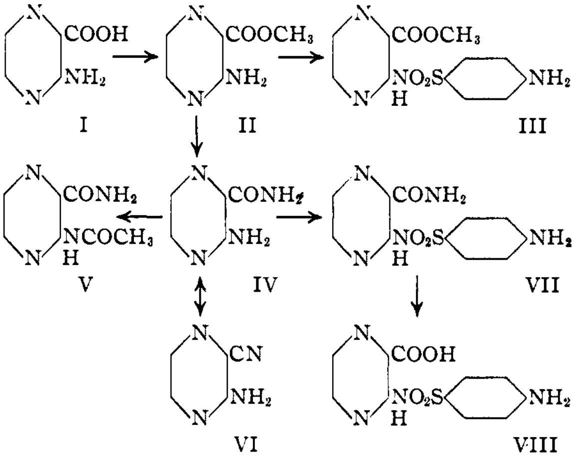
BY RUDOLPH C. ELLINGSON, ROBERT L. HENRY AND FRANCIS G. MCDONALD

The chemical literature describes relatively few derivatives of the simple heterocyclic ring, pyrazine. This may be due to the unsatisfactory methods available for making pyrazine compounds. The observation that lumazines can be hydrolyzed by alkali[1,2] provides a satisfactory method for preparing aminopyrazine-carboxylic acids. The availability of aminopyrazine-carboxylic acids from the alkaline hydrolysis of lumazines makes possible the synthesis of several aminopyrazine derivatives with substituents other than alkyl and aryl groups. These substituents are halogen atoms, amino, cyano, hydroxy, carbamyl and carboxy groups.

In addition to making and studying simple pyrazine derivatives, our object has been to use them in the synthesis of substituted sulfapyrazines. The substituted sulfapyrazines that have been reported have only alkyl[1,3] and aryl[1] groups in the pyrazine ring.

We have included in this paper only those derivatives which are readily obtained from 3-aminopyrazinoic acid.[1,4] Some of these new aminopyrazine derivatives have been converted to the corresponding sulfonamides. The chart shows the routes by which these compounds were made.

Attempts to prepare 3-sulfanilamidopyrazinoic acid (VIII) by condensation of 3-aminopyrazinoic acid (I) with acetylsulfanilyl chloride followed by deacetylation were unsuccessful. The reaction gave tars and a small quantity of a brick-red powder which we were unable to purify. This result was unexpected because the pyridine analog, 2-aminonicotinic acid,[5] has been reported to condense satisfactorily.



In the condensation of 3-aminopyrazinamide (IV) with acetylsulfanilyl chloride we have assumed that the acetylsulfanilyl radical becomes attached to the amino nitrogen and not to the amido nitrogen. Since sulfonamide VII, thus obtained, can be hydrolyzed to compound VIII and this in turn decarboxylated to 2-sulfanilamidopyrazine,[6] this assumption would seem to be correct.

Attempts to degrade 3-aminopyrazinamide (IV) to 2,3-diaminopyrazine by the Hofmann reaction were unsuccessful. When the same reaction was tried on the acetyl derivative (V), two unexpected compounds were obtained. One melts with decomposition in a sealed tube at about 335–338°. The other does not melt up to 350° although it begins to darken at 260°. These two compounds will be given further consideration in a later paper.

To obtain 3-aminopyrazinenitrile (VI) compound IV was dehydrated in pyridine by means of phosphorus pentoxide. To prove that com-

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[1] Weijlard, Tishler and Erickson, THIS JOURNAL, **67**, 802 (1945).

[2] In 1942 Weijlard, *et al.*, privately informed us that they had produced pyrazine derivatives by the hydrolysis of lumazine with concentrated sulfuric acid. It occurred to us, and apparently also to Weijlard, *et al.*, that similar cleavages might be effected by alkali.

[3] Joiner and Spoerri, THIS JOURNAL, **63**, 1929 (1941).

[4] Gabriel and Sonn, *Ber.*, **40**, 4850 (1907).

[5] May and Baker Co., (J. A. Ewins and M. A. Philips), British patent 516,288.

[6] (a) Ellingson, THIS JOURNAL, **63**, 2524 (1941); (b) **Raiziss**, Clemence and Freifelder, *ibid.*, **63**, 2739 (1941); (c) Sausville and Spoerri, *ibid.*, **63**, 3153 (1941).