stability constants[9] indicate that the chelate effect is substantially smaller for octahedral nickel(II) than for square-planar palladium(II), on the order of 100–200 for $\mathrm{Ni(en)^{2+}}$ compared with $\mathrm{Ni(NH_3)_2{}^{2+}}$, in contrast to the value of 10^4 indicated above for palladium(II). Thus the general distinction between dissociative modes of reaction for octahedral complexes and associative modes for square-planar complexes nicely parallels the difference in the relative magnitudes of the equilibrium chelate effect.

A kinetic explanation for the chelate effect in octahedral complexes thus depends on the smaller rate of ring opening of ethylenediamine relative to dissociation of ammonia, resulting in $(k_2/k_{-2}) > (k'_2/k'_{-2})$, and on the possible influence of internal conjugate base formation by ethylenediamine, suggested by Rorabacher.[14] Substitution of $\mathrm{Ni(H_2O)_6{}^{2+}}$ by ethylenediamine is some 50 times faster than substitution by ammonia, an observation inconsistent with the simple model of a dissociative mechanism. Rorabacher proposed that the second amine group of the diamine forms a hydrogen bond with a coordinated water, forming an incipient conjugate base on the nickel(II) ion. This results in more rapid loss of water from the metal ion and an enhanced rate of substitution by the first amine group of the diamine. The larger value of k_1 for ethylenediamine relative to ammonia does not account for the chelate effect, however, for if the transition-state energy for the process represented by k_1 is lowered by internal conjugate base formation, then according to the principle of microscopic reversibility the transition-state energy for the reverse process k_{-1} is lowered similarly and the ratio of the rates k_1/k_{-1} remains constant.

An explanation of the chelate effect is provided by a simple extension of the internal conjugate base mechanism. Although there is no direct experimental evidence available, it seems reasonable that in the half-bonded intermediate $\mathrm{Ni(H_2O)_5(en-)^{2+}}$ the free end of the amine will remain hydrogen bonded as in the transition state and will be consequently more stable. The chelate effect may thus reflect a larger value of $K_1 = k_1/k_{-1}$ for ethylenediamine relative to ammonia. Thus, in contrast to substitution on a square-planar complex in which the larger value of k_2 is responsible for the kinetic chelate effect, in the octahedral system the origin of the kinetic chelate effect is in k_1/k_{-1}, as well as in a smaller value of k_{-2} common to both systems. The chelate effect, which is observed for both square-planar and octahedral complexes, must be explained kinetically by distinctly different mechanisms, a consequence of the distinctly different modes of reactivity of the two classes of complexes.

[14] D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

CONTRIBUTION FROM THE INSTITUTE OF INORGANIC CHEMISTRY,
UNIVERSITY OF BASEL, CH-4000 BASEL, SWITZERLAND

Ternary Complexes in Solution. VIII. Complex Formation between the Copper(II)–2,2'-Bipyridyl 1:1 Complex and Ligands Containing Oxygen and/or Nitrogen as Donor Atoms[1,2]

BY ROLF GRIESSER AND HELMUT SIGEL[3]

Received November 3, 1969

The stability constants of the ternary $\mathrm{Cu^{2+}}$ complexes containing 2,2'-bipyridyl and as a second ligand ethylenediamine, glycine anion, malonic acid dianion, or pyrocatechol dianion were determined by potentiometric titration. For the equilibrium $\mathrm{CuA_2 + CuB_2 \rightleftharpoons 2CuAB}$, the corresponding constants are $\log X = 1.10$, 3.05, 5.49, and 6.15 ($I = 0.1$; temperature 25°). All four ternary complexes are more stable than one would expect for purely statistical reasons ($\log X = 0.6$). Furthermore, the stability constants show that the $\mathrm{Cu^{2+}}$–2,2'-bipy 1:1 complex has discriminating qualities toward the second ligand to be coordinated; it rather prefers to form ternary complexes with those ligands that contain O as donor atoms. In addition, the formation constants for the reactions between the $\mathrm{Cu^{2+}}$–2,2'-bipy 1:1 complex and the dianions of malonic acid or pyrocatechol are greater than those for the corresponding reactions with the free (hydrated) $\mathrm{Cu^{2+}}$ ion. To get a broader basis for the evaluation of the reasons for the high stability of these ternary complexes, results taken from the literature were included in the Discussion. The conclusions drawn from a total of 20 examples of ternary $\mathrm{Cu^{2+}}$ complexes are that the most important driving forces for the formation of ternary complexes are electronic effects (π system of the ligands), besides coulombic effects (neutralization of charge in ternary complexes), and lower steric hindrance compared with the corresponding binary bis complexes.

In several papers it has been stated that ligands containing O as donor atoms form stabler complexes with the $\mathrm{Cu^{2+}}$–2,2'-bipy 1:1 complex (eq 1) than with the free (hydrated) $\mathrm{Cu^{2+}}$ ion (eq 2). Hence, according to eq 3 positive $\Delta \log K$ values were ob-

$$\mathrm{Cu(bipy) + L \rightleftharpoons Cu(bipy)L}$$

$$K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)L}} = \frac{[\mathrm{Cu(bipy)L}]}{[\mathrm{Cu(bipy)}][\mathrm{L}]} \qquad (1)$$

---

[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; see Abstract No. BIOL 53.

[2] Part VII: P. R. Huber, R. Griesser, B. Prijs, and H. Sigel, *European J. Biochem.*, **10**, 238 (1969).

[3] Correspondence should be addressed to this author.

$$\mathrm{Cu} + \mathrm{L} \rightleftharpoons \mathrm{CuL} \qquad K^{\mathrm{Cu}}_{\mathrm{CuL}} = \frac{[\mathrm{CuL}]}{[\mathrm{Cu}][\mathrm{L}]} \qquad (2)$$

$$\Delta \log K = \log K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)L}} - \log K^{\mathrm{Cu}}_{\mathrm{CuL}} \qquad (3)$$

served.[4-7] This is very surprising, since usually $K^{M}_{ML} > K^{ML}_{ML_2}$,[8] due to the fact that more coordination positions are available for bonding of the first ligand to a given metal ion than for the second ligand. With ligands containing N as donor atoms, the values for $\Delta \log K$ are negative.[5] With "mixed" ligands, containing O and N as donors, intermediate values were observed.[9,10]

In these cases, the stability constants according to eq 1 were determined under the assumption that the complex formation between Cu^{2+} and 2,2′-bipyridyl is complete. This assumption is reasonable and will be confirmed during this work. Besides the possibility of characterizing the stability of ternary complexes by eq 3, there is another one (eq 4 and 5)[11] which, however, needs more data.

$$\mathrm{CuA_2} + \mathrm{CuB_2} \rightleftharpoons 2\mathrm{CuAB} \qquad X = \frac{[\mathrm{CuAB}]^2}{[\mathrm{CuA_2}][\mathrm{CuB_2}]} \qquad (4)^{12}$$

$$\log X = 2 \log \beta^{\mathrm{Cu}}_{\mathrm{CuAB}} - (\log \beta^{\mathrm{Cu}}_{\mathrm{CuA_2}} + \log \beta^{\mathrm{Cu}}_{\mathrm{CuB_2}}) \qquad (5)^{13}$$

To learn more about the driving forces which lead to the formation of mixed-ligand complexes, several systems containing Cu^{2+}, 2,2′-bipyridyl, and another ligand with O and/or N atoms as donors were investigated by potentiometric titration. These systems will be characterized according to eq 3 and 5.

Experimental Section

Materials.—2,2′-Bipyridyl, ethylenediamine, oxalic acid, malonic acid, pyrocatechol, $Cu(ClO_4)_2 \cdot 6H_2O$, and $NaClO_4$ were from Fluka AG, Buchs, Switzerland. $HClO_4$ and potassium hydrogen phthalate were from Merck AG, Darmstadt, Germany.

Measurements.—The titrations were carried out under N_2 in solutions with ionic strength $I = 0.1$ ($NaClO_4$) at 25° with a Metrohm potentiograph E 336 and Metrohm UX glass electrodes. Standardization of NaOH for titration was effected with potassium hydrogen phthalate. The exact Cu^{2+} concentration of the stock solution was determined with ethylenediamine-N,N,N′,N′-tetraacetic acid.

Determination of the Acidity Constants of the Ligands.—$K^{H}_{H_2L}$ and K^{H}_{HL} of ethylenediamine were determined by titrating 50 ml of aqueous 1.3×10^{-3} M $HClO_4$ and $NaClO_4$ ($I = 0.1$) in the presence and absence of the ligand (6×10^{-4} M) under N_2 with 0.1 M NaOH[2] and those of malonic acid were determined by titrating 25 ml of aqueous 3×10^{-3} M $HClO_4$ with and without ligand (7.2×10^{-3} M) using 0.5 M NaOH ($I = 0.1$; temperature 25°).

The acidity constants of glycine[9] and $K^{H}_{H_2L}$ of pyrocatechol[2] were taken from our earlier work. The value for pK^{H}_{HL} of pyrocatechol was from a study by Perrin[14] (*cf.* also ref 15) and that for 2,2′-bipyridyl from a report by Anderegg.[16]

Determination of the Stability Constants of the Binary Complexes.—The conditions of measurements for the determination of the stability constants, K^{Cu}_{CuL}, were the same as for the acidity constants, but a part of $NaClO_4$ was replaced by $Cu(ClO_4)_2$ with the ratio $Cu^{2+}:L = 1:1$. Titrations of solutions without ligand were used as a basis for the evaluation.

The calculation of K^{Cu}_{CuL} was done by taking into account the species H_2L, HL, L, Cu, CuL, and CuL_2. From the equations summarizing the total concentration of L and Cu^{2+} and from that for the neutralization degree for each point of the titration curve, a value for K^{Cu}_{CuL} can be obtained. Previously, $K^{CuL}_{CuL_2}$ was determined[17] from titrations where L was in excess with regard to Cu^{2+}. $K^{CuL}_{CuL_2}$ of malonic acid was taken from the work of Davies[18] and the constants of the Cu^{2+}–2,2′-bipy complexes were from the work of Anderegg.[16]

Determination of the Stability Constants of the Ternary Complexes.—The conditions of measurements for the titrations of the ternary complexes were the same as for the binary ones, but the solutions contained equivalent amounts of 2,2′-bipyridyl, Cu^{2+}, and the other ligand (L). The evaluation of the titration curves was done using curves obtained using the same solutions but without L.

In the literature (*cf.*, *e.g.*, ref 19–21), ways are described for determination of the stability constants of ternary complexes. Our calculations, similar to those of Näsänen and Koskinen,[22,23] were performed with a computer (IBM 1620) using the iteration method described by Zajicek.[24] The species taken into account were H_2A, HA, A, H_2B, HB, B, CuA_2, CuA, CuB_2, CuB, Cu, and CuAB, and the calculated equilibrium constant was β^{Cu}_{CuAB}.

Results

The acidity constants of the ligands and the stability constants of the binary Cu^{2+} complexes which were used for the calculations of the stability constants of the ternary complexes are given in Table I. The results obtained for the formation of ternary complexes between the Cu^{2+}–2,2′-bipy 1:1 complex and ethylenediamine, glycine anion, malonic acid dianion, or pyrocatechol dianion are shown in Table II. Originally, it was intended to use oxalate instead of malonate. However, in the latter case a precipitate is formed already at very low pH (*cf.* also ref 4). The elementary analysis shows that a mixed 2,2′-bipy–Cu^{2+}–oxalate complex is formed.[25]

The values in Table II for $\Delta \log K$ and $\log X$ were calculated according to eq 3 and 5, respectively, and those for $\log K^{Cu(bipy)}_{Cu(bipy)L}$ according to the equation

$$\log K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)L}} = \log \beta^{\mathrm{Cu}}_{\mathrm{Cu(bipy)L}} - \log K^{\mathrm{Cu}}_{\mathrm{Cu(bipy)}} \qquad (6)$$

Instead of considering the reaction between the Cu^{2+}–

---

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

[5] H. Sigel, *Chimia* (Aarau), **21**, 489 (1967).

[6] H. Sigel, K. Becker, and D. B. McCormick, *Biochim. Biophys. Acta*, **148**, 655 (1967).

[7] R. Griesser, B. Prijs, and H. Sigel, *Inorg Nucl. Chem. Letters*, **4**, 137 (1968).

[8] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

[9] H. Sigel and R. Griesser, *Helv. Chim. Acta*, **50**, 1842 (1967).

[10] H. Sigel, *Angew. Chem.*, **80**, 124 (1968); *Angew. Chem., Intern. Ed. Engl.*, **7**, 137 (1968).

[11] M. Bonnet and R. A. Pâris, *Bull. Soc. Chim. France*, 747 (1966).

[12] A and B are bidentate ligands.

[13] $\beta^{Cu}_{CuAB} = [CuAB]/([Cu][A][B])$; $\beta^{Cu}_{CuA_2} = [CuA_2]/([Cu][A]^2)$; $\beta^{Cu}_{CuB_2} = [CuB_2]/([Cu][B]^2)$.

[14] D. D. Perrin, *Nature*, **182**, 741 (1958).

[15] C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **90**, 3379 (1968).

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

[17] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941.

[18] C. W. Davies, *J. Chem. Soc.*, 910 (1935).

[19] R. Näsänen, P. Meriläinen, and S. Lukkari, *Acta Chem. Scand.*, **16**, 2384 (1962).

[20] R.-P. Martin and R. A. Pâris, *Bull. Soc. Chim. France*, 80 (1964).

[21] I. G. Sayce, *Talanta*, **15**, 1397 (1968); D. D. Perrin and V. S. Sharma, *J. Chem. Soc., A*, 446 (1968).

[22] R. Näsänen and M. Koskinen, *Suomen Kemistilehti, B*, **40**, 23 (1967).

[23] R. Näsänen and M. Koskinen, *ibid., B*, **40**, 108 (1967).

[24] O. T. Zajicek, *J. Chem. Educ.*, **42**, 622 (1965); *cf.* also N. Ingri and L. G. Sillén, *Acta Chem. Scand.*, **16**, 173 (1962).

[25] *Anal.* Calcd for $C_{12}H_8N_2O_4Cu$: C, 46.83; H, 2.62; N, 9.10. Found: C, 46.54; H, 2.83; N, 9.10.

TABLE I

NEGATIVE LOGARITHMS OF ACIDITY CONSTANTS OF THE LIGANDS AND LOGARITHMS OF STABILITY CONSTANTS OF THEIR BINARY Cu^{2+} COMPLEXES ($I = 0.1$; 25°)

Ligand	$pK^{H}_{H_2L}$	pK^{H}_{HL}	Log K^{Cu}_{CuL}	Log $K^{Cu}_{CuL_2}$	Log $\beta^{Cu}_{CuL_2}$
2,2′-Bipyridyl[a]	. . .	4.49	8.00	5.60	13.60
Ethylenediamine[b]	7.10 ± 0.03	9.89 ± 0.03	10.44 ± 0.06	9.16	19.60
Glycine[b]	2.33 ± 0.01	9.68 ± 0.01	8.27 ± 0.01	6.92	15.19
Malonic acid	2.62 ± 0.03	5.30 ± 0.02	5.10 ± 0.05	2.55[c]	7.65
Pyrocatechol[b]	9.32 ± 0.03	13.00[d]	13.96 ± 0.02	11.07	25.03

[a] These values are taken from the work of Anderegg.[16] [b] These values are also used in connected work: glycine, ref 9; ethylenediamine and pyrocatechol, ref 2. [c] This value is taken from the work of Davies.[18] [d] This value is taken from the work of Perrin;[14] *cf.* also ref 15.

TABLE II

LOGARITHMS OF STABILITY CONSTANTS OF SOME TERNARY 2,2′-bipy–Cu^{2+}–LIGAND COMPLEXES ($I = 0.1$; 25°)

Ligand	Log $\beta^{Cu}_{Cu(bipy)L}$	Log $K^{Cu(bipy)}_{Cu(bipy)L}$[a]	Log $K^{CuL}_{CuL(bipy)}$[b]	Δ log K[c]	Log X[d]
Ethylenediamine	17.15 ± 0.03	9.15	6.71	−1.29	1.10
Glycine	15.92 ± 0.01	7.92	7.65	−0.35	3.05
Malonic acid	13.37 ± 0.04	5.37	8.27	+0.27	5.49
Pyrocatechol	22.39 ± 0.03	14.39	8.43	+0.43[e]	6.15

[a] Calculated according to eq 6. [b] Calculated according to eq 7. [c] Calculated according to eq 3. [d] Calculated according to eq 5. [e] L'Heureux and Martell determined $\Delta \log K = +0.36$.[4]

2,2′-bipy 1:1 complex and another ligand, L (*cf.* eq 1), one can also consider the reaction between CuL and 2,2′-bipyridyl. The corresponding equilibrium constants, $K^{CuL}_{CuL(bipy)}$, were calculated according to eq 7 and are also given in Table II. An extension of eq 3 shows (*cf.* eq 8) that the differences between $K^{Cu(bipy)}_{Cu(bipy)L}$ or $K^{CuL}_{CuL(bipy)}$ and the corresponding values, K^{Cu}_{CuL} or $K^{Cu}_{Cu(bipy)}$, are the same. Hence, the influence of both ligands in a ternary complex is mutual and of the same size. Both ligands are either stabilized or destabilized in their coordination to the same metal ion.[5,6]

$$\log K^{CuL}_{CuL(bipy)} = \log \beta^{Cu}_{Cu(bipy)L} - \log K^{Cu}_{CuL} \qquad (7)$$

$$\Delta \log K = \log K^{Cu(bipy)}_{Cu(bipy)L} - \log K^{Cu}_{CuL} = \log K^{CuL}_{CuL(bipy)} - \log K^{Cu}_{Cu(bipy)} \qquad (8)$$

As already mentioned, in several earlier studies[4-7] stability constants according to eq 1 of ternary 2,2′-bipy–Cu^{2+}–ligand complexes have been determined by the assumption that in a 1:1 mixture of Cu^{2+} and 2,2′-bipyridyl the formation of the Cu^{2+}–2,2′-bipy 1:1 complex is complete. This assumption allows one to calculate the stability constants of the ternary complexes in a way usual for binary complexes. To see how this simplification influences the values, *e.g.*, log $K^{Cu(bipy)}_{Cu(bipy)L}$, the titration data were also evaluated under this assumption. The results showed that the agreement between the two methods is very good; *cf.* ref 26. Hence, it is obvious that the mentioned assumptions are reasonable. This result allows us to include also data obtained under these assumptions in General Conclusions (Table III), where we shall discuss the reasons for the stability of ternary complexes.

Discussion

The Δ log K values for the ternary complexes containing 2,2′-bipyridyl and the dianions of pyrocatechol or malonic acid are positive (Table II). The order of Δ log K (approximately +0.4) is the same as observed before with other O ligands[4-6] and confirms the observations that the presence of 2,2′-bipyridyl favors the coordination of these ligands to Cu^{2+}. For the 2,2′-bipy–Cu^{2+}–en system, a negative Δ log K value (−1.3) is observed. In agreement with these results, $\Delta \log K = -0.35$ for the "mixed" O–N ligand, glycine; this value is between those found for pure O or N ligands.

The observation of a negative Δ log K value means that the ligand under consideration forms a more stable complex with the free (hydrated) Cu^{2+} ion than with the Cu^{2+}–2,2′-bipy 1:1 complex;[27] however, it does not mean that no ternary complex is formed in solutions containing equimolar mixtures of two different ligands and Cu^{2+}. A more general statement about the conditions in such solutions can be made considering eq 4 and the corresponding equilibrium constant, X (eq 5). The value expected for X on statistical reasons is 4; *i.e.*, $\log X = 0.6$.[28,29] Even in the case of the 2,2′-bipy–Cu^{2+}–en system where a strongly negative Δ log K value is observed, the value for log X is still greater than the statistical one (Table II). The ternary complexes containing the dianions of pyrocatechol or malonic acid are more stable by a factor of approximately 10^5 than expected for statistical reasons.

The high concentrations of ternary complexes that

[26] Log $K^{Cu(bipy)}_{Cu(bipy)L}$, calculated by taking into account only the species Cu(bipy), Cu(bipy)L, H_2L, HL, and L, is: for L = ethylenediamine, 9.29 ± 0.04 (9.15); glycine, 7.88 ± 0.01[9] (7.92); malonic acid, 5.33 ± 0.03 (5.37); pyrocatechol, 14.35 ± 0.03 (14.39). The values given in parentheses are the corresponding ones from Table II, which were calculated taking into account the species Cu(bipy), $Cu(bipy)_2$, Cu(bipy)L, CuL, CuL_2, Cu, H(bipy), bipy, H_2L, HL, and L.

[27] It is informative to compare for given conditions the degree of complex formation in binary mixtures containing Cu^{2+} and ligand in the ratio 1:1 with those of the ternary mixtures 2,2′-bipyridyl:Cu^{2+}:ligand = 1:1:1. The results of such calculations for 10^{-3} *M* solutions at pH 6.0 for L = ethylenediamine are 69% CuL in the binary system and 50% Cu(bipy)L in the ternary one; for L = pyrocatechol dianion 62% CuL is formed in the binary mixture and 72% Cu(bipy)L in the ternary one.

[28] R. DeWitt and J. I. Watters, *J. Am. Chem. Soc.*, **76**, 3810 (1954).

[29] S. Kida, *Bull. Chem. Soc. Japan*, **29**, 805 (1956).

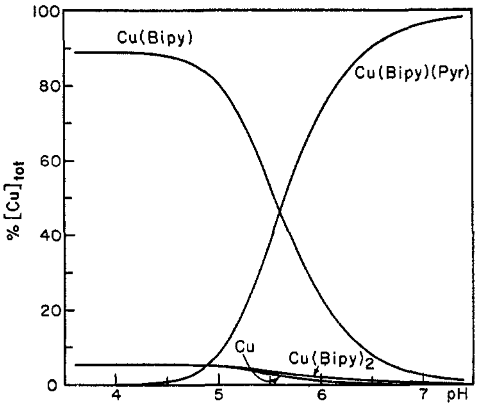

Figure 1.—Variation with pH of the concentrations (given as the percentage of the total Cu^{2+} present) of the several species present in an aqueous solution of Cu^{2+}, 2,2′-bipyridyl, and pyrocatechol (each 10^{-3} *M*); computed with the constants of Tables I and II. Cu(pyr) reaches its maximal concentration at pH 6 with 1.2%; $Cu(pyr)_2$ is less than 0.05% at pH <8.

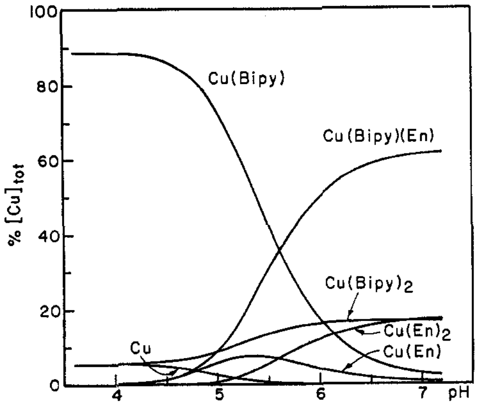

Figure 2.—Variation with pH of the concentrations (given as the percentage of the total Cu^{2+} present) of the several species present in an aqueous solution of Cu^{2+}, 2,2′-bipyridyl, and ethylenediamine (each 10^{-3} *M*); computed with the constants of Tables I and II.

occur in 1:1:1 mixtures can be seen from Figures 1 and 2 where the percentage of the total concentration of Cu^{2+} in the several species is shown in dependence on pH. The concentrations were computed using the results of Tables I and II. In the 2,2′-bipy–Cu^{2+}–pyrocatechol system, the concentration of the ternary complex reaches nearly 100% of the total Cu^{2+} present at high pH (Figure 1). In the 2,2′-bipy–Cu^{2+}–en system, the concentration of the ternary complex is considerably less but still remarkable (Figure 2). In all the systems, the ternary complex and the binary bis complexes tend to approach limiting values with increasing pH.

General Conclusions

In the last section, we saw that the Cu^{2+}–2,2′-bipy 1:1 complex has discriminating qualities toward other ligands; it preferably coordinates O-containing ligands, and the resulting ternary complexes are remarkably stable. To get a broader basis for the attempt to find the reasons for this behavior and to see whether or not these qualities are generally due to Cu^{2+}–N ligand 1:1 complexes, additional stability data for ternary Cu^{2+} complexes are given in Table III.[30–34] A part of the values for Δ log *K* and log *X* were already given by the several authors and the others were calculated according to eq 3 (=8) and 5 using the data available in the literature. Even though the conditions of measurement, *i.e.*, *I* and temperature, were somewhat different for the several systems, it is possible to draw some general conclusions from the data of Table III.

Probably the most evident fact is that positive Δ log *K* values are observed only with 2,2′-bipy–Cu^{2+}–O ligand systems. It is of interest to note that quite generally the largest contribution to log *X*, for which eq 5 as well as eq 9 holds, comes from the ligand which has the greatest difference in stability between the 1:1 and 1:2 complexes.

$$(\log K^{\mathrm{CuB}}_{\mathrm{CuBA}} - \log K^{\mathrm{CuA}}_{\mathrm{CuA_2}}) + (\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} - \log K^{\mathrm{CuB}}_{\mathrm{CuB_2}}) = \log X \quad (9)$$

TABLE III

COMPARISON OF THE STABILITY OF SOME TERNARY Cu^{2+} COMPLEXES

No.	Ligand[a] A	Ligand[a] B	Δ log K^b	Log *X*	*I*	Temp, °C	Ref
0	A	B		0.6^c			28, 29
1	bipy	DSP	+0.87	$\sim 6.4^d$	0.1	25	4, 30
2	bipy	pyr	+0.43	6.15	0.1	25	*e*
3	bipy	Ssal	+0.45	5.9^f	0.1	25	4, 14
4	bipy	sal	+0.27	5.7^f	0.1	25	4, 14
5	bipy	ma	+0.27	5.49	0.1	25	*e*
6	bipy	gly	−0.35	3.05	0.1	25	*e*
7	bipy	GA	−0.4	2.8	0.1	25	10
8	bipy	en	−1.29	1.10	0.1	25	*e*
9	ha	pyr	−0.48	4.86	0.1	25	2
10	ha	ser	−0.58	2.95^g	0.15	37	31
11	ha	en	−1.43	1.54^g	0.15	37	31
12	en	pyr	−0.76	2.65	0.1	25	2
13	en	ox	−1.1	1.3^h	1.0	25	32
14	en	ser	−0.87	0.79^g	0.15	37	31
15	en	PDA	−1.53	0.96	0	25	23
16	en	DEE	−1.40	1.83	→0	25	23
17	en	IDE	−2.3	1.9	→0.1	30	34
18	Ssal	bipy	+0.45	5.9^f	0.1	25	4, 14
19	Ssal	Men		1.83	0.1	25	19
20	Ssal	$(NH_3)_2$	−1.19	1.56	1.0	25	11
21	Ssal	gly	−1.20	1.02	1.0	25	11, 20

[a] Abbreviations used: bipy, 2,2′-bipyridyl; DEE, N,N′-diethylethylenediamine; DSP, 3,5-disulfopyrocatechol tetraanion; en, ethylenediamine; GA, glycine amide; gly, glycine anion; ha, histamine; IDE, iminodiacetic acid dianion; ma, malonic acid dianion; Men, 1,2-diaminopropane; ox, oxalic acid dianion; PDA, 1,3-propylenediamine; pyr, pyrocatechol dianion; sal, salicylic acid dianion; ser, serine anion; Ssal, 5-sulfosalicylic acid trianion. [b] Calculated according to eq 8. [c] Statistical value. [d] Calculated with the data for the ternary complex of L'Heureux and Martell[4] and those for the binary complexes of Näsänen.[30] The values of ref 30 were corrected due to the different acidity constants given in ref 4 and 30; this correction leads to a value for log *X* which is too small rather than too large. [e] This work. [f] Calculated with the data of L'Heureux and Martell[4] and log $K^{\mathrm{CuL}}_{\mathrm{CuL_2}}$ of Perrin.[14] [g] Calculated with the values given by Perrin, Sayce, and Sharma.[31] [h] Calculated with the values given by Schaap and McMasters;[32] values determined by other authors are 1.4,[33] 1.1,[29] and 1.0.[28]

---

(30) R. Näsänen, *Suomen Kemistilehti*, *B*, **33**, 111 (1960).

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

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

(33) J. I. Watters, *ibid.*, **81**, 1560 (1959).

(34) W. E. Bennett, *ibid.*, **79**, 1290 (1957).

As for the driving forces which lead to the formation of ternary complexes, one has to mention, in addition to the statistical reasons,[28,29] the neutralization of charge in ternary complexes like ethylenediamine–Cu^{2+}–oxalic acid dianion. This latter is neutral compared with the corresponding binary 1:2 complexes which have a charge of 2.[32] This means enthalpy (coulombic) and entropy (release of the orientation of solvent molecules) effects favor the formation of the ternary complex.[4] Indeed, the log X value of the ethylenediamine–Cu^{2+}–oxalic acid dianion system (**13** in Table III) is significantly larger than the statistical value.

That steric hindrance[23,35] in the binary complexes may increase the stability of the ternary complexes where steric hindrance is lower is suggested from systems **15–17** in Table III. The bulky groups of N,N′-diethylethylenediamine in the Cu^{2+} 1:1 complex favor more the coordination of ethylenediamine than a second ligand of the same kind (**16**). Similar reasoning is true for the Cu^{2+} 1:1 complex with the tridentate ligand iminodiacetic acid (**17**).

Very recently the high stability of ternary Cu^{2+} complexes containing 2,2′-bipyridyl or 1,10-phenanthroline was attributed to steric hindrance in the corresponding Cu^{2+} 1:2 complexes.[36] However, this effect cannot be really important, since positive Δ log K values are observed in 2,2′-bipyridyl–O ligand systems (*cf.* **1–5** in Table III). So it is hard to see why the coordination of the pyrocatechol dianion to the hydrated Cu^{2+} ion should be sterically more hindered than the coordination of the same ligand to the Cu^{2+}–2,2′-bipy 1:1 complex; if in this example any steric hindrance occurs, one would expect just the opposite. Also the log X values of 2,2′-bipy–Cu^{2+}–O ligand systems are by a factor of 10^4–10^5 greater than the ethylenediamine ones (**12** and **13**). Therefore, the explanations given so far can only be part of the reasons for the increased stability of ternary complexes.

Since the only difference between systems **2** and **12** in Table III is the N ligand, the additional stability-increasing effects have to be due to the qualities of 2,2′-bipyridyl (*cf.* also ref 5). The main differences between 2,2′-bipyridyl and ethylenediamine are: (a) 2,2′-bipyridyl induces a stronger ligand field at the Cu^{2+} ion than ethylenediamine and (b) 2,2′-bipyridyl is bound to Cu^{2+} through a σ donor bond as is ethylenediamine, but the former ligand is also a π acceptor (π bonds; back-donation); hence, the resulting charge on the Cu^{2+} ion in the 1:1 complexes is higher with 2,2′-bipyridyl.[37] According to (a) the distorted octahedral $Cu(H_2O)_6{}^{2+}$ ion will be somewhat more strongly distorted toward a square-planar coordination sphere by the coordination of 2,2′-bipyridyl, thus, creating the "right" geometry for the coordination of the second ligand, which will be especially favored due to (b) if its donors are negatively charged O atoms.

In accordance with these explanations are the stabilities observed for ternary complexes containing histamine (**9–11** in Table III); their stabilities are between those of the systems containing 2,2′-bipyridyl or ethylenediamine. The Cu^{2+}–histamine 1:1 complex has still quite remarkable discriminating qualities which may be important in biological systems. The results obtained so far for the stability of ternary complexes containing 1,10-phenanthroline are also in agreement with the above statement. The log X values for the 1,10-phenanthroline–Cu^{2+}–2-picoline carboxylic acid[38] and the 1,10-phenanthroline–Cu^{2+}–8-hydroxyquinoline complexes[38,39] are 3.92 and 3.71 which is very reasonable compared with the values of Table III. The log X values obtained for several ternary Cu^{2+} complexes containing 5-sulfosalicylic acid trianion (**18–21**) and another ligand also fit in the described picture.

Besides the importance of the π system of the N ligand for the stability of ternary Cu^{2+} complexes, the π system of the O ligand seems also to have some (but a smaller) effect. The log X value of the ethylenediamine–Cu^{2+}–pyrocatechol complex is about 1.3 log units greater than that of the ethylenediamine–Cu^{2+}–oxalic acid system. This suggests that in complexes like 2,2′-bipyridyl–Cu^{2+}–pyrocatechol a cooperative effect may occur between the π systems of the two ligands bound to the same Cu^{2+}. In line with this assumption are results obtained for several ternary 2,2′-bipyridyl–Cu^{2+}–carboxylate complexes: aromatic carboxylic acid anions (derivatives of benzoate) form somewhat more stable complexes with the Cu^{2+}–2,2′-bipy 1:1 complex than aliphatic carboxylic acid anions (acetate, etc.);[7] complex formation with the hydrated Cu^{2+} ion is the same for both kinds of carboxylic acid anions. Of interest in this connection is that the ultraviolet spectra of the 8-quinolinolato–Cu^{2+}–arylhydroxycarboxylato complexes[40] show considerable interaction of the metal ion "d" electrons with the π system of the 8-quinolinolate, and little interaction with the π system of the arylhydroxycarboxylic acids.

Another explanation for the great stability of ternary Cu^{2+} complexes containing aromatic N ligands, like 2,2′-bipyridyl, can be given according to Pearson's "hard and soft rule": hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases.[41] After Pearson, Cu^{2+} is neither hard nor soft but is borderline; the same is true for the pyridyl group. Going across, for example, the

---

(35) R. Näsänen and P. Tilus, *Suomen Kemistilehti, B*, **42**, 11 (1969).

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

(37) That the differences are due to π bonds and not the increase in s character of the N atoms (sp^2 in 2,2′-bipyridyl and sp^3 in ethylenediamine) follows from an investigation of the ternary Cu^{2+} complexes containing pyrocatechol and 4-(2-pyridyl)imidazole or picolylamine. The stability of the ternary complex with the previous N-ligand is between those containing 2,2′-bipyridyl or picolylamine. This is in agreement with the fact that the imidazole group is a poorer π acceptor than the pyridyl group: P. R. Huber, R. Griesser, and H. Sigel, to be submitted for publication.

(38) J. P. Scharff and M. R. Pâris, *Bull. Soc. Chim. France*, 1782 (1967).

(39) J. P. Scharff and M. R. Pâris, *Compt. Rend.*, **263**, 935 (1966).

(40) S. G. Schulman, W. P. Kilroy, and H. Gershon, *J. Phys. Chem.*, **72**, 3372 (1968).

(41) R. G. Pearson, *J. Chem. Educ.*, **45**, 581, 643 (1968).

3d transition series from Ca^{2+} to Zn^{2+}, the ions become softer as a consequence of the increasing number of d electrons.[41] Since π bonds are formed and back-donation occurs from the coordination of 2,2′-bipyridyl to Cu^{2+}, the d-electron content on Cu^{2+} decreases; that is it becomes more hard. Hence, through the combination of the borderline 2,2′-bipyridyl with the borderline Cu^{2+}, a harder species is created which is more favored to combine with O than with N ligands (the hardness increases in the series: $CH_3^- < NH_2^- < OH^- < F^-$ (*cf.* ref 41); this behavior is opposite to the "symbiotic" effect described by Jørgensen.[42]

The importance of ternary complexes in metal ion catalyzed reactions is well known. For example, the Cu^{2+}-catalyzed decomposition of H_2O_2 is strongly dependent on the kind of ligand bound to the metal ion.[43] Also, the rate of the metal ion catalyzed decarboxylation of acetonedicarboxylate, oxaloacetate, or dimethyloxaloacetate is increased by coordination of the metal ion to an aromatic ligand, *e.g.*, 2,2′-bipyridyl, compared with the aqueous metal ions,[44] while no enhancement is observed with aliphatic amines.[45] In addition, the hydrolysis of diisopropyl fluorophosphate is catalyzed through several Cu^{2+} complexes, among which the Cu^{2+}–2,2′-bipy 1:1 complex is especially effective; furthermore, the complexes of L-histidine, 1,10-phenanthroline, and imidazole are better catalysts than that of glycine.[46] Such observations and the described stability rules suggest that the difference in the reaction rate is closely connected with the stability of the ternary complexes formed during the reactions.

Acknowledgments.—We wish to thank Professor Dr. D. B. McCormick (Cornell University, Ithaca, N. Y.) for helpful comments. The measurements were performed with the skillful technical assistance of Miss R. Baumbusch, Miss G. Baum, and Mr. A. Tàlos. The computer, IBM 1620, was made available by the Rechenzentrum der Universität Basel. This investigation was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.

[42] C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).

[43] H. Sigel, *Angew. Chem.*, **81**, 161 (1969); *Angew. Chem., Intern. Ed. Engl.*, **8**, 167 (1969).

[44] R. W. Hay and K. N. Leong, *Chem. Commun.*, 800 (1967); P. R. Boutchev and V. Michaylova, *J. Inorg. Nucl. Chem.*, **29**, 2945 (1967); J. V. Rund and R. A. Plane, *J. Am. Chem. Soc.*, **86**, 367 (1964).

[45] J. V. Rund and K. G. Claus, *Inorg. Chem.*, **7**, 860 (1968).

[46] T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens, and R. Proper, *J. Am. Chem. Soc.*, **77**, 922 (1955).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, A.C.T., AUSTRALIA, AND UNIVERSITY OF QUEENSLAND, ST. LUCIA, BRISBANE, QUEENSLAND, AUSTRALIA

Racemization and Oxygen-18-Exchange Studies of Heterochelate Chromium(III) Complexes with the Ligands 2,2′-Bipyridine, 1,10-Phenanthroline, and Oxalate Ion. I. Racemization of the Bis(oxalato)2,2′-bipyridinechromate(III) and the Bis(oxalato)-1,10-phenanthrolinechromate(III) Anions

BY J. A. BROOMHEAD,[1a] N. KANE-MAGUIRE,[1b] AND I. LAUDER[1b]

Received December 8, 1969

The kinetics of racemization of the anions $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ (ox = oxalate ion; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline) fit the expression rate = $(k_1 + k_2[H^+] + k_3[H^+]^2)$[complex]. At 25° and unit ionic strength respective values are: $k_1 = 1.82 \times 10^{-4}$ sec^{-1}, $k_2 = 2.44 \times 10^{-4}$ M^{-1} sec^{-1}, $k_3 = 1.15 \times 10^{-4}$ M^{-2} sec^{-1}; $k_1 = 2.43 \times 10^{-4}$ sec^{-1}; $k_2 = 2.73 \times 10^{-4}$ M^{-1} sec^{-1}, $k_3 = 1.34 \times 10^{-4}$ M^{-2} sec^{-1}. Divalent metal ions catalyze the racemization reaction and give a rate expression similar to that for acid catalysis. Arrhenius parameters have been measured and previous work extended. An intramolecular racemization mechanism involving contributions from half-bonded oxalato ligands and from twist processes is suggested. Acid-catalyzed oxygen-18 exchange with solvent water follows the rate expression rate = $k'[H^+]$[complex], up to 1 M acid. All eight oxygen atoms of the oxalato ligands are exchanged at the same rate, and though the racemization results support a half-bonded oxalate mechanism for oxygen exchange, an interchange process cannot be eliminated. Divalent metal ions do not induce oxygen exchange. The danger in equating oxygen exchange and racemization rate data is discussed.

Introduction

Most studies on the racemization of metal complexes have been concerned with individual compounds rather than an interrelated series. The advantages of the last mentioned approach have been demonstrated previously in relation to nickel(II) complexes.[2] When a postulated mechanism includes factors common to more than one complex, then a more reliable interpretation may ensue. For this reason the series $Cr(ox)_2phen^-$, $Cr(ox)_2bipy^-$, $Cr(ox)(phen)_2^+$, and $Cr(ox)(bipy)_2^+$ (phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine; ox = oxalate ion) has been prepared and characterized.[3]

---

[1] (a) Australian National University. (b) University of Queensland.

[2] J. A. Broomhead and F. P. Dwyer, *Australian J. Chem.*, **16**, 51 (1963).

[3] (a) J. A. Broomhead, M. Dwyer, and N. Kane-Maguire, *Inorg. Chem.*, **7**, 1388 (1968); (b) J. A. Broomhead, *Australian J. Chem.*, **15**, 228 (1962).