Inorganic Chemistry, Vol. 18, No. 2, 1979 **425**

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Ternary Complexes in Solution. 31.[1] Effect of the Varying π-Accepting Properties of Several Bipyridyl-like Ligands on the Stability of Mixed-Ligand Complexes Also Containing Pyrocatecholate and Cobalt(II), Nickel(II), Copper(II), or Zinc(II)

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Received June 9, 1978

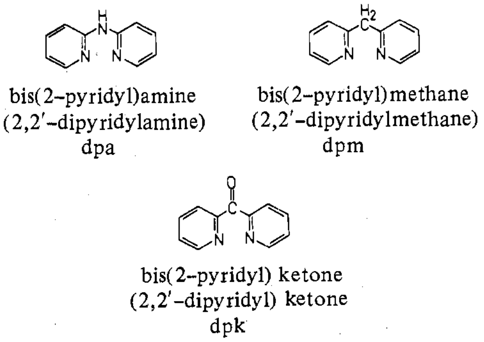
The stability constants of the ternary Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes containing pyrocatecholate (pyr) and, as a second ligand, a heteroaromatic N base, namely, bis(2-pyridyl)amine (2,2′-dipyridylamine, dpa), bis(2-pyridyl)methane (2,2′-dipyridylmethane, dpm), or bis(2-pyridyl) ketone (2,2′-dipyridyl ketone, dpk), were determined in aqueous solution by potentiometric titration ($I = 0.1$ M, $NaClO_4$; 25 °C). For the equilibrium $M(pyr)_2 + M(dpx)_2 \rightleftharpoons 2M(dpx)(pyr)$, where dpx = dpa, dpm, or dpk, the following constants, log X, were determined: Co(dpa)(pyr) 3.79 (0.69), Co(dpm)(pyr) 4.79 (1.13); Ni(dpa)(pyr) 3.95 (0.37), Ni(dpm)(pyr) 4.47 (0.43); Cu(dpa)(pyr) 6.17 (0.37), Cu(dpm)(pyr) 5.8 (0.66), Cu(dpk·H_2O)(pyr) 6.6 (0.82) [dpk·H_2O = geminal diol of dpk]; Zn(dpa)(pyr) 3.92 (0.57), Zn(dpm)(pyr) 4.31 (0.83). The constants given in parentheses are due to $\Delta \log K_M = \log K^{M(dpx)}_{M(dpx)(pyr)} - \log K^{M}_{M(pyr)}$ and refer to the equilibrium $M(dpx)^{2+} + M(pyr) \rightleftharpoons M(dpx)(pyr) + M^{2+}$. All of these mixed-ligand complexes are considerably more stable than one would expect from purely statistical reasons. In addition, all metal ions form the more stable ternary complex, as is especially evident from the $\Delta \log K_M$ values, with this heteroaromatic N base which is the better π acceptor; i.e., the tendency for the formation of the M(dpx)(pyr) complexes decreases within the series dpk > dpm > dpa. This demonstrates that for the enhanced stability of ternary complexes (with Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}) containing an O donor and a heteroaromatic N base the π-acceptor properties of the latter are crucial, but it should be noted that the stability enhancement with Ni^{2+} is less pronounced than with its neighboring elements.

Among the ternary complexes containing 3d ions, those with Cu^{2+} are by far the best studied;[2,3] it is evident that certain ligand combinations lead to a discriminating behavior and to an increased stability.[4] The latter is especially pronounced if the mixed-ligand complex is formed by a heteroaromatic N base like 2,2′-bipyridyl and an O donor like malonate or pyrocatecholate.[5] This enhanced stability is lost if the heteroaromatic N base is replaced by an aliphatic amine like ethylenediamine[6] or an amine with an aromatic moiety like 1,2-diaminobenzene.[7] It was concluded that the stability of the ternary complex depends crucially on the π-accepting qualities of the heteroaromatic N base.[6,8,9]

Mixed-ligand systems containing Mn^{2+}, Co^{2+}, Ni^{2+}, or Zn^{2+} have been studied to a much lesser extent,[2,4,9-12] and while for Mn^{2+} complexes similar evidence has been given[13] as described in the preceding paragraph for Cu^{2+} systems, there is no systematic study available which deals with the influence of the π-accepting qualities of the heteroaromatic N base on the stability of ternary complexes formed with Co^{2+}, Ni^{2+}, or Zn^{2+}. To overcome this gap we investigated complexes of these metal ions with a series of ligands which are closely related in their ligating groups but which differ in their π-acceptor ability.

An amino group attached to an aromatic ring as in aminobenzene has a +M effect; i.e., it enhances the electron density on the ring due to the interaction of the nitrogen lone pair with the π system of the aromatic moiety. Contrary, a carbonyl function as in benzaldehyde has a −M effect; i.e., it reduces the electron density on the ring through its electron-withdrawing effect.[14] As a pyridyl moiety with a low electron density can act as a better acceptor of π back-bonding electrons from a d-metal ion than a moiety with a higher electron density, one may expect that the π-acceptor ability increases within the ligand series bis(2-pyridyl)amine (2,2′-dipyridylamine, dpa) < bis(2-pyridyl)methane (2,2′-dipyridylmethane, dpm) < bis(2-pyridyl) ketone (2,2′-dipyridyl ketone, dpk) (see Chart I). In fact, bis(2-pyridyl)amine behaves in CD[15] and in structural[16] studies of mixed-ligand Cu^{2+} complexes in a way similar to that of 2,2′-bipyridyl or 1,10-phenanthroline, and bis(2-pyridyl) ketone is generally expected to exhibit, due to the keto group, enhanced π back-bonding qualities compared with those of 2,2′-bipyridyl.[17] As the second ligand for the formation of the ternary complexes, pyrocatecholate (pyr) was chosen.

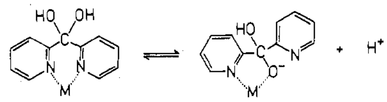
Chart I


bis(2-pyridyl)amine
(2,2′-dipyridylamine)
dpa

bis(2-pyridyl)methane
(2,2′-dipyridylmethane)
dpm

bis(2-pyridyl) ketone
(2,2′-dipyridyl) ketone
dpk

Scheme I



When we started this work from the three heteroaromatic N bases (Chart I), the binary metal ion systems in aqueous solutions of bis(2-pyridyl)amine[18] and bis(2-pyridyl)methane[19] had already been studied and had shown essentially a behavior similar to that of 2,2′-bipyridyl. With bis(2-pyridyl) ketone the matter turned out to be more complicated:[20] in neutral aqueous solution the ligand exists as the ketone,[17b,20] while in alkaline solution a deprotonated geminal diol is formed ($pK_a = 13.61$; $I = 0.1$ M, 25 °C).[20] Furthermore, there is convincing evidence that in aqueous solution bis(2-pyridyl) ketone is N,N coordinated to metal ions but that the ligand exists in these complexes as the geminal diol.[20] Of course, with an sp^3 carbon, the configuration of this ligand corresponds more to the one of bis(2-pyridyl)methane and bis(2-pyridyl)amine, but the π-accepting properties of the geminal diol are expected to be somewhat smaller than those of the ketone, as the geminal diol has only a −I effect, while the −M effect of the carbonyl group is lost.[14]

The matter is further complicated by the fact that the metal ion coordinated geminal diol form of bis(2-pyridyl) ketone rearranges under deprotonation of the diol moiety to an N,O coordinated complex (Scheme I; for details see ref 20).

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Unfortunately, the loss of this proton occurs in the same or even in a lower pH range as the ionization of pyrocatechol in the ternary systems with Co^{2+}, Ni^{2+}, and Zn^{2+}. Only in the mixed-ligand Cu^{2+} system does the ionization of pyrocatechol occur in a pH range low enough to allow the determination of the stability of the neutral $Cu(dpk{\cdot}H_2O)(pyr)$ complex, in which the geminal diol form of bis(2-pyridyl) ketone is N,N coordinated.[21,22] With the two other heteroaromatic N bases (see Chart I) the stability of all of the ternary M(dpx)(pyr) complexes[21] with $M^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+}, or Zn^{2+} could be determined, and it became thus evident that the π-accepting property of the heteroaromatic N base is crucial indeed for the stability of the ternary complexes with all of these metal ions. On the basis of these results and on the earlier observations with Mn^{2+} (ref 13) and Cu^{2+} (ref 3) it may thus be anticipated as a general rule that ternary complexes with the divalent metal ions of the second half of the 3d series are especially stable if they are formed with a heteroaromatic N base and an O donor.

Experimental Section

Materials. The metal ion perchlorates, pyrocatechol (puriss) and bis(2-pyridyl)amine were from Fluka AG, Buchs, Switzerland. Materials used for synthesis were 1-bromobutane, pyridine-2-carbaldehyde, and thionyl chloride from Merck AG, Darmstadt, Germany, and 2-bromopyridine from Merck-Schuchardt, Hohenbrunn near München, Germany. The bis(2-pyridyl) ketone was the same as used earlier.[20]

Synthesis. The bis(2-pyridyl)methane was prepared by the method of Beyerman and Bontekoe[23] and always freshly distilled over sodium before use. Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.32; H, 5.98; N, 16.41.

The bis(2-pyridyl)amine obtained from Fluka AG was converted to the hydrochloride by dissolving the free base in 1 equiv of HCl. The crude product, obtained by evaporation of this solution, was recrystallized twice from ethanol/ether and the hygroscopic needles were isolated (mp 173–175 °C). Anal. Calcd for $C_{10}H_{10}N_3Cl$: C, 57.84; H, 4.85; N, 20.23; Cl, 17.07. Found: C, 57.29; H, 4.85; N, 19.80; Cl, 16.91.

Measurements and Determination of Equilibrium Constants. The acidity constants of the ligands and the stability constants of the binary systems were taken from studies of Anderegg and Bühler[18,19] or from our own earlier work.[5,11,20] The stability constants of the ternary complexes were measured by automatic potentiometric pH titrations (25 °C; $I = 0.1$ M, $NaClO_4$),[5] i.e., by titration of 50 mL of aqueous solutions of the reactants ($[M^{2+}]:[dpx]:[pyr] = 1:1:1$ to 1:1:6) under N_2 with 1 mL of 0.1 N NaOH. The concentrations used in the Co^{2+}, Ni^{2+}, Zn^{2+}/dpa, dpm/pyr systems were $[M^{2+}] = [dpx] = 3 \times 10^{-4}$–$4.5 \times 10^{-4}$ M and $[pyr] = 3 \times 10^{-4}$–2.7×10^{-3} M; in the corresponding Cu^{2+} systems the concentrations used were $[Cu^{2+}] = [dpa] = [pyr] = 5 \times 10^{-4}$ M and $[Cu^{2+}] = [dpm]$ or $[dpk] = [pyr] = 8 \times 10^{-4}$ M.

The stability constant $\beta^{M}_{M(dpx)(pyr)}$ was calculated as described[5] by taking into account the species H^+, $H_2(dpx)^{2+}$, $H(dpx)^+$, dpx, $H_2(pyr)$, $H(pyr)^-$, pyr^{2-}, M^{2+}, $M(dpx)^{2+}$, $M(dpx)_2{}^{2+}$, M(pyr), $M(pyr)_2{}^{2-}$, and M(dpx)(pyr). This means the complexes $M(dpx)_2(pyr)$ and $M(dpx)(pyr)_2{}^{2-}$ were neglected; that this is justified under our experimental conditions[5,11] was recently also confirmed by Daniele et al.[24] In addition, as we calculated a $\beta^{M}_{M(dpx)(pyr)}$ value every 0.1 pH unit, a drift in the values, and hence the appearance of an additional species which was not considered, became immediately obvious and the collection of data was then stopped. Furthermore, the data were evaluated only in this pH range where hydrolysis of the metal ion was negligible; this was checked by titrating the M^{2+}/dpx systems also in the absence of pyr. With dpk only the ternary system with Cu^{2+} could be studied for the reasons outlined already in the Introduction.[22]

The stability constants were calculated from at least six independent titration curves. The errors given are three times the standard error of the mean value or the sum of the probable systematic errors, whichever is the larger.

Results

The stability constants of a ternary system are defined by eq 1–3. The overall stability constant $\beta^{M}_{M(dpx)(pyr)}$, which was experimentally determined, is connected with $K^{M(dpx)}_{M(dpx)(pyr)}$ and $K^{M(pyr)}_{M(pyr)(dpx)}$ by eq 4 and 5, respectively.

$$M^{2+} + dpx + pyr^{2-} \rightleftharpoons M(dpx)(pyr)$$

$$\beta^{M}_{M(dpx)(pyr)} = [M(dpx)(pyr)]/([M][dpx][pyr]) \tag{1}$$

$$M(dpx)^{2+} + pyr^{2-} \rightleftharpoons M(dpx)(pyr)$$

$$K^{M(dpx)}_{M(dpx)(pyr)} = [M(dpx)(pyr)]/([M(dpx)][pyr]) \tag{2}$$

$$M(pyr) + dpx \rightleftharpoons M(dpx)(pyr)$$

$$K^{M(pyr)}_{M(pyr)(dpx)} = [M(dpx)(pyr)]/([M(pyr)][dpx]) \tag{3}$$

$$\log K^{M(dpx)}_{M(dpx)(pyr)} = \log \beta^{M}_{M(dpx)(pyr)} - \log K^{M}_{M(dpx)} \tag{4}$$

$$\log K^{M(pyr)}_{M(pyr)(dpx)} = \log \beta^{M}_{M(dpx)(pyr)} - \log K^{M}_{M(pyr)} \tag{5}$$

One way to quantify the stability of ternary complexes is according to eq 6,[2-6] i.e., by comparing the difference in

$$\begin{aligned} \Delta \log K_M &= \log K^{M(dpx)}_{M(dpx)(pyr)} - \log K^{M}_{M(pyr)} \\ &= \log K^{M(pyr)}_{M(pyr)(dpx)} - \log K^{M}_{M(dpx)} \end{aligned} \tag{6}$$

stability, e.g., for the reaction between $M(dpx)^{2+}$ or $M(aq)^{2+}$ and pyr^{2-}. The value of $\Delta \log K_M$ is the logarithm of the equilibrium constant due to eq 7. In general, *negative* values

$$M(dpx)^{2+} + M(pyr) \rightleftharpoons M(dpx)(pyr) + M^{2+} \tag{7}$$

for $\Delta \log K_M$ (eq 6) are expected, since usually $K^{M}_{ML} > K^{ML}_{ML_2}$. This is in accordance with the statistical values obtained for the coordination of two different bidentate ligands to a regular and to a distorted octahedral coordination sphere, i.e., $\Delta \log K_{oh} = -0.4$ and $\Delta \log K_{do} \simeq -0.9$, respectively.[3]

The other approach commonly used to quantify the stability of a ternary complex is based on the equilibrium constant, X, as defined by eq 8;[3,15,25] log X may be calculated according to eq 9. The statistical value for log X is for all geometries

$$M(dpx)_2{}^{2+} + M(pyr)_2{}^{2-} \rightleftharpoons 2M(dpx)(pyr)$$

$$X = [M(dpx)(pyr)]^2/([M(dpx)_2][M(pyr)_2]) \tag{8}$$

$$\begin{aligned} \log X &= 2 \log \beta^{M}_{M(dpx)(pyr)} - (\log \beta^{M}_{M(dpx)_2} + \log \beta^{M}_{M(pyr)_2}) \\ &= (\log K^{M(pyr)}_{M(pyr)(dpx)} - \log K^{M(dpx)}_{M(dpx)_2}) + \\ &\qquad (\log K^{M(dpx)}_{M(dpx)(pyr)} - \log K^{M(pyr)}_{M(pyr)_2}) \end{aligned} \tag{9}$$

of the coordination sphere of a metal ion the same and is 0.6.[25,26]

In Figure 1 a representative set of experimental data obtained from the potentiometric titrations is shown. The pH of the reaction solution is plotted against the neutralization degree for the binary Co^{2+}- and Cu^{2+}/pyr systems, as well as for the corresponding ternary systems containing in addition bis(2-pyridyl)amine, bis(2-pyridyl)methane, or bis(2-pyridyl) ketone. As the formation of complexes shifts the buffer region of the ligand to lower pH values, it is immediately obvious from Figure 1 that all the Cu^{2+} complexes are more stable than the Co^{2+} complexes. But more important, as the binary M^{2+}/dpx complexes are nearly completely formed, it is evident (despite the somewhat different concentrations) that the deprotonation of pyrocatechol in the ternary Co^{2+} and Cu^{2+} systems occurs at a lower pH compared with that in the corresponding binary systems. This means the ternary Co(dpx)(pyr) and Cu(dpx)(pyr) complexes are more stable than the corresponding binary Co(pyr) and Cu(pyr) complexes, and hence we shall obtain *positive* $\Delta \log K_M$ values (see eq 6) in all these cases.

Furthermore, from Figure 1 it is evident that for both metal ion systems the stability of the ternary complexes depends on the participating heteroaromatic N base; i.e., the tendency for the formation of the ternary M(dpx)(pyr) complexes increases

Table I. Negative Logarithms of the Acidity Constants of the Ligands

ligand (L)	$pK^{H}_{H_2L}$	pK^{H}_{HL}
dpa[18]		7.14
dpm[19]	2.69	5.18
dpk[20]		3.06
pyr[5]	9.32	13.00

Table II. Logarithms of the Stability Constants of the Binary M^{2+} Complexes

ligand (L)	M^{2+}	$\log K^{M}_{ML}$	$\log K^{ML}_{ML_2}$	$\log \beta^{M}_{ML_2}$
dpa[18]	Co^{2+}	4.72	4.20	8.92
	Ni^{2+}	6.25	5.78	12.03
	Cu^{2+}	8.05	5.51	13.56
	Zn^{2+}	3.75	3.20	6.95
dpm[19]	Co^{2+}	3.46	2.82	6.28
	Ni^{2+}	5.02	4.15	9.17
	Cu^{2+}	6.7	5.1	11.8
	Zn^{2+}	2.81	2.39	5.20
$dpk\cdot H_2O$[20,a]	Cu^{2+}	5.13	3.1	8.2
pyr[5,11]	Co^{2+}	8.61	6.72	15.33
	Ni^{2+}	8.89	6.15	15.04
	Cu^{2+}	13.96	11.07	25.03
	Zn^{2+}	9.90	7.67	17.57

[a] See text and left-hand side of Scheme I.

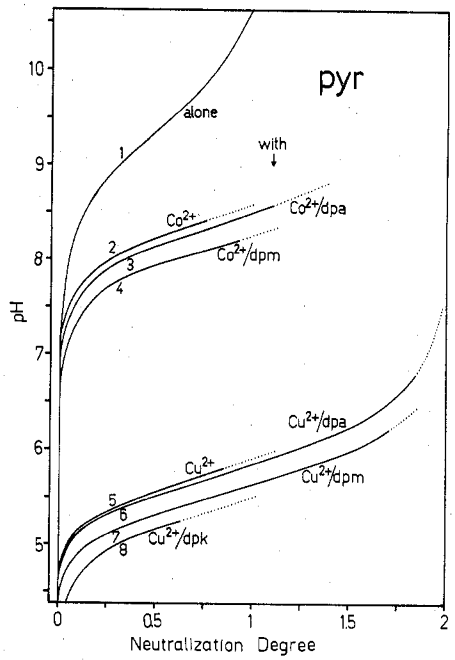

Figure 1. Dependence of neutralization degree upon pH during potentiometric titration of pyrocatechol without (1) and with metal ions (2, 5) or metal ions and dpx (3, 4, 6–8) in aqueous solution ($I = 0.1$ M, $NaClO_4$; 25 °C). The dotted-line portions extended toward higher degrees of neutralization indicate uncertainty due to hydrolysis or the pH range where the calculated constants begin to "drift" (see Experimental Section). Concentrations of the reaction solutions are (1) [pyr] = 8×10^{-4} M, (2) $[Co^{2+}]$ = [pyr] = 8×10^{-4} M, (3) and (4) [dpa] or [dpm] = $[Co^{2+}]$ = [pyr] = 4.5×10^{-4} M, (5) $[Cu^{2+}]$ = [pyr] = 8×10^{-4} M, (6) [dpa] = $[Cu^{2+}]$ = [pyr] = 5×10^{-4} M, and (7) and (8) [dpm] or [dpk] = $[Cu^{2+}]$ = [pyr] = 8×10^{-4} M. The volume of the reaction solutions was 50 mL; the titration was carried out with 0.1 M NaOH.

in the series dpa < dpm < dpk. It seems important to note that, as we have seen, all of these crucial and decisive—though only qualitative—results can be drawn directly from the potentiometric titrations without any calculation.

The acidity constants of the ligands[5,18-20] and the stability constants of the binary Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes[5,11,18-20] which were used in the evaluation of the ternary systems are given in Tables I and II, respectively. The stability constant computed for the ternary complexes from the experimental data (cf. Figure 1) was $\log \beta^{M}_{M(dpx)(pyr)}$ which is due to the overall equilibrium (1). This constant and related stability constants of the ternary complexes are listed in Table III, together with the values calculated for $\Delta \log K_M$ (eq 6 and 7) and $\log X$ (eq 8 and 9) and two related systems.[6a,27] It should be added here that in the ternary Cu^{2+}/dpk/pyr system, bis(2-pyridyl) ketone coordinates, as already outlined for the binary complexes in the introduction, in its geminal diol form (Scheme I) over the two pyridyl nitrogens;[28] i.e., the ternary complex should be formulated as $Cu(dpk\cdot H_2O)(pyr)$.[22]

Discussion

From the values listed in Table III for $\log X$ and especially from those due to $\Delta \log K_M$ it is evident that for all of the metal ions studied the ternary complexes formed with pyrocatecholate and bis(2-pyridyl)methane are more stable than those formed with bis(2-pyridyl)amine.[31] For Cu^{2+}, the values obtained with bis(2-pyridyl) ketone also exceed those with dpm, thus showing that the stability of the ternary complex with $dpk\cdot H_2O$ is larger than with dpm or dpa. As the coordinating sites in all of these ligands are identical and only the bridging groups between the two pyridyl moieties are different, the observed differences in stability of the ternary complexes for a given metal ion can solely be attributed to the different π-accepting properties of these three heteroaromatic N bases (see introduction and Chart I). Hence, these results show unambiguously that what was already found earlier for ternary heteroaromatic N base/O donor complexes containing Cu^{2+} (cf. ref 3) or Mn^{2+} (cf. ref 13) is also true for these with

Table III. Logarithms of the Equilibrium Constants of the Ternary dpx/M^{2+}/pyr Systems and Some Related Data ($I = 0.1$ M, $NaClO_4$; 25 °C)

dpx	M^{2+}	$\log \beta^{M}_{M(dpx)(pyr)}$ (eq 1)	$\log K^{M(dpx)}_{M(dpx)(pyr)}$ (eq 2 and 4)	$\log K^{M(pyr)}_{M(pyr)(dpx)}$ (eq 3 and 5)	$\log X$ (eq 8 and 9)	$\Delta \log K_M$ (eq 6 and 7)
dpa	Co^{2+}	14.02 ± 0.04	9.30	5.41	3.79	0.69
	Ni^{2+}	15.51 ± 0.04	9.26	6.62	3.95	0.37
	Cu^{2+}	22.38 ± 0.03	14.33	8.42	6.17	0.37
	Zn^{2+}	14.22 ± 0.06	10.47	4.32	3.92	0.57
dpm	Co^{2+}	13.20 ± 0.08	9.74	4.59	4.79	1.13
	Ni^{2+}	14.34 ± 0.06	9.32	5.45	4.47	0.43
	Cu^{2+}	21.32 ± 0.04	14.6	7.36	5.8	0.66
	Zn^{2+}	13.54 ± 0.07	10.73	3.64	4.31	0.83
$dpk\cdot H_2O$[a]	Cu^{2+}	19.91 ± 0.04	14.78	5.95	6.6	0.82
prop[27]	Cu^{2+}				4.11	−0.69
en[6a,27]	Cu^{2+}				2.65	−0.76

[a] See text.

Co^{2+}, Ni^{2+}, and Zn^{2+}; this means that a ternary complex becomes more stable with better π-accepting properties of the participating heteroaromatic N base.

That the π-accepting properties of the heteroaromatic N base are decisive for the stability of the ternary complexes is confirmed from a comparison of the data due to the Cu(prop)(pyr) complex with the other data of the ternary Cu^{2+} complexes in Table III. However, the size of the chelate ring is also among the factors[3,27,32] influencing the stability of mixed-ligand complexes as is obvious from the data due to Cu(en)(pyr).

There is one further interesting point: the stability of mixed-ligand Ni^{2+} complexes is less influenced by the π-accepting qualities of a participating heteroaromatic N base, as was also observed before.[11] Thus, Ni(dmp)(pyr) is a ternary complex formed with a good π acceptor and still the values for $\log X$ and $\Delta \log K_M$ are smaller than those of the corresponding complexes with Co^{2+} and Cu^{2+}. It is therefore not surprising that the difference in the $\Delta \log K_M$ values for M(dpa)(pyr) and M(dpm)(pyr) is the smallest for Ni^{2+} among all investigated metal ions (Table III). In other words, the participation of a heteroaromatic N base with good π-acceptor properties does enhance the stability of ternary complexes with Ni^{2+} considerably less than it favors the one of the complexes with its neighboring elements, i.e., Co^{2+} and Cu^{2+}. Maybe the relative instability of the mixed-ligand complexes formed with Ni^{2+} and its restricted availability are reasons[13] that this metal ion does not occur widely in biological systems.

Acknowledgment. The elemental analyses were kindly performed in the microanalytical laboratories (Dr. W. Padowetz) of the CIBA-GEIGY AG, Basel. The computers were made available by the Zentralstelle für Elektronische Datenverarbeitung des Kantons Basel-Stadt (IBM 370/158) and by the Rechenzentrum der Universität Basel (Univac 1108). These supports and a research grant from the Swiss National Science Foundation are gratefully acknowledged.

Registry No. Co(dpa)(pyr), 68332-12-7; Ni(dpa)(pyr), 68332-13-8; Cu(dpa)(pyr), 68332-14-9; Zn(dpa)(pyr), 68332-15-0; Co(dpm)(pyr), 68345-02-8; Ni(dpm)(pyr), 68332-16-1; Cu(dpm)(pyr), 68332-17-2; Zn(dpm)(pyr), 68332-18-3; Cu(dpk·H_2O)(pyr), 68332-19-4.

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(21) Abbreviations: bpy, 2,2′-bipyridyl; dpa, bis(2-pyridyl)amine (2,2′-dipyridylamine); dpk, bis(2-pyridyl) ketone (2,2′-dipyridylketone); dpk·H_2O, geminal diol of dpk; dpm, bis(2-pyridyl)methane (2,2′-dipyridylmethane); dpx = dpa, dpk, or dpm (see Chart I); en, ethylenediamine; L, general ligand; M, general metal ion; phen, 1,10-phenanthroline; prop, 1,3-propylenediamine; pyr, pyrocatecholate.
(22) We did not attempt to determine the stability of the ternary complexes containing the deprotonated geminal diol form of bis(2-pyridyl) ketone,[20] as in these complexes the coordination pattern is different and no longer comparable to the M(dpx)(pyr) complexes and is, hence, not in line with the aim of this work.
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(28) This is evident from a plot of $\log K^{\mathrm{Cu(pyr)}}_{\mathrm{Cu(pyr)(dpx)}}$ vs. $pK^{\mathrm{H}}_{\mathrm{H(dpx)}}$ (analogous to those shown in ref 20), which suggests related coordinating properties for all three dpx ligands. It may be added that several authors[17,29,30] have shown that in solid metal ion complexes dpk is coordinated over its two nitrogen atoms and that a trace of H_2O present during the preparation of the compounds[17a] is enough to transform the ketone into a geminal diol.
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