Inorg. Chem. **1989**, *28*, 3805-3807

Contribution from the Department of Inorganic and Analytical Chemistry,
Kossuth L. University, Debrecen 10, H-4010 Hungary

Hydrolytic Reactions of Copper(II) Bipyridine Complexes

István Fábián

Received March 4, 1988

The hydrolytic reactions of Cu(II)–2,2′-bipyridine complexes have been studied in aqueous solutions at 25 °C and in 1.0 M KNO_3. The formation of the ternary hydroxo complexes $Cu_2(bpy)_2(OH)_2^{2+}$, $Cu(bpy)(OH)_2$, $Cu_2(bpy)_4(OH)^{3+}$, and $Cu(bpy)_2(OH)^+$ (bpy = 2,2′-bipyridine) were verified by using pH-metry and a ^1H NMR relaxation method. The logarithms of the overall stability constants for these species are 7.27 ± 0.02, −9.10 ± 0.02, 23.46 ± 0.05, and 5.38 ± 0.02, respectively. The line-broadening effect of the paramagnetic species on the NMR signal of the bulk solvent is discussed.

Introduction

Ternary systems including Cu^{2+}, 2,2′-bipyridine (bpy), and a second ligand have frequently been used for modeling complex equilibria of biological relevance.[1-7] In many papers by Sigel et al. and others the extreme affinity of bipyridine complexes toward oxygen-donor ligands has been demonstrated[8-15] and the observed extra stabilization was interpreted in terms of a specific π interaction.[8-10] In spite of these results little attention has been paid to the hydrolytic reactions of the parent complexes in which the simplest O-donor coordinates to the central ion.

In 1955 Wagner-Jauregg et al. first reported the formation of hydroxo bipyridine complexes,[16] and in 1957 Martell et al. published a p*K* value for the mono(bipyridine) complex.[17] A year later Ryland et al. demonstrated the strong tendency of the monohydroxo species to form a dimer ($Cu_2(bpy)_2(OH)_2^{2+}$) and also verified the formation of the dihydroxo complex ($Cu(bpy)(OH)_2$).[18] Their results were supported by others.[19-22] No literature data are available for the hydrolysis of $Cu(bpy)_2^{2+}$.

In the present work the hydrolysis of the mono- and bis(bipyridine) complexes of copper(II) are studied by using pH-metry and a ^1H NMR relaxation method.

Experimental Section

Materials. Stock solutions of Cu^{2+}, KNO_3, and bpy were prepared from reagent grade chemicals (REANAL). The ligand and KNO_3 were recrystallized from water twice. The bpy solutions were kept in the dark to avoid any photodecomposition. The ionic strength was adjusted to 1.0 M with KNO_3.

The pH-metric and the NMR measurements were carried out as titrations. Aliquots of the samples (25 cm^3) were titrated with standard KOH solutions. The total concentration of the metal ion and the metal ion to ligand concentration ratio were varied in the range 7.96×10^{-4}–1.59×10^{-2} M and from 1:1 to 1:2.3, respectively.

Methods. A Radiometer PHM-52 type pH meter equipped with a GK-2322C combined electrode was used for pH measurements. The electrode was calibrated for H^+ concentration according to the method of Irving et al.[23] (log $K_W{}^c$ was calculated to be −13.78). The reproducibility of the pH measurements was ±0.003 pH unit (±0.006 above pH 12). A Newport N-20 type NMR spectrometer operating at a 2.5-MHz frequency was used to measure the T_2 relaxation time of water protons by the simple echo technique.[24] The reproducibility of the NMR measurements was 5%. All measurements were performed at 25 ± 0.2 °C. The temperature dependence of the relaxation time was measured between 0 and 80 °C.

Results and Discussion

In the first set of pH-metric titrations the bpy:Cu^{2+} concentration ratio was kept at approximately 1:1 with a very slight ligand excess in order to avoid any pH effect caused by the hydrolysis of the metal ion. Precalculations on these data have reaffirmed former literature results,[18-22] i.e. the formation of the complex $Cu_2(bpy)_2(OH)_2^{2+}$ (at approximately neutral pH) and the liberation of further protons in the alkaline range.

In the second set of titrations the ligand to metal ion concentration ratio was 2:1. For these titration curves the formation function—i.e. the average number of the liberated protons vs pH—was calculated by assuming only the formation of mononuclear hydroxo complexes of 2:1 stoichiometry for bpy and Cu^{2+}. The diversity of the curves (Figure 1) indicates that this assumption is not applicable in the studied system, and for the correct interpretation of the experimental data the following reactions also have to be considered: polymerization reactions of $Cu(bpy)_2^{2+}$ through hydroxide bridges; the formation of mono(bipyridine) hydroxo complexes in significant concentration.

Further titrations were carried out by varying both the ligand to metal ion concentration ratio and the total concentrations. The data from all of the pH-metric curves were evaluated simultaneously by using the program PSEQUAD.[25] In the course of the fitting procedure the number and the composition of the hydroxo species in the equilibrium models were systematically varied and their stability constants were calculated. $Hbpy^+$ and the parent complexes were included in these calculations with fixed stability constants (Table I).

---

(1) Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 134.
(2) Huber, P. R.; Griesser, R.; Prijs, B.; Sigel, H. *Eur. J. Biochem.* **1969**, *10*, 238.
(3) Malik, G. S.; Singh, S. P.; Tandon, J. P. *Monatsh. Chem.* **1979**, *110*, 149.
(4) Kumar, K.; Prasad, D. R.; Nigam, P. C. *Monatsh. Chem.* **1984**, *115*, 731.
(5) Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 1527.
(6) Prasad, K.; Mohan, M. S. *J. Coord. Chem.* **1987**, *16*, 1.
(7) Sigel, H. *Chimia* **1987**, *11*, 41 and references therein.
(8) Griesser, R.; Sigel, H. *Inorg. Chem.* **1970**, *9*, 1238.
(9) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945.
(10) Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394.
(11) Daniele, P. G.; Ostacoli, G.; Vanni, A. *Ann. Chim. (Rome)* **1975**, *65*, 465.
(12) Munakata, M.; Harada, M.; Niina, S. *Inorg. Chem.* **1976**, *15*, 1727.
(13) Bonomo, R. P.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1851.
(14) Arena, G.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *Inorg. Chim. Acta* **1978**, *27*, 31.
(15) Patel, P. J.; Patel, V. K.; Battacharya, P. K. *Inorg. Chem.* **1982**, *21*, 3163.
(16) Wagner-Jauregg, T.; Hackley, B. E., Jr.; Lies, T. A.; Owens, O. O.; Proper, R. *J. Am. Chem. Soc.* **1955**, *77*, 922.
(17) Martell, A. E.; Chaberek, S., Jr.; Courtney, R. C.; Westerback, S.; Hyytiainen, H. *J. Am. Chem. Soc.* **1957**, *79*, 3036.
(18) Ryland, L. B.; Ronay, G. S.; Fowkes, F. M. *J. Phys. Chem.* **1958**, *62*, 798.
(19) Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 525.
(20) Perrin, D. D.; Sharma, V. S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1271.
(21) Ostacoli, G.; Daniele, P. G.; Vanni, A. *Ann. Chim. (Rome)* **1975**, *65*, 197.
(22) Arena, G.; Cali, R.; Rizzarelli, E.; Sammartano, S. *Thermochim. Acta* **1976**, *17*, 155.
(23) Irving, H. M.; Miles, M. G.; Pettit, L. D. *Anal. Chim. Acta* **1967**, *38*, 475.
(24) Farrar, T. C.; Becker, E. D. *Pulse and Fourier Transform NMR*; Academic Press: New York, London, 1971.
(25) Zékány, L.; Nagypál, I. In *Computational Methods for the Determination of Formation Constants*; Leggett, D. J., Ed.; Plenum: New York, 1985; p 291.

0020-1669/89/1328-3805$01.50/0

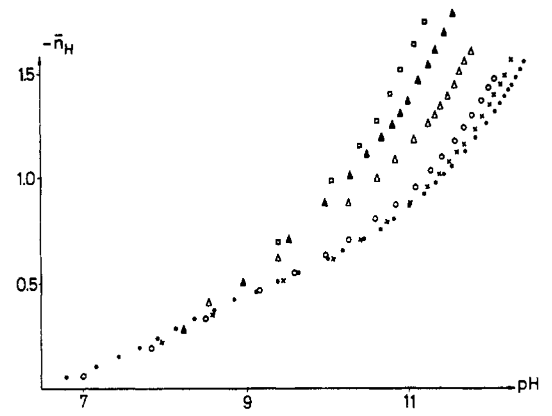

Figure 1. Formation functions for the hydrolysis of the $Cu(bpy)_2^{2+}$ complex: (●) $T_{Cu} = 1.59 \times 10^{-2}$ M, $T_{bpy} = 3.22 \times 10^{-2}$ M; (×) $T_{Cu} = 1.11 \times 10^{-2}$ M, $T_{bpy} = 2.25 \times 10^{-2}$ M; (○) $T_{Cu} = 7.96 \times 10^{-3}$ M, $T_{bpy} = 1.61 \times 10^{-2}$ M; (△) $T_{Cu} = 3.18 \times 10^{-3}$ M, $T_{bpy} = 6.43 \times 10^{-3}$ M; (▲) $T_{Cu} = 1.59 \times 10^{-3}$ M, $T_{bpy} = 3.22 \times 10^{-3}$ M; (□) $T_{Cu} = 7.96 \times 10^{-4}$ M, $T_{bpy} = 1.61 \times 10^{-3}$ M.

The fitting procedure has shown that more than one equilibrium model is suitable for the interpretation of the pH-metric data. The fitting parameter, i.e. the average deviation in the measured and calculated volumes of the titrant, agreed within 10% for the equivalent models. The lack of a unique mathematical solution indicates the formation of two or more hydroxo complexes in the same concentration and pH range. The observed pH effect may not be characteristic of the speciation if the overlapping hydrolytic reactions cannot be separated by varying the total concentrations of the components.

While the formation of the complexes $Cu_2(bpy)_2(OH)_2^{2+}$ and $Cu_2(bpy)_4(OH)^{3+}$ could be justified, few other species could substitute each other in the equilibrium models, without changing considerably the fitting parameter and the stability constants for the above complexes. For each of the complex pairs $Cu(bpy)(OH)_2$, $Cu_2(bpy)_2(OH)_3^+$ and $Cu(bpy)_2(OH)^+$, $Cu_2(bpy)_3(OH)_2^{2+}$ the formation of one species had to be considered to get a reliable description of the system. If both of the corresponding complexes were included in the equilibrium models, the calculation became ill conditioned. ^{1}H NMR relaxation was chosen as an independent method to identify the complexes formed in this system.

The line-broadening effect of paramagnetic species on the NMR signals of the bulk solvent has been discussed by Swift and Connick in detail.[26] According to their results the paramagnetic contribution to the observed line width ($1/T_{2p}$) is given as the linear combination of the concentrations of the paramagnetic species if they participate in two site-exchange reactions only

$$1/T_{2p} = \sum r_i c_i \tag{1}$$

$$1/T_{2p} = 1/T_{2m} - 1/T_{20} \tag{2}$$

where T_{2m} is the measured relaxation time of the given nucleus, T_{20} is the relaxation time in absence of paramagnetic complexes, and r_i and c_i are the molar relaxation coefficient and the equilibrium concentration of the given species, respectively. In other words, ^{1}H NMR line broadening can be used for equilibrium calculations (like monochromatic photometry) as it is described elsewhere in detail.[30]

While mononuclear Cu^{2+} complexes exhibit paramagnetism, and the hydroxo species significantly broaden the ^{1}H NMR signal of the bulk water in aqueous solutions, the dimers are antiferromagnetic. As a consequence, in the Cu^{2+}–2,2′-bipyridine system a very small excess line broadening could be expected at high pH if the dimers were formed predominantly from the above-mentioned pairs of complexes. The relaxation rate vs pH curves for a few typical NMR titrations are depicted in Figure 2. Since the relaxation rate steadily increased on increasing the pH, these curves clearly illustrate the formation of at least one mononuclear hydroxo complex in alkaline solutions.

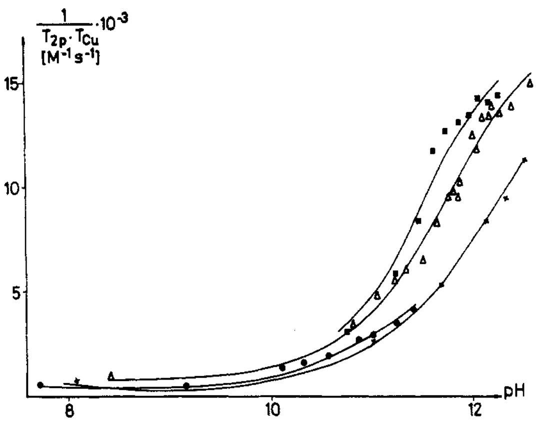

Figure 2. Paramagnetic contribution to the relaxation rate of water protons normalized for total copper(II) concentration as a function of pH: (×) $T_{Cu} = 1.59 \times 10^{-2}$ M, $T_{bpy} = 3.22 \times 10^{-2}$ M; (●) $T_{Cu} = 1.12 \times 10^{-2}$ M, $T_{bpy} = 2.25 \times 10^{-2}$ M; (△) $T_{Cu} = 3.19 \times 10^{-3}$ M, $T_{bpy} = 6.44 \times 10^{-3}$ M; (■) $T_{Cu} = 1.60 \times 10^{-3}$ M, $T_{bpy} = 3.22 \times 10^{-3}$ M. The solid lines represent calculated curves.

Table I. Stability Constants and Relaxation Coefficients for the Copper(II) Bipyridine Hydroxo Complexes

complex[d]	log β[a]	r_i, M^{-1} s^{-1}
$Cu(bpy)^{2+}$	9.06[b]	$(1.57 \pm 0.05) \times 10^3$
$Cu(bpy)_2^{2+}$	14.96[b]	$(6.8 \pm 0.8) \times 10^2$
$Cu(bpy)_3^{2+}$	18.21[c]	
$Cu_2(bpy)_2(OH)_2^{2+}$	7.27 ± 0.02	
$Cu(bpy)(OH)_2$	-9.10 ± 0.02	$(1.78 \pm 0.03) \times 10^4$
$Cu_2(bpy)_4(OH)^{3+}$	23.46 ± 0.05	
$Cu(bpy)_2(OH)^+$	5.38 ± 0.02	$(3.7 \pm 0.2) \times 10^3$

[a] $\beta_{ijk} = [Cu_i(bpy)_j(OH)_k^{2i-k}][H^+]^k/[Cu^{2+}]^i[bpy]^j$. [b] From ref 28. [c] $\log K^{Cu(bpy)_2}{}_{Cu(bpy)_3} = 3.25$.[29] [d] Protonation constant of the ligand: $\log K = 4.64$.[27]

In the final fitting procedure the log β_i and r_i values were calculated for the hydroxo complexes, by simultaneously fitting the NMR and the pH-metric data.[31] The molar relaxation coefficients of the parent complexes were also calculated. A reasonable description of the NMR data could be obtained only if both complexes $Cu(bpy)(OH)_2$ and $Cu(bpy)_2(OH)^+$ were included in the applied equilibrium model. In this case the formation of complexes $Cu_2(bpy)_2(OH)_3^+$ and $Cu_2(bpy)_3(OH)_2^{2+}$ were rejected, as their calculated stability constants were unrealistically small with extremely high standard deviations. The final result is given in Table I.

Since most of the previously published data for this system are expressed as acid dissociation constants, the equilibrium constants for reactions 3–6 were calculated.

$$2Cu(bpy)^{2+} = Cu_2(bpy)_2(OH)_2^{2+} + 2H^+ \qquad \log K_1 = -10.85 \tag{3}$$

$$Cu(bpy)^{2+} = Cu(bpy)(OH)_2 + 2H^+ \qquad \log K_2 = -18.16 \tag{4}$$

$$2Cu(bpy)_2^{2+} = Cu_2(bpy)_4(OH)^{3+} + H^+ \qquad \log K_3 = -6.46 \tag{5}$$

$$Cu(bpy)_2^{2+} = Cu(bpy)_2(OH)^+ + H^+ \qquad \log K_4 = -9.54 \tag{6}$$

---

(26) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

(27) Szabó, K.; Nagypál, I.; Fábián, I. *Talanta* **1983**, *30*, 801.

(28) Szabó, K. Thesis, Kossuth University, Debrecen, Hungary, 1984.

(29) Debreczeni, F.; Nagypál, I. *Inorg. Chim. Acta* **1982**, *57*, 135.

(30) Korondán, I.; Nagypál, I. *Inorg. Chim. Acta* **1983**, *73*, 131.

(31) The main advantage of the applied program (PSEQUAD) is that it can be used for simultaneous evaluation of different types of experimental data. In the present case the fitting parameter was calculated as a weighted sum of $\sum(1/T_{i,m} - 1/T_{i,c})^2$ (for the NMR data) and $\sum(v_{i,m} - v_{i,c})^2$ (for the pH-metric data). T is the spin–spin relaxation time, v is the volume of the titrant, and the indexes m and c denote measured and calculated data, respectively. For further detail see ref 25.

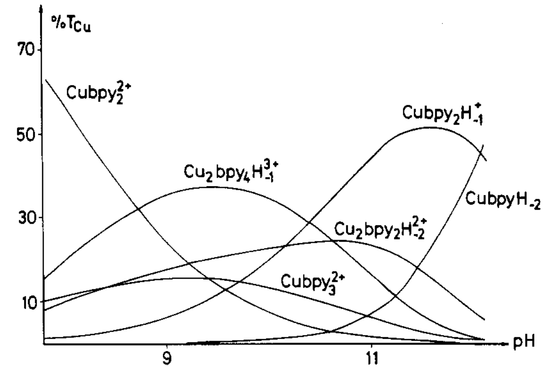

Figure 3. Concentration distribution for the Cu^{2+}–2,2′-bipyridine system (T_{Cu} = 7.96 × 10^{-3} M; T_{bpy} = 1.61 × 10^{-2} M; $[Cu_i(bpy)_jH_{-k}{}^{2i-k}] = [Cu_i(bpy)_j(OH)_k{}^{2i-k}]$).

The value for log K_1 is in excellent agreement with literature data: −10.74,[18] −10.81,[19] −11.06,[20] −10.62,[21] −10.60.[22] The dissociation constant for reaction 4 is considerably smaller than that given by Ryland et al. (log K_2 = −16.28).[18] The observed difference in K_2 is perhaps caused by the different experimental conditions as well as by the approximations involved in the graphic evaluation method used in that early work. No literature data are available for complexes $Cu_2(bpy)_4(OH)^{3+}$ and $Cu(bpy)_2(OH)^+$.

The most striking feature of this system is that the hydroxide group can displace one bipyridine molecule from the $Cu(bpy)_2{}^{2+}$ complex in moderately alkaline solutions (Figure 3). In principle analogous reactions may also influence the equilibria of ternary Cu^{2+}–2,2′-bipyridine–B ligand systems, but significant hydroxo complex formation has been reported only for a few systems in the pH range used for the calculation of the stability constant of the Cu(bpy)B complex.

The paramagnetic contribution to the line width is attributed to fast proton-exchange reactions between the coordination spheres of the paramagnetic complexes and the bulk water. While in the case of the parent complexes these reactions can proceed through the coordinated water molecules only, for hydroxo complexes another pathway is available via the OH^- group(s); thus, r_i can be written in the form

$$r_i = r_{i1} + r_{i2} \tag{7}$$

r_{i1} and r_{i2} denote the relaxation coefficients characteristic for the coordinated H_2O and OH^-, respectively. The relaxation effect of the parent complexes is roughly proportional to the number of the water molecules in the coordination sphere with an average of r = 366 M^{-1} s^{-1} per H_2O unit. On this basis r_{i1} can be estimated for $Cu(bpy)(OH)_2$ and $Cu(bpy)_2(OH)^+$ by assuming that two and one water molecules are coordinated in these complexes, respectively. The relaxation coefficients for the two species are r_{i1} = 733 and 366 M^{-1} s^{-1} and r_{i2} = 17 100 and 3327 M^{-1} s^{-1}, respectively.

The temperature dependence of $1/T_{2p}$ has been measured at different ligand and metal concentrations. In the applied pH range (11.2–13.4) the paramagnetic line broadening is exclusively attributed to the complexes $Cu(bpy)(OH)_2$ and $Cu(bpy)_2(OH)^+$. $1/T_{2p}$ steadily decreased on increasing the temperature regardless of the composition or the pH of the samples. This observation clearly indicates that the paramagnetic contribution to the measured line width is relaxation-controlled for both hydroxo species;[26] i.e. r_i can be expressed in the form

$$r_i = \frac{1}{[H_2O]} \frac{x}{T_{2B}} \tag{8}$$

where x and T_{2B} are the number of the exchangable protons and the paramagnetic relaxation time for the given coordination sphere, respectively.

The paramagnetic relaxation times (T_{2B}) for the hydroxide protons of the complexes $Cu(bpy)(OH)_2$ and $Cu(bpy)_2(OH)^+$ are 1.1 × 10^{-6} and 2.7 × 10^{-6} s, respectively. These relaxation times are considerably shorter than the corresponding values for other ternary hydroxo complexes—for $CuL_2(OH)$ (L = *N*-methylglycine) T_{2B} = 3.7 × 10^{-6} s[32] and for $Cu(NTA)(OH)^{2-}$ (NTA = nitrilotriacetate) T_{2B} = 7.0 × 10^{-6} s[33]—and comparable or even shorter than for the tetrahydroxo complex ($Cu(OH)_4{}^{2-}$): T_{2B} = 1.6 × 10^{-6} s.[32] These results strongly suggest a coordinative interaction between the central ion and the OH^- group much stronger than the usual in the case of bipyridine complexes. The phenomenon is the consequence of the typical π interaction between this aromatic ligand and copper(II).[8-10] The back-coordination of the d electrons to the π^* orbital of the ligand(s) significantly reduces the electron density on the metal ion; thus, it forms stronger bonds with electron-rich ligands such as OH^-. In the case of other hydroxo species the lack of such an electronic effect results in longer paramagnetic relaxation time for the OH^- proton.

Acknowledgment. I am indebted to Professor István Nagypál for helpful discussions.

---

(32) Debreczeni, F.; Polgár, J.; Nagypál, I. *Inorg. Chim. Acta* **1983**, *71*, 195.
(33) Debreczeni, F.; Nagypál, I. *Inorg. Chim. Acta* **1983**, *72*, 61.