

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231356066>

Spectral properties of mixed-ligand copper(II) complexes and their corresponding binary parent complexes

ARTICLE *in* INORGANIC CHEMISTRY · NOVEMBER 1972

Impact Factor: 4.76 · DOI: 10.1021/ic50117a036

CITATIONS

62

READS

8

3 AUTHORS, INCLUDING:



[F\(rances\) Ann Walker](#)

The University of Arizona

240 PUBLICATIONS 8,648 CITATIONS

SEE PROFILE



[Donald Bruce McCormick](#)

Emory University

283 PUBLICATIONS 4,184 CITATIONS

SEE PROFILE

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF CALIFORNIA, SAN FRANCISCO, CALIFORNIA 94132, THE INSTITUTE OF INORGANIC CHEMISTRY, UNIVERSITY OF BASEL, CH-4000 BASEL, SWITZERLAND, AND THE SECTION OF BIOCHEMISTRY AND MOLECULAR BIOLOGY AND GRADUATE SCHOOL OF NUTRITION, CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

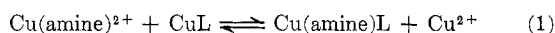
Spectral Properties of Mixed-Ligand Copper(II) Complexes and Their Corresponding Binary Parent Complexes

By F. ANN WALKER,*^{1a} HELMUT SIGEL,^{2b} AND DONALD B. MCCORMICK^{1c}

Received January 3, 1972

The ternary complex, $\text{Cu}(2,2'\text{-bipy})(\text{ox})$, has been prepared and compared with the binary parent complexes $\text{Cu}(2,2'\text{-bipy})_2(\text{ClO}_4)_2$ and $\text{K}_2\text{Cu}(\text{ox})_2$. The mixed-ligand complex, $\text{Cu}(2,2'\text{-bipy})(\text{pyr})$, was also prepared and compared with $\text{Cu}(8\text{-HQ})_2$. The solids were characterized by elemental analysis and infrared spectra. The epr and reflectance spectra indicate unequivocally that the ternary cases are definite complexes and not mixtures of the corresponding binary parent complexes. In all of the ternary complexes, the epr parameters indicate a square-planar coordination sphere for $\text{Cu}(\text{II})$. These complexes, as well as several species containing 3,5-disulphopyrocatecholate (Tiron), have also been studied in the glassy state (ethylene glycol-water glasses) and in aqueous solution at room temperature. Again, the epr parameters and the absorption spectra indicate clearly that mixed-ligand species are formed in solution. Furthermore, based on these data it is suggested that π bond formation is more important in the ternary complexes than in the binary ones.

Studies of the thermodynamics of mixed-ligand systems reveal that ternary complexes are often more stable than expected from statistical reasons.¹⁻¹¹ However, rather unique qualities are observed for mixed bidentate ligand Cu^{2+} complexes containing an aromatic amine and a second ligand with O as donor atoms.⁸⁻⁵ Such ternary complexes are extremely stable. For example, pyrocatecholate forms a more stable complex with $\text{Cu}(\text{bipy})^{2+}$ than with $\text{Cu}(\text{aq})^{2+}$.^{4,6,12} Hence, equilibrium 1 lies to the right, and for the corresponding constant, $\Delta \log K$,¹³ positive values are obtained (cf. Table I). This result is in contrast to the general rule, $K^{\text{Cu}}_{\text{CuL}} > K^{\text{Cu}}_{\text{CuL}_2}$.¹⁴



Systematic studies¹¹ have demonstrated that for the observation of a positive value for $\Delta \log K$, an aromatic amine must be involved. Thus, if 2,2'-bipyridyl is replaced by ethylenediamine, the stability of the ternary complex decreases sharply (cf. Table I). Therefore, π bonding must be important for the stability of the mixed-ligand complexes. The π system of the ligand with O as donors also has some influence but a less pronounced one, as a comparison between the systems containing oxalate or pyrocatecholate shows.¹⁵ Addi-

TABLE I
STABILITY OF SEVERAL TERNARY Cu^{2+} COMPLEXES

System	Log X^a	$\Delta \log K^b$
2,2'-Bipyridyl- Cu^{2+} -oxalate ⁷	4.9 ^c	0.7 ^c
2,2'-Bipyridyl- Cu^{2+} -pyrocatecholate ⁴	6.15	0.43
2,2'-Bipyridyl- Cu^{2+} -Tiron(tetraanion) ⁸	5.76	0.11
Ethylenediamine- Cu^{2+} -pyrocatecholate ¹⁰	2.65	-0.76
Ethylenediamine- Cu^{2+} -oxalate ⁹	1.3	-1.1

^a $X = [\text{Cu}(\text{amine})\text{L}]^2 / [\text{Cu}(\text{amine})_2][\text{CuL}_2]$ corresponding to the equilibrium $\text{Cu}(\text{amine})_2 + \text{CuL}_2 \rightleftharpoons 2\text{Cu}(\text{amine})\text{L}$. ^b Cf. eq 1. ^c This value is only estimated; cf. ref 7.

tionally, studies of the kinetics of mixed-ligand complex formation revealed that the rates for the reaction between $\text{Cu}(\text{bipy})^{2+}$ and $\text{Cu}(\text{aq})^{2+}$ with amino acid anions are comparable.^{16,17}

With these results in mind, we began a study of the spectral properties, *i.e.*, infrared, electronic, and epr spectra, of several mixed-ligand Cu^{2+} complexes containing 2,2'-bipyridyl as one ligand. The aim was to learn more about the general qualities of ternary complexes and, if possible, to obtain information about the electron distribution in such systems. The solid complex, $\text{Cu}(\text{bipy})(\text{ox})$, and its parent complexes, $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ and $\text{K}_2\text{Cu}(\text{ox})_2$, were prepared.¹² $\text{Cu}(\text{bipy})(\text{pyr})$ was also made and compared with $\text{Cu}(8\text{-HQ})_2$. Additionally, these complexes and the binary and ternary ones with Tiron were studied in solution.

Experimental Section

Materials.—Oxalic acid, pyrocatechol, 2,2'-bipyridyl, and 8-hydroxyquinoline were obtained from Eastman Organic Chemicals. The dihydrate of 8-hydroxyquinoline-5-sulfonic acid was purchased from Aldrich Chemical Co., Tiron was from J. T. Baker Chemical Co., and ethylene glycol from Matheson Coleman and Bell. $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was from Alfa Inorganics, and ^{63}CuO from Oak Ridge National Laboratories.

Apparatus.—A Corning Model 12 research pH meter with a glass electrode was used for the adjustment of pH.

Reflectance and solution absorption spectra were measured on a Cary 14 spectrophotometer. The reflectance spectra could be recorded only over the range of the visible (tungsten) light source (330–760 nm).

Infrared spectra were taken, both as Nujol mulls and KBr pellets, on a Perkin Elmer Infracord. No shifts of peaks were

(1) (a) San Francisco State College. (b) University of Basel. (c) Cornell University.

(2) R. DeWitt and J. I. Watters, *J. Amer. Chem. Soc.*, **76**, 3810 (1954).

(3) S. Kida, *Bull. Chem. Soc. Jap.*, **29**, 805 (1956).

(4) H. Sigel, *Chimia*, **21**, 489 (1967).

(5) (a) R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970); (b) R. Griesser and H. Sigel, *ibid.*, **10**, 2229 (1971).

(6) G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).

(7) H. Sigel, P. R. Huber, and R. F. Pasternack, *Inorg. Chem.*, **10**, 2226 (1971).

(8) H. Sigel, P. R. Huber, R. Griesser, and B. Prijs, results to be submitted for publication.

(9) W. B. Schaap and D. L. McMasters, *J. Amer. Chem. Soc.*, **83**, 4699 (1961).

(10) P. R. Huber, R. Griesser, B. Prijs, and H. Sigel, *Eur. J. Biochem.*, **10**, 235 (1969).

(11) P. R. Huber, R. Griesser, and H. Sigel, *Inorg. Chem.*, **10**, 945 (1971).

(12) Abbreviations used: 2,2'-bipyridyl, bipy; general ligand, L; glycinate, Gly; 8-hydroxyquinoline, 8-HQ; 8-hydroxyquinoline-5-sulfonate, 8-HQ-5-S; oxalate, ox; pyrocatecholate, pyr; 3,5-disulphopyrocatecholate, Tiron.

(13) $\Delta \log K = \log K^{\text{Cu}}_{\text{Cu}(\text{amine})\text{L}} - \log K^{\text{Cu}}_{\text{CuL}_2}$.

(14) L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

(15) For a discussion of the general aspects of the stability of ternary complexes, see ref 5.

(16) R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, **92**, 6146 (1970).

(17) R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, **11**, 276 (1972).

TABLE II
 ELEMENTAL ANALYSIS AND VISIBLE CHARACTERISTICS OF SEVERAL SOLID BINARY AND TERNARY Cu²⁺ COMPLEXES

Complex ^{1a}	% Cu		% C		% H		% O		% N		Visible characteristics
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Cu(bipy)(ox)	20.65	20.69	46.83	46.44	2.62	2.50	20.80	20.93	9.10	9.15	Turquoise (bluish green) powder
Cu(bipy) ₂ (ClO ₄) ₂ ^b	11.05	10.90	41.79	41.18	2.89	3.00	22.27	21.89	9.75	9.56	Fine blue crystals
K ₂ Cu(ox) ₂ ·c	19.99		15.12				40.28				Bright blue crystals
+1H ₂ O	18.92	18.77	14.31	14.88	0.60	1.00	42.88	42.01			
Cu(bipy)(pyr) ^a	19.38	18.69	58.62	57.43	3.69	4.25	9.76	10.39	8.55	8.03	Dark brown powder
+1H ₂ O	18.37		55.57		4.08		13.88		8.10		
Cu(8-HQ) ₂	18.06	17.86	61.44	61.21	3.44	3.28	9.09	9.36	7.96	7.91	Mustard yellow powder
[Cu(bipy)(OH)] ₂ ·(ClO ₄) ₂ ^d	18.90	18.83	35.73	36.17	2.70	2.64	23.80	23.48	8.33	8.33	Bluish gray (violet) powder

^a Hygroscopic complexes. ^b % Cl: 12.34 (calcd), 12.33 (found). ^c % K: 24.61 (calcd), 23.29 (calcd with 1H₂O), 22.99 (found). ^d % Cl: 10.55 (calcd), 10.80 (found).

noted on comparison of the spectra obtained from samples in each of these media.

Epr spectra were recorded on either a Varian E-3 or E-9 epr spectrometer. The microwave frequency was measured using DPPH ($g = 2.0036$). Glassy and polycrystalline epr spectra were recorded at 77°K, and solution spectra at ambient temperature (~22°). Several experiments were performed with tubes sealed under high vacuum, no influence of the air was observed on the spectra.

Solid Complexes.—Two of the preparations are described in detail: the first complex is a new compound, and in the second case a procedure superior to a published one is given.

Cu(bipy)(pyr).—Ten millimoles of each reactant was used. Pyrocatechol was dissolved in 10 ml of H₂O and 2.5 ml of acetone. Copper perchlorate was dissolved in 10 ml of H₂O and 2,2'-bipyridyl in 10 ml of 50% aqueous acetone. Upon combination of these two solutions precipitation occurred. While stirring, this suspension was slowly added to the pyrocatechol solution. A blue-green solution of pH 3 resulted. The pH was adjusted to 8 with 2 N NaOH and a brown precipitate obtained. The filtered complex was washed twice with water and twice with acetone, yield approximately 95%.

Cu(bipy)(ox).—Ten millimoles of each reactant was used. Oxalic acid was dissolved in 70 ml of water and the pH adjusted to 6 with NaOH; then 10 ml of acetone was added. 2,2'-Bipyridyl was dissolved in 20 ml and copper perchlorate in 10 ml of 50% aqueous acetone. These two solutions were combined, and the oxalate solution was added with stirring; a precipitate formed. This mixture was stirred for an additional 30 min and filtered. The complex was washed three times with water and once with acetone, yield 77%. In this way anhydrous Cu(bipy)(ox) was obtained directly (cf. also the section on polycrystalline samples), and not the dihydrate as described by Sone, *et al.*¹⁸

The compounds, Cu(bipy)₂(ClO₄)₂, [Cu(bipy)(OH)]₂(ClO₄)₂, K₂[Cu(ox)₂], and Cu(8-HQ)₂, were prepared similarly; cf. also ref 19–22.

The elemental analysis (performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y.) of these complexes together with their visible characteristics are assembled in Table II. Attempts to prepare K₂[Cu(pyr)₂] and Cu(bipy)-(H₂O)_n(ClO₄)₂ or Cu(bipy)(OH)₂ failed.

Complexes in Solution.—Solutions of the complexes were prepared either by dissolving the solids or by preparation of the complex solutions as described below. The results appeared to be identical. Solutions containing ⁶³⁺⁶⁵Cu were used to find the best conditions for the glassy epr spectra; the experiments were then repeated with ⁶³Cu.

⁶³CuO was dissolved in perchloric acid to produce aqueous

solutions of ⁶³Cu(ClO₄)₂ of accurately known concentration. Samples of the complexes were prepared by combining aliquots of ⁶³Cu(ClO₄)₂ or ⁶³⁺⁶⁵Cu(ClO₄)₂ and the required ligand(s). The desired complex species were obtained by adjusting the pH of each solution to a value (see later in Table IV) in accord with the acidity constants of the ligands and the stability constants of their corresponding complexes: bipy-Cu²⁺-ox system and parent complexes, ref 7; bipy-Cu²⁺-pyr system and parent complexes, ref 4; bipy-Cu²⁺-Tiron system and parent complexes, where L = Tiron: $pK_{HL}^{H_2L} = 7.66$, $pK_{HL}^{HL} = 12.55$, $\log K_{CuL}^{CuL} = 14.28$, $\log K_{CuL}^{CuL_2} = 11.14$; $\log \beta_{Cu(bipy)L}^{Cu(bipy)L} = 22.39$ ($I = 0.1$, 25°);⁸ 8-HQ and 8-HQ-5-S and the corresponding Cu²⁺ complexes, ref 6, 14, 23.

After adjustment of the pH, ethylene glycol and distilled water were added to produce solutions in which the final Cu²⁺ concentration was 10⁻³ M. The solvent ratios were varied in order to obtain the best resolution of the glassy spectrum. The best ratio was usually found to be 3:1 or 2:1 ethylene glycol:water. No dependence of the epr parameters on the solvent composition was observed over the range of solvent ratios studied.

Results and Discussion

A. Polycrystalline Samples.—The parameters of the infrared, visible-reflectance, and epr spectra of the polycrystalline binary and ternary Cu²⁺ complexes are listed in Table III. The infrared spectra confirm the elemental analyses with regard to composition of the complexes. Excluding the binuclear complex, [Cu(bipy)(OH)]₂(ClO₄)₂, the epr data are typical for axially symmetric complexes ($g_1 = g_{||}$, $g_2 = g_{\perp}$) in which the coordination geometry is at least approximately square planar, and the unpaired electron is in the $d_{x^2-y^2}$ orbital of copper.²⁴ An exception to this general observation is data due to the complex, Cu(bipy)(ox), for which three g values are observed. It is interesting to note that their values are within the experimental error of those published for the compound Cu(bipy)₂(ox), 2.236, 2.122, 2.069.²⁴ However, the infrared spectra are rather different; Hathaway, *et al.*,²⁴ reported oxalate absorptions at 1665, 1630, 1610, 1295, and 825 cm⁻¹, whereas we observe no peak at 825 cm⁻¹, but additional peaks (which we attribute to oxalate) at 1590 and 795 cm⁻¹.

The similarity in epr parameters between Cu(bipy)(ox) (this work) and Cu(bipy)₂(ox) (ref 24) suggests that the latter complex was also Cu(bipy)(ox), co-crystallized with excess bipyridyl. Additionally, in

(18) K. Sone, S. Utsuno, and T. Ogura, *J. Inorg. Nucl. Chem.*, **31**, 117 (1969).

(19) F. M. Jaeger and J. A. Dijk, *Z. Anorg. Chem.*, **227**, 273 (1936).

(20) C. M. Harris, E. Sinn, W. R. Walker, and P. R. Williams, *Aust. J. Chem.*, **21**, 631 (1968).

(21) "Gmelins Handbuch der anorganischen Chemie," 8th ed, Kupfer (No. 60), Part B, Lieferung 3, 1965, p 1047.

(22) Cf. ref 21, Lieferung 4, 1966, p 1697.

(23) C. F. Richard, R. L. Gustafson, and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 1033 (1959).

(24) B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 2219 (1969).

TABLE III
PARAMETERS OF THE INFRARED, REFLECTANCE, AND ESR SPECTRA OF THE POLYCRYSTALLINE
BINARY AND TERNARY Cu^{2+} COMPLEXES

Complex ^{1,2}	Infrared spectra, ^a cm^{-1}	Electronic spectra, kK	Esr spectra ^b			Relative esr signal intensity
			g_1	g_2	g_3	
$\text{Cu}(\text{bipy})(\text{ox})$	bipy: 3050 (w), 1590 (s), 1490 (m), 1445 (s), 1250 (m), 1175, 1160 (m), 1110 (m), 1055 (m), 1035, 1020 (m), 985 (w), 905 (w), 777 (s, b), 735 (s) ox: 1660 (s, b), 1590 (s), 1360 (w), 1290 (s), 795 (s), 750 (w) H_2O : 3400 (w)	14.1 14.3 ^c	2.228	2.126	2.066	200
$\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$	bipy: 3050 (w), 1660 (w), 1610 (m), 1570 (m), 1500 (m), 1480 (m), 1450 (s), 1320 (m), 1255 (m), 1180, 1160 (w), 1035, 1020 (w), 900 (w), 775 (s, b), 733 (s) ClO_4 : 1090 (s, b), 933 (w)	14.5 13.9, 9.7 ^c 15.1 ^d	2.20 ^e	2.060 2.050 ^d		125
$\text{K}_2\text{Cu}(\text{ox})_2 \cdot \text{H}_2\text{O}$	ox: 1660, 1630 (s, b), 1405 (s, b), 1340 (w), 1275 (s), 895 (m), 860 (m), 800 (s, b) H_2O : 3400 (m), 1110 (m)	14.9 14.7 ^c	2.285	2.074		400
$\text{Cu}(\text{bipy})(\text{pyr})$	bipy: 3000 (w), 1630 (w), 1600 (m), 1560 (m), 1475 (s), 1440 (m), 1310 (m), 1250 (s), 1210 (w), 1165, 1150 (m), 1120, 1100 (m), 1055 (w), 1030, 1022 (m), 977 (w), 905 (w), 767 (s), 730 (s) pyr: 3000 (w), 1475 (s), 1405 (w), 1250 (s), 890 (w), 864 (m), 813 (w), 792 (s), 746, 740 (s)	20.8 (CT) ^e	2.18 ^e	2.089		67
$\text{Cu}(\text{8-HQ})_2$	8-HQ: 3000 (w), 1600, 1570 (m), 1540 (w), 1500 (s), 1465 (s), 1435 (w), 1380 (s), 1325 (s), 1280 (m), 1235, 1225 (m), 1180 (m), 1150 (w), 1120 (s), 1055 (w), 1035 (m), 855 (w), 837 (w), 822 (s), 807 (s), 788 (s), 746 (s), 734 (m), 725 (s)	14.5	2.186	2.061		162
$[\text{Cu}(\text{bipy})(\text{OH})]_2(\text{ClO}_4)_2$	bipy: 3100 (w), 1610 (m), 1575 (m), 1500 (m), 1480 (s), 1322 (m), 1258 (m), 1220 (w), 1178, 1165 (m), 1125 (m), 1038, 1024 (m), 987 (m), 905 (m), 775 (s, b), 734 (s) OH: 3400 (m), 2000 (w), 1675 (w), 1015 (m), 880 (m, b) ClO_4 : 1084 (s, b), 935 (w)	17.4 (sh) ^f 14.4	h	h	h	1

^a Key: w, weak; m, medium; s, strong; b, broad. ^b g values ± 0.006 . ^c Reference 18. ^d Reference 24. ^e Charge-transfer band. ^f Shoulder. ^g Estimated from broad band. ^h Reference 30.

solution we could find no evidence for a mixed ligand species containing greater amounts of bipyridyl than that present in $\text{Cu}(\text{bipy})(\text{ox})$.⁷ It appears to us that the species, $\text{Cu}(\text{bipy})_2(\text{ox})$, does not exist in solution nor in the solid state.

Although square-planar $\text{Cu}(\text{bipy})(\text{ox})$, $\text{Cu}(\text{bipy})(\text{pyr})$, and $\text{Cu}(\text{8-HQ})_2$ ²⁵ do not have C_4 rotation axes, the latter two display axial symmetry in the solid state, while $\text{Cu}(\text{bipy})(\text{ox})$ does not (*cf.* Table III). It should be noted, however, that the average of g_2 and g_3 for solid $\text{Cu}(\text{bipy})(\text{ox})$ is 2.096, and this value is very similar to that of 2.089 for g_{\perp} for $\text{Cu}(\text{bipy})(\text{pyr})$. It may be that the crystal lattice imposes more distortion on the planar coordination geometry of $\text{Cu}(\text{bipy})(\text{ox})$ than of $\text{Cu}(\text{bipy})(\text{pyr})$, thus reducing the apparent symmetry to the expected D_{2h} . All three of these complexes, as well as $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$ and $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$, show very similar (axially symmetric) epr spectra in frozen ethylene glycol-water glasses (*cf.* discussion of spectra taken in the glassy state, and Table IV).

The epr data of Table III make it quite clear that the compound which we have formulated as $\text{Cu}(\text{bipy})(\text{ox})$ is *not* the disproportionation product $[\text{Cu}(\text{bipy})_2][\text{Cu}(\text{ox})_2]$, as suggested by Sone, *et al.*,¹⁸ from reflectance

spectral measurements. The epr spectra of the magnetically concentrated polycrystalline samples of $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ and $\text{K}_2\text{Cu}(\text{ox})_2$ are not in any way superimposable with that of $\text{Cu}(\text{bipy})(\text{ox})$, nor are the values of g_1 , g_2 , or g_3 of the latter compound in any way similar to those of g_1 and g_2 of the two copper complexes formed if disproportionation did take place. That $\text{Cu}(\text{bipy})(\text{ox})$ is a defined complex and not a mixture of the corresponding binary parent complexes is additionally confirmed by the results of our reflectance absorption spectra; $\text{Cu}(\text{bipy})(\text{ox})$ absorbs at longer wavelengths than either of the parent complexes.

Attempts to prepare a simple Cu^{2+} -bipy 1:1 complex were unsuccessful. The only compound that could be isolated was the hydrolyzed dimer with the formula $[\text{Cu}(\text{bipy})(\text{OH})]_2(\text{ClO}_4)_2$ (*cf.* Table II for analysis). Previous studies of the equilibrium constants in aqueous solution had already revealed that the only existing hydrolyzed species is the dimer, $[\text{Cu}(\text{bipy})(\text{OH})]_2^{2+}$.²⁶ The crystal structure of $[\text{Cu}(\text{bipy})(\text{OH})]_2(\text{NO}_3)_2$ has been reported.²⁷ The magnetic moment of our sample, $[\text{Cu}(\text{bipy})(\text{OH})]_2(\text{ClO}_4)_2$, is 1.77 BM/copper at 25°, which is higher than a typical spin-only moment. A variable temperature magnetic susceptibility study of

(25) *Cf.* ref 22, p 1698; J. A. Bevan, D. P. Graddon, and J. F. McConnell, *Nature (London)*, **199**, 373 (1963); R. C. Hoy and R. H. Morris, *Acta Crystallogr.*, **22**, 476 (1967).

(26) D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, **28**, 1271 (1966).

(27) R. J. Majeste and E. A. Mayers, *J. Phys. Chem.*, **74**, 3497 (1970).

[Cu(bipy)(OH)(H₂O)]₂(SO₄)·3H₂O (which has been shown to contain five-coordinate Cu(II)²⁸) has shown that it has a magnetic moment per copper of 1.94 BM at 25° and 2.04 BM at 84°K, which suggests that it has a triplet ground state with the singlet excited state lying about 48 cm⁻¹ higher in energy.^{28,29} This compound, and also the nitrate and perchlorate salts, should therefore exhibit triplet epr spectra. Barnes, *et al.*,³⁰ have very recently reported the epr spectrum of [Cu(bipy)(OH)]₂(ClO₄)₂ and other [Cu(bipy)(OH)]₂²⁺ salts. Our sample gives essentially the same spectrum, except that the high field peak is of lower relative intensity than that shown in Figure 4 of ref 30.

B. Glassy Epr Samples. Coordination Sphere of Cu(II).—Although it is reasonable to conclude that the mononuclear binary and ternary Cu²⁺ complexes discussed so far probably all have at least approximate square-planar geometry, the coordination number and geometry of these complexes in aqueous solution is more difficult to establish. Usually Cu²⁺ prefers in aqueous solution a square-planar (or grossly distorted octahedral) coordination sphere, as can be judged from the stabilities^{14,31} of its complexes and their catalytic behavior.³² The only significant exceptions to this rule are the Cu²⁺ complexes formed with ligands of good π -accepting qualities, *e.g.*, *o,o'*-phenanthroline or 2,2'-bipyridyl. With these ligands 1:3 complexes may be easily formed.^{14,33} In fact, it has been shown that [Cu(bipy)₂(H₂O)]₂²⁺ exists mainly as the cis isomer at room temperature.³⁴ However, the structure and epr spectrum of this complex at low temperatures in the glassy state is unknown due to disproportionation to the mono and tris complexes.^{35,36}

For the work described herein, it is important to note that, with the exception of the Cu²⁺-bipyridyl complexes, all the complexes formed between Cu²⁺ and oxalate, pyrocatecholate, Tiron, 8-hydroxyquinolate or its 5-sulfonate (*i.e.*, the ligands of Tables III and IV) show only two stepwise formation constants. As already mentioned, this is true with most bidentate ligands.¹⁴ It holds also for the ternary complexes containing 2,2'-pyridyl, which are discussed herein.^{4,7,8} Although this suggests that the geometry of the bis complexes of bidentate ligands is trans with respect to the remaining "free" coordination sites, the extent to which water molecules solvate these in solution is not known. It is clear, however, that the strength of this solvation interaction, if it exists, is small, since all of the compounds listed in Tables II and III could be prepared in anhydrous form (although K₂Cu(ox)₂ and

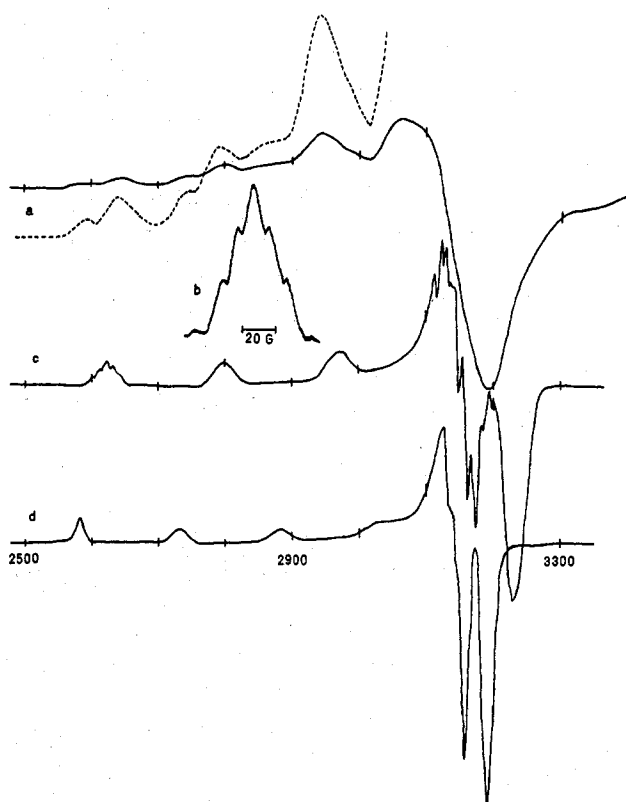


Figure 1.—Glassy epr spectra of (a) "Cu(bipy)₂²⁺" in 67% ethylene glycol-33% water. Dashed line shows magnification of low-field lines, previously shown to be due to Cu(bipy)²⁺ and Cu(bipy)₂²⁺.³⁸ (b) Cu(bipy)(ox) in 40% ethylene glycol-60% water; (d) Cu(ox)₂²⁻ in 67% ethylene glycol-33% water.

Cu(bipy)(pyr) tended to pick up water when exposed to the atmosphere). For simplicity, therefore we choose to omit waters of hydration in our formulation of these complexes in solution or in the glassy state, even though weak solvation may in fact be present.

Evidence for Ternary Complex Formation in the Glassy State and in Solution.—The epr spectrum of a typical ternary complex, Cu(bipy)(ox), is shown in Figure 1c, with the lowest field parallel line magnified to show superhyperfine splittings due to two nitrogen nuclei³⁷ (Figure 1b). This spectrum is clearly different from those of the two binary parent complexes, Cu(ox)₂²⁻ (*cf.* Figure 1d) and "Cu(bipy)₂²⁺"³⁸ (*cf.* Figure 1a), and is certainly not the superposition of these other two spectra. Figure 1 thus unequivocally proves the existence of the ternary complex Cu(bipy)(ox) as a unique compound in the glassy state, and confirms the titration data which had previously indicated the existence of this ternary complex.⁷

Table IV lists glassy epr and solution electronic spectral data for the complexes of interest in this work. These data confirm the visual impressions of Figure 1 that the ternary complex Cu(bipy)(ox) is unique; it is different from any of the possible binary parent complexes. In addition, Table IV presents glassy epr data for two other ternary complexes, Cu(bipy)(pyr) and

(28) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).

(29) J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *ibid.*, 1593 (1970).

(30) J. A. Barnes, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **11**, 144 (1972).

(31) D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc. A*, 1755 (1967).

(32) H. Sigel, *Angew. Chem.*, **81**, 161 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 167 (1969).

(33) G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963); H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

(34) M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968).

(35) F. A. Walker and H. Sigel, *Inorg. Chem.*, **11**, 1162 (1972).

(36) It has very recently been shown (H. Nakai, *Bull. Chem. Soc. Jap.*, **44**, 2412 (1971)) that in the solid state Cu(bipy)₂(ClO₄)₂ "is a tetragonally distorted octahedron; the four nitrogen atoms of bipyridine molecules are arranged in a flattened tetrahedral manner (av Cu-N = 1.99 Å), the least-squares plane of these atoms making an equatorial plane, while the polar positions are occupied by the two oxygen atoms of perchlorate anions, the Cu-O distances being 2.45 and 2.73 Å."

(37) It has been pointed out that the ¹⁴N superhyperfine structure observed around g_{\parallel} is $A_{\parallel}(^{14}\text{N})$ and that observed around g_{\perp} is $1/2(A_{\parallel} + A_{\perp})(^{14}\text{N})$, on the average, since the principal axis of nitrogens bonded along the x and y axes of Cu is perpendicular to the principal axis of the complex.

(38) As mentioned, the glassy epr spectrum of "Cu(bipy)₂²⁺" at 77°K has been shown to be largely a superposition of the epr spectra of the disproportionation products Cu(bipy)²⁺ and Cu(bipy)₂²⁺.³⁸

TABLE IV
 ELECTRONIC AND ESR SPECTRAL PARAMETERS FOR BINARY AND TERNARY Cu^{2+} COMPLEXES IN
 AQUEOUS SOLUTION OR MIXED SOLVENTS

Complex ^{1a}	pH ^a	Electronic spectra, kK	Esr parameters of ^{63}Cu complexes in ethylene glycol-water glasses at 77°K					
			$g_{ }$	g_{\perp}	$10^4 A_{ } $, cm ⁻¹	$10^4 A_{\perp} $, cm ⁻¹	$10^4 A_{ N} $, cm ⁻¹	$10^4 A_{\perp N} $, cm ⁻¹
$\text{Cu}(\text{aq})^{2+}$	1.0	12.6 12.6 ^b	2.422	2.087	134	$\leq 11^e$	<i>g</i>	<i>g</i>
$\text{Cu}(\text{Tiron})^{2-}$	6.0	14.1	2.327	2.072	164	$\sim 11^e$	<i>g</i>	<i>g</i>
$\text{Cu}(\text{Tiron})_2^{6-}$	8.0	15.05	2.280	2.066	179	22	<i>g</i>	<i>g</i>
$\text{Cu}(\text{ox})_2^{2-}$	5.5	14.5 14.0 ^c	2.318	2.071	164	$\leq 8^e$	<i>g</i>	<i>g</i>
$\text{Cu}(\text{bipy})_2^{2+}$	2.5	13.6, 11.1	2.308	2.068	166	7	~ 14	$\sim 10^e$
$\text{Cu}(\text{bipy})_3^{2+}$	5.5	13.9, 10.8 13.9, 10.5 ^b 13.5, 11.1 ^c	<i>e, f</i>	<i>e, f</i>	<i>e, f</i>	<i>f</i>	<i>f</i>	<i>f</i>
$\text{Cu}(\text{bipy})_3^{2+}$	5.5	14.7, 9.1	2.266	2.070	161	13	16	10
$\text{Cu}(\text{bipy})(\text{ox})$	5.0	15.8 15.8 ^c	2.258	2.063	183	24	11	10
$\text{Cu}(\text{bipy})(\text{pyr})$	7.5	~ 16.1 (sh), ^d 23.4	2.249	2.069	186	22	12	11
$\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$	6.0	16.1	2.251	2.067	176	25	14	11
$\text{Cu}(\text{8-HQ})_2$	8.5	16.4	2.244	2.064	177	~ 24	13	11
$\text{Cu}(\text{8-HQ-5-S})_2^{2-}$	8.5	16.4	2.248	2.066	177	~ 24	13	11

^a Cf. Experimental Section. ^b C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955); "Absorption Spectra and Chemical Bonding in Complexes." Pergamon Press, Oxford, 1964, p 124. ^c Reference 18. ^d Shoulder. ^e Not resolved. ^f See ref 35, 39. ^g Not expected.

$\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$, and the related complexes, $\text{Cu}(\text{8-HQ})_2$ and $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$. The electronic spectra and epr parameters for these five complexes are remarkably similar to each other, and markedly different from those of the binary complexes. They show consistently smaller values of $g_{||}$ and larger values of $|A_{\perp}|$, and generally larger values of $|A_{||}|$ than the related binary complexes.

Bonding Coefficients for Ternary Complexes. Possible Evidence for π Back-Bonding.—The epr parameters of Table IV may be used to estimate the bonding coefficients, β_1^2 and ϵ^2 , which describe the fraction of copper d orbitals used in σ and out-of-plane π bonding, respectively.^{39,40} The σ -bonding parameter β_1^2 describes the covalency of the σ bond between copper and its ligands, $\beta_1^2 = 1$ if the bond is totally ionic and $\beta_1^2 = 0.5$ if it is completely covalent. Using the ^{14}N splitting constants and eq 12 and 13 of ref 39, we find that $\beta_1^2 \approx 0.85$ for the ternary complexes and 0.83 for $\text{Cu}(\text{bipy})_3^{2+}$ (cf. Table V). (Where use of eq 12 and 13 of ref 39 gave slightly different values, the value of β_1^2 reported in Table V is the average. In general β_1^2 is reliable to ± 0.02 .) If instead, β_1^2 is calculated from $A_{||}(\text{Cu})$ using eq 10 of ref 39, we find $\beta_1^2 = 0.76$ –0.80 for the ternary (including $\text{Cu}(\text{8-HQ})_2$ and $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$) complexes, and 0.80–0.85 for the binary complexes, with the exception of $\text{Cu}(\text{bipy})_3^{2+}$, which has $\beta_1^2 = 0.74$.

The crudeness of the two methods used for calculation of β_1^2 is great enough that the differences in the magnitude of β_1^2 calculated from each of the two methods are probably not significant, although the calculation based on ^{14}N superhyperfine splittings may more accurately reflect the covalency of the Cu^{2+} –bipy bonds, while the calculation based on $A_{||}(\text{Cu})$ may more accurately reflect the average covalency of all bonds. However, if this were the case, we would expect the value of β_1^2 for $\text{Cu}(\text{bipy})_3^{2+}$ to remain the same, no matter how it is calculated. Since it changes by about the same amount as do the values of β_1^2 for the ternary complexes, the

 TABLE V
 BONDING PARAMETERS, β_1^2 AND ϵ^2 , AND THE FERMI CONTACT
 TERM, κ_0 , FOR SEVERAL BINARY AND TERNARY Cu^{2+}
 COMPLEXES, CALCULATED FROM THE EPR DATA OF TABLE IV
 AND THOSE DETERMINED IN AQUEOUS SOLUTION

Complex	Bonding parameters				κ_0
	From ^{14}N		From $A_{ }(\text{Cu})$		
	β_1^2	ϵ^2	β_1^2	ϵ^2	
$\text{Cu}(\text{aq})^{2+}$			0.83	1.0	0.29
$\text{Cu}(\text{Tiron})^{2-}$			0.85	0.80	0.32
$\text{Cu}(\text{Tiron})_2^{6-}$			0.84	0.77	0.30
$\text{Cu}(\text{ox})_2^{2-}$			0.80	0.89	0.31
$\text{Cu}(\text{bipy})_2^{2+}$	0.83	0.79	0.80	0.82	0.30
$\text{Cu}(\text{bipy})_3^{2+}$					0.24
$\text{Cu}(\text{bipy})_3^{2+}$	0.83	0.70	0.74	0.78	0.25
$\text{Cu}(\text{bipy})(\text{ox})$	0.86	0.73	0.79	0.78	0.32
$\text{Cu}(\text{bipy})(\text{pyr})$	0.86	0.68	0.80	0.73	0.32
$\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$	0.83	0.72	0.77	0.77	0.32
$\text{Cu}(\text{8-HQ})_2$	0.85	0.70	0.76	0.78	0.31
$\text{Cu}(\text{8-HQ-5-S})_2^{2-}$	0.85	0.71	0.77	0.79	0.32

differences in β_1^2 obtained by each of the two methods of calculation do not appear significant. However, the internal differences within one calculation method appear to be significant, indicating that σ bonding between Cu^{2+} and the ligands is less covalent in the binary complexes, with the exception of $\text{Cu}(\text{bipy})_3^{2+}$, than in the ternary (including $\text{Cu}(\text{8-HQ})_2$ and $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$) complexes. It is interesting to note that the β_1^2 values of $\text{Cu}(\text{bipy})(\text{ox})$ or $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$ are identical or even lower (indicating increasing covalency) than the β_1^2 values of $\text{Cu}(\text{ox})_2^{2-}$ or $\text{Cu}(\text{Tiron})_2^{6-}$ (cf. Table V).

It is unfortunate that β_1^2 for *trans*- $\text{Cu}(\text{bipy})_2^{2+}$ is not known,³⁸ since this would allow a comparative estimate of π back-bonding in binary and ternary Cu –bipy complexes. One tentative estimate of the value of β_1^2 (and ϵ^2) for *trans*- $\text{Cu}(\text{bipy})_2^{2+}$ might be obtained by averaging the values calculated for β_1^2 (and ϵ^2) for $\text{Cu}(\text{bipy})_2^{2+}$ and $\text{Cu}(\text{bipy})_3^{2+}$. One measure of the reliability of such an average would be the existence of a constant value for the Fermi contact term, κ_0 , for the three Cu^{2+} –bipy complexes.⁴⁰ Since κ_0 may be calculated from the isotropic values $\langle a \rangle$ and $\langle g \rangle$, obtained either from solution epr spectra or from glassy spectra (Table IV) [$\langle a \rangle = 1/8(A_{||} + 2A_{\perp})$ and $\langle g \rangle = 1/8(g_{||} + 2g_{\perp})$], it is possible to obtain κ_0 for all three Cu^{2+} –bipy complexes,

(39) C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A*, 2289 (1969).

(40) K. E. Falk, E. Ivanova, B. Roos, and T. Vanngard, *Inorg. Chem.*, **9**, 556 (1970).

as well as for all other binary and ternary complexes of interest here

$$\kappa_0 = \frac{|\langle a \rangle|}{P} + \Delta g_0 \quad (2)$$

where $P = 388 \times 10^{-4} \text{ cm}^{-1}$ and $\Delta g_0 = \langle g \rangle - 2.0023$. The calculated values of κ_0 are listed in Table V. It is immediately obvious that $\text{Cu}(\text{bipy})_2^{2+}$ and $\text{Cu}(\text{bipy})_3^{2+}$ are unique. They have significantly smaller calculated values of κ_0 than do all of the other binary and ternary complexes. The smaller values of κ_0 for these two complexes are indicative of a smaller degree of 4s character in the orbital of the unpaired electron for $\text{Cu}(\text{bipy})_2^{2+}$ and $\text{Cu}(\text{bipy})_3^{2+}$.⁴⁰ Since $\text{Cu}(\text{bipy})_2^{2+}$ exists mainly as the cis isomer at room temperature,³⁴ it and also $\text{Cu}(\text{bipy})_3^{2+}$ probably have significant trigonal distortions from octahedral symmetry, in contrast to the approximately square-planar geometry of the other Cu^{2+} complexes of Table V. Therefore, it would not be unreasonable to expect that $\text{Cu}(\text{bipy})_2^{2+}$ and $\text{Cu}(\text{bipy})_3^{2+}$ have significantly different amounts of 4s character in the hybrid bonding orbitals of Cu, in addition to different interactions with excited vibronic states of the complexes.⁴⁰ Therefore, it is not surprising that κ_0 is considerably different for these two complexes than for the complexes which are expected to have a square-planar geometry. It thus appears that the only possibly reliable comparison of β_1^2 (and ϵ^2) values between ternary complexes and the binary Cu^{2+} -bipy complexes must be with $\text{Cu}(\text{bipy})_2^{2+}$. This complex, however, is itself a "ternary complex", since it must have two water molecules, in addition to 2,2'-bipyridyl, in the plane.

Of more potential interest than β_1^2 is ϵ^2 , the out-of-plane π -bonding parameter, which should be sensitive to back-donation from the filled T_{2g} orbitals of Cu to the π^* orbitals of the ligand (if any). A value of 1 for ϵ^2 indicates that no π bonding occurs. If ϵ^2 is calculated from ^{14}N splittings, the values obtained range from 0.68 to 0.72 for all complexes which have resolved ^{14}N splittings. If ϵ^2 is instead calculated from $A||(^{63}\text{Cu})$, values of 0.73–0.79 are obtained for $\text{Cu}(\text{bipy})_3^{2+}$, $\text{Cu}(\text{8-HQ})_2$, $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$, and all three ternary complexes (Table V). In either case, significant back-donation is found to be present in these compounds. The ϵ^2 values for $\text{Cu}(\text{bipy})_2^{2+}$, $\text{Cu}(\text{ox})_2^{2-}$, and $\text{Cu}(\text{aq})^{2+}$ reflect the decreasing importance of back-donation in these complexes. A comparison of ϵ^2 due to $\text{Cu}(\text{ox})_2^{2-}$ and $\text{Cu}(\text{Tiron})_2^{6-}$ demonstrates the importance of the aromatic system, present in Tiron, for the out-of-plane π bonding. The same is evident from a comparison of ϵ^2 for $\text{Cu}(\text{bipy})(\text{ox})$ with $\text{Cu}(\text{bipy})(\text{pyr})$; here $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$ is more similar to $\text{Cu}(\text{bipy})(\text{ox})$, probably due to the electron-withdrawing properties of the sulfonate groups which are not present in pyrocatecholate.⁷

If, as suggested above, one uses $\text{Cu}(\text{bipy})_2^{2+}$ as the standard for comparison with the ternary complexes, one observes that in all cases, ϵ^2 is smaller for the ternary complexes, which indicates more π back-bonding in these cases. One might expect that the ternary complexes, which contain the rather "soft"⁴¹ bidentate 2,2'-bipyridyl, which is a good π acceptor, and a "hard" bidentate ligand with O as donors, which is a better σ donor than bipyridyl, are favored for an increased back-

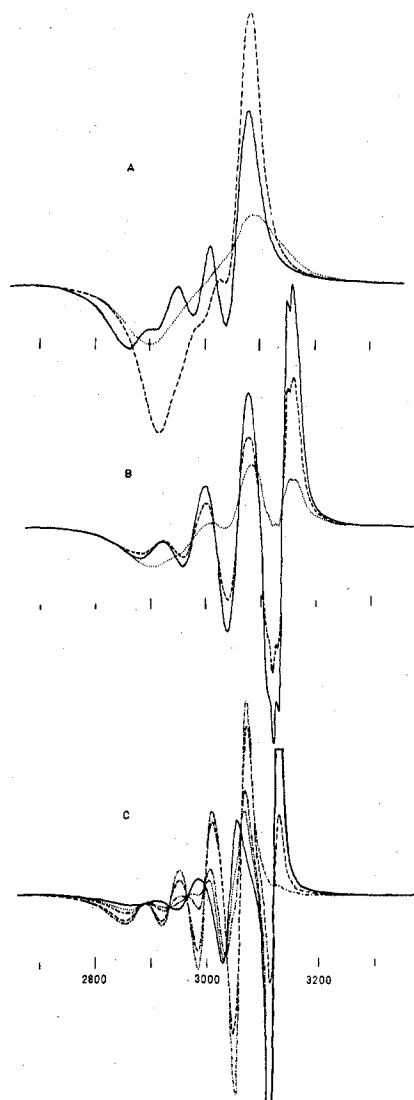


Figure 2.—Epr spectra of the ternary bipy- Cu^{2+} -Tiron system and of the corresponding binary systems (each reactant was $10^{-3} M$) in aqueous solution at 22° . Percentages of each species calculated from data of ref 8 (cf. Experimental Section).

Part A						
Lines in fig	Cu:bipy	pH	% Cu^{2+}	% $\text{Cu}(\text{bipy})_2^{2+}$	% $\text{Cu}(\text{bipy})_3^{2+}$	% $\text{Cu}(\text{bipy})_2^{2+}$
—	1:1	6.0	5.5	86.4	5.5	
----	1:2	6.0		8.1	85.0	6.8
....	1:10	6.0			2.4	97.6
Part B						
Lines in fig	Cu:bipy:Tiron	pH	% $\text{Cu}(\text{bipy})_2^{2+}$	% $\text{Cu}(\text{bipy})_3^{2+}$	% $\text{Cu}(\text{Tiron})_2$	% $\text{Cu}(\text{bipy})_2^{2+}$
----	1:1:1	6.0	1.5	0.7	0.7	97.1
—	1:1:5	6.0			0.1	99.4
....	1:5:1	6.0		59.7		40.2
Part C						
Lines in fig	Cu:Tiron	pH	% $\text{Cu}(\text{Tiron})$		% $\text{Cu}(\text{Tiron})_2$	
----	1:2	6.0	53.0		46.9	
----	1:5	6.0	15.9		84.0	
----	1:2	8.0	1.4		98.5	
....	1:10	6.0	6.9		93.0	
—	1:10	8.0			99.9	

donation to the π^* orbitals of bipyridyl. In fact, the ϵ^2 values due to all three ternary complexes are significantly lower than the value of 0.82 for $\text{Cu}(\text{bipy})_2^{2+}$.

Additionally, the averages of ϵ^2 for the parent complexes $\text{Cu}(\text{bipy})^{2+}$ and $\text{Cu}(\text{ox})_2^{2-}$ are remarkably higher than ϵ^2 due to the corresponding ternary complex $\text{Cu}(\text{bipy})(\text{ox})$. This is in line with earlier assumptions upon the importance of π bonding for the stability of mixed-ligand complexes.^{3-5,11} Furthermore, a comparison of ϵ^2 of $\text{Cu}(\text{bipy})(\text{ox})$ (0.78) with the one (0.73) due to $\text{Cu}(\text{bipy})(\text{pyr})$ (the β_1^2 values are practically the same for both ternary complexes) demonstrates an increasing importance of the π bond and supports the earlier assumption,^{4,11} based on stability data of ternary complexes (*cf.* Table I), of a cooperative effect between the π systems of the two ligands present in $\text{Cu}(\text{bipy})(\text{pyr})$. Unfortunately, the values of ϵ^2 for $\text{Cu}(\text{Tiron})_2^{6-}$ and $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$ do not follow these trends. This may be due to charge effects, due to the extended π system in $\text{Cu}(\text{Tiron})_2^{6-}$, or due to the limitations of such calculations of bonding coefficients. The fact that the binary and ternary complexes involving Tiron do not follow the expected trends suggests that the determination of bonding coefficients from epr parameters is at best approximate, and that it is not wise to rely too heavily on small changes in these coefficients.

Electronic Spectra. Evidence for π Back-Bonding.

Data obtained from the visible spectral parameters (*cf.* Table IV) may be used to strengthen the tentative conclusions above concerning π back-bonding. The visible band, usually assigned to the transition $a_g \rightarrow b^*_{1g}$ in a complex of D_{2h} symmetry,⁴⁰ appears at higher energy in the ternary complexes than in the binary complexes in which the ligands are all oxygen or all nitrogen donors. This indicates that either b^*_{1g} is higher in energy, due to a stronger σ bond, or else a_g is lower in energy, due to a stronger π bond, or both, in the ternary complexes than in the binary complexes.

C. Solution Epr Samples.—The epr parameters, $\langle g \rangle$ and $\langle a \rangle$, observed for the water soluble complexes, $\text{Cu}(\text{Tiron})^{2-}$, $\text{Cu}(\text{Tiron})_2^{6-}$, $\text{Cu}(\text{bipy})^{2+}$, $\text{Cu}(\text{bipy})_3^{2+}$, $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$, and $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$, at 22° in aqueous solution, are in good agreement with those calculated from the glassy epr data of Table IV and are therefore not listed.

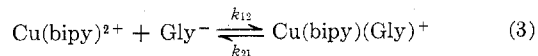
The epr spectra of the bipy-Cu^{2+} -Tiron system and the corresponding binary parent systems are shown in Figure 2, together with the predicted concentrations of each species, calculated from the appropriate equilibrium constants of the coupled equilibria (*cf.* Experimental Section). The equilibrium constants are available only at an ionic strength of 0.1 *M*, while for the epr measurements of Figure 2 the ionic strength was approximately 3×10^{-3} *M*. Nevertheless, the concentrations of the various species should be fairly similar under these two sets of conditions, particularly for the Cu^{2+} -bipy complexes (Figure 2A), since ionic strength effects should be minor in this case. It can therefore be said that Figure 2A shows the epr spectra of $\text{Cu}(\text{bipy})^{2+}$, $\text{Cu}(\text{bipy})_2^{2+}$, and $\text{Cu}(\text{bipy})_3^{2+}$, to the extent that each of these can be isolated from the other two and from free Cu^{2+} , and to the extent that exchange with these other species does not broaden or otherwise distort the spectrum of the species of interest.

Likewise, Figure 2C shows the epr spectrum of $\text{Cu}(\text{Tiron})^{2-}$ (dot-dash-dot line) and of $\text{Cu}(\text{Tiron})_2^{6-}$ (solid line). Even though the calculated ratios of

species (*cf.* caption, Figure 2) indicate that the dot-dash line of Figure 2C should contain nearly equal amounts of the 1:1 and 1:2 complexes, the appearance of the spectrum clearly indicates that the 1:1 species is present to at least 96%. (Note the size of the peak at 3115 G, which is due to the 1:2 complex.) Using the height of the peak at 3115 G it is possible to calculate an approximate equilibrium constant for the addition of the second Tiron ligand to $\text{Cu}(\text{Tiron})^{2-}$. The value obtained is $\log K^{\text{Cu}(\text{Tiron})_2}_{\text{Cu}(\text{Tiron})} \approx 10.5$,⁴² this is in fair agreement with the value obtained from potentiometric titrations ($\log K^{\text{Cu}(\text{Tiron})_2}_{\text{Cu}(\text{Tiron})} = 11.14$),⁸ if one takes into account the different experimental conditions and methods. Since in this case the reactants are both highly charged, the equilibrium constants would be expected to show significant ionic strength dependence.

Of additional interest in Figure 2C is the existence of "isosbestic points" in the epr spectra as the concentration of the Tiron anion is increased, either by addition of more Tiron or by raising the pH. Six sharp isosbestic points are observed, which clearly indicate the presence of only two species in the solution. This is of interest because it has not been possible to detect the addition of a third ligand by titration methods.⁸ If there were a third step of ligand addition, then the solid line of Figure 2C should certainly depart significantly from the isosbestic points. Since it does not, we can say that the epr data from this work are in agreement with the conclusion⁸ that only two stepwise equilibria exist. This indicates that the two Tiron ligands probably adopt a planar configuration, leaving the remaining two coordination sites *trans* to each other, and thus unreactive to a third bidentate ligand.⁴³

An important consideration in the above discussion of isosbestic points is the fact that their existence implies that the rate of exchange of Cu^{2+} present in $\text{Cu}(\text{Tiron})^{2-}$ or $\text{Cu}(\text{Tiron})_2^{6-}$, when the solution contains a mixture of the two, is slow on the epr time scale. If it were rapid, we would see the weighted average of the two epr spectra, which would certainly not exhibit isosbestic points. In particular, the highest field line, which occurs at 3055 G for $\text{Cu}(\text{Tiron})^{2-}$ and 3115 G for $\text{Cu}(\text{Tiron})_2^{6-}$, would be found at some position intermediate between these two points for a solution containing a mixture of the two species if they were exchanging rapidly on the epr time scale.^{44,45} A kinetic study of the system



by temperature jump techniques has shown $k_{12} = 1.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{21} = 19 \text{ sec}^{-1}$.¹⁶ Assuming that the rates of exchange of $\text{Cu}(\text{Tiron})^{2-}$ and $\text{Cu}(\text{Tiron})_2^{6-}$ are similar to those of $\text{Cu}(\text{Gly})^+$ and $\text{Cu}(\text{bipy})(\text{Gly})^+$,¹⁶ the lifetimes of the two Tiron species would be orders of magnitude longer than 10^{-8} sec for any reasonable

(42) The stability constant, based on the epr experiments, was calculated by taking into account the acidity constants determined earlier.⁸

(43) Of course, charge effects are also unfavorable for addition of a third Tiron anion, since the charge on or in the vicinity of Cu^{2+} in $\text{Cu}(\text{Tiron})_2^{6-}$ is -2 , and the third Tiron ligand would provide another unit of -2 to the Cu^{2+} center, aside from the charge of the sulfo groups.

(44) J. A. Pople, W. G. Schneider, and J. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 218-225.

(45) F. A. Walker, Ph.D. Thesis, Brown University, 1966; F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).

fractions of each species (e.g., 0.2–0.8); hence, no exchange is observable within the slow-exchange region of the epr time scale.^{44,45}

The epr spectrum of $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$ (cf. Figure 2B) is unique, as in the case of the glassy epr spectra. It differs from both the spectra of the three Cu^{2+} -bipy complexes and the two Cu^{2+} -Tiron complexes. Thus we are assured that this is indeed a unique species, a ternary complex, at room temperature. The solution epr spectrum of $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$ is markedly similar to that of $\text{Cu}(\text{bipy})(\text{Tiron})^{2-}$, including ^{14}N superhyperfine structure on the highest field line, as is true for the latter species (cf. Figure 2B). This again confirms the great similarity between $\text{Cu}(\text{8-HQ-5-S})_2^{2-}$ and the ternary complexes, as already concluded above, on the basis of glassy epr data.

The amounts of the ternary complex present, as observed in the three spectra of Figure 2B, do not agree very well with the amounts calculated from the stability data (cf. caption to Figure 2B).⁸ This is probably

again an ionic strength effect, since the two reactants are of opposite charge.

Acknowledgments.—Epr spectra were recorded in the Department of Biochemistry, Cornell University, and at Varian Associates, Palo Alto, Calif. The authors wish to thank Professor J. O. Edwards and the Department of Chemistry, Brown University, Providence, R. I., for use of the Cary 14 reflectance attachment, and Professor Henry Taube, Department of Chemistry, Stanford University, for use of the Faraday balance. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (F. A. W.), the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung (H. S.), and the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, Research Grant Am-08721 and the State University of New York (D. B. M.) for support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO 44106

Kinetics of Zinc-Glycine Interactions in Aqueous Solution

By J. A. MICELI AND J. E. STUEHR*

Received May 24, 1972

Two concentration and pH dependent relaxation times in the millisecond time region have been observed for the aqueous zinc-glycine system by means of temperature-jump spectrometry. The faster of the times was measured in dilute solutions. The process responsible was shown to be the formation of the monoglycinate complex from the reaction of zinc with free glycine anion. The overall second-order rate constant is $1.5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° and $I = 0.1 \text{ M}$. The slower time, observed only in concentrated glycine solutions, was attributed to the formation of the bis glycinate complex accompanied by a rate-determining unimolecular rearrangement. The rate constant for the latter was estimated to be 93 sec^{-1} . The structure change is postulated to be tetrahedral \rightarrow octahedral.

Introduction

Considerable information now exists for the kinetics of interactions of metal ions with organic and inorganic ligands.^{1,2} In particular, much effort has been directed toward characterizing the solvent lifetimes within the inner coordination spheres of the alkaline earth cations and several of the first row transition elements (especially Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}). Considerably less is known about the complexation kinetics of other metal ions.

An examination of the literature indicates that very few kinetic investigations have involved divalent zinc, with which this article is concerned. One of the first studies was that of Wilkins³ between zinc(II) and an azo dye, pyridine-2-azo-*p*-dimethylaniline, for which he obtained a complexation rate constant of $4 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° . Perhaps the most detailed study to date was that of Maass,⁴ who reported kinetic data for the interactions between zinc(II) and acetate and sulfate by means of ultrasonic absorption measurements. The value of the characteristic ligand penetration rate

constant (presumably equal to the solvent lifetime rate constant $k_{\text{H}_2\text{O}}$ in the inner coordination sphere of the metal ion) ranged from 3×10^7 to $1 \times 10^8 \text{ sec}^{-1}$ at 25° . Other kinetic studies involving murexide,^{4,5} 2,2'-dipyridyl, and 1,10-phenanthroline⁶ have yielded complexation rate constants ranging from 1×10^6 to $7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. Thus, several different investigations have come to substantially different conclusions as to the rate of ligand penetration into the primary coordination sphere for divalent zinc.

Divalent zinc is potentially an extremely interesting system in view of the structural possibilities proposed by Swift.⁷ In a temperature-jump study of $\text{Zn}(\text{NO}_3)_2$, he reported a concentration-independent relaxation time ($\tau \approx 0.13 \text{ sec}$ at 25°). He attributed this time to a structural interconversion between tetrahedral $\text{Zn}(\text{H}_2\text{O})_4^{2+}$ and another configuration, presumably octahedral. If this indeed is the cause of this relaxation, then it should be possible to obtain independent evidence for it by studying the interactions between zinc and a ligand which imposes a different geometry on the

(1) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(2) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

(3) R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964).

(4) G. Maass, *Z. Phys. Chem. (Frankfurt am Main)*, **60**, 138 (1968).

(5) A. Bewick and P. Robertson, *Trans. Faraday Soc.*, **63**, 678 (1967).

(6) R. Holyer, C. Hubbard, S. Kettle, and R. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

(7) T. J. Swift, *ibid.*, **3**, 526 (1964).