B(6,8) may behave in an unusual fashion, probably involving hydrogen-exchange and/or spin-coupling processes. It should be noted that the assignments suggested here are quite similar to the results found earlier for $B_{10}H_{12}(\text{ligand})_2$ derivatives.[3]

The X-ray crystal structure of $B_9H_{14}^-$ has been shown to fit a 2613 topological representation and to be different than that of $B_9H_{13}(CH_3CN)$.[14] At room temperature in solution both the ^{11}B and proton nmr spectra suggest that $B_9H_{14}^-$ is undergoing a relatively fast hydrogen atom exchange process. There are three boron atom environments of area 3 each with one nonexchanging hydrogen attached to each of the nine boron atoms and five rapidly exchanging hydrogen atoms. In the case of the anionic derivative $B_9H_{13}(NCS)^-$ a ^{11}B nmr spectrum quite similar to that of the neutral $B_9H_{13}(\text{ligand})$ derivatives was observed. Thus in this case the rapid exchange process described above is not operative.

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Ternary Complexes in Solution. IX. The Stability-Increasing Effect of the Pyridyl and Imidazole Groups on the Formation of Mixed-Ligand–Copper(II)–Pyrocatecholate Complexes[1,2]

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The stability constants of the ternary Cu^{2+} complexes containing pyrocatecholate and, as a second ligand, 2,2′-bipyridyl, 4-(2′-pyridyl)imidazole, 2-picolylamine, 4-aminomethylimidazole, and ethylenediamine were determined by potentiometric titration. For the equilibrium $Cu(\text{pyrocatecholate})_2^{2-} + Cu(\text{amine})_2^{2+} \rightleftharpoons 2Cu(\text{pyrocatecholate})(\text{amine})$ the corresponding constants are $\log X = 6.15, 5.47, 4.64, 3.46$, and 2.65 ($I = 0.1$; temperature 25°). All five mixed-ligand complexes are more stable than one would expect on purely statistical grounds ($\log X = 0.6$). The importance of the π system of the N ligand for the stability of the ternary complexes is obvious from the given series. The imidazole group, often suggested as a binding site for metal ions in enzymes, clearly has qualities similar to those of the pyridyl group; *i.e.*, the stability of ternary Cu^{2+} complexes containing these groups is increased.

With ligands containing O as donor atoms, Cu^{2+}–2,2′-bipyridyl forms ternary complexes that are more stable than the corresponding binary Cu^{2+}–O ligand 1:1 complexes.[2,4–6] In addition, the Cu^{2+}–2,2′-bipy 1:1 complex has discriminating qualities: O rather than N ligands are more stably bound.[2,5] For the Cu^{2+}–histamine 1:1 complex a similar but less pronounced behavior was found.[7]

It was suggested[2,5] that the "aromaticity" of the ligand containing N as donor atoms is important for the stability of the resulting mixed-ligand complexes. To test this hypothesis, the following series of bidentate N ligands was chosen and the stability of their ternary complexes with Cu^{2+} and pyrocatecholate was determined by potentiometric titrations: 2,2′-bipyridyl,[8] 4-(2′-pyridyl)imidazole, 2-picolylamine, 4-aminomethylimidazole, and ethylenediamine.[8]

One way to characterize the stability of ternary complexes is according to eq 1, *i.e.*, by comparing the difference in stability between eq 2 and 3.[9] The connection

$$\Delta \log K = \log K^{Cu(NL)}_{Cu(NL)pyr} - \log K^{Cu}_{Cu(pyr)} \qquad (1)$$

$$Cu(NL) + pyr \rightleftharpoons Cu(NL)pyr$$
$$K^{Cu(NL)}_{Cu(NL)pyr} = [Cu(NL)pyr]/([Cu(NL)][pyr]) \qquad (2)$$

$$Cu + pyr \rightleftharpoons Cu(pyr)$$
$$K^{Cu}_{Cu(pyr)} = [Cu(pyr)]/([Cu][pyr]) \qquad (3)$$

between eq 2 and 4 is given by eq 5. Another way to

$$Cu + NL + pyr \rightleftharpoons Cu(NL)pyr$$
$$\beta^{Cu}_{Cu(NL)pyr} = [Cu(NL)pyr]/([Cu][NL][pyr]) \qquad (4)$$

$$\log K^{Cu(NL)}_{Cu(NL)pyr} = \log \beta^{Cu}_{Cu(NL)pyr} - \log K^{Cu}_{Cu(NL)} \qquad (5)$$

characterize the stability of ternary complexes is by eq 6 and 7.

$$Cu(NL)_2 + Cu(pyr)_2 \rightleftharpoons 2Cu(NL)(pyr)$$
$$X = [Cu(NL)pyr]^2/([Cu(NL)_2][Cu(pyr)_2]) \qquad (6)$$

$$\log X = 2 \log \beta^{Cu}_{Cu(NL)pyr} - (\log \beta^{Cu}_{Cu(NL)_2} + \log \beta^{Cu}_{Cu(pyr)_2}) \qquad (7)$$

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[8] The 2,2′-bipyridyl–Cu^{2+}-pyrocatecholate[2] and the ethylenediamine–Cu^{2+}–pyrocatecholate[7] systems were already investigated in different connections; these results[2,7] are also used now.

[9] Abbreviations: pyrocatecholate, pyr; ligand with N as donor atom, NL; general ligand, L. Charges are omitted in all equations.

TABLE I

NEGATIVE LOGARITHMS OF ACIDITY CONSTANTS OF THE LIGANDS AND LOGARITHMS OF STABILITY CONSTANTS OF THEIR BINARY Cu^{2+} COMPLEXES ($I = 0.1$ ($NaClO_4$), 25°)[9]

Ligand	$pK^{H}_{H_2L}$	pK^{H}_{HL}	Log K^{Cu}_{CuL}	Log $K^{CuL}_{CuL_2}$	Log $\beta^{Cu}_{CuL_2}$
2,2′-Bipyridyl[2]	−0.2[a]	4.49[b]	8.00[b]	5.60[b]	13.60[b]
4-(2′-Pyridyl)imidazole[c]	1.33	5.49	8.76	6.40	15.16
2-Picolylamine	2.05 ± 0.02	8.70 ± 0.01	9.72 ± 0.03	7.75	17.47
4-Aminomethylimidazole	4.73 ± 0.02	9.35 ± 0.01	9.22 ± 0.03	7.95	17.17
Ethylenediamine[7]	7.10	9.89	10.44	9.16	19.60
Pyrocatecholate[2,7]	9.32	13.00[d]	13.96	11.07	25.03

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TABLE II

LOGARITHMS OF STABILITY CONSTANTS OF SOME TERNARY PYROCATECHOLATE–Cu^{2+}–N LIGAND COMPLEXES ($I = 0.1$ ($NaClO_4$), 25°)[9]

N ligand	Log $\beta^{Cu}_{Cu(NL)pyr}$	Log $K^{Cu(NL)}_{Cu(NL)pyr}$[a]	Log $K^{Cu(pyr)}_{Cu(pyr)NL}$[b]	Δ log K	Log X
2,2′-Bipyridyl[2]	22.39	14.39	8.43	+0.43	6.15
4-(2′-Pyridyl)imidazole	22.83 ± 0.03	14.07	8.87	+0.11	5.47
2-Picolylamine	23.57 ± 0.04	13.85	9.61	−0.11	4.64
4-Aminomethylimidazole	22.83 ± 0.04	13.61	8.87	−0.35	3.46
Ethylenediamine[7]	23.64	13.20	9.68	−0.76	2.65

[a] Log $K^{Cu(NL)}_{Cu(NL)pyr}$ was calculated according to eq 5 (*cf.* ref 2) and independently by taking into account only the species Cu(NL), Cu(NL)pyr, H_2pyr, Hpyr, and pyr (*i.e.*, it was assumed that the Cu(NL) 1:1 complex is formed for 100% and this before the reaction with pyr occurs): 14.35,[2] 2,2′-bipyridyl; 13.98 ± 0.04, 4-(2′-pyridyl)imidazole; 13.76 ± 0.03, picolylamine; 13.55 ± 0.08, 4-aminomethylimidazole; 13.23 ± 0.08, ethylenediamine. A comparison of these results with those of the table suggests that this simplification is reasonable; this will be of importance for the corresponding ternary NL–Cu–adenosine 5′-monophosphate complexes: P. R. Huber and H. Sigel, unpublished results. [b] Calculated according to log $K^{Cu(pyr)}_{Cu(pyr)NL}$ = log $\beta^{Cu}_{Cu(NL)pyr}$ − log $K^{Cu}_{Cu(pyr)}$.

The values expected for Δ log K (eq 1) are negative ($K^{M}_{ML} > K^{ML}_{ML_2}$), because more coordination positions are available for bonding of the first ligand to a given metal ion than for the second ligand. The value expected for X on statistical grounds is 4, *i.e.*, log X = 0.6.[10]

Experimental Section

Materials.—4-(2′-Pyridyl)imidazole was synthesized according to Clemo, Holmes, and Leitch.[11] 4-Aminomethylimidazole dihydrochloride was made starting from fructose to 4-hydroxymethylimidazole,[12] oxidizing with HNO_3 to the aldehyde,[13] preparing the oxime,[14] and reducing with H_2 (atmospheric pressure, 5% Pd on C) in methanol saturated with HCl.[15] α-Picolylamine was from Dr. F. Raschig GmbH, Ludwigshafen, Germany. For all other materials see ref 2.

Measurements.—These were done as previously described.[2]

Determination of Equilibrium Constants.—All constants were measured by potentiometric titrations (25°, $I = 0.1$ ($NaClO_4$)). The acidity constants of the ligands and the stability constants of the binary complexes were calculated as described recently.[2] The stability constant, $\beta^{Cu}_{Cu(NL)pyr}$ (eq 4), of the ternary systems was computed[2] (IBM 1620) from the data obtained by titrating solutions containing a 1:1:1 Cu:NL:pyr ratio and by taking into account the species H_2(NL), H(NL), NL, Cu(NL), $Cu(NL)_2$, H_2pyr, Hpyr, pyr, Cu(pyr), $Cu(pyr)_2$, Cu, and Cu(NL)pyr.[9] By titrating solutions containing Cu^{2+} alone or a 1:1 Cu:NL ratio it was shown that hydrolysis could be ignored in the pH region used for the evaluation of the data.

The uncertainties given in Tables I and II are 3 times the standard deviation (which results in a more than 99% security that the "right" value is within the given limits): $\sqrt{\Sigma\Delta^2/N(N-1)}$. Δ is the difference between a measured and the average value, and N the total number of values. The given data are the results of at least three independent titrations (done on different days), and each titration curve was evaluated at at least eight different pH values, *i.e.*, $N \geqslant 24$.

Results and Discussion

The acidity constants of the ligands and the stability constants of their binary Cu^{2+} complexes are given in Table I. Table II contains the constants of the mixed-ligand–Cu^{2+} complexes formed by pyrocatecholate and a second ligand with N as the donor atom.

In all cases reported here Δ log K is less negative than one might expect from the value of log $K^{CuL}_{CuL_2}$ − log K^{Cu}_{CuL} (*cf.* Table I), and in two cases even positive values of Δ log K are obtained (Table II). In addition, the values for X are greater than expected statistically by factors of 10^2 through 3×10^5. That the greatest part of the increased stability is not due to a simple neutralization of charge in the ternary complex compared with the two binary ones (both have a charge of 2) is evident from the ethylenediamine–Cu^{2+}–oxalate system[16] with log X = 1.3.[2] The stability of the ternary N ligand–Cu^{2+}–pyrocatecholate complexes (Table II) increases by changing the N ligand in the series ethylenediamine < 4-aminomethylimidazole < 2-picolylamine < 4-(2′-pyridyl)imidazole < 2,2′-bipyridyl. Therefore, the "aromaticity" of the N ligand is decisive; ethylenediamine forms only σ bonds with Cu^{2+}, whereas 2,2′-bipyridyl is additionally able to form π bonds (back-donation); *i.e.*, the given series is an order of increasing π-acceptor qualities.[17] A change in the systems from the pyridyl to an imidazole group shows that the latter is not quite as effective a π acceptor. This is what one would expect.

Besides the obvious importance of the π system of the N ligand for the stability of the ternary Cu^{2+} complexes, the π system of the O ligand also has some effect. The log X value of the ethylenediamine–Cu^{2+}–pyro-

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(17) For a further discussion, see ref 2. In addition, it is of interest to note that the stability of the ternary complexes investigated here increases with decreasing basicity of the N ligand; in fact, if the sum of $pK^{H}_{H_2L}$ and pK^{H}_{HL} is plotted against Δ log K or log X, straight lines with negative slopes result. This problem is under further investigation and shall be discussed later together with additional examples.

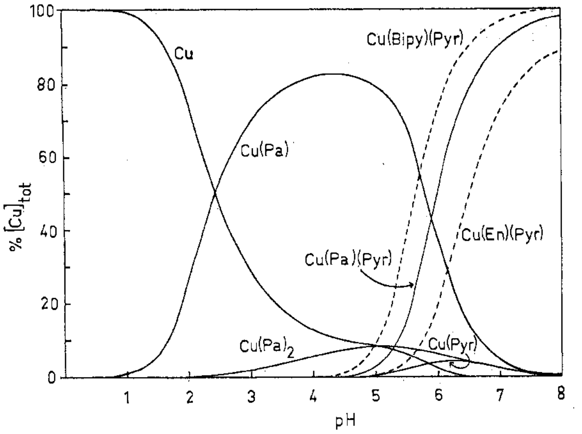

Figure 1.—Variation with pH of the concentrations (given as the percentage of the total Cu^{2+} present) of the several species present in an aqueous solution of Cu^{2+}, 2-picolylamine (pa), and pyrocatecholate (pyr) (each 10^{-3} *M*); $Cu(pyr)_2$ is less than 0.4% at pH <8. For comparison the concentration of the ternary complex in the systems containing 2,2′-bipyridyl (bipy) or ethylenediamine (en) instead of 2-picolylamine is also given (dashed lines). All data were computed with the constants given in Tables I and II.

catecholate complex (*cf.* Table II) is about 1.3 log units[2] greater than that of the ethylenediamine–Cu^{2+}–oxalate system.[16] This suggests that in complexes like 2,2′-bipyridyl–Cu^{2+}–pyrocatecholate a cooperative effect may occur between the π systems of the two ligands bound to the same Cu^{2+}.[18]

As an example, the concentrations of the several species present in the ternary system 2-picolylamine–Cu^{2+}–pyrocatecholate are given in Figure 1. At higher pH values the concentration of the mixed complex dominates strongly and all concentrations tend to approach limiting values. Of special interest is a comparison between the mentioned system and the formation of the ternary complexes containing 2,2′-bipyridyl or ethylenediamine (dashed lines) instead of 2-picolylamine. This evidently demonstrates the larger stability of the ternary 2,2′-bipyridyl–Cu^{2+}–pyrocatecholate complex, as this one is formed in the lowest pH range and reaches the highest concentration.

One of the main conclusions from this investigation is that not only the pyridyl but also the imidazole group has a stability-increasing effect on the formation of ternary Cu^{2+} complexes with ligands containing O as donor atoms. In this connection it is of interest to note the observation of Girotti and Breslow[19] that copper(II) acetate is bound more firmly to ribonuclease than Cu^{2+} and at least some of the binding sites offered by ribonuclease are imidazole groups. Considering this example, it can be hoped that by further systematic studies of mixed-ligand complexes at least in part an answer may be found to the question:[20] What are the control mechanisms that determine the coordination and coordination tendency of metal ions in biological systems?

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The Influence of π-Bonding Ligands upon the Properties of an Associated Ethylenediamine Ligand[1]

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The influence of certain π-bonding ligands upon (a) the acidity of an associated σ-bonding ethylenediamine ligand and (b) ligand lability in complexes of platinum(II) is evaluated *via* deprotonation reactions and nmr and tga data.

It has been known for some time that stability in coordinated ethylenediamine increases with increase in the charge on the transitional metal ion about which the ligand is coordinated.[2,3] More recently it has been shown that, while $[Pt(en)_2]I_2$ and its Pd analog are not deprotonated by the relatively weakly basic ammonia molecule, introduction of one bipy ligand enhances the acidity of the remaining en ligand.[4,5] Accordingly, it was of interest to investigate the effect of other π-bonding or potentially π-bonding ligands upon proton lability in an associated en ligand.

Experimental Section

Unless otherwise indicated, all experimental methods, including analytical procedures, were the same as those described in recent publications from this laboratory.[3,4,6] All of the platinum(II) complexes employed in this work were prepared and characterized as described elsewhere.[7]

Although most of the reactions reported here were carried out in liquid ammonia at or below −33.5°, it was necessary in some cases to expose the complexes to liquid ammonia at higher temperatures. For this purpose a modified Soxhlet-type extractor was employed and a typical procedure was as follows. A small sample (0.8–0.9 g) of the complex in an extraction thimble was placed in the extractor and the system was evacuated for >8

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[1] Abbreviations: 2,2′-bipyridine, bipy; pyridine, py; 1,2-bis(diphenylarsine)ethane, EDA; 1,2-bis(diphenylphosphine)ethane, EDP; ethylenediamine, en; en minus *n* protons, en-*n*H; diethylenetriamine, dien; *N,N*-dimethylethylenediamine, udmen; *N,N′*-dimethylethylenediamine, sdmen; *N,N,N′*-trimethylethylenediamine, tmen; 1,2-dicyanoethylene-1,2-dithiolato ion, MNT; 1,10-phenanthroline, phen.

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