Anal. Calcd. for $C_{11}H_{10}O_2Ru$: C, 47.88; H, 3.65; O, 11.60; Ru, 36.86. Found: C, 48.21; H, 3.89; O, 11.21; Ru, 37.0.

In a similar experiment in which ruthenocene was replaced with an equimolar quantity of ferrocene, the yields of ferrocenemonocarboxylic acid and ferrocene-1,1'-dicarboxylic acid were 24 and 9%, respectively.

A methyl ester was prepared readily from a solution of the mono-acid in methanol containing a trace of sulfuric acid. Recrystallization from methanol and water gave monocarbomethoxyruthenocene as white leaflets, m.p. 107–107.5°.

Anal. Calcd. for $C_{12}H_{12}O_2Ru$: C, 49.71; H, 4.18. Found: C, 49.64; H, 4.31.

Ruthenocenedicarboxylic acid (XVI) was best prepared by the procedure described by Mayo, *et al.*,[26] for the synthesis of ferrocene-1,1'-dicarboxylic acid. A cold solution of 100 ml. of diethyl ether containing 0.090 mole of *n*-butyllithium was added rapidly under nitrogen to a suspension of 3.48 g. (0.015 mole) of ruthenocene in 100 ml. of tetrahydrofuran maintained at −50°. After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature over about a 1 hr. period, during which time all the ruthenocene dissolved. The reaction mixture was stirred for an additional 17 hr. at room temperature, then cooled, carbonated and hydrolyzed. After Soxhlet extraction of the crude acid (4.175 g.), evaporation of the ether extracts and recrystallization of the residue gave 0.035 g. (1% yield) of ruthenocenemonocarboxylic acid, m.p. 235–238° dec. The insoluble residue was recrystallized from glacial acetic acid, yielding 4.102 g. (86% yield) of yellow crystals of ruthenocenedicarboxylic acid, which melted with much decomp. at approximately 325°, with slight charring from 300°; neut. equiv. calcd.. 159.9; neut. equiv. found, 161.3.

Anal. Calcd. for $C_{12}H_{10}O_4Ru$: C, 45.05; H, 3.15; O, 20.01; Ru, 31.79. Found: C, 44.97; H, 3.38; O, 20.50; Ru, 31.70.

In a similar experiment in which ruthenocene was replaced with an equimolar quantity of ferrocene, the yields of ferrocenemonocarboxylic acid and ferrocene-1,1'-dicarboxylic acid were 35 and 39%, respectively.

The preparation of osmocene acids was made in an analogous manner from 0.700 g. (0.00218 mole) of osmocene and 0.0131 mole of *n*-butyllithium in diethyl ether–tetrahydrofuran 1:1. The crude osmocene acids were vacuum sublimed at 220°, producing a white crystalline sublimate (0.600 g.) and leaving an appreciable dark residue. The sublimate began to decompose slowly at 245° and decomp. was complete at 333°.

Anal. Calcd. for $C_{11}H_{10}OsO_2$: C, 36.25; H, 2.77; Os, 52.20; O, 8.78. Calcd. for $C_{12}H_{10}OsO_4$: C, 35.28; H, 2.47; Os, 46.57; O, 15.67. Found: C, 35.32; H, 2.94; Os, 48.75; O, 12.90.

On this basis, the sublimate consisted of approximately 42 mole % osmocenemonocarboxylic acid and 58 mole % osmocenedicarboxylic acid. It is quite possible that partial decarboxylation occurred during the sublimation at 220°, since later tests with the sublimate indicated that some decomposition began to occur at this temperature.

Phenylation of ruthenocene was made according to procedures reported for the facile arylation of ferrocene.[11,14] In general, experiments involving the use of acetone or glacial acetic acid as the solvent were less successful, due to the marked decrease in solubility of ruthenocene in these solvents compared to ferrocene.

In an experiment in which 0.0034 mole of ruthenocene in diethyl ether solution was treated for 17 hr. with a 12 molar excess of benzenediazonium chloride, chromatography of the reaction product on an alumina column (eluting with benzene–ether mixtures) produced considerable unreacted ruthenocene and developed several orange-yellow bands. Selective elution of these bands resulted in only traces of products, although one band gave 0.067 g. of an orange solid, m.p. 203–205°. An infrared spectrum of this material exhibited 3 bands in the carbon–hydrogen stretching region (3012, 2899 and 2841 cm.$^{-1}$), bands at 1733, 1595 and 687 cm.$^{-1}$ attributable to a phenyl group, a very strong band at 827 cm.$^{-1}$ attributable to ruthenocene (carbon–hydrogen bending vibration), as well as ruthenocene bands at 1002 and near 1100 cm.$^{-1}$, which would indicate the presence of an unsubstituted cyclopentadienyl ring.

Acknowledgments.—The authors wish to thank Dr. H. P. Fritz for aid in interpretation of the infrared spectra and Mr. W. Semmlinger for determination of the dissociation constants of the carboxylic acids. We also wish to express our appreciation to Baker and Co., Inc., Newark, N. J., for a gift of ruthenium chloride which made possible a portion of this investigation. M. D. R. is indebted to the National Science Foundation for a post-doctoral fellowship for the year 1957–1958.

MUNICH, WEST GERMANY

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY AND LABORATORIO DE FÍSICA NUCLEAR UNIVERSIDAD DE CHILE]

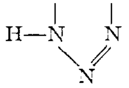
Metal Tetrazole Complexes: Bis-(5-aminotetrazolato)-copper(II)

BY CARL H. BRUBAKER, JR.[1]

RECEIVED JUNE 5, 1959

Two crystalline forms of bis-(5-aminotetrazolato)-copper(II) have been prepared and characterized. Visible and ultraviolet spectra of aqueous copper(II)-5-aminotetrazole solution have been examined. Continuous variation experiments reveal 1:2 interactions and a formation constant for the complex in solution has been determined and is about 10^{12}. Infrared studies suggest coördination involves the ring and not the 5-amino group. Acids decompose the complexes and bring about rupture of the tetrazole ring, while decomposition by ammonia does not affect the ring.

Since tetrazole and a variety of substituted tetrazoles are available at Michigan State University,[2] it appeared to be worthwhile to examine the possible coördination of several, especially tetrazole and some 5-substituted tetrazoles, with metallic ions. One can envision a number of possible ways in which the class of compounds



might engage in coördination and in inner complex formation, if the acidic 1-H were replaced by a metal–nitrogen bond.

Preliminary experiments revealed interactions between copper(II), nickel(II) and platinum(II) and tetrazole. 5-Aminotetrazole was more plenti-

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[2] R. M. Herbst, Department of Chemistry.

ful at the start of this work, so a detailed study of the copper(II)–5-aminotetrazole interaction was undertaken.

Wilson and co-workers[3] have prepared various group VIII metal complexes with 1,2,3-benzotriazole and Popov[4] has investigated complexing of pentamethylenetetrazole with halogens, polyhalides and with silver ion.

Experimental

Tetrazole and 5-aminotetrazole (anhydrous and monohydrate) were obtained from R. M. Herbst and since the elementary analyses supplied indicated high purity, only titration with standard NaOH was used as a check of purity These titrations indicated 99.95% purity for CH_2N_4, 100.0% for CH_3N_5 and 100.7% for $CH_3N_5 \cdot H_2O$. Solutions were prepared by dissolving weighed amounts of the compounds in water to make solutions of the desired molarities.

J. T. Baker "Analyzed" $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were employed at Michigan State and Merck (Germany) $CuSO_4 \cdot 5H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ at the Universidad de Chile. $Cu(ClO_4)_2$ solutions were prepared by dissolving copper oxide in a slight excess of perchloric acid.

Copper determinations in solutions and in solid compounds were done either colorimetrically or polarographically in 2 N NH_3 + 2 N NH_4Cl against copper standards, prepared by dissolving weighed quantities Mallinckrodt or Merck CuO in a minimum quantity of nitric acid, boiling to remove nitrogen oxides and diluting to volume. Solid copper compounds were similarly decomposed in nitric acid before copper determinations were made.

Determination of C, H, N in the copper complexes were provided by commercial analytical houses and by Samuel Trumper, Escuela de Medicina, Universidad de Chile.

Spectrophotometric examinations were made by use of Beckman model DK-2 model DU and Hilger, "Uvispec" (Courtesy, Facultad de Química y Farmacia, Universidad de Chile) spectrophotometers. All quantitative data reported were taken with the DU and "Uvispec" instruments.

Infrared spectra were obtained with mulls in mineral oil, hexachlorobutadiene and perfluorokerosene by use of a Perkin–Elmer model 21 instrument.

$Cu(CH_2N_5)_2$ (Light Green).—Aqueous solutions of $CuSO_4$ and CH_3N_5 or $NaCH_2N_5$ are mixed in any proportion and a light green material separates which cannot be washed free of small amounts of sulfate without its being converted to a blue material.

$Cu(NO_3)_2$ and CH_3N_5 solutions mixed in a $^1/_2$ proportion give a green solution and after being heated at 95° for one hour a pale green material, which cannot be washed free of nitrate, separates. X-Ray powder patterns are identical with those for the green compound prepared from $CuSO_4$.

$CuCl_2$ and CH_3N_5 solutions in water or 95% ethanol give the same pale green material (by X-ray comparison). The green substances were washed several times by centrifuging, dried to constant weight *in vacuo* and stored over barium oxide. Heating to 75–100° causes decomposition and evolution of HCN and an amorphous solid of indefinite composition results. The compound decomposes more vigorously, when heated more strongly.

Anal. Calcd. for 89.0% $Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$ + 11.0% $CuSO_4$: Cu, 26.9; C, 8.96; N, 51.7; H, 1.85. Found: Cu, 27.0; C, 9.13; N, 51.8; H, 1.84. Calcd. for 87.8% $Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$ + 12.2% $Cu(NO_3)_2 \cdot 3H_2O$: Cu, 26.3; N, 51.0. Found: Cu, 25.8; N, 51.0.

The analyses indicate a composition of slightly less than two $CH_2N_5^-$ per copper (1.75 and 1.80 for the sulfate and nitrate preparations, respectively), but since the samples contained small amounts of sulfate or nitrate, it is likely that the copper determinations are high due to the presence of occluded copper nitrate or sulfate. Analyses of other similar preparations all indicated impurities of copper nitrate or sulfate of 10 to 15%.

$Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$.—A crystalline hemihydrate of bis-(5-aminotetrazolato)-copper(II) is formed when solutions of $Cu(NO_3)_2$ or $Cu(ClO_4)_2$ or supernatant liquids from the preparation of the light green material are allowed to stand at room temperature for ten days to two weeks. A bright blue material forms slowly and after about three weeks no trace of copper remains in the supernate, if a slight excess of CH_3N_5 or $NaCH_2N_5$ is used. The blue material seems to contain one to two waters per copper, but when pumped *in vacuo* until constant weight is reached or when dried over barium oxide, it becomes dark green and analyses indicate a hemihydrate.

Anal. Calcd. for $Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$: Cu, 26.3; N, 58.1; C, 9.96; H, 2.08. Found: Cu, 26.6; N, 58.2; C, 10.9; H, 2.54.

This material gives the same X-ray powder pattern and copper analysis (26.0–26.6%) regardless of the nature of the copper salt used and there are no detectable traces of NO_3^- or $SO_4^=$ in the preparations from $Cu(NO_3)_2$ or $CuSO_4$.

If this dark green material is heated for several days at 100° decomposition occurs and a dark crystalline product (with a different powder pattern) results, which contains 27.5 to 28.8% copper. When the dark green hemihydrate is heated strongly it decomposes with a pop.

If the light green material is digested with water on a steam-bath or washed repeatedly to remove traces of $SO_4^=$, Cl^- or NO_3^-, it gradually turns blue and eventually, after drying, gives the X-ray pattern of the $Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$, but copper content is high. Since no traces of foreign anions remain, some hydrolysis is indicated (Cu, 27.0–31.6%).

Both the light green and dark hemihydrate materials are insoluble in water, alcohol, acetone, 4-methyl-2-pentanone, ether, dioxane, benzene and chloroform. They are readily decomposed by excess ammonia and dilute acids.

When either substance is dissolved in excess ammonia the characteristic blue of the copper(II)-ammonia complex is developed, but if the ammonia is carefully neutralized with HCl or H_2SO_4 the light green substance precipitates immediately.

If the light green material is treated with dilute HCl or H_2SO_4, it immediately decomposes and HCN is liberated. The complex is not recovered on neutralization of the acid. The hemihydrate likewise decomposes on acidification, but no HCN is given off. The complex is not recovered on neutralization of the acid. This decomposition of the tetrazole ring upon acidification of the complexes is now being studied.

The spectrum of $Cu(NO_3)_2$ with two parts $NaCH_2N_5$ or excess CH_3N_5 shows a maximum at 690 mμ and a large absorption which goes off scale in the ultraviolet, but beginning at about 400–450 mμ. The ultraviolet portion is similar to that of $NaCH_2N_5$, but much more intense and the $NaCH_2N_5$ absorption does not extend into the visible region.

Continuous variation studies were made with the $Cu(NO_3)_2$ + CH_3N_5 solutions at 0.03 and 0.05 total molarity at both 690 and 350 mμ. Maxima occur at $(CH_3N_5)/(Cu^{++}) = 2$.

Spectra were examined for solutions of 0.02 M $Cu(NO_3)_2$ and various concentrations of CH_3N_5. In Table I the absorbances at 690 mμ are given. As larger and larger amounts of 5-aminotetrazole are added, the maximum at 800 mμ (aquo-complex) shifts to shorter wave lengths and higher absorbancies, ending at 690 mμ and nearly twice the absorbancy of the aquo-complex at 800 mμ.

Results and Discussion

The compositions of the compounds and the continuous variation studies clearly indicate a 1/2 interaction between copper(II) and 5-aminotetrazole and appear to be 5-aminotetrazolato complexes. The shifting of the copper(II) maximum to shorter wave lengths and the intensification and possible shifting of the ultraviolet absorption of $CH_2N_5^-$, suggest coördination rather than simple salt formation.

It has been possible to calculate a formation constant for the bis-(5-aminotetrazolato)-copper(II) in 0.02 M $Cu(NO_3)_2$ solution from the absorbancies in Table I.

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(3) R. F. Wilson and L. J. Baye, THIS JOURNAL, **80**, 2652 (1958); R. F. Wilson and C. M. Womack, Jr., *ibid.*, **80**, 2065 (1958); R. F. Wilson and L. E. Wilson, *ibid.*, **77**, 6204 (1955); **78**, 2370 (1956); *Anal. Chem.*, **28**, 93 (1956).

(4) A. I. Popov, Carla Castellani Bisi and M. Craft, THIS JOURNAL, **80**, 6513 (1958); A. I. Popov, private communication.

TABLE I

ABSORBANCIES AT 690 mμ OF SOLUTIONS OF 0.02 M $Cu(NO_3)_2$ AND VARIOUS QUANTITIES OF 5-AMINOTETRAZOLE (A_∞ = 0.415)

(CH_3N_6), M	A_{690}	$\bar{n}$	$[H^+] \times 10^2$,[a] M	$[HT] \times 10^2$, M
0.0000	0.105	0	0	0
.0160	.178	0.472	0.945	0.655
.0240	.205	.646	1.29	1.11
.0328	.233	.826	1.65	1.63
.0440	.260	1.00	2.00	2.40
.0520	.277	1.11	2.22	2.98
.0520	.279	1.12	2.24	2.96
.0600	.297	1.24	2.48	3.52
.0680	.310	1.32	2.64	4.16
.0880	.340	1.51	3.03	5.77
.133	.390	1.84	3.68	9.62
.160	.408	1.95	3.91	12.1
.200	.413	1.99	3.98	16.0[a]

[a] NOTE ADDED IN PROOF.—Measurements of pH of these solutions show that it is necessary to correct for the interaction between free H^+ and free 5-aminotetrazole to form $CH_4N_5^+$. Using experimental (H^+) and correcting (CH_3N_5) for the formation of $CH_4O_5^+$, the slope (equation 5) is 4.24 and the intercept 0.442. Thus, $K = 0.12$ and $K_1 = 2.5 \times 10^{11}$.

If the limiting absorbancy at 690 mμ is taken as that of 0.02 M $Cu(CH_2N_5)_2$, then one may calculate the degree of formation, α, as $(A - A_0)$ $(A_\infty - A_0)$. A is the absorbancy of any solution of 0.02 M Cu^{++} and CH_3N_5, A_0 that of 0.02 M $Cu(NO_3)_2$ or other uncomplexed copper salt and A_∞ that of 0.02 M $Cu(CH_2N_5)_2$.

Then Bjerrum's $\bar{n}$ is given as[5]

$$= 2\alpha = 2 \times \frac{A - A_0}{A_\infty - A_0} = \frac{C_{HT} - (HT)}{C_{Cu}} \qquad (1)$$

C_{HT} and C_{Cu} are the total CH_3N_5 and $Cu(NO_3)_2$ concentrations and (HT) the concentration of unbound 5-aminotetrazole. Consider the equilibria[6]

$$\begin{gathered} HT = H^+ + T^- \quad K_A = 6.8 \times 10^{-7} \\ \underline{Cu^{++} + 2T^- = CuT_2\ K_1} \\ Cu^{++} + 2HT = CuT_2 + 2H^+ \\ K_A{}^2K_1 = K \end{gathered} \qquad (2)$$

Moreover we can write

$$nC_{Cu} = C_{HT} - (HT) = (H^+) \qquad ^a(3)$$

and

$$C_{HT} - nC_{Cu} = (HT)$$

Further[5]

$$\bar{n} = \frac{2(CuT_2)}{(Cu^{++}) + (CuT_2)} = \frac{2K(Cu^{++})(HT)^2/(H^+)^2}{(Cu^{++})(1 + K(HT)^2/(H^+)^2)}$$
$$= \frac{2K(HT)^2/(H^+)^2}{1 + K(HT)^2/(H^+)^2} \qquad (4)$$

and

$$\frac{1}{\bar{n}} = \frac{1}{2K} \times \frac{(H^+)^2}{(HT)^2} + \frac{1}{2} \qquad (5)$$

Then (H^+) and (HT) can be calculated by equations 3 and a graph of $1/\bar{n}$ *versus* $(H^+)^2/(HT)^2$ should give a straight line with slope $1/2K$ and intercept $1/2$. The intercept is slightly less than 1/2 and the slope is 0.81 ± 0.05 which gives $K = 0.61$ and K_1 is then 1.3×10^{-12}. A standard graph[5] of $\bar{n}$ *vs.* log (T) suggests no CuT^+ is formed and so this simpler treatment is used. It seems, then, that, in aqueous solution the complex is very strong, an observation which is also supported by the 690 mμ (14,500 cm.$^{-1}$) absorption of the copper complex.[7] While it is evident that stable complexes are formed, it is yet to be shown whether coördination by the 5-aminotetrazolate ion involves the primary amino nitrogen or only the ring.

Since preliminary studies show that almost exactly parallel behavior and compounds result when tetrazole is used and similar behavior is also indicated with 5-phenyltetrazole and with 1-ethyletetrazole, there can be but little doubt that it is coördination with the ring only. However, the relatively low values of formation constants for the silver–pentamethylenetetrazole[4] ($\sim 10^2$) and our observation of very little interaction between copper and 1,5-dimethyltetrazole, indicate that a replaceable ring hydrogen is needed.

Infrared Spectra.—As further evidence of ring involvement, the infrared spectra of CH_3N_5, $CH_3N_5 \cdot H_2O$, $NaCH_2N_5$, $Cu(CH_2N_5)_2$(light green) and $Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$ are offered in Table II. By making use of the three mulling agents, mineral oil, hexachlorobutadiene and perfluorokerosene, it has been possible to examine the virtually entire region of interest (2.0–12.0 μ) and to uncover some features of the 5-aminotetrazole spectrum, not previously recorded.[8,9]

Of particular interest are the N–H stretching vibrations at 3510 and 3390 cm.$^{-1}$ in the 5-amino-

TABLE II

INFRARED ABSORPTION BANDS[a] OF 5-AMINOTETRAZOLE, SODIUM 5-AMINOTETRAZOLATE AND THE COPPER(II) COMPLEXES, MINERAL OIL, HEXACHLOROBUTADIENE AND PERFLUOROKEROSENE MULLS (IN CM.$^{-1}$)

CH_3N_5	$CH_3N_5 \cdot H_2O$	$NaCH_2N_5$	$Cu(CH_2N_6)_2$ lt. green	$Cu(CH_2N_5)_2 \cdot {}^1/_2H_2O$
3510(s)	3510(s)	3400(s)	3450(s)	3395(s)
3390(s)	3390(s)	3333(s)	3370(s)	3333(s)
3230(s)	3230(s)	3230(ms)	3230(m)	3230(m)
3130(m)				
2940(m)	2940(m)			
2780(m)	2820(m)			
2630(m)	2630(m)			
2500(ms)	2500(ms)			
2360(m)	2380(m)	2360(w)	2360(w)	2360(w)
1790(w)	1790(w)			
1675(s)	1680(s)			
1640(s)	1650(s)	1630(s)	1630(s)	1630(s)
1610(m)	1610(m)	1540(s)	1550(s)	1550(m)
		1505(ms)	1460(m)	1460(m)
1450(m)	1450(m)	1450(ms)	1440(m)	1440(s)
1290(s)	1290(s)	1250(m)	1275(m)	1300(m)
1270(w)	1270(w)	1200(w)		
1160(s)	1160(s)	1130(s)	1160(m)	1150(mw)
		1105(s)	1110(ms)	1075(ms)
1060(s)	1060(s)	1050(w)	1040(m)	1040(m)
990(s)	990(s)	1000(mw)	969(mw)	962(mw)
901(ms)	901(ms)			

[a] s, strong; m, medium; w, weak intensity.

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(5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

(6) E. Bauer, *Z. physik. Chem.*, **23**, 409 (1897); R. M. Herbst, private communication.

(7) J. Bjerrum and C. Klixbiill Jørgensen, *Rec. trav. chim.*, **75**, 658 (1956).

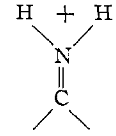
(8) E. Lieber, D. Levering and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

(9) D. R. Murphy and J. P. Picard, *J. Org. Chem.*, **19**, 1807 (1954).

tetrazole. In the sodium salt these appear at 3400 and 3333 cm.$^{-1}$ and at 3450 and 3370 in the light green and 3395 and 3333 in the hemihydrate. Since no lowering of frequency, compared to the sodium salt, is observed, bonding to the 5-amino group is not suggested.

Considerably more details than have been previously described are found in the 2940–2500 cm.$^{-1}$ region and presumably represent the ring N–H group. These bands are not present in salt or complexes.

In the 1680–1440 cm.$^{-1}$ region are a number of sharp bands including the one previously unknown, at 1450–1440 cm.$^{-1}$. The 1675 and 1640 and 1610 absorptions have been discussed[8–10] and are attributed variously to exo-amino bending (1675–1640) and to —N=N— or



If the latter is the correct assignment for 1610 cm.$^{-1}$, it should not appear in any of the salts. The 1450 cm.$^{-1}$ band may be the missing C=N (endo) and the 1300–1250 cm.$^{-1}$ band may be the exo C–N stretch.

In the 1160–900 cm.$^{-1}$ region are a number of bands, which have been attributed to ring vibrations.[8–10] Basic differences are shown between the simple sodium salt and the complexes which suggest ring involvement. Coördination involving the ring would probably not be between two adjacent nitrogen atoms and so it is probable that the copper atom is not in the plane of the ring.

Ring participation is also indicated by its rupture on treatment of the complexes with dilute acids.

Acknowledgment.—The author wishes to thank the Fulbright Commission and the U. S. Atomic Energy Commission which supported this work in Chile and the U. S., respectively. Thanks are also due R. M. Herbst, who supplied the various tetrazoles and gave considerable helpful advice, and Eduardo Schalscha for his invaluable ass.stance in obtained hard-to-find materials in Chile.

EAST LANSING, MICHIGAN
SANTIAGO, CHILE

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[10] D. Percival, Ph.D. Thesis, Michigan State College, 1955.

[CONTRIBUTION FROM THE EASTERN RESEARCH LABORATORY OF THE DOW CHEMICAL COMPANY]

Some Reactions of the Bis-[Salicylaldimine]-Cu(II) Chelates

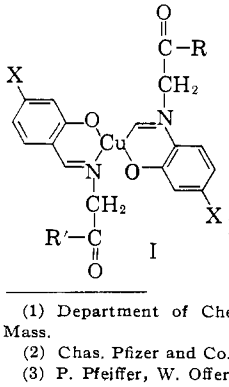
BY HERBERT S. VERTER[1] AND ALBERT E. FROST[2]

RECEIVED NOVEMBER 4, 1958

Several new Schiff bases having the bis-[salicylaldimine]-Cu(II) structure were prepared. Transesterification and amidation reactions were performed on bis-[salicylaldimine]-Cu(II) chelates derived from amino acid esters and a mechanism is proposed to explain rapid ester exchange of the bidentate chelates and absence of ester exchange under comparable conditions in the tridentate chelates. A reaction involving ligand exchange is reported.

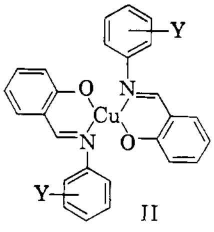
It is of considerable interest to study the reactions of simple metal chelate systems in order to gain an insight into the more complex systems in which metals are involved.

This project was modelled after some experiments of Pfeiffer which seemed capable of further extension.[3] Pfeiffer's experiments involved transesterifications on the amino acid ester portion of bis-[N-(carboxymethyl methyl ester)-salicylaldimine]-Cu(II), Ia (R = OMe, X = H). For example, refluxing Ia in *n*-butyl alcohol for ten minutes gives Ib (R = OBu, X = H).



I

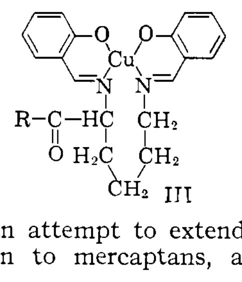
Ia, R = OMe	X = H
Ib, R = OBu	X = H
Ic, R = NHBu	X = H
Id, R = NHCH$_2$COOMe	X = H
Ie, R = OMe	X = Cl
If, R = OMe	X = OH
Ig, R = NHBu	X = OH
Ih, R = NHBu	X = Cl
Ii R = OBu	X = Cl



II

IIa, Y = *o*-Cl
IIb, Y = *m*-Cl
IIc, Y = *p*-Cl
IId, Y = *o*-NO$_2$
IIe, Y = *m*-NO$_2$
IIf, Y = *p*-NO$_2$
IIg, Y = *o*-NO$_2$, *p*-OMe
IIh, Y = H
IIi, Y = *o*-OC$_2$H$_5$
IIj, Y = *m*-OC$_2$H$_5$
IIk, Y = *p*-OC$_2$H$_5$
IIl Y = *o*-OMe
IIm, Y = *m*-COOMe
IIn, Y = *p*-COOMe
IIo, Y = *o*-COOMe

Several of Pfeiffer's experiments on bis-[N-(carboxymethyl methyl ester)-salicylaldimine]-Cu(II) (Ia) were repeated successfully. In addition, a successful transesterification was run on Ie (R = OMe, X = Cl) with butyl alcohol to produce Ii (R = OBu, X = Cl).



III

IIIa, R = OMe
IIIb, R = NHBu
IIIc, R = OBu
IIId, R = OEt

In an attempt to extend the transesterification reaction to mercaptans, and formation of thiol

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[3] P. Pfeiffer, W. Offerman and H. Werner, *J. prakt. Chem.*, **159**, 313 (1942).