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Ternary Complexes in Solution. XI. Complex Formation between the Cobalt(II)-, Nickel(II)-, Copper(II)-, and Zinc(II)-2,2'-Bipyridyl 1:1 Complexes and Ethylenediamine, Glycinate, or Pyrocatecholate¹

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The stability constants of the ternary Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} complexes containing 2,2'-bipyridyl and, as a second ligand, ethylenediamine, glycinate, or pyrocatecholate were determined by potentiometric titration. For the equilibrium, $\text{M}(2,2'\text{-bipyridyl})_2 + \text{M}(\text{ligand})_2 \rightleftharpoons 2\text{M}(2,2'\text{-bipyridyl})(\text{ligand})$ ($\text{M} = \text{metal}$), the corresponding constants are as follows: with Co^{2+} , $\log X = 0.68, 1.12, 4.11$; with Ni^{2+} , $\log X = 0.68, 0.75, 3.71$; with Cu^{2+} , $\log X = 1.10, 3.05, 6.15$; with Zn^{2+} , $\log X = 0.36, 0.72, 2.98$ ($I = 0.1$; 25°). Most of the mixed-ligand complexes are more stable than one would expect from purely statistical reasons ($\log X = 0.6$). Furthermore, the stability constants show that the M^{2+} -2,2'-bipyridyl 1:1 complexes have discriminating qualities toward the second ligand to be coordinated; they preferentially form ternary complexes with those ligands that contain O as donor atoms. In addition, the formation constants for the reactions between the Co^{2+} -, Ni^{2+} -, and Cu^{2+} -2,2'-bipyridyl 1:1 complexes and pyrocatecholate are greater than those for the corresponding reactions with the free (hydrated) metal ion. To get a broader basis for the conclusions, results taken from the literature are included in the Discussion. It is shown that mixed-ligand complexes containing Cu^{2+} are more stable than those with Co^{2+} , Ni^{2+} , or Zn^{2+} , at least as long as a pyridyl or an imidazole group is involved with the complex formation. Additionally, if these ligand groups are present, the ternary complexes formed with Co^{2+} are more stable than those with Ni^{2+} .

The investigation of mixed-ligand complexes containing Cu^{2+} showed that those ligands having a pyridyl or an imidazole group favor the stability of the ternary complex.² This can even lead to such surprising stabilities as observed, for example, with the 2,2'-bipyridyl- Cu^{2+} -pyrocatecholate system: pyrocatecholate forms a more stable complex with $\text{Cu}(\text{bipyridyl})^{2+}$ than with $\text{Cu}(\text{aq})^{2+}$.^{3,4} Another interesting result of these studies is the discriminating abilities of the Cu^{2+} -2,2'-bipyridyl 1:1 complex.^{3,5} 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 Cu^{2+} , the latter ligand is preferably bound to added Cu^{2+} -2,2'-bipyridyl.

These few mentioned facts show that mixed-ligand- Cu^{2+} complexes are relatively well investigated in contrast to ternary complexes containing other metal ions. Therefore, in the present work mixed-ligand complexes with Co^{2+} , Ni^{2+} , and Zn^{2+} were studied. To allow comparisons with the results of the earlier investigations³ with Cu^{2+} , 2,2'-bipyridyl was used as one ligand and ethylenediamine, glycinate, or pyrocatecholate as the other. All constants were determined by potentiometric titrations ($I = 0.1$; 25°).

Experimental Section

Materials and Measurements.—The metal ion perchlorates were obtained from Fluka AG, Buchs, Switzerland. The other reagents were the same as used earlier.³ All constants were measured by potentiometric titrations (25° ; $I = 0.1$, NaClO_4), carried out under N_2 with 0.1 M NaOH, as described.³

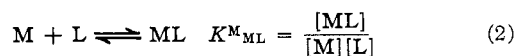
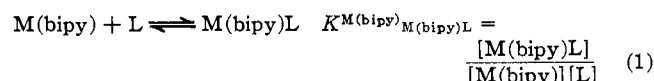
Determination of the Stability Constants of the Complexes.—In principle, the constants were determined as described recently^{2,3} but with the following exceptions. In the case of Ni^{2+} and glycinate, equilibrium was reached only after some time; therefore, the titrations were carried out over 2 hr rather than the usual 20 min. The stability constants of the 1:1 complexes between glycinate and Co^{2+} or Zn^{2+} agreed very well with those

given by Anderegg;⁶ therefore, we used his stability constants for the corresponding 1:2 complexes without a redetermination. To avoid precipitation, the constants for the pyrocatecholate 1:2 complexes were determined in solutions that were 2.9×10^{-4} to 7.2×10^{-3} M in pyrocatecholate and 1.4×10^{-4} M in metal ion. The titrations were done for this case with 2×10^{-3} M NaOH. The stability constants determined are in the order of those reported by Tyson and Martell.⁷

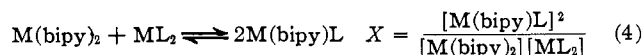
The stability constants of the binary and of the ternary complexes were computed as described recently.³ The uncertainties given in the tables are 3 times the standard deviation.³

Results

There are two convenient ways to characterize the stability of mixed-ligand complexes. The one is based on the difference of stability constants, $\Delta \log K$ (eq 1-3), and the other on the "disproportionation" constant, $\log X$ (eq 4 and 5).⁸



$$\Delta \log K = \log K^{\text{M}(\text{bipy})\text{L}}_{\text{M}(\text{bipy})\text{L}} - \log K^{\text{MML}}_{\text{ML}} \quad (3)$$



$$\log X = 2 \log \beta^{\text{M}(\text{bipy})\text{L}} - (\log \beta^{\text{M}(\text{bipy})_2} + \log \beta^{\text{MML}_2}) \quad (5)$$

Generally, one would expect to observe negative values for $\Delta \log K$ (eq 3), since usually it holds that $K^{\text{MML}}_{\text{ML}} > K^{\text{MML}_2}_{\text{ML}_2}$.⁹ This is 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. The method using eq 4 for characterization is somewhat more "objective," as the value expected for X can be deduced from statistical arguments: $X = 4$, i.e., $\log X = 0.6$ (eq 5).^{10,11}

(6) G. Anderegg, *Helv. Chim. Acta*, **44**, 1673 (1961).(7) C. A. Tyson and A. E. Martell, *J. Amer. Chem. Soc.*, **90**, 3379 (1968).

(8) Abbreviations used: M, general metal ion; L, general ligand; AHT, 2-acetyl-3-hydroxythiophene; ATP, adenosine 5'-triphosphate; bipy, 2,2'-bipyridyl; en, ethylenediamine; gly, glycinate; ha, histamine; ser, serinate.

(9) L. G. Silén and A. E. Martell, *Chem. Soc. Spec. Publ.*, **No. 17** (1964).(10) R. DeWitt and J. I. Watters, *J. Amer. Chem. Soc.*, **76**, 3810 (1954).(11) S. Kida, *Bull. Chem. Soc. Jap.*, **29**, 805 (1956).(1) Part X: H. Sigel, P. R. Huber, and R. F. Pasternack, *Inorg. Chem.*, **10**, 2226 (1971).(2) P. R. Huber, R. Griesser, and H. Sigel, *ibid.*, **10**, 945 (1971).(3) R. Griesser and H. Sigel, *ibid.*, **9**, 1238 (1970).(4) G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).(5) H. Sigel, *Chimia*, **21**, 489 (1967).

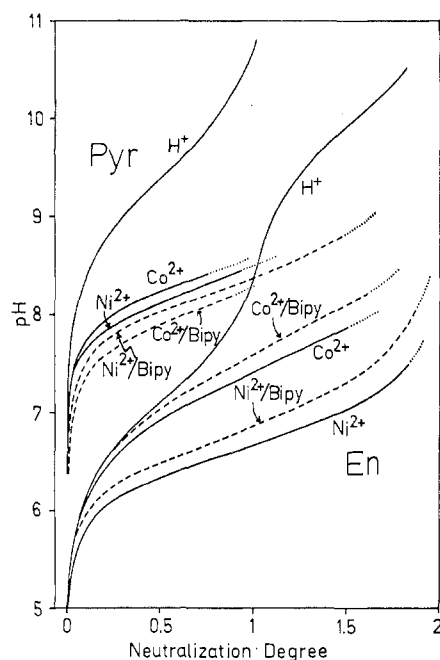


Figure 1.—Dependence of neutralization degree upon pH during potentiometric titration of pyrocatechol (Pyr) or ethylenediamine (En) without and with metal ion (—) or metal ion and 2,2'-bipyridyl (---) in aqueous solution ($I = 0.1$; 25°). Portions of lines (...) extended toward higher degrees of neutralization indicate uncertainty due to hydrolysis. Pyrocatechol was $8 \times 10^{-4} M$, as were the other reactants when added. Ethylenediamine was $6 \times 10^{-4} M$, as were the other reactants when added. The volume of the reaction solution was 50 ml. Titration was done with 0.1 M NaOH.

In Figure 1 the dependence of the degree of neutralization upon pH is given for the binary and ternary complexes of ethylenediamine and pyrocatechol with Co^{2+} and Ni^{2+} . Comparing the curves resulting from the titrations of ethylenediamine and Co^{2+} or Ni^{2+} in a ratio of 1:1 with those curves where, in addition, 2,2'-bipyridyl was present (ratio of 1:1:1), one sees that with both metal ions the deprotonation of ethylenediamine occurs in the presence of 2,2'-bipyridyl at higher pH values. This means the ternary complex is less stable than the corresponding binary one; in other words, the values we shall obtain for $\Delta \log K$ are negative. With the systems containing pyrocatechol, things are different. The deprotonation in the ternary systems occurs at a lower pH, especially remarkable with Co^{2+} . This means the ternary complexes are more stable than the corresponding binary ones, and we shall obtain *positive* $\Delta \log K$ values in these cases.

The acidity constants of the ligands and the stability constants of the binary Co^{2+} , Ni^{2+} , and Zn^{2+} complexes which were used for the calculations of the stability constants of the ternary complexes are given in Tables I and II. The results obtained for the formation of ternary complexes between the M^{2+} -2,2'-bipyridyl

TABLE I
NEGATIVE LOGARITHMS OF ACIDITY CONSTANTS
OF THE LIGANDS ($I = 0.1$; 25°)

Ligand	$pK_{H_2L}^H$	pK_{HL}^H	Ligand	$pK_{H_2L}^H$	pK_{HL}^H
2,2'-Bipyridyl	-0.2 ^a	4.49 ¹²	Glycine ^a	2.33	9.68
Ethylenediamine ^a	7.10	9.89	Pyrocatechol ^a	9.32	13.00

^a R. H. Linnel and A. Kaczmarczyk, *J. Phys. Chem.*, **65**, 1196 (1961).

TABLE II
LOGARITHMS OF STABILITY CONSTANTS OF
THE BINARY M^{2+} COMPLEXES
($I = 0.1$; 25°)

Ligand	M^{2+}	Log K_{ML}^{ML}	Log $K_{ML_2}^{ML_2}$	Log $\beta_{ML_2}^M$
2,2'-Bipyridyl ¹²	Co^{2+}	6.06	5.36	11.42
	Ni^{2+}	7.13	6.88	14.01
	Cu^{2+}	8.00	5.60	13.60
	Zn^{2+}	5.30	4.53	9.83
Ethylenediamine ^a	Co^{2+}	5.38 ± 0.04	4.86	10.24
	Ni^{2+}	6.97 ± 0.05	6.18	13.15
	Cu^{2+}	10.44 ^a	9.16 ^a	19.60 ^a
	Zn^{2+}	5.59 ± 0.14	5.02	10.61
Glycinate	Co^{2+}	4.63 ± 0.01	3.87 ^b	8.50
	Ni^{2+}	5.83 ± 0.02	4.91 ^b	10.74
	Cu^{2+}	8.27 ^a	6.92 ^a	15.19 ^a
	Zn^{2+}	4.96 ± 0.07	4.23 ^b	9.19
Pyrocatecholate	Co^{2+}	8.61 ± 0.04	6.72	15.33
	Ni^{2+}	8.89 ± 0.03	6.15	15.04
	Cu^{2+}	13.96	11.07 ^a	25.03 ^a
	Zn^{2+}	9.90 ± 0.08	7.67	17.57

^a The stability constants $\log K_{ML_2}^{ML_2}$ determined for the 1:3 complexes are 3.55 for Co^{2+} , 4.38 for Ni^{2+} , and 3.78 for Zn^{2+} .
^b $\log K_{NiL_2}^{NiL_2} \sim 3.3$.

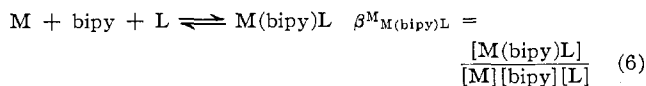
1:1 complex and ethylenediamine, glycinate, or pyrocatecholate are shown in Table III. The constant com-

TABLE III
LOGARITHMS OF STABILITY CONSTANTS OF SOME TERNARY
2,2'-BIPYRIDYL- M^{2+} -LIGAND COMPLEXES ($I = 0.1$; 25°)^a

Ligand	M^{2+}	Log $\beta_{M(bipy)L}^M$	Log $K_{M(bipy)L}^{M(bipy)L}$	Log $K_{MLML(bipy)}^{MLML(bipy)}$
Ethylenediamine	Co^{2+}	11.17 ± 0.06	5.11	5.79
	Ni^{2+}	13.92 ± 0.08	6.79	6.95
	Cu^{2+}	17.15	9.15	6.71
	Zn^{2+}	10.40 ± 0.06	5.10	4.81
Glycinate	Co^{2+}	10.52 ± 0.01	4.46	5.89
	Ni^{2+}	12.75 ± 0.05	5.62	6.92
	Cu^{2+}	15.92	7.92	7.65
	Zn^{2+}	9.87 ± 0.11	4.57	4.91
Pyrocatecholate	Co^{2+}	15.43 ± 0.12	9.37	6.82
	Ni^{2+}	16.38 ± 0.03	9.25	7.49
	Cu^{2+}	22.39	14.39	8.43
	Zn^{2+}	15.19 ± 0.08	9.89	5.29

^a The constants for the mixed-ligand complexes containing Cu^{2+} are taken from ref 3.

puted from the experimental data (*cf.* Figure 1) was $\log \beta_{M(bipy)L}^M$ which is due to the overall equilibrium 6. The constant $\log K_{M(bipy)L}^{M(bipy)L}$, according to eq 1, was calculated from eq 7. Of course, instead of considering the reaction between the M^{2+} -2,2'-bipyridyl 1:1 complex and another ligand, L, one can also consider the reaction between ML and 2,2'-bipyridyl. The corresponding equilibrium constant, $K_{MLML(bipy)}^{MLML(bipy)}$, was calculated according to eq 8 and is also given in Table III. To obtain a more complete picture necessary for a profound discussion, the results obtained earlier³ with the mentioned systems and Cu^{2+} are included in the tables.



$$\log K_{M(bipy)L}^{M(bipy)L} = \log \beta_{M(bipy)L}^M - \log K_{M(bipy)}^M \quad (7)$$

$$\log K_{MLML(bipy)}^{MLML(bipy)} = \log \beta_{M(bipy)L}^M - \log K_{ML}^{ML} \quad (8)$$

The equilibrium constant $\log \beta_{M(bipy)L}^M$ was calculated taking into account the species H, H_2L , HL, L, ML, ML_2 , $H_2(bipy)$, H(bipy), bipy, M(bipy), $M(bipy)_2$, $M(bipy)L$, and M .³ In other words, no 1:3 complexes were considered. This is reasonable, as under our experimental conditions (titration of 1:1:1 mixtures), the

concentrations of these species are negligible. In addition, most of the species already taken into account occur also only in very minor concentrations. This becomes obvious from calculations with only the species H, H₂L, HL, L, M(bipy), and M(bipy)L assuming that in a 1:1 mixture of M²⁺ and 2,2'-bipyridyl the formation of the M²⁺-2,2'-bipyridyl 1:1 complex is complete.¹² This allows one to calculate the stability constants $\log K^{M(bipy)}_{M(bipy)L}$ (eq 1) of the ternary complexes in a way usual for binary complexes. As an example, the results obtained under these assumptions for the 2,2'-bipyridyl-M²⁺-glycinate systems are given (the values in parentheses are those of Table III): $\log K^{M(bipy)}_{M(bipy)gly}$ for M = Co²⁺, 4.39 ± 0.01 (4.46); Ni²⁺, 5.53 ± 0.02 (5.62); Cu²⁺, 7.88 (7.92);⁸ Zn²⁺, 4.62 ± 0.07 (4.57). The agreement between these constants and those obtained by the more explicit calculation is surprisingly good for all four metal ions. The same was observed by doing the analogous calculations for the 2,2'-bipyridyl-M²⁺-ethylenediamine and the 2,2'-bipyridyl-M²⁺-pyrocatecholate systems.

It is of interest to note that the order of the overall stability constants, $\beta^M_{M(bipy)L}$, according to eq 6 follows the Irving-Williams series¹³ for all three mixed-ligand systems given in Table III. The same is generally also true for the constants $K^{ML}_{ML(bipy)}$ and $K^{M(bipy)}_{M(bipy)L}$, the latter having one exception in the 2,2'-bipyridyl-M²⁺-pyrocatecholate system, where the constant due to Co²⁺ is slightly greater than that due to Ni²⁺. The same behavior is observed for the corresponding M²⁺-pyrocatecholate 1:2 complexes (cf. Table II) and is also known from other examples.¹⁴ Quite generally the differences in stabilities within the Irving-Williams series are always less pronounced with ligands containing O as donor atoms than with those containing N or S.¹⁴

By using the results of Tables II and III, the values for $\Delta \log K$ (eq 3) and $\log X$ (eq 5) were calculated and are summarized for the three mixed-ligand systems in Table IV. These data cannot be ordered correspond-

TABLE IV

COMPARISON OF THE STABILITY OF THE TERNARY 2,2'-BIPYRIDYL-M²⁺-LIGAND COMPLEXES

M ²⁺	—Ethylenediamine—		—Glycinate—		—Pyrocatecholate—	
	$\Delta \log K$	$\log X$	$\Delta \log K$	$\log X$	$\Delta \log K$	$\log X$
Co ²⁺	-0.27	0.68	-0.17	1.12	+0.76	4.11
Ni ²⁺	-0.18	0.68	-0.21	0.75	+0.36	3.71
Cu ²⁺	-1.29	1.10	-0.35	3.05	+0.43	6.15
Zn ²⁺	-0.49	0.36	-0.39	0.72	-0.01	2.98

ing to the Irving-Williams series¹³ despite the fact that the latter was followed by the overall stability constants (eq 6) of the ternary complexes. However, as expected according to Figure 1, the $\Delta \log K$ values are negative for the 2,2'-bipyridyl-M²⁺-ethylenediamine systems. The corresponding $\log X$ values (eq 4 and 5) are about in the statistical order; that is, they are close to 0.6 with the only exception being the Cu²⁺ complex. In the 2,2'-bipyridyl-M²⁺-glycinate systems also all the $\Delta \log K$ values are negative, but only the $\log X$ values of the Ni²⁺ and Zn²⁺ complexes are about in the statistical

order; the $\log X$ value of the Co²⁺ complex is somewhat larger and that of the Cu²⁺ complex significantly larger. As expected on the basis of the neutralization curves (Figure 1) obtained for the 2,2'-bipyridyl-M²⁺-pyrocatecholate systems with Co²⁺ and Ni²⁺, the $\Delta \log K$ values are positive as are those with Cu²⁺. Indeed, all four mixed-ligand complexes are considerably more stable than expected statistically.

Discussion

The results summarized in Table IV show that the stability of the mixed-ligand 2,2'-bipyridyl-M²⁺-ligand complexes increases within the following series of ligands: ethylenediamine < glycinate < pyrocatecholate. This is partly (cf. later) due to an increasingly better neutralization of charge in the ternary complexes compared with the binary ones, e.g., M(2,2'-bipyridyl)₂²⁺ + M(pyrocatecholate)₂²⁻ ⇌ 2M(2,2'-bipyridyl)(pyrocatecholate). Similarly to Cu(2,2'-bipyridyl)₂²⁺, but less pronounced, the corresponding complexes with Co²⁺, Ni²⁺, and Zn²⁺ show a discriminating behavior; ligands with O atoms as donors are preferably bound.

A second, more surprising point following from the values of $\log X$ in Table IV is that the mixed-ligand complexes containing Ni²⁺ are less stable than those with Co²⁺ or Cu²⁺. It seems that this is a general feature as long as an aromatic amine is involved. This view is supported by the values calculated for $\log X$ from results given by Perrin, Sayce, and Sharma (Table V).¹⁵

TABLE V

VALUES OF $\log X^a$ (CORRESPONDING TO EQ 4) FOR THE TERNARY SYSTEMS HISTAMINE-M²⁺-ETHYLENEDIAMINE, HISTAMINE-M²⁺-SERINATE, AND ETHYLENEDIAMINE-M²⁺-SERINATE

M ²⁺	ha-M-en	ha-M-ser	en-M-ser
Co ²⁺	0.62	1.23	0.95
Ni ²⁺	0.53	0.95	1.18
Cu ²⁺	1.54	2.95	0.79
Zn ²⁺	0.64	1.22	1.13

^a These $\log X$ values were calculated according to eq 5 using the results published by Perrin, Sayce, and Sharma.¹⁵

Again in the systems histamine-M²⁺-ethylenediamine and histamine-M²⁺-serinate, the mixed-ligand complexes with Ni²⁺ are less stable than those with Co²⁺ or Cu²⁺. In the case of ethylenediamine-M²⁺-serinate, this is no longer true. The reason for this result is probably that in the latter system only a ligand with aliphatic amino groups is present. In other words, for the observation of an increased stability in a mixed-ligand-Co^{II} complex (compared with the stability of the corresponding Ni²⁺ complex) it seems to be a condition that an aromatic N donor like a pyridyl or an imidazole group is involved.

The generality of the relatively great stability of mixed-ligand-Co²⁺ complexes, compared with those containing Ni²⁺, can be further supported by some results obtained for the 2,2'-bipyridyl-M²⁺-2-acetyl-3-hydroxythiophene⁹ and the 2,2'-bipyridyl-M²⁺-adenosine 5'-triphosphate complexes.¹⁶ The values of $\Delta \log K$ given in Table VI are greater for the Co²⁺ complexes than they are for the corresponding Ni²⁺ complexes.

(12) G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963).

(13) H. Irving and R. J. P. Williams, *Nature (London)*, **162**, 746 (1948); *J. Chem. Soc.*, 3192 (1953).

(14) H. Sigel and D. B. McCormick, *Accounts Chem. Res.*, **3**, 201 (1970).

(15) D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc. A*, 1755 (1967); 446 (1968); 2060 (1969).

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

TABLE VI
 $\Delta \text{LOG } K$ VALUES^a (EQ 3) FOR THE TERNARY SYSTEMS
 2,2'-BIPYRIDYL-M²⁺-2-ACETYL-3-HYDROXYTHIOPHEN
 AND 2,2'-BIPYRIDYL-M²⁺-ADENOSINE 5'-TRIPHOSPHATE

M ²⁺	bipy-M-AHT	bipy-M-ATP
Co ²⁺	+0.07	-0.07
Ni ²⁺	-0.05	-0.40
Cu ²⁺	+0.46	+0.53
Zn ²⁺	0.00	+0.05

^a These results were obtained under the assumption of complete formation of the 1:1 complex in a 1:1 mixture of M²⁺ and 2,2'-bipyridyl (see text) and are taken from earlier work: AHT,⁵ ATP.¹⁶

To see how important the "neutralization of charge in the ternary complexes" is as a driving force leading to the formation of mixed-ligand complexes, some additional examples of such systems are given in Table VII.

TABLE VII
 VALUES OF LOG X (CORRESPONDING TO EQ 4) FOR SEVERAL
 MIXED-LIGAND SYSTEMS CONTAINING NO DONOR
 GROUP WITH "AROMATICALLY" BOUND NITROGEN^a

System	Log X
Ethylenediamine-Cu ²⁺ -oxalate	1.0, ^b 1.1, ^c 1.3, ^d 1.4 ^e
Ethylenediamine-Zn ²⁺ -oxalate	1.09 ^f
Ethylenediamine-Cd ²⁺ -oxalate	0.71, ^f 1.1 ^d
Glycinate-Cu ²⁺ -5-sulfosalicylate	1.02 ^g
Glycinate-Ni ²⁺ - α -alaninate	1.29 ^h
Ethylenediamine-Cu ²⁺ -1,3-propylenediamine	0.96 ⁱ

^a The log X values (if not already given in the papers) were calculated according to eq 5 using the results of the cited literature. ^b Reference 10. ^c Reference 11. ^d W. B. Schaap and D. L. McMasters, *J. Amer. Chem. Soc.*, **83**, 4699 (1961). ^e J. I. Watters, *ibid.*, **81**, 1560 (1959). ^f Y. Kanemura and J. I. Watters, *J. Inorg. Nucl. Chem.*, **29**, 1701 (1967). ^g R.-P. Martin and R. A. Pâris, *Bull. Soc. Chim. Fr.*, 80 (1964). ^h R.-P. Martin and R. A. Pâris, *ibid.*, 3170 (1964). ⁱ R. Näsänen and M. Koskinen, *Suom. Kemistilehti B*, **40**, 23 (1967).

None of these mixed-ligand systems contains a donor group with an "aromatic" nitrogen and no steric hindrance occurs; *i.e.*, none of the ligands has a real bulky group that might strongly favor the formation of a ternary complex. Therefore, from systems 1 through 3 (and 4), we learn that the neutralization of charge according to $\text{MA}_2^{2+} + \text{MB}_2^{2-} \rightarrow 2\text{MAB}$ leads to an increase of log X by only about 0.6 log unit, compared with the statistical value,^{10,11} log X = 0.6. The very little steric hindrance as may occur in systems 5 (due to the methyl group of α -alaninate) and 6 (due to the change in ring size of the chelate, *cf.* also ref 1) favors the mixed-ligand complexes also very insignificantly (by about 0.4 log unit).

Taking into account the conclusions from the last paragraph and considering now the 2,2'-bipyridyl-M²⁺-pyrocatecholate systems (Table IV) in which the neutralization of charge is in the order as discussed above and steric hindrance is surely of minor importance, if at all, we have left unexplained an additional increase of the stability of the ternary complexes (based on log X = 0.6 (statistics) + 0.6 (charge) + 0.4 (steric hindrance) = 1.6) of about 1.4–4.6 log units. This difference has to be due to the π systems of 2,2'-bipyridyl and pyrocatecholate, as this is the only significant difference between these two ligands and those occurring in Table

VII. In fact, 2,2'-bipyridyl is known to be a good π acceptor and Cu²⁺ a good π donor; here the formation of π bonds is obvious.^{2,3} In addition, comparative studies³ gave evidence that the π system of a ligand containing O as donor atoms is also of importance but less so than the π system of the ligand with N atoms.² Using this concept which proved to be valid for the explanation of the stability of mixed-ligand-Cu²⁺ complexes, one can understand why the 2,2'-bipyridyl-Zn²⁺-pyrocatecholate complex is less stable by a factor of about 10³ than the corresponding Cu²⁺ complex. Due to its d¹⁰ electron configuration, Zn²⁺ is a much poorer π -electron donor, but still it is one.¹⁷

Why Co²⁺ is somewhat more effective in the formation of mixed-ligand complexes than Ni²⁺, at least as long as π bonding is important, is hard to say. In this connection, it is of interest to note the observations of Burger and Pintér,¹⁸ who showed that halide or pseudo-halide ions are bound more strongly by the Co^{II}(dimethylglyoxime)₂ complex than by the Co_{aq}²⁺ ion. This was attributed to a greater coordination tendency of the 3d₂ orbital in the low-spin Co^{II}(dimethylglyoxime)₂ complex toward the electron pair of the monofunctional ligand than of the orbitals in a high-spin aquo complex. It may well be that a final explanation for the present results will be found along these lines.

In conclusion, the results presented show that in all the systems mixed-ligand complexes are formed and that those containing Cu²⁺ are significantly more stable than those with Co²⁺, Ni²⁺, or Zn²⁺. In addition, there is good evidence that the ternary Co²⁺ complexes are more stable than the corresponding Ni²⁺ ones, at least as long as ligand groups containing "aromatic" N donors (like the pyridyl or imidazole groups) are involved.

In general, further studies of the formation and stability of mixed-ligand complexes will be followed by an increasing understanding of the driving forces leading to such complexes. As a result, we may hope that our understanding of catalytic processes,^{19,20} including the special cases of enzyme-metal ion-substrate complexes,¹⁴ also increases.

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