

TABLE I
EVALUATION OF K_d AT pH 7

C_{HC^+}, M	C_{Ag^+}, M	$E,$ volts versus s.c.e.	$[Ag^+]$	$\frac{C_{Ag^+} - [Ag^+]}{C_{HC^+} - C_{Ag^+} + [Ag^+]}$
5.85×10^{-3}	7.67×10^{-4}	0.3412	3.09×10^{-4}	0.085
5.78×10^{-3}	1.52×10^{-3}	.3624	5.64×10^{-4}	.201
5.73×10^{-3}	2.26×10^{-3}	.3758	9.02×10^{-4}	.309
5.68×10^{-3}	2.99×10^{-3}	.3857	1.26×10^{-3}	.438
5.64×10^{-3}	3.70×10^{-3}	.3931	1.68×10^{-3}	.560
5.60×10^{-3}	4.42×10^{-3}	.3994	2.12×10^{-3}	.695
5.53×10^{-3}	5.46×10^{-3}	.4067	2.82×10^{-3}	.908
5.48×10^{-3}	6.31×10^{-3}	.4117	3.44×10^{-3}	1.10
5.43×10^{-3}	7.15×10^{-3}	.4159	4.06×10^{-3}	1.32

evaluated from these four plots to be 2.2×10^{-3} with an average deviation of 0.3×10^{-3} .

Figure 2 shows the plot of equation 7 at pH values ranging from 5.60 to 7.75. C_{HC^+} varied from 1×10^{-3} to $6 \times 10^{-3} M$, and the range of C_{Ag^+} used was from 5×10^{-4} to $5 \times 10^{-3} M$. The intercept gave for $\log K_d$ a value of -2.61 , corresponding to a dissociation constant of 2.46×10^{-3} which agreed well with the value obtained by the previous plots.

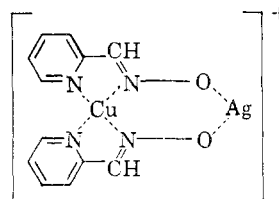
Preparation of Silver(I) Bis-(pyridine-2-aldoxime)-copper(II) Perchlorate Monohydrate.—Recrystallized monohydrogen bis-(pyridine-2-aldoxime)-copper(II) nitrate was dissolved in water and mixed with a slight excess of silver nitrate and sodium perchlorate. The mixture was heated on a steam bath and very slowly neutralized with sodium hydroxide to a final pH of 7.2. The green silver complex salt which precipitated upon neutralization was filtered, washed with several portions of distilled water and air dried.

Anal. Calcd. for $Cu(C_5H_5N_2O)_2AgClO_4 \cdot H_2O$: C, 27.1; H, 2.26; N, 10.5. Found: C, 26.96; H, 2.25; N, 10.21.

Discussion

The linearity of the plots confirms the fact that there is interaction between silver(I) ion and bis-

(pyridine-2-aldoxime)-copper(II) ions and that a one-to-one complex is formed. The plot on Fig. 2 shows deviation from linearity in the region of lower pH values. This deviation probably is due to the protonation of the monohydrogen and the silver complexes, which has been shown to be possible. The first dissociation constant of the dihydrogen bis-(pyridine-2-aldoxime)-copper(II) ion representing dissociation into the monohydrogen species and hydrogen ion has previously been reported as 1.7×10^{-3} .¹ The isolation of the silver complex compound furnished further proof for the one-to-one composition. The most likely structure for the silver complex is



where the silver(I) ion is chelated. Infrared spectrum of the compound indicates this structure as the spectrum is very similar to that of monohydrogen bis-(pyridine-2-aldoxime)-copper(II) perchlorate. As expected, the absorption band at 1600 cm^{-1} , which has been shown to be due to O-H stretching of the intramolecularly bonded hydrogen species, is not observed in the spectrum of the silver complex.¹

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK AND THE UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT]

Complexes of Copper with Pyridine-2-aldoxime¹

BY C. H. LIU AND CHUI FAN LIU

RECEIVED MAY 8, 1961

The one-to-two complex of copper(II) with pyridine-2-aldoxime has been shown by pH titrations to behave as a dibasic acid. The successive dissociation constants are 1.7×10^{-3} and 2.0×10^{-7} . The dihydrogen sulfate and the monohydrogen bromide, chloride, iodide, nitrate and perchlorate of bis-(pyridine-2-aldoxime)-copper(II) have been prepared. Infrared spectra show hydrogen bonded O-H stretching bands at 1710 and 1600 cm^{-1} for the dihydrogen and monohydrogen complexes. Their spectra after deuteration are consistent with these observations. On the basis of these evidences, it appears that the complex has the *cis* configuration. Intramolecular hydrogen bonding would stabilize one of the hydrogens and decrease its acidity compared to the other. Polarographic studies indicate that the copper(II) complex is reducible in two steps, first to the one-to-two copper(I) complex and then to copper amalgam. The dissociation constants of the copper(II) and copper(I) complexes are 2.1×10^{-19} and 3.3×10^{-16} , respectively.

Introduction

Very few ligands containing both an aromatic nitrogen heterocycle and an oxime group at the alpha position have been studied. Geometrically, this arrangement of the coordinating groups is similar to that found in 2,2'-dipyridyl and 1,10-phenanthroline which are known to form stable complexes with many metal ions. Unlike 2,2'-dipyridyl and 1,10-phenanthroline, these ligands are unsymmetrical and should give rise to *cis-trans* isomerism in the two-to-one complexes,

(1) Part of this work was done at the University of Michigan, Ann Arbor, Michigan. Presented at the 138th meeting of the American Chemical Society, New York.

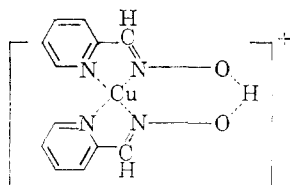
provided the four coordinated nitrogens are not arranged in a tetrahedral structure. Moreover, the *cis* configuration should be capable of intramolecular hydrogen bonding analogous to that found in dimethylglyoxime complexes.

In earlier studies, complexes between pyridine oximes and divalent metal ions were prepared and isolated as two-to-one inner complexes; that is, the oxime hydrogens on both of the ligand molecules were lost. Tschugaev obtained the platinum(II) and palladium(II) complexes of phenyl-2-pyridine ketoxime.^{2a} Emmert and Diehl studied the

(2) (a) L. A. Tschugaev, *Ber.*, **39**, 3382 (1906). (b) B. Emmert and K. Diehl, *ibid.*, **62**, 1735 (1929).

complexes of methyl-2-pyridine ketoxime with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II).^{2b} More recently, Krause and Busch reported the complexes of nickel(II), palladium(II) and platinum(II) with pyridine-2-aldoxime.³ No attempt was made to study intramolecular hydrogen bonding in these complexes, and their configurations were not examined.

The present investigation is concerned with the complexes between copper(II) and pyridine-2-aldoxime. The complexes have been found to contain two molecules of the ligand to each copper(II) ion. Special attention is directed to the configuration of the complexes and the intramolecular hydrogen bonding which necessitates a *cis* arrangement as indicated below.



Experimental Results and Discussion

Preparation of Compounds. Dihydrogen Bis-(pyridine-2-aldoxime)-copper(II) Sulfate Trihydrate.

Pyridine-2-aldoxime was obtained from Aldrich Chemical Company, Milwaukee, and used without further purification. A solution of 2.44 g. of pyridine-2-aldoxime in 50 ml. of 95% ethanol was added to 2.50 g. of cupric sulfate pentahydrate dissolved in 60 ml. of water. The resulting dark green solution was heated on the steam-bath for an hour and left to evaporate at room temperature. Bluish green crystals formed gradually. These were separated from the solution, recrystallized from water and air dried.

Anal. Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2\text{H}_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$: C, 31.44; H, 3.93; N, 12.22. Found: C, 31.78; H, 3.96; N, 12.58.

Monohydrogen Bis-(pyridine-2-aldoxime)-copper(II) Nitrate.—To a solution of 2.42 g. of cupric nitrate trihydrate in 30 ml. of water were added 2.44 g. of pyridine-2-aldoxime dissolved in the minimum required amount of 95% ethanol. The solution turned dark green, and crystals formed upon standing. These were filtered out, recrystallized from water and air dried.

Anal. Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2\text{H}]\text{NO}_3$: C, 39.05; H, 2.98; N, 18.97. Found: C, 39.08; H, 3.01; N, 18.92.

Monohydrogen Bis-(pyridine-2-aldoxime)-copper(II) Chloride.—To a solution of 1.70 g. of cupric chloride dihydrate in 40 ml. of water were added 2.44 g. of pyridine-2-aldoxime in the minimum required amount of 95% ethanol. The solution turned dark green, and crystals separated almost immediately. These were filtered out, recrystallized from water and air dried.

Anal. Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2\text{H}]\text{Cl}$: C, 42.11; H, 3.22; N, 16.37. Found: C, 42.24; H, 3.29; N, 16.25.

(3) R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 4830 (1960).

Monohydrogen Bis-(pyridine-2-aldoxime)-copper(II) Bromide, Iodide and Perchlorate.—These were easily obtained by adding an alkali salt of the desired anion to an aqueous solution of the purified dihydrogen bis-(pyridine-2-aldoxime)-copper(II) sulfate trihydrate. Crystals formed immediately upon addition in each case.

The sulfate, nitrate and chloride were also analyzed polarographically with respect to their copper(II) and pyridine-2-aldoxime contents by the standard addition method. In a phosphoric acid-sodium dihydrogen phosphate buffer where the total phosphate concentration was 0.2 *F* and whose *pH* was adjusted to 2, the complex was substantially decomposed. Copper(II) was reducible to copper amalgam in a two electron step and pyridine-2-aldoxime was reducible in a four electron step presumably to the corresponding protonated amine. The half-wave potentials for the reduction of copper(II) and of pyridine-2-aldoxime were, respectively, -0.01 and -0.50 volt *versus* the saturated calomel electrode. At higher *pH*'s, the reduction potential of the ligand was shifted to more negative values as expected. With 0.005% Triton X-100 added as maximum suppressor, well-defined waves were obtained which were tested and found to be of analytical utility. The results from polarographic analysis confirmed the elemental analyses in all cases.

***pH* Titrations.**—Leeds and Northrup and Beckman *pH* meters were used in these titrations. Solutions of the ligand at concentrations from 0.01 to 0.1 *F* were titrated with standard 0.1 *F* hydrochloric acid and sodium hydroxide solutions. Results showed the K_a for the oxime hydrogen to be 9.1×10^{-11} and the K_b for the heterocyclic nitrogen to be 3.8×10^{-11} . Next, solutions of the complex were made by mixing standard solutions or solid portions of pyridine-2-aldoxime with standard copper(II) sulfate, chloride and nitrate solutions; the mole ratio between the ligand and copper(II) in the final solutions was always kept at two to one. These solutions were then titrated with a standard sodium hydroxide solution. In the case of sulfate, solutions of the complex at concentrations from 0.01 to 0.05 *F* were titrated whereas in the case of chloride and nitrate, the concentration of the complex had to be kept below 0.01 *F* for precipitates which were later identified as the monohydrogen form of the complex formed at higher concentrations. Practically identical titration curves were obtained in all cases. The complex in solution behaved as a dibasic acid with two distinct equal steps of neutralization. The total available acid hydrogen was always two moles per mole of the complex. Results from these titrations and from a number of similar titrations involving the isolated and purified complexes gave for the successive dissociation constants for the two acid hydrogens of bis-(pyridine-2-aldoxime)-copper(II) 1.7×10^{-8} and 2.0×10^{-7} . The titration curves of the dihydrogen and monohydrogen complex chlorides in solution with sodium hydroxide are shown on the following figure; a titration curve of hydrochloric acid is also given for comparison.

These results suggest that in solution the complex exists in either the *cis* or the *trans* form rather than as a mixture of the two isomers. Furthermore, the *cis* configuration appears to be more likely as intramolecular hydrogen bonding, which is possible only when the compound is in the *cis* form, would make one of the hydrogens less acidic. Jones and Soper⁴ first suggested that internal hydrogen bonding might account for the large ratio of the first to the second ionization constants, K_1/K_2 , of some dibasic acids, notably carbonic acid. Stabilization of the monohydrogen ion through an internal hydrogen bonded ring would result in increased ionization of the first acid hydrogen and decreased ionization for the second. McDaniel and Brown⁵ noted that the K_1/K_2 ratio of many dicarboxylic acids showed a remarkable variation with structure, particularly noticeable in the case of *cis-trans* isomerism. Table I lists their comparisons of the K_1 and K_2 of the *cis* and *trans* isomers of some dibasic acids along with the successive dissociation constants of dihydrogen bis-(pyridine-2-aldoxime)-copper(II). It should be

TABLE I

IONIZATION CONSTANTS FOR DIBASIC ACIDS^a

Acid	K_1	K_2	K_1/K_2
Fumaric	9.57×10^{-4}	4.13×10^{-5}	23.2
Maleic	1.2×10^{-2}	5.95×10^{-7}	20,200
<i>trans</i> -Cyclopentane 1,2-dicarboxylic	2.2×10^{-4}	7.4×10^{-6}	29.7
<i>cis</i> -Cyclopentane 1,2-dicarboxylic	4.7×10^{-4}	3.4×10^{-7}	1380
<i>trans</i> -Carbonic	1.52×10^{-4}	4.78×10^{-5}	31.8
<i>cis</i> -Carbonic	4.59×10^{-3}	4.94×10^{-9}	929,000
Dihydrogen-bis-(pyridine-2-aldoxime)-copper(II)	1.7×10^{-3}	2.0×10^{-7}	8500

^a In water at 25°.

pointed out that there is an added complication in the case of dihydrogen bis-(pyridine-2-aldoxime)-copper(II) ion. The acid hydrogen released from the first dissociation would tend to interact with the heterocyclic nitrogen of the pyridine ring, weakening the chelate and introducing another equilibrium for consideration. However, in view of the weak basicity of this heterocyclic nitrogen, this adverse effect should not be strong enough to distort the picture. It is also conceivable that the dihydrogen compound isolated is actually the bisulfate of the monohydrogen complex. In solution, however, the interaction between hydrogen ion and the monohydrogen complex is unmistakable and well defined as shown by the pH titrations.

Infrared Studies.—Infrared spectra were obtained on a Perkin-Elmer Model 21 Infrared Spectrometer equipped with sodium chloride optics. Nujol mulls were employed in all cases. Spectra of dihydrogen bis-(pyridine-2-aldoxime)-copper(II) sulfate and of the bromide, chloride, nitrate and perchlorate of monohydrogen bis-(pyridine-2-aldoxime)-copper(II) were obtained. In the case of the dihydrogen complex, a band at 1710 cm^{-1} was observed. The spectra of the other salts showed absorption bands at 1600 cm^{-1} .

(4) I. Jones and F. G. Soper, *J. Chem. Soc.*, 133 (1936).

(5) D. H. McDaniel and H. C. Brown, *Science*, **118**, 370 (1953).

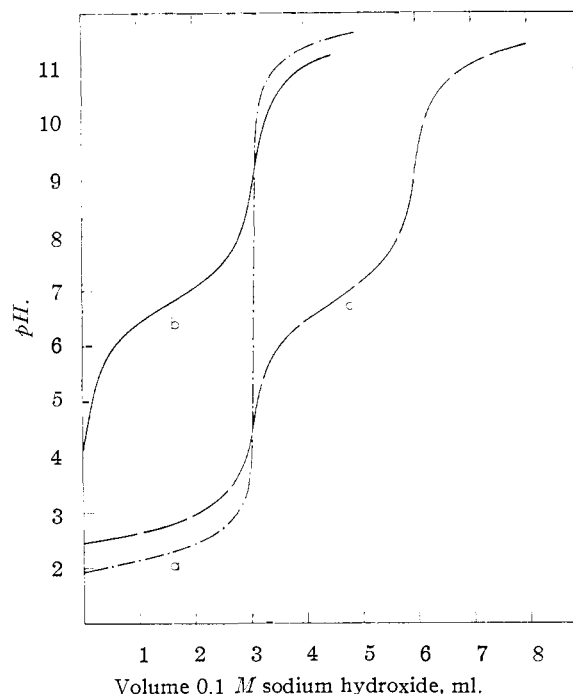


Fig. 1.—Titration curves: a, 0.01 *F* hydrochloric acid; b, 0.01 *F* bis-(pyridine-2-aldoxime)-copper(II) chloride; c, 0.01 *F* cupric chloride-0.02 *F* pyridine-2-aldoxime.

These bands are attributed to O-H stretching of the intramolecularly hydrogen-bonded oxime O-H group. The bands are quite within the range of the bands described by Rundle and Parasol, who investigated the dimethylglyoxime complexes of copper(II), nickel(II) and palladium(II).⁶ Similarly, Fujita, Nakahara and Tsuchida described O-H stretching frequencies of cobalt(III)-dimethylglyoxime complexes as essentially in the same range.⁷ To test the validity of the assignment of the bands at 1710 and 1600 cm^{-1} , dihydrogen bis-(pyridine-2-aldoxime)-copper(II) sulfate and monohydrogen bis-(pyridine-2-aldoxime)-copper(II) chloride were deuteriated. The bands at 1710 and 1600 cm^{-1} were absent in the spectra of the deuteriated complexes while the rest of the spectra remained identical with those of the original compounds before deuteriation.

Polarographic Studies.—All polarograms were obtained on a Sargent Model XXI polarograph. A Meites-Meites type of polarographic cell was used with a built-in saturated calomel reference electrode. The supporting electrolyte used was a sodium phosphate buffer in which the total phosphate concentration was 0.2 *F* and whose pH was adjusted to 12. The high pH was employed so that pyridine-2-aldoxime would exist essentially in the anionic form. An excessively high pH was avoided because there had been evidence that some monodentate ligands tended to enter additional coordination positions of square planar copper(II) complexes.⁸ The bis-(pyridine-

(6) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

(7) A. Fujita, A. Nakahara and R. Tsuchida, *ibid.*, **23**, 1541 (1955).

(8) J. Steigman, C. H. Liu and D. Gaskill, paper presented at the Meeting-in-Miniature, New York Section, American Chemical Society, March, 1960.

2-aldoxime)-copper(II) concentration was $1 \times 10^{-3} F$ in all cases while the excess ligand concentration varied between 0.02 and 0.08 F . From electrocapillary curves, the complex and ligand were shown not to be appreciably surface active. Triton X-100, 0.005%, was added as maximum suppressor. Each solution was allowed to equilibrate in a thermostat kept at $25 \pm 0.01^\circ$ and thoroughly de-aerated with a stream of oxygen-free nitrogen before a polarogram was measured. Well-defined double waves, representing two one electron reduction steps, were obtained in all cases. Conventional log plots indicated reversibility of the waves. A typical set of results showing the half-wave potentials of the first and second waves at various concentrations of the ligand is given in Table II.

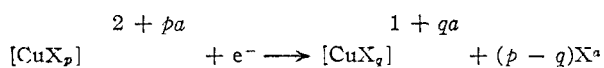
TABLE II

HALF-WAVE POTENTIALS OF BIS-(PYRIDINE-2-ALDOXIME)-COPPER(II)^a

Concentration of pyridine-2-aldoxime, F	Half-wave potentials versus s.c.e.	
	First wave	Second wave
0.0810	-0.328	-0.582
.0692	- .329	- .574
.0339	- .325	- .542
.0162	- .324	- .504

^a Mercury column, 45 cm.; flow rate of mercury, 2.06 mg. sec.⁻¹; drop time at the potential of the saturated calomel electrode, 4.5 sec.

For the reduction of a copper(II) complex with p coordinated ligands, X, of charge a to a copper(I) complex with q coordinated ligands

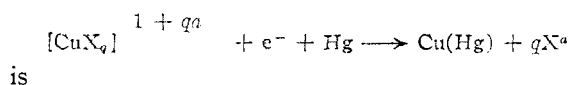


Lingane⁹ has shown the equation relating the half-wave potentials of the complex and simple ion reductions at 25°

$$(E_{1/2})_c - (E_{1/2})_s = 0.05915 \log \frac{K_{dII}}{K_{dI}} - (p-q) 0.05915 \log C_x f_x$$

(9) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

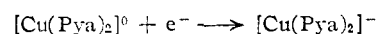
where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complex and simple ions, K_{dII} and K_{dI} are the dissociation constants of the copper(II) and copper(I) complexes, C_x is the concentration of the ligand and f_x is its activity coefficient. The ratios of the diffusion coefficients and the activity coefficients of the simple and complex copper(II) and copper(I) ions are assumed to be unity. The analogous equation for the reduction of the copper(I) complex to copper amalgam



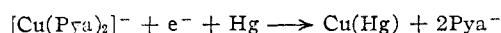
$$(E_{1/2})_c - (E_{1/2})_s = 0.05915 \log K_{dI} - q 0.05915 \log C_x f_x$$

with similar assumptions regarding the diffusion coefficients and activity coefficients of the simple and complex copper(I) ions. If the activity coefficient of the ligand X is considered a constant since a constant ionic strength has been used, it may be incorporated into the dissociation constants, and the concentration of the ligand may be introduced directly into the equation, thus obviating any corrections. Naturally, the dissociation constants thus obtained would be valid only for the ionic strength used. The half wave potentials for the reduction of copper(II) to copper(I) and for the reduction of copper(I) to copper amalgam are taken as -0.079 and 0.143 volts versus the saturated calomel electrode.¹⁰

The experimental results have shown that the reduction of bis-(pyridine-2-aldoxime)-copper(II) follow the steps



and



where Pya is the abbreviation for pyridine-2-aldoxime. The dissociation constants for bis-(pyridine-2-aldoxime)-copper(II) and bis-(pyridine-2-aldoxime)-copper(I) are 2.1×10^{-19} and 3.3×10^{-15} , respectively.

(10) E. I. Oustatt and H. A. Laitinen, *J. Am. Chem. Soc.*, **72**, 4724 (1950).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

Malonate as a Bridging Group for Electron Transfer

BY GEORGE SVATOS AND HENRY TAUBE

RECEIVED APRIL 12, 1961

When malonate is the bridging group in the reaction of acid malonatopentamminecobalt(III) ion with Cr^{++} , a term in the rate law first order in (H^+) is observed in addition to the acid independent term and the term inverse in (H^+) . The term first order in (H^+) is absent when the methylene hydrogens are replaced by C_2H_5 . This and other observations suggest that the acid dependent term involves dissociation of a methylene hydrogen under the combined influence of acid and the reducing agent, the resulting system of delocalized electrons serving to conduct the electron from Cr^{++} to the Co(III) center.

We are reporting the results of kinetic studies done on the reaction of Cr^{++} with acid malonatopentamminecobalt(III). The study was undertaken because we were interested in the effect

which chelation of Cr^{++} by the malonate ligand in the activated complex might exert on the rate of the reaction and in what might be learned by comparing the kinetic data with those observed