

metal-halogen vibrations which do not involve cation motions. The two lower energy bands,  $E_{1u}(c)$  and  $A_{2u}(b)$ , involve cation translations and appear at significantly lower frequencies in the spectrum of  $TiNiCl_3$  compared with those of the cesium and rubidium salts. On the other hand, changing the halogen affects the energies of all five active vibrations. In the spectra of  $CsNiI_3$ ,  $CsNiBr_3$ , and  $CsNiCl_3$ , the frequencies of corresponding bands increase in the order,  $I < Br < Cl$ , which is expected considering the masses of the different halide ions.

The frequencies of the internal vibrations of the  $M^{II}X_3$  anionic chain vary significantly from metal ion to metal ion. The frequencies of the three high-energy bands in the spectra of  $CsVCl_3$ ,  $(CH_3)_4NMnCl_3$ ,<sup>13</sup>  $CsFeCl_3$ ,  $CsCoCl_3$ , and  $CsNiCl_3$ , generally follow the trend, in order of increasing frequency,  $Mn < Fe < Co < Ni < V$ . (The three high-energy bands in the spectrum of  $(CH_3)_4NMnCl_3$  appear at 220, 170, and 148  $cm^{-1}$ .) Assuming that the small differences between the masses of the various metal ions do not strongly affect the vibrational frequencies within this series of compounds, the trend suggests that the force constants for the metal-halogen bonds follow the crystal field stabilization energies for the metal ions. For high-spin octahedral complexes the CFSE is at a maximum for the  $d^3$  and  $d^8$  configurations and is at a minimum for the  $d^5$  configuration. The  $d^3$ ,  $d^8$ , and  $d^5$  configurations correspond to the vanadium, nickel, and manganese salts, respectively.

**Registry No.**  $CsMgCl_3$ , 12371-11-8;  $CsVCl_3$ , 20959-74-4;  $CsCrCl_3$ , 13820-84-3;  $CsMnCl_3$ , 14219-53-5;  $CsFeCl_3$ , 15611-69-5;  $CsCoCl_3$ , 15305-74-5;  $CsNiCl_3$ , 15455-69-3;  $KNiCl_3$ , 15530-90-2;  $TiNiCl_3$ , 28480-14-0;  $RbNiCl_3$ , 18894-62-7;  $CsNiBr_3$ , 15455-70-6;  $CsMnBr_3$ , 36482-50-5;  $CsNiI_3$ , 38496-65-0;  $CsCuCl_3$ , 18437-47-3.

**Acknowledgment.** We gratefully acknowledge Tulane University for the support of this work.

(13) Including the manganese salt in these comparisons may not really be valid since the  $(CH_3)_4N^+$  ion is much larger than the  $Cs^+$  ion. The difference in cation size might lead to longer metal-halogen distances in  $(CH_3)_4NMnCl_3$ .

Contribution from the Institute of Inorganic Chemistry,  
University of Basel, CH-4056 Basel, Switzerland

### Ternary Complexes in Solution. XV.<sup>1</sup> Mixed-Ligand Copper(II) Complexes with 2,2'-Bipyridyl or 1,10-Phenanthroline and Pyrocatecholate or Derivatives Thereof

Helmut Sigel,\* Peter R. Huber, Rolf Griesser, and Bernhard Prijs

Received August 22, 1972

Systematic studies of mixed-ligand  $Cu^{2+}$  complexes revealed a surprisingly high stability of those ternary complexes formed by an aromatic amine and a second ligand with O as donor atoms.<sup>2</sup> For example, pyrocatecholate forms a more stable complex with  $Cu(bipy)^{2+}$  than with

$Cu(aq)^{2+}$ .<sup>3,4</sup> It was shown that one of the intrinsic factors governing the stability of these mixed-ligand complexes is the  $\pi$ -acceptor qualities of the amine.<sup>2</sup> From this point of view it is of interest to compare the stability of ternary complexes containing either 2,2'-bipyridyl or 1,10-phenanthroline and especially to see how large the expected stability increase with 1,10-phenanthroline actually is.<sup>5,6</sup>

Furthermore, there are several hints in the literature<sup>2,4,7</sup> that the  $\pi$  system of the ligand with O as donor atoms also has some influence on the stability of complexes and that, more important, "cooperative effects" may occur between the  $\pi$  systems of two ligands bound to the same  $Cu^{2+}$ . To test this hypothesis several derivatives of pyrocatecholate have been included in the present investigation. The stabilities of ternary complexes containing either 2,2'-bipyridyl or 1,10-phenanthroline and one of the following bidentate ligands with O as donors were determined: pyrocatechol (1,2-dihydroxybenzene), tiron (1,2-dihydroxybenzene-3,5-disulfonate), pyrogallol 1-methyl ether (1,2-dihydroxy-3-methoxybenzene), and 6,7-dihydroxy-naphthalene-2-sulfonate.

### Experimental Section

**Materials.** Tiron (disodium salt), pyrogallol 1-methyl ether, and 1,10-phenanthroline were purchased from Fluka AG, Buchs, Switzerland. 6,7-Dihydroxynaphthalene-2-sulfonate (sodium salt) was from Schuchardt, Munich. The other reagents were the same as used earlier.<sup>4</sup>

**Measurements and Determination of Constants.** The acidity constants,  $K_{HL}^H$ , of the ligands with hydroxy groups were determined<sup>8</sup> by adjusting a series of appropriate pH values of solutions ( $I = 0.1$ ,  $NaClO_4$ ;  $25^\circ$ ) containing these ligands and by recording the absorption spectra of these solutions with a Beckman DB Spectrophotometer connected with a W+W Electronic Hi-speed Recorder, Model 202. In the case of tiron the solutions were  $1.4 \times 10^{-4}$  M and the spectra were evaluated at 254, 278, and 330 nm; with pyrogallol 1-methyl ether (evaluation at 300 nm) and 6,7-dihydroxynaphthalene-2-sulfonate (evaluation at 244 and 266 nm) the concentrations were  $1.8 \times 10^{-4}$  and  $1.8 \times 10^{-5}$  M, respectively.

All the other constants were measured by potentiometric titrations ( $I = 0.1$ ,  $NaClO_4$ ;  $25^\circ$ ), carried out under  $N_2$  with 0.1 N NaOH (cf. ref 4). The stability constants of the binary and of the ternary complexes were computed as described previously.<sup>4,9-11</sup> The uncertainties given in the tables are 3 times the standard deviation.<sup>2</sup>

The acidity constants,  $K_{HL}^H$ , of 2,2'-bipyridyl and 1,10-phenanthroline and the stability constants of the corresponding

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

(4) R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).

(5) As 1,10-phenanthroline has  $\pi$ -acceptor qualities like 2,2'-bipyridyl,<sup>6</sup> an increase in stability must be expected for the corresponding ternary  $Cu^{2+}$  complexes.

(6) W. J. Eilbeck, F. Holmes, G. G. Phillips, and A. E. Underhill, *J. Chem. Soc. A*, 1161 (1967).

(7) F. A. Walker, H. Sigel, and D. B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).

(8) H. Sigel and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1701 (1964).

(9) In the calculation of the stability constant,  $\beta_{Cu-Cu(Am)(OL)}$ , of the ternary complexes the following species were taken into account in all systems:<sup>10</sup> H,  $H_2(Am)$ ,  $H(Am)$ ,  $Am$ ,  $Cu(Am)$ ,  $Cu(Am)_2$ ,  $H_2(OL)$ ,  $H(OL)$ ,  $OL$ ,  $Cu(OL)$ ,  $Cu(OL)_2$ ,  $Cu$ ,  $Cu(Am)(OL)$ .<sup>4</sup> In the systems containing 1,10-phenanthroline (P) the species  $HP_2^+$  and  $HP_3^+$ , detected by Fahsel and Banks,<sup>11</sup> do not occur in significant concentrations under our experimental conditions:  $[Cu^{2+}]_{tot} = [P]_{tot} \leq 8 \times 10^{-4}$  M; the complex  $CuP^{2+}$  is formed for nearly 100% already at low pH values ( $pH > 2.5$ ). The species  $HP_2^+$  and  $HP_3^+$  are perceptible only at  $[P]_{free} > 10^{-3}$  M.<sup>11</sup> Additionally, calculations were carried out under the assumption that the formation of the copper(II)-amine 1:1 complex is complete; i.e., only the species  $Cu(Am)$ ,  $Cu(Am)(OL)$ ,  $H_2(OL)$ ,  $H(OL)$ ,  $OL$ , and H were taken into account. Still, the results obtained under this simplification are practically identical with those given in the tables (cf. also ref 1, 2, 4).

(10) Abbreviations: Am, amine; L, general ligand; OL, ligand with O as donor atoms. The coordinating forms of the ligands OL are the anions. Charges are omitted in all equations.

(11) M. J. Fahsel and C. V. Banks, *J. Amer. Chem. Soc.*, **88**, 878 (1966).

(1) Part XIV: P. R. Huber and H. Sigel, *Z. Naturforsch. B*, **27**, 1319 (1972).

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

Table I. Negative Logarithms of Acidity Constants of the Ligands and Logarithms of Stability Constants of Their Binary Cu<sup>2+</sup> Complexes (*I* = 0.1; 25°)<sup>10</sup>

Ligand	pK <sup>H</sup> <sub>H<sub>2</sub>L</sub>	pK <sup>H</sup> <sub>HL</sub>	Log K <sup>Cu</sup> <sub>CuL</sub>	Log K <sup>CuL</sup> <sub>CuL<sub>2</sub></sub>	Log β <sup>Cu</sup> <sub>CuL<sub>2</sub></sub>
Pyrocatechol <sup>4</sup>	9.32	13.00 <sup>14,15</sup>	13.96	11.07	25.03
Tiron	7.66 ± 0.02	12.55 ± 0.09	14.28 ± 0.02	11.14	25.42
Pyrogallol 1-methyl ether	9.31 ± 0.01	12.10 ± 0.03	13.00 ± 0.01	10.06	23.06
6,7-Dihydroxynaphthalene-2-sulfonate	8.17 ± 0.01	12.40 ± 0.06	13.83 ± 0.01	11.01	24.84
2,2'-Bipyridyl <sup>a</sup>	-0.2 <sup>a</sup>	4.49	8.00	5.60	13.60
1,10-Phenanthroline <sup>a</sup>	-1.6 <sup>a</sup>	4.95	9.25	6.75	16.00

<sup>a</sup> Reference 12; 20°.Table II. Logarithms of Stability Constants of Some Ternary Aromatic Am-Cu<sup>2+</sup>-OL Complexes (*I* = 0.1; 25°)<sup>10</sup>

Ligand, OL	Log β <sup>Cu</sup> <sub>Cu(Am)OL</sub>	Log K <sup>Cu(Am)</sup> <sub>Cu(Am)OL</sub>	Log K <sup>Cu(OL)</sup> <sub>Cu(OL)Am</sub>
Amine = 2,2'-Bipyridyl			
Pyrocatechol <sup>4</sup>	22.39	14.39	8.43
Tiron	22.39 ± 0.02	14.39	8.11
Pyrogallol 1-methyl ether	21.39 ± 0.01	13.39	8.39
6,7-Dihydroxynaphthalene-2-sulfonate	22.52 ± 0.06	14.52	8.69
Amine = 1,10-Phenanthroline			
Pyrocatechol	23.56 ± 0.03	14.31	9.60
Tiron	23.44 ± 0.01	14.19	9.16
Pyrogallol 1-methyl ether	22.56 ± 0.01	13.31	9.56
6,7-Dihydroxynaphthalene-2-sulfonate	23.90 ± 0.07	14.65	10.07

Table III. Comparison of the Stability of Some Ternary Cu<sup>2+</sup> Complexes

No.	Amine	Second ligand <sup>10</sup>	Δ log K	log X	Ref
1	2,2'-Bipyridyl	Pyrocatechol	0.43	6.15	4
2		Tiron	0.11	5.76	a
3		Pyrogallol 1-methyl ether	0.39	6.12	a
4		6,7-Dihydroxynaphthalene-2-sulfonate	0.69	6.60	a
5	1,10-Phenanthroline	Pyrocatechol	0.35	6.09	a
6		Tiron	-0.09	5.46	a
7		Pyrogallol 1-methyl ether	0.31	6.06	a
8		6,7-Dihydroxynaphthalene-2-sulfonate	0.82	6.96	a
9	Ethylenediamine	Pyrocatechol	-0.76	2.65	b, 2
10		Oxalic acid	-1.1	1.3	c
11	1,10-Phenanthroline	8-Hydroxyquinoline-5-sulfonate		3.71	d
12		Pyridine-2-carboxylic acid		3.92	d

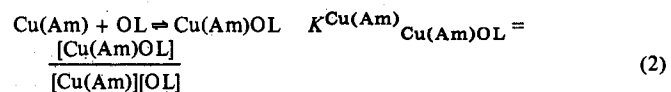
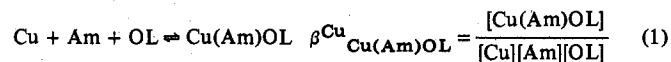
<sup>a</sup> This work. <sup>b</sup> P. R. Huber, R. Griesser, B. Prijs, and H. Sigel, *Eur. J. Biochem.*, **10**, 238 (1969). <sup>c</sup> W. B. Schaap and D. L. McMasters, *J. Amer. Chem. Soc.*, **83**, 4699 (1961); cf. also ref 4. <sup>d</sup> J.-P. Scharff and M. R. Paris, *Bull. Soc. Chim. Fr.*, 1782 (1967).

binary Cu<sup>2+</sup> complexes were taken from the work of Anderegg.<sup>12</sup> The acidity constants, K<sup>H</sup><sub>H<sub>2</sub>L</sub>, due to 2,2'-bipyridyl and 1,10-phenanthroline are from a report by Linnell and Kaczmarczyk,<sup>13</sup> and the value for K<sup>H</sup><sub>HL</sub> of pyrocatechol is from a study by Perrin<sup>14</sup> (cf. also ref 15). The stability constants of the binary copper(II)-pyrocatecholate system and the ternary 2,2'-bipyridyl-copper(II)-pyrocatecholate system are the same as determined recently.<sup>4</sup>

## Results and Discussion

The acidity constants of the ligands and the stability constants of their binary Cu<sup>2+</sup> complexes are given in Table I. Table II contains the constants of the mixed-ligand Cu<sup>2+</sup> complexes formed by 2,2'-bipyridyl or 1,10-phenanthroline and pyrocatechol or a derivative thereof. For the ternary complexes the overall constant log β<sup>Cu</sup><sub>Cu(Am)OL</sub> according to equilibrium 1 was computed.<sup>4,9,10</sup> The constant log K<sup>Cu(Am)</sup><sub>Cu(Am)OL</sub> according to equilibrium 2 was calculated from eq 3. Of course, one may also consider the reaction between Cu(OL) and one of the amines; the corresponding

equilibrium constant log K<sup>Cu(OL)</sup><sub>Cu(OL)Am</sub> was calculated according to eq 4 and is also listed in Table II.



$$\log K^{\text{Cu(Am)}}_{\text{Cu(Am)OL}} = \log \beta^{\text{Cu}}_{\text{Cu(Am)OL}} - \log K^{\text{Cu}}_{\text{Cu(Am)}} \quad (3)$$

$$\log K^{\text{Cu(OL)}}_{\text{Cu(OL)Am}} = \log \beta^{\text{Cu}}_{\text{Cu(Am)OL}} - \log K^{\text{Cu}}_{\text{Cu(OL)}} \quad (4)$$

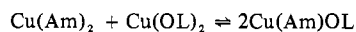
There are two convenient ways to characterize the stability of mixed-ligand complexes. One is according to eq 5, i.e., by comparing the difference in stability, Δ log K, e.g., for the reaction between Cu(Am)<sup>2+</sup> or Cu(aq)<sup>2+</sup> and the ligand OL.<sup>16</sup> The other is based on the "disproportionation" constant,

(16) The difference Δ log K is of course also the logarithm of an equilibrium constant, which is due to Cu(Am) + Cu(OL) ⇌ Cu(Am)OL + Cu.

(12) G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963).  
 (13) R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.*, **65**, 1196 (1961).  
 (14) D. D. Perrin, *Nature (London)*, **182**, 741 (1958).  
 (15) C. A. Tyson and A. E. Martell, *J. Amer. Chem. Soc.*, **90**, 3379 (1968).

$\log X$ , as defined by equilibrium 6 (calculation with eq 7). Generally, one would expect to observe negative values for  $\Delta \log K$  (eq 5), since usually it holds that  $K^{\text{Cu}}_{\text{CuL}} > K^{\text{Cu}}_{\text{CuOL}}$  (cf. Table I). The method using equilibrium 6 for characterization is somewhat more "objective," as the value expected for  $X$  can be deduced from statistical arguments:  $X = 4$ , i.e.,  $\log X = 0.6$ .<sup>17</sup>

$$\Delta \log K = \log K^{\text{Cu(Am)}}_{\text{Cu(Am)OL}} - \log K^{\text{Cu}}_{\text{Cu(OL)}} = \log K^{\text{Cu(OL)}}_{\text{Cu(OL)Am}} - \log K^{\text{Cu}}_{\text{Cu(Am)}} \quad (5)$$



$$X = \frac{[\text{Cu(Am)OL}]^2}{[\text{Cu(Am)}_2][\text{Cu(OL)}_2]} \quad (6)$$

$$\log X = 2 \log \beta^{\text{Cu}}_{\text{Cu(Am)OL}} - (\log \beta^{\text{Cu}}_{\text{Cu(Am)}_2} + \log \beta^{\text{Cu}}_{\text{(OL)}_2}) \quad (7)$$

By using the results of Tables I and II, the values for  $\Delta \log K$  (eq 5) and  $\log X$  (eq 7) were calculated. These data are listed in Table III, together with some results taken from the literature. The  $\Delta \log K$  values observed by Martell, *et al.*,<sup>3,18</sup> for the 2,2'-bipyridyl-copper(II)-pyrocatecholate system (+0.36)<sup>3,18</sup> and the 1,10-phenanthroline-copper(II)-pyrocatecholate system (+0.31)<sup>18</sup> are in excellent agreement with the present results. The same is true for the 2,2'-bipyridyl-copper(II)-tiron system (+0.03)<sup>18,19</sup> and the 1,10-phenanthroline-copper(II)-tiron system (-0.14).<sup>18</sup>

A comparison of the data of the mixed-ligand systems containing 2,2'-bipyridyl and a ligand with O as donor atoms, 1-4 in Table III, demonstrates unequivocally that the electron density in the ligand OL has a significant influence on the stability of the ternary  $\text{Cu}^{2+}$  complexes: electron-withdrawing substituents lower the stability (tiron, 2; cf. also ref 7) and electron-donating "substituents" (the naphthalene derivative, 4) increase it.<sup>20</sup> The systems containing 1,10-phenanthroline (5-8) instead of 2,2'-bipyridyl reveal the same picture but even more pronounced: while the difference between the lowest and highest values of  $\log X$  for the 2,2'-bipyridyl systems is about 0.8 log unit, the same difference for the systems with 1,10-phenanthroline is about 1.5 log units. Hence,  $\text{Cu(phen)}^{2+}$  is somewhat more sensitive toward the electron distribution on the ligand with O as donor atoms as is  $\text{Cu(bipy)}^{2+}$ .

However, as a first approximation one may still say that the stability-increasing effect of 1,10-phenanthroline is of the same order as the one due to 2,2'-bipyridyl. Ternary complexes containing an aromatic amine are significantly more stable as the ones containing an aliphatic amine (cf. 1, 5, and 9).<sup>2</sup> A comparison of the systems 1, 5, 9, and 10 shows not only the influence of the  $\pi$  systems of the ligand with N donors but, additionally, the one of the ligand with O donors (cf. also ref 5).<sup>21</sup>

The discriminating qualities toward the second ligand to be coordinated have unequivocally been demonstrated for the  $\text{Cu}^{2+}$ -2,2'-bipy complex. This means, if an aqueous

solution contains a ligand with N and another one with O as donor atoms, both ligands having the same coordination tendency toward  $\text{Cu(aq)}^{2+}$ , the latter ligand is preferably bound to  $\text{Cu(bipy)}^{2+}$ .<sup>4</sup> The same qualities may be surmised for  $\text{Cu(phen)}^{2+}$ . In fact, the systems 11 and 12 of Table III give good evidence for such behavior: the ternary complexes formed with "mixed" ligands containing N and O as donor atoms are remarkably less stable than the ones formed with ligands having only O as donor atoms (5-8).

**Registry No.** 2,2'-Bipyridyl, 366-18-7; 1,10-phenanthroline, 66-71-7; pyrocatechol, 120-80-9; tiron, 149-45-1; pyrogallol 1-methyl ether, 934-00-9; 6,7-dihydroxynaphthalene-2-sulfonate, 135-53-5.

**Acknowledgments.** The measurements were performed with the skillful technical assistance of Miss M. Nicholson and Miss R. Baumbusch. The computer, IBM 1620, was made available by the Rechenzentrum der Universität Basel. This work was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.

Contribution from the Departments of Chemistry, California State University, San Diego, California 92115, and University of Florida, Gainesville, Florida 32601

### Enhanced Acidity of Protic Chelate Complexes

Larry E. Bennett,\* Robert H. Lane, Michael Gilroy, Frank A. Sedor, and James P. Bennett, Jr.

Received September 6, 1972

The acidity of protic ligands is an important characteristic of many coordination complexes. In connection with redox studies to be reported elsewhere, we have obtained additional evidence in support of enhanced acidities for protic *chelate* complexes relative to their monodentate analogs. An interpretation of the data appears to require the recognition of at least one influence which previously has not been considered in regard to the acidity of protic complexes.

### Experimental Section

**Preparation of Complexes.** Glycolatobis(ethylenediamine)cobalt(III) perchlorate was prepared by the method used for the glycinate analog.<sup>1</sup> *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl (2.0 g) and freshly prepared Ag<sub>2</sub>O (0.81 g) were ground periodically with 4 ml of H<sub>2</sub>O in a mortar for 1 hr. AgCl was removed by filtration and washed with portions of boiling water until the combined filtrate and washings totaled 10-12 ml. NaOOCCH<sub>2</sub>OH (0.9 g) was added and the solution evaporated on a steam bath until a thick crust formed. After cooling to room temperature the mixture was filtered and the precipitate washed twice with absolute ethanol. The solid was dissolved in 10 ml water to which 10 ml of saturated NaClO<sub>4</sub> solution was added to precipitate the perchlorate salt. Recrystallization was effected by dissolving the salt in the minimum amount of water and adding solid NaClO<sub>4</sub> to make the solution ~4 M in perchlorate. The solution was cooled to 0° and the precipitate was filtered, washed twice with absolute ethanol and twice with diethyl ether, and dried overnight under vacuum; yield 1.3 g. *Anal.* Calcd for [Co(en)<sub>2</sub>(OOCCH<sub>2</sub>O)]ClO<sub>4</sub>: C, 20.45; H, 5.15; N, 15.0; Co, 16.7. Found: C, 20.36; H, 5.12; N, 15.7; Co, 16.6.

2-Aminoethanolbis(ethylenediamine)cobalt(III) perchlorate was

(17) R. DeWitt and J. I. Watters, *J. Amer. Chem. Soc.*, **76**, 3810 (1954); S. Kida, *Bull. Chem. Soc. Jap.*, **29**, 805 (1956).

(18) G. F. Condiak and A. E. Martell, *J. Inorg. Nucl. Chem.*, **31**, 2455 (1969).

(19) The value  $\Delta \log K = +0.87$ , as observed in ref 3, is certainly too high.

(20) 2,3-Dihydroxynaphthalene is too insoluble to be studied. The influence of the methoxy substituent (3) is obviously too weak to be significant.

(21) For a general discussion of the factors governing the stability of mixed-ligand complexes cf. ref 4 and R. Griesser and H. Sigel, *Inorg. Chem.*, **10**, 2229 (1971).

\* Address correspondence to this author at California State University.

(1) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 1590 (1966).