

[KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

Complexes of Copper(II) and Some 5-Substituted Tetrazoles

BY NED A. DAUGHERTY AND C. H. BRUBAKER, JR.

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The complexes of Cu(II) and 5-phenyltetrazole and some substituted 5-phenyltetrazoles have been studied. Bis-(5-phenyltetrazolato)-copper(II), $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$, has been characterized. Monotetrazole complexes $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$ and $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{Cl}$ also have been prepared. Visible and ultraviolet spectra of $\text{Cu}^{++} + \text{C}_7\text{H}_5\text{N}_4$ in methanol have been studied as have the infrared spectra of the solids. The 5-phenyltetrazolate ion seems to satisfy two coordination positions on copper. 5-*o*-Chloro- and 5-*m*-chlorophenyltetrazole and 5-*o*-tolyltetrazole give solids of the form CuT_2 (T = tetrazole) but 5-*p*-nitro and 5-*p*-chlorophenyltetrazole form compounds of the type $\text{Cu}_2\text{T}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. With 5-*p*-methoxyphenyltetrazole and 5-*p*-tolyltetrazole solids form which do not correspond to any simple formula and probably are not pure. Studies of the effects of aqueous anions on the rapidity of formation and structure of precipitates of bis-(5-aminotetrazolato)-copper(II) were made. It was found that Cl^- , SO_4^{2-} and NO_2^- cause the $\text{Cu}(\text{CN}_5\text{H}_2)_2$ to form rapidly as the light green phase, while the dark green (blue) phase separated only very slowly when the anions were ClO_4^- , NO_3^- , PO_4^{3-} , $\text{C}_2\text{H}_3\text{O}_2^-$, Br^- , HCO_2^- . With Cl^- and SO_4^{2-} the amounts of solid depended on the concentrations of the anions, but the $\text{Cu}(\text{CN}_5\text{H}_2)_2$ contained only traces of Cl^- or SO_4^{2-} . The effect probably is due to nucleation of the light green solid by a trace of some solid chloro- or sulfato-complex.

The preparation and properties of two crystalline copper complexes of 5-aminotetrazole have been reported recently.¹ The anion of the copper salt used determined which of the two complexes formed, but only trace amounts of the anion are found in the solids. Although 5-aminotetrazole is relatively stable in the presence of acids, the complexes are reported to decompose with rupture of the tetrazole ring in the presence of dilute acids. Although infrared spectra suggest that the amino group is not coordinated, the exact nature of the metal-tetrazole bond is unknown. The complexes are reported to be insoluble in a wide variety of solvents.

These properties suggested that metal-tetrazole complexes are somewhat unusual and prompted the further investigation of tetrazole complexes. This paper reports the preparation and properties of some copper complexes of 5-aryltetrazoles. The anion effect in the formation of solid copper complexes of 5-aminotetrazole also was investigated.

Experimental

Materials.—Reagent grade chemicals were used throughout this investigation. The tetrazoles used were either obtained from R. M. Herbst² or were prepared by the method of Finnegan and Henry.³ The melting points and equivalent weights of the tetrazoles were determined to verify purity.

Analytical Methods.—The copper content of the solid complexes was determined colorimetrically as described previously.¹ Samples for analysis were decomposed either by treatment with hot nitric acid or by dissolution in 5 *M* NH_3 + 5 *M* NH_4Cl .

Determinations of C, H, N in the complexes were made by commercial analytical houses.

The tetrazolate content of the complexes was determined gravimetrically by precipitation of the tetrazoles, at pH 6.0–6.5, as their silver salts. Silver salts of 5-substituted tetrazoles have been used as a means of characterizing 5-substituted tetrazoles.⁴ Samples for analysis were decomposed by treatment with alcoholic NaOH. The samples were filtered and the residues were washed repeatedly with distilled water. The filtrate and washings were acidified to pH 6.0–6.5 and a 10% excess of AgNO_3 was added to precipitate the tetrazole. The precipitates were digested, filtered and dried to constant weight at 90°.

The sulfate content of the complexes was determined gravimetrically by precipitation of the sulfate as BaSO_4 .

The samples were decomposed by treatment with alcoholic NaOH. The samples were filtered and the residues were washed thoroughly with distilled water. After acidification, a calculated excess of BaCl_2 was added to the filtrates to precipitate the sulfate. The precipitates were filtered and ignited to constant weight.

Crystalline Copper Complexes of 5-Phenyltetrazole. $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$.—When methanol solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{C}_7\text{H}_5\text{N}_4$ are mixed in any proportion, a dark blue solution results from which a dark blue, crystalline solid separates within a few hours. The blue solid seems to contain one or two waters per copper. Drying the blue solid to constant weight *in vacuo* over $\text{Mg}(\text{ClO}_4)_2$ yields the blue monohydrate, $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$.

Anal. Calcd. for $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$: Cu, 17.1; C, 45.2; H, 3.8; N, 30.2. Found: Cu, 17.1; C, 45.7; H, 3.7; N, 29.7.

If the monohydrate is dried in an oven at 110° for 2 or 3 days or *in vacuo* over $\text{Mg}(\text{ClO}_4)_2$ for several weeks, a bronze colored solid containing 18.0% Cu, corresponding to $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2$, is produced. The anhydrous $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2$ rapidly turns blue upon exposure to moist air.

$\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$.—When a methanol solution prepared by mixing methanol solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 5-phenyltetrazole, $\text{C}_7\text{H}_5\text{N}_4$, in a 1:2 ratio is diluted with a large volume of water, a blue solid separates at once. The solid contains 16.5% Cu and yields an X-ray powder pattern identical with the pattern of $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$. However, if $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{C}_7\text{H}_5\text{N}_4$ dissolved in methanol are mixed in a 1:1 mole ratio and diluted with water, a pale blue solid containing 28.5% Cu separates at once. Analyses indicate that the solid is $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$.

Anal. Calcd. for $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$: Cu, 28.2; C, 37.3; H, 2.7; N, 24.8. Found: Cu, 28.5; C, 38.2; H, 2.8; N, 24.8.

The reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{C}_7\text{H}_5\text{N}_4$ in 95% ethanol results in the slow formation of a pale blue solid. The blue solid gives the X-ray powder pattern of $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$. The solid contains 27.7% Cu and 62.9% $\text{C}_7\text{H}_5\text{N}_4$. Calcd. for $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$: Cu, 28.2; $\text{C}_7\text{H}_5\text{N}_4$, 64.3.

The complex $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$ slowly dissolves in 6 *N* H_2SO_4 . Neutralization of the acid solution produces a pale blue solid which, after drying, gives an X-ray powder pattern identical with the pattern of $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$.

Stirring a suspension of $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$ in water for 20 hr. at room temperature produces a solid, which when dried at 110°, appears to be a mixture of two compounds, $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2$ and $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$.

$\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{Cl}$.—When solutions of anhydrous CuCl_2 and 5-phenyltetrazole, $\text{C}_7\text{H}_5\text{N}_4$, in absolute alcohol are mixed and allowed to stand 3 or 4 weeks in a stoppered flask, a brown solid separates. The brown solid has an X-ray powder pattern different from the patterns obtained from $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$.

Analyses indicate that the solid might be a mixture of $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{Cl}$ and CuCl_2 .

The Reactions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 5-Phenyltetrazole, $\text{C}_7\text{H}_5\text{N}_4$.—If 40 ml. of 0.10 *M* $\text{C}_7\text{H}_5\text{N}_4$ and 20 ml. of 0.10 *M* $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in methanol solution are mixed, no

(1) C. H. Brubaker, *J. Am. Chem. Soc.*, **82**, 82 (1960).

(2) Department of Chemistry, Michigan State University.

(3) W. Finnegan and R. Henry, *J. Am. Chem. Soc.*, **81**, 3250 (1959).(4) R. Herbst and J. Mihina, *J. Org. Chem.*, **15**, 1082 (1950).

visible reaction occurs at the time of mixing. If the reaction mixture is allowed to stand overnight, a small amount of a bluish-purple solid separates. If the solution stands for several more weeks no significant additional amount of solid is found. The purple solid gave an X-ray pattern different from any copper complex previously prepared. Analyses failed to establish the material as a pure compound.

If 95% ethanol is used as the solvent, the mixing of 40 ml. of 0.10 M $C_7H_8N_4$ and 20 ml. of $Cu(NO_3)_2 \cdot 3H_2O$ produces a blue solution which rapidly becomes turbid. A green solid separates within 5 minutes and after 10 more minutes, the green solid turns blue. The blue solid contains 30.5% Cu, but comparison of X-ray powder patterns indicates that it is primarily $Cu(C_7H_8N_4)OH$ (which contains only 28.2% Cu). In a duplicate experiment, the green solid turned blue as it was sucked dry in the filter. The solid gave an X-ray powder pattern identical with the pattern of the solid obtained from the reaction in methanol.

When the reaction is carried out in absolute alcohol at 0°, a green solution is obtained. A purple solid slowly separates from the cold methanol solution. The purple, blue crystals also give an X-ray pattern identical with the pattern of the solid obtained, using methanol as the solvent. Copper and tetrazolate analyses indicate the solid contains 17.9% Cu and 73.1% $C_7H_8N_4^-$, corresponding to a $C_7H_8N_4^- : Cu^{++}$ molar ratio of 1.79. It is probably not a pure compound.

Infrared Spectra of the Copper- $C_7H_8N_4$ Complexes.—The infrared spectra of $C_7H_8N_4$, $NaC_7H_8N_4$, $Cu(C_7H_8N_4)_2 \cdot H_2O$, $Cu(C_7H_8N_4)OH$ and $Cu(C_7H_8N_4)Cl$ were obtained by use of the KBr disc technique. Several bands in the 3077–2519 cm^{-1} region of the spectrum of $C_7H_8N_4$ are missing in the spectrum of the sodium salt. Apparently these bands are due to the ring N–H group. These bands are also missing in the spectra of the copper complexes, indicating loss of the ring hydrogen during complex formation.

Lieber, *et al.*,⁶ have examined the infrared spectra of some tetrazoles and have attributed bands in the 1100–900 cm^{-1} region to tetrazole ring vibration. The spectra of the complexes differ from the spectrum of the simple sodium salt in this region. These data are given in Table I.

TABLE I

INFRARED ABSORPTION (IN CM^{-1}) OF 5-PHENYLTETRAZOLE, SODIUM 5-PHENYLTETRAZOLATE AND THE COPPER(II) COMPLEXES OF 5-PHENYLTETRAZOLE IN KBr DISCS

s, strong; m, medium; w, weak absorption

$C_7H_8N_4$	$NaC_7H_8N_4$	$Cu(C_7H_8N_4)_2 \cdot H_2O$	$Cu(C_7H_8N_4)OH$	$Cu(C_7H_8N_4)Cl$
3571mw	3690s		3636ms	3571m
	3509s	3484s		3448m
3226mw	3279s			3390m
3155m		3125m	3125m	
3077m				3049m
2985ms			2985m	
2915ms				
2755s				
2653s				
2584s				
2519s				
	2309w			
2000mw	1972w		1961w	1961w
1923m	1908w		1898w	1905w
1880m				
1776w				
1754w				
1724w	1704m			
1675w	1658w	1650m		
1623ms		1626m	1639w	
1577s			1613w	1613m

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

1497ms		1538mw	1531mw	1527m
1479ms	1479ms			
1443w	1453s		1453s	1456s
1391s	1391s	1398ms	1389s	1381mw
	1374ms	1376m	1366mw	1366m
				1339w
				3112w
1294m	1285mw	1287mw	1282mw	1285m
1255m	1266w	1267mw	1266mw	1253w
				1242w
	1215w	1217m	1209m	1209ms
1167s	1149m	1183m	1181mw	1195m
				1178mw
	1134m	1161mw		1156mw
	1127m	1130m	1127m	1135m
1103w	1105w	1101w	1096mw	
1087ms	1096w	1081m	1075m	1073m
1057ms	1075m			1066m
				1044w
1036m	1027mw	1036w	1031mw	1033mw
1015m	1012mw	1014m	1008m	1015ms
994ms	996w			
959mw				
924mw	917w	922mw	956 broad band (s)	929mw
	909w		914 m	
792m	786mw	789m	781mw	784m
783mw	725s	731s	722s	745s
725s	704s	694s	698ms	699ms
703s				694ms

Copper Complexes of $C_7H_8N_4$ in Solution. The Visible Spectrum of $CuSO_4 \cdot 5H_2O + C_7H_8N_4$ in Methanol.—The addition of $C_7H_8N_4$ to methanol solutions of $CuSO_4 \cdot 5H_2O$ shifts the 830 $m\mu$ peak of the copper solution to a shorter wave length. A 20:1 tetrazole to copper ratio gives an absorption maximum at 730 $m\mu$, but it appears that further addition of $C_7H_8N_4$ would shift the maximum to a still shorter wave length. The addition of the tetrazole produces a very strong absorption in the ultraviolet. As with $Cu(II)$ and 5-aminotetrazole¹ an isosbestic point occurs at 830 $m\mu$, the maximum for uncomplexed copper ion. The absorption in the ultraviolet is similar to that of the tetrazolate ion but is more intense. No maximum is observed down to 218 $m\mu$, but only a general increase in absorption.

Continuous Variation Studies in the $CuSO_4 \cdot 5H_2O - C_7H_8N_4$ System.—Continuous variation studies, in methanol, of $CuSO_4 \cdot 5H_2O$ and $C_7H_8N_4$ were carried out at both 720 and 880 $m\mu$. Samples were prepared from stock methanol solutions of $CuSO_4 \cdot 5H_2O$ and $C_7H_8N_4$. The absorbances of the samples were measured, using a Beckman DU spectrophotometer, about 30 minutes after the samples had been prepared. No variation of absorbancy with time was observed. Studies at both wave lengths indicate a 1:1 copper-tetrazole interaction.

Crystalline Copper Complexes of Other 5-Aryltetrazoles.—The copper complexes of several 5-aryltetrazoles were prepared in an identical manner to those of 5-phenyltetrazole. The complexes were prepared by mixing 2.4×10^{-3} mole of $CuSO_4 \cdot 5H_2O$ dissolved in about 10 ml. of methanol with 10^{-2} mole of the tetrazole dissolved in 100 ml. of methanol. The resulting solutions were allowed to stand in stoppered flasks until crystallization of the complexes occurred. The solid complexes were separated by filtration and washed with methanol until the washings were SO_4^{--} free. The solids were dried *in vacuo* over $Mg(ClO_4)_2$. The solid complexes are described below.

5-*o*-Chlorophenyltetrazole.—Dark blue crystals separate from a methanol solution of the reactants a week to 10 days after the reactants are combined. After having been dried, the crystals are bronze colored.

Anal. Calcd. for $Cu(C_7H_7N_4Cl)_2$: Cu, 15.0; $C_7H_7N_4Cl^-$, 85.0. Found: Cu, 15.0; $C_7H_7N_4Cl^-$, 84.3.

5-*m*-Chlorophenyltetrazole.—The dark blue crystals obtained from the reaction become blue-grey when they are

dried. Analyses indicate that the material probably is impure $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{Cl})_2 \cdot \text{H}_2\text{O}$.

Anal. Calcd. for $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{Cl})_2 \cdot \text{H}_2\text{O}$: Cu, 14.4; C, 38.0; H, 2.3; N, 25.4. Found: Cu, 15.5; C, 37.0; H, 2.5; N, 24.8.

5-*p*-Chlorophenyltetrazole.—Mixing methanol solutions of the reactants produces a blue solution. After 48 hr. pale blue crystals begin to separate from the solution. When the crystals are sucked dry on a filter, the color of the solid changes to green. After repeated washings with methanol, the solid still contains SO_4^{2-} .

Copper, tetrazolate and SO_4^{2-} analyses suggest a composition of $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{Cl})_2 \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$.

Anal. Calcd. for $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{Cl})_2 \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$: Cu, 20.6; $\text{C}_7\text{H}_4\text{N}_4\text{Cl}^-$, 58.2; SO_4^{2-} , 15.5. Found: Cu, 20.4; $\text{C}_7\text{H}_4\text{N}_4\text{Cl}^-$, 58.0; SO_4^{2-} , 15.3.

5-*p*-Nitrophenyltetrazole.—The complex was obtained as bright blue crystals which also contain SO_4^{2-} .

Anal. Calcd. for $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{O}_2^-)_2 \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$: Cu, 19.9; $\text{C}_7\text{H}_4\text{N}_4\text{O}_2^-$, 59.5; SO_4^{2-} , 15.0. Found: Cu, 19.3; $\text{C}_7\text{H}_4\text{N}_4\text{O}_2^-$, 59.9; SO_4^{2-} , 14.9.

5-*o*-Tolyltetrazole.—A crystalline hemi-hydrate of $\text{Cu}(\text{C}_8\text{H}_7\text{N}_4)_2$ was prepared by combining 5.0×10^{-3} mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 50 ml. of methanol with 1.0×10^{-2} mole of the tetrazole dissolved in 100 ml. of methanol. The resulting dark blue solution begins to deposit dark blue crystals 12 hr. after the solutions have been mixed. After having been dried over $\text{Mg}(\text{ClO}_4)_2$ the color of the solid changes to brown. The brown solid is very hygroscopic and turns blue on brief exposure to moist air. Drying the brown solid to constant weight at 110° results in a weight loss of 2.1% and produces an ash green solid. The brown solid appears to be $\text{Cu}(\text{C}_8\text{H}_7\text{N}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.

Anal. Calcd. for $\text{Cu}(\text{C}_8\text{H}_7\text{N}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: Cu, 16.3; $\text{C}_8\text{H}_7\text{N}_4^-$, 81.3; H_2O , 2.3. Found: Cu, 16.3; $\text{C}_8\text{H}_7\text{N}_4^-$, 81.3; wt. loss on heating, 2.1.

5-*p*-Methoxyphenyltetrazole.—A green crystalline solid is obtained from a methanol solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{C}_8\text{H}_8\text{N}_4\text{O}$. The green solid contains 20.1% Cu, 61.8% $\text{C}_8\text{H}_7\text{N}_4\text{O}^-$ and 11.3% SO_4^{2-} . This composition corresponds to a $\text{Cu}:\text{C}_8\text{H}_7\text{N}_4\text{O}^-:\text{SO}_4^{2-}$ molar ratio of 2.8:3.0:1. No definite formula can be assigned on the basis of these analytical results. Although the solid appears to be homogeneous, it is probably a mixture of compounds. It is interesting to note that the composition calculated for an equimolar mixture of $\text{Cu}(\text{C}_8\text{H}_7\text{N}_4\text{O})\text{OH}$ and $\text{Cu}_2(\text{C}_8\text{H}_7\text{N}_4\text{O})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (Calcd: Cu, 22.0; $\text{C}_8\text{H}_7\text{N}_4\text{O}^-$, 60.7; SO_4^{2-} , 11.1) is in fair agreement with the observed values.

5-*p*-Tolyltetrazole.—A light green solid complex was obtained. The solid contains 20.8% Cu, 69.9% $\text{C}_8\text{H}_7\text{N}_4^-$ and 7.5% SO_4^{2-} corresponding to a $\text{Cu}:\text{C}_8\text{H}_7\text{N}_4^-$ molar ratio of 1:1.34. A formula has not been assigned to this solid, which is probably a mixture of compounds.

Effects of Some Anions on the Formation of Bis-(5-aminotetrazolato)-copper(II).—In a previous paper,¹ it was reported that some anions, such as SO_4^{2-} and Cl^- , caused bis-(5-aminotetrazolato)-copper(II)· $\text{Cu}(\text{CN}_6\text{H}_2)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ to precipitate rapidly as green crystals, slightly contaminated with CuSO_4 or CuCl_2 . However, NO_3^- or ClO_4^- had no such effects and $\text{Cu}(\text{CN}_6\text{H}_2)_2$ precipitated only after standing for a week or more and then appeared as a blue solid which changed to dark green $\text{Cu}(\text{CN}_6\text{H}_2)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ after being dried over BaO . The X-ray powder patterns of the two $\text{Cu}(\text{CN}_6\text{H}_2)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ compounds were different. Therefore, the effects of other anions were studied and attempts were made to study quantitatively the effects of SO_4^{2-} and Cl^- .

Various amounts of Na_2SO_4 , NaCl , KBr , Na_2PO_4 , NaHCO_3 , NaNO_2 and $\text{NaC}_2\text{H}_3\text{O}_2$ were added to mixtures of $\text{Cu}(\text{NO}_3)_2$ (0.02 M) and CN_6H_2 (0.04 M). Only SO_4^{2-} , Cl^- and NO_2^- caused any precipitation.

In the cases of SO_4^{2-} and Cl^- , solutions were prepared at various concentrations of one part $\text{Cu}(\text{NO}_3)_2$ plus two parts CN_6H_2 and varying amounts of the anions were added. The extent of precipitation was measured by weighing the precipitates (in the more concentrated, ca. 0.1 M Cu^{++} , solutions) and by using a Beckman, Model DU, spectrophotometer to measure turbidities of the more dilute solution (ca. 10^{-3} M Cu^{++}). The amounts of SO_4^{2-} and Cl^-

added were comparable to or less than the amounts of Cu^{++} present.

Since turbidity appeared slowly with Cl^- , some studies of turbidity vs. time were made as a function of (Cl^-).

Results

Three crystalline copper complexes of 5-phenyltetrazole, $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{OH}$ and $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4)\text{Cl}$, have been prepared and characterized. Copper complexes of other 5-aryltetrazoles also have been isolated as crystalline solids from methanol solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and the tetrazoles. In general, copper ion and 5-aryltetrazoles form complexes of the general formula CuT_2 , where T = a tetrazolate anion. However, 5-*p*-nitro and 5-*p*-chlorophenyltetrazole react with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in methanol to yield crystalline complexes having the formulas $\text{Cu}_2\text{T}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. In all of the cases studied, the tetrazole coordinates as an anion and there is no evidence that more than two tetrazoles coordinate per copper ion.

An experimental difficulty encountered in the preparation of pure, solid complexes is that no methods for purification of the solids have been found. The solids cannot be recrystallized, since they are insoluble in a wide variety of solvents such as water, alcohols, dimethylformamide, benzene, dioxane, acetone, acetonitrile, chloroform and ethyl acetate. The complexes are decomposed by aqueous acids and aqueous or liquid ammonia. The solids decompose when heated and cannot be sublimed or distilled. Washing the solids with excess solvent sometimes converts one crystalline form of a complex to another¹ or results in extensive hydrolysis of the complex.

Continuous variation studies of the reaction of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 5-phenyltetrazole point to the existence of a 1:1 copper-tetrazole complex species in solution. However, it should be mentioned that ideal conditions for such a study do not exist at either 720 or 380 $\text{m}\mu$. At 720 $\text{m}\mu$ the absorption peak of the complex overlaps the absorption peak of uncomplexed Cu^{++} and 380 $\text{m}\mu$ does not correspond to an absorption maximum but is merely a convenient wave length at which the complex is the only strongly absorbing species.

In the previous paper,¹ it was reported that the light green compound, bis-(5-aminotetrazolato)-copper(II), could be decomposed by dilute acids and that the tetrazole ring was broken in the process. This reaction has been investigated, and it was found that only a small amount of the 5-aminotetrazole was decomposed; at least 90% was recovered. Some HCN and what was probably N_2 were formed.

Discussion

At present, little is known about the nature of the metal-tetrazole bond. Analytical results and infrared spectra indicate that 5-substituted tetrazoles coordinate as anions. However, Popov⁶ has isolated silver complexes of metrazole, indicating that loss of the ring hydrogen is not necessary in order for coordination to occur.

There are a number of ways that coordination between metal ions and tetrazoles could occur.

(6) A. Popov and R. Holni, *J. Am. Chem. Soc.*, **81**, 3250 (1959).

Perhaps the simplest type of bonding would be "simple" donation of an electron pair by one of the nitrogen atoms of the tetrazole ring to the metal ion. If bonding occurred in this manner, one might expect copper to coordinate four ligands, as it does in its imidazole complexes.⁷⁻⁹

Since the tetrazolate anion seems to satisfy two coordination sites on the copper ion, coordination could occur by the formation of bonds to two distinct nitrogen atoms of the tetrazole ring. Coordination probably would not involve two adjacent nitrogen atoms of the tetrazole ring which means that if coordination occurs in this manner, the tetrazole rings would not be coplanar with the copper ion.

The electronic structure of the tetrazole ring has a marked similarity to the electronic structure of cyclopentadiene. Another possible mode of bonding is coordination of the metal ion to the π -electron system of the tetrazolate anion. If this type of bonding were encountered, one might expect the copper complexes to be soluble in organic solvents.

In fact, the almost complete lack of solubility of the copper complexes in a wide variety of solvents might suggest a polymeric structure in the solid state. There are several structures that one can visualize in which the tetrazolate anions are shared by more than one copper ion.

A determination of the structure of the solid complexes from X-ray data has not been made. The patterns indicate that the unit cell is large.

The dark blue solution obtained by mixing

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methanol solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{C}_7\text{H}_8\text{N}_4$ suggests that a soluble complex is formed on mixing the reactants. The intensity of the blue color remains constant until the solid complex begins to separate from the solution. The blue solid is not soluble in methanol. Such behavior suggests that the structure of the solid complex may be different from the structure of the complex in solution.

The "anion effect" observed in the reaction of Cu^{++} with CN_5H_3 is not well understood. The fact that SO_4^- is much more effective, in producing turbidity, than any of the other anions examined suggests that the anion plays a rather specific role in the reaction. The poor effectiveness of basic anions such as $\text{C}_2\text{H}_3\text{O}_2^-$ and $\text{PO}_4^{=}$ compared to SO_4^- indicate that the effect is not an acid-base phenomenon. The lack of effect by $\text{PO}_4^{=}$ leads one to believe the effect is not entirely one of coagulation of a colloidal material.

It is suggested, therefore, that rapid nucleation of the $\text{Cu}(\text{CN}_5\text{H}_2)_2$ requires a small amount of some complex which contains $\text{SO}_4^{=}$, Cl^- or NO_2^- and which may be insoluble. If that is the case the sulfate complex must form at once, but the chloride one only slowly, since the appearance of solid in the chloride case is slow and depends on (Cl^-) .

Although a systematic study of the roles of some anions on precipitation of tetrazole complexes has been made only with Cu^{++} and CN_5H_3 , one must point out that it seems to be quite general for metal ions and tetrazoles.

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

Chelate Stabilities of Certain Oxine-type Compounds. III. Schiff Bases¹

BY T. J. LANE, C.S.C., AND A. J. KANDATHIL

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The acid dissociation constants for three types of Schiff bases structurally similar to 8-hydroxyquinoline have been determined in 50% v./v. dioxane-water at 25° and the chelate stabilities of these ligands with $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cd}(\text{II})$ have been obtained by Calvin-Bjerrum potentiometric titration technique. The differences in values obtained for the basicities of the ligands have been explained by electron donating tendency of the substituents and by hydrogen bonding. The formation constants of these ligands with the metal ions studied are lower than those of the corresponding 8-hydroxyquinoline chelates due to unfavorable steric factors but are higher than those of the 4-hydroxybenzimidazoles because of more favorable nitrogen-oxygen distance. The stability constants for the metal chelates of the Schiff bases increase with increase in ligand basicity except when the size of the metal chelate ring or the presence of adjacent groups affects these values.

In the previous papers^{2,3} the chelate stabilities of 4-hydroxybenzimidazoles, 4-hydroxybenzoxazoles and 4-hydroxybenzothiazoles with divalent metal ions have been reported. In the present paper are presented and discussed the stability values obtained for the metal chelates of three

types of Schiff bases represented by the formulas where $\text{R}=\text{H}$, CH_3 , OCH_3 and OH . Compounds of type A are structural analogs of 8-hydroxyquinoline and contain the same chelating system $-\text{O}-\text{C}=\text{C}-\text{N}=\text{}$, the difference being that the nitrogen atom is not part of a ring. Type B and type C compounds have been included to study the effect of varying the size of the chelate ring and of introducing an *ortho* substituent, respectively.

Materials.—N-Benzylidene-*o*-hydroxyaniline (compound I, Table I), N-(4-methylbenzylidene)-*o*-hydroxyaniline

(1) Presented in part before the Inorganic Chemistry Division of the 138th National Meeting of the A.C.S. at New York, N. Y., September, 1960.

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