TABLE IV

OSCILLATOR STRENGTHS OF THE ABSORPTION BANDS[a]

Compound	Solvent	$f\nu_3$	$f\nu_2$	$f\nu_3/f\nu_2$
$((C_6H_5)_3MeP)_2[NiCl_4]$	CH_3CN	2.30×10^{-3}	2.01×10^{-4}	11.4
	CH_3NO_2	2.21×10^{-3}	2.35×10^{-4}	9.40
	$0.1\ M\ ((C_6H_5)_3MeP)Cl$ in CH_3NO_2	2.24×10^{-3}	1.42×10^{-4}	15.8
$((C_6H_5)_4P)_2[NiBr_4]$	CH_3NO_2	3.12×10^{-3}	4.85×10^{-4}	6.44
	CH_3CN	2.97×10^{-3}	4.28×10^{-4}	6.94
	$0.1\ M\ ((C_6H_5)_3\text{-}n\text{-}BuP)Br$ in CH_3CN	3.15×10^{-3}	2.61×10^{-4}	12.1
$[Ni((C_6H_5)_3PO)_2Br_2]$	Acetone	1.59×10^{-3}	1.63×10^{-4}	9.75
$[Ni((C_6H_5)_3PO)_2I_2]$	C_6H_5Cl	2.06×10^{-3}	1.08×10^{-4}	19.1
$[Ni((C_6H_5)_3AsO)_2Cl_2]$	C_6H_5Cl	1.52×10^{-3}	1.21×10^{-4}	12.6
$[Ni((C_6H_5)_3AsO)_2Br_2]$	C_6H_5Cl	2.92×10^{-3}	1.79×10^{-4}	16.3

[a] The estimates include all absorption in the region of the ν_i concerned. Thus, for the ν_2 bands, the intensity of the absorption known to be due to solvolyzed species is included.

heavy ultraviolet absorption trailing off into the region of ν_3 makes accurate intensity assessment difficult.

The most striking aspect of the intensity data is the relatively high intensity of the bands of the tetrahedral nickel(II) complexes as compared to the band intensities for octahedral complexes of nickel(II). The ratio is about 10^2. This effect is quite general, having been found for Co-(II),[21,22] Mn(II)[23,24] and Cu(II),[17] and Ballhausen and Liehr have discussed the possible reasons for it.[25] The intensity ratios show that

(22) F. A. Cotton and M. Goodgame, J. Am. Chem. Soc., 83, 1777 (1961).

(23) D. M. L. Goodgame and F. A. Cotton, J. Chem. Soc., Aug.(1961).

(24) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, J. Am. Chem. Soc., in press.

(25) C. J. Ballhausen and A. D. Liehr, J. Mol. Spect., 2, 342 (1958); 4, 190 (1960).

ν_3 is generally 10 to 20 times stronger than ν_2. This is in agreement with the fact that in the strong field limit ν_3 remains a one-electron transition while ν_2 becomes a two-electron transition.

It is also noteworthy that the intensity of ν_3 is relatively insensitive to solvolysis effects, whereas for ν_2 the solvolyzed species are more strongly absorbing than are the $[NiX_4]^{2-}$ ions.

# Hetero-binuclear Chelates of Copper(II) and Silver(I)

BY C. H. LIU AND CHUI FAN LIU

Interaction between silver(I) ion and bis-(pyridine-2-aldoxime)-copper(II) ion has been investigated by potentiometric measurements. The hetero-binuclear chelate involved has also been isolated as the perchlorate and examined by infrared spectroscopy.

In a previous investigation,[1] it has been shown that monohydrogen bis-(pyridine-2-aldoxime)-copper(II) ion has the structure
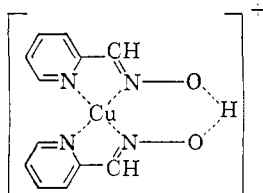
The acidic hydrogen is intramolecularly bonded in a six-membered ring. From this structure, it would appear that the complex itself might form chelates with other metal ions through the oximate

(1) C. H. Liu and Chui-Fan Liu, work presented at the 138th National Meeting of the American Chemical Society, New York, 1960.

groups. The present work is concerned with the interaction between the complex ion and silver(I) ion. This interaction has been studied by measuring the two competing equilibria

$$HC^+ \rightleftharpoons H^+ + C^0$$

$$AgC^+ \rightleftharpoons Ag^+ + C^0$$
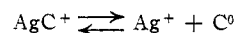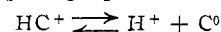
where HC^+ is the monohydrogen bis-(pyridine-2-aldoxime)-copper(II) ion, AgC^+ is the analogous silver complex, and C^0 is the basic form of the complex. For the second equilibrium, neglecting activity coefficients

$$K_d = \frac{[Ag^+][C^0]}{[AgC^+]} \qquad (1)$$

and

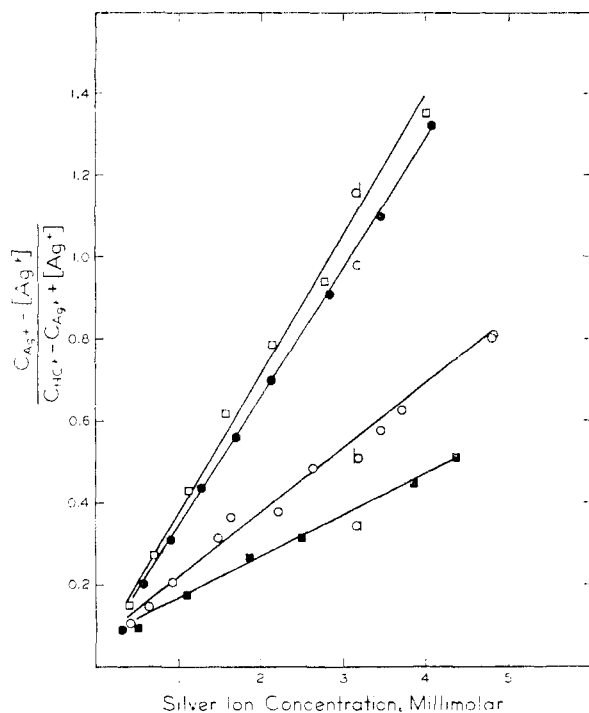$$[Ag^+] = \frac{K_d[AgC^+]}{[C^0]} \qquad (2)$$

Fig. 1.—Plots of $C_{Ag^+} - [Ag^+]/C_{HC^+} - C_{Ag^+} + [Ag^+]$ versus $[Ag^+]$ at constant pH's: a, pH = 6.0, K_d = 1.7 × 10^{-3}; b, pH = 6.5, K_d = 2.4 × 10^{-3}; c, pH = 7.0, K_d = 2.1 × 10^{-3}; d, pH = 7.5, K_d = 2.5 × 10^{-3}.

where the brackets designate the equilibrium molar concentrations of the species in question. Let C_{HC^+} be the total molar concentration of the complex in all forms and C_{Ag^+} be the total molar concentration of silver(I) ion in all forms.

$$C_{HC} = [AgC^+] + [HC^+] + [C^0] \qquad (3)$$

and

$$C_{Ag^+} = [AgC^+] + [Ag^+] \qquad (4)$$

if the pH of the solution is such that the extent of protonation of HC$^+$ and AgC$^+$ to form the respective protonated species is negligible. Furthermore, the dissociation constant of monohydrogen bis-(pyridine-2-aldoxime)-copper(II) ion has been determined to be 2.0 × 10^{-7}.[1]

$$[HC^+] = \frac{[H^+][C^0]}{2.0 \times 10^{-7}} \qquad (5)$$

Combining equations 2, 3, 4 and 5

$[Ag^+] =$

$$K_d \left(\frac{2.0 \times 10^{-7} + [H^+]}{2 \times 10^{-7}} \right) \left(\frac{C_{Ag^+} - [Ag^+]}{C_{HC^+} - C_{Ag^+} + [Ag^+]} \right) \qquad (6)$$

Thus, if $C_{Ag^+} - [Ag^+]/C_{HC^+} - C_{Ag^+} + [Ag^+]$ is plotted against $[Ag^+]$, the slope of the straight line should be equal to $(2.0 \times 10^{-7} + [H^+]/2.0 \times 10^{-7})K_d$. $[Ag^+]$ may be measured experimentally by direct potentiometry with a silver indicator electrode. K_d can be evaluated in this manner if pH is held constant.

Rearrangement of equation 6 yields

$$\frac{[Ag^+](C_{HC^+} - C_{Ag^+} + [Ag^+])}{C_{Ag^+} - [Ag^+]} = \left(1 + \frac{[H^+]}{2.0 \times 10^{-7}} \right) K_d \qquad (7)$$

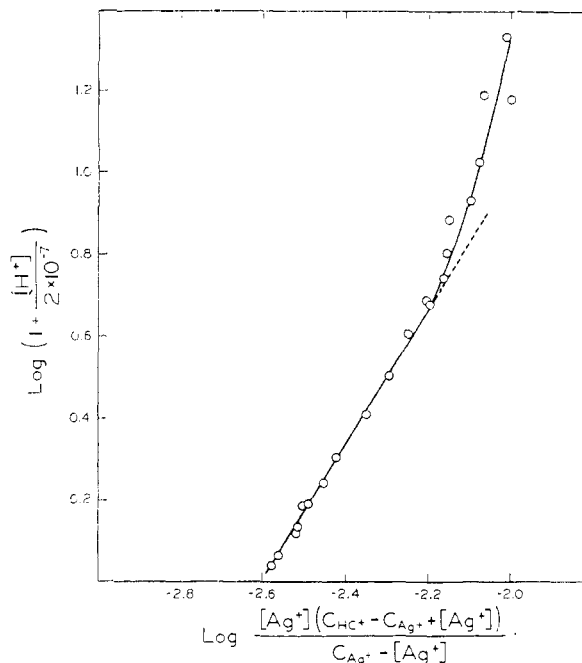Thus, a plot of log $(1 + [H^+]/2.0 \times 10^{-7})$ against

Fig. 2.—Plot of log $(1 + ([H^+]/2.0 \times 10^{-7}))$ versus log $[Ag^+](C_{HC^+} - C_{Ag^+} + [Ag^+])/C_{Ag^+} - [Ag^+]$; intercept = −2.61; K_d = 2.46 × 10^{-3}.

log $[Ag^+](C_{HC^+} - C_{Ag^+} + [Ag^+])/C_{Ag^+} - [Ag^+]$ should result in a straight line with the intercept equal to log K_d. A wide range of pH values and of silver(I) ion concentrations can be employed in making this plot.

Experimentally, C_{Ag^+} should be kept small compared to C_{HC^+}, and relatively high pH values should be used. Any complications due to further reactions of hydrogen ion and silver ion with the monohydrogen and the analogous silver complexes could then be avoided.

Experimental Results

Potential was measured with a Rubicon portable potentiometer, and pH measurements were made with a line operated Leeds and Northrup pH-meter. Infrared spectra were obtained on a Perkin–Elmer Model 21 Infrared Spectrometer equipped with sodium chloride optics.

Monohydrogen bis-(pyridine-2-aldoxime)-copper(II) nitrate was prepared by the same procedure as described previously.[1] The product was twice recrystallized from water and air dried. Standard solutions of this compound were made by direct weighing and standardized by pH titrations with a standard 0.1 M sodium hydroxide solution. In these titrations, the acidic hydrogen of the complex was neutralized. The results of the titrations usually agreed with the direct weighings to within 1%.

Silver ion concentrations were determined with a silver chloride–silver electrode from a standard working curve measured in 0.01 M KNO$_3$, which closely approximated the ionic strength of the solutions in the experiments. The logarithm of silver concentrations was plotted against potential in volts versus the saturated calomel electrode.

Standard solutions of monohydrogen bis-(pyridine-2-aldoxime)-copper(II) nitrate and silver nitrate solutions were mixed to obtain various values of C_{HC^+} and C_{Ag^+}, and pH was adjusted to the desired value by the addition of sodium hydroxide. Constant pH values of 6.0, 6.5, 7.0 and 7.5 were employed in separate experiments; C_{HC^+} varied between 2 × 10^{-3} and 1 × 10^{-2} M while C_{Ag^+} was in the range from 7 × 10^{-4} to 7 × 10^{-3} M. A typical set of results is presented in Table I.

Figure 1 shows the linear plots of equation 6 at pH values of 6.0, 6.5, 7.0 and 7.5. The dissociation constant, K_d, was

TABLE I

EVALUATION OF K_d AT pH 7

C_{HC^+}, M	C_{Ag^+}, M	E, volts versus s.c.e.	[Ag$^+$]	$\dfrac{C_{Ag^+} - [Ag^+]}{C_{HC^+} - C_{Ag^+} + [Ag^+]}$
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 6×10^{-3} M, and the range of C_{Ag^+} used was from 5×10^{-4} to 5×10^{-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 $Cu(C_6H_5N_2O)_2AgClO_4 \cdot H_2O$: 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
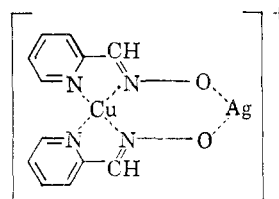
where the silver(I) ion is chelated. Infrared spectrum of the compound indicates this structure as the spectrum is very similar to that of monohydrogen bis-(pyridine-2-aldoxime)-copper(II) perchlorate. As expected, the absorption band at 1600 cm.$^{-1}$, which has been shown to be due to O–H stretching of the intramolecularly bonded hydrogen species, is not observed in the spectrum of the silver complex.[1]

Complexes of Copper with Pyridine-2-aldoxime[1]

BY C. H. LIU AND CHUI FAN LIU

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-aldoxim)-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^{-15}, 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 coördinating 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,

provided the four coördinated 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

(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.

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