CO), $Rh(bpy)_2(CO)H^{2+}$ is a relatively efficient catalyst for the water gas shift reaction (~1 turnover/h). The pH dependence of the catalytic rates (maximum at pH 3) suggests that either metallocarboxylic acid formation or decarboxylation is rate determining.

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Registry No. Rh, 7440-16-6; $[Rh(bpy)_2(CO)H]^{2+}$, 96293-15-1; $[Rh(bpy)_2]^+$, 47386-82-3; $[Rh(phen)_2]^+$, 56713-18-9; $[Rh(Me_2bpy)_2]^+$, 96293-16-2; $[Rh(CO)_2Cl]_2(\mu$-4,4'-bpy), 26173-13-7.

Supplementary Material Available: Table SII giving WGS reaction data and Figures S1–S3 giving hydrogen production rates as a function of solvent, temperature, rhodium concentration, and CO pressure (7 pages). Ordering information is given on any current masthead page.

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

Ternary Complexes in Solution. 45.[1] Intramolecular Aromatic-Ring Stacking Interactions in Dependence on the Ligand Structure, Geometry of the Coordination Sphere of the Metal Ion, and Solvent Composition

RAMAN MALINI-BALAKRISHNAN, KURT H. SCHELLER, ULRICH K. HÄRING, ROGER TRIBOLET, and HELMUT SIGEL*

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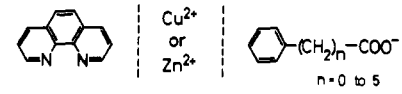
Stability constants of mixed-ligand M(phen)(PheCA)$^+$ complexes (M = Cu^{2+}, Zn^{2+}; phen = 1,10-phenanthroline; $PheCA^-$ = benzoate, 2-phenylacetate, 3-phenylpropionate, 4-phenylbutyrate, 5-phenylvalerate, 6-phenylcaproate) have been determined by potentiometric pH titration in aqueous solution and in 50% (v/v) ethanol- or dioxane/water and compared with the stabilities of the corresponding formate or acetate complexes. The ternary complexes containing phenylalkanecarboxylates ($PheCA^-$) are significantly more stable due to intramolecular stacking between the phenyl residue of the $PheCA^-$ ligands and the phen molecule. The formation degree of the intramolecular stacks in the Cu^{2+} and Zn^{2+} complexes was calculated, and the position of the intramolecular equilibrium between the opened and stacked isomer was determined: the stacked isomers occur between about 15 and 60% depending on the geometry of the coordination sphere of the bridging metal ion (Cu^{2+} (tetragonal)/Zn^{2+} (tetrahedral or octahedral)) and on the number of methylene groups between the phenyl residue and the coordinating carboxylate group (the "best fit" is usually reached with 2-phenylacetate). Addition of ethanol or dioxane to an aqueous solution may further favor intramolecular stack formation, contrary to the experience with simple unbridged binary stacking adducts, which are destabilized by the addition of ethanol or dioxane. The introduction of substituents into the phenyl residue of 2-phenylacetate influences the stability of the intramolecular stacks; especially a nitro group in the para position reduces considerably its formation degree. Replacement of the phenyl residue by the larger naphthyl moiety favors stacking and in 50% aqueous dioxane formation degrees of nearly 80% are reached, e.g., in Cu(phen)[2-(α-naphthyl)acetate]$^+$. The indole residue exhibits similar stacking properties. With regard to the side chains of amino acids it is interesting to note that the tendency to form intramolecular stacks in ternary complexes decreases in the series indole > phenyl > imidazole; the position of the last residue is based on measurements carried out with a pyrrole derivative as model ligand.

Metal ions are able to promote hydrophobic and aromatic-ring stacking interactions between suitable groups of different molecules, provided these molecules contain also ligating sites that allow the formation of mixed-ligand complexes.[2] Examples are the intramolecular ligand/ligand interactions within ternary complexes between suitable side chains of coordinated amino acids[3,4] or the corresponding interactions in mixed-ligand complexes of nucleotides and amino acids.[2,4] The systems mentioned are all of great interest with regard to biological systems.[5] However, due to the complicated nature of the ligands involved, it is difficult to study systematically the effect of structural alterations.

To overcome this handicap and to learn something about the factors that govern the formation degree of intramolecular aromatic-ring stacks, we initiated a comprehensive study that involves the components shown in Chart I. The series of phenylalkanecarboxylate ligands ($PheCA^-$)[6] allows a systematic variation of

Chart I



the distance between the coordinating carboxylate group and the phenyl moiety, which may form stacks with the also metal ion coordinated 1,10-phenanthroline. Indeed, in Cu(phen)(PheCA)$^+$ in aqueous solution intramolecular stacking interactions occur,[1] and the extent depends on the number of methylene groups be-

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(6) Abbreviations: Ac^-, acetate; $ArCA^-$, arylalkanecarboxylate, e.g., α-$NPAc^-$, PAc^-; bpy, 2,2'-bipyridyl; Bz^-, benzoate; CA^-, carboxylate ligand; IAc^-, 3-indoleacetate; IPr^-, 3-indolepropionate; L, general ligand; M^{2+}, general divalent metal ion; MBz^-, *p*-methylbenzoate; $MOPAc^-$, 2-(*p*-methoxyphenyl)acetate; $MPSAc^-$, carboxylatomethyl *p*-methylphenyl sulfide; NBz^-, *p*-nitrobenzoate; $NPAc^-$, 2-(*p*-nitrophenyl)acetate; α-$NPAc^-$, 2-(α-naphthyl)acetate; β-$NPAc^-$, 2-(β-naphthyl)acetate; $NPSAc^-$, carboxylatomethyl *p*-nitrophenyl sulfide; PAc^-, 2-phenylacetate; PBu^-, 4-phenylbutyrate; PCa^-, 6-phenylcaproate; $PheCA^-$, phenylalkanecarboxylates, e.g. Bz^-, PAc^-, etc.; phen, 1,10-phenanthroline; PPr^-, 3-phenylpropionate; Pr^-, propionate; $PSAc^-$, carboxylatomethyl phenyl sulfide (= 2-(phenylthio)acetate = phenylmercaptoacetate); PVa^-, 5-phenylvalerate; $PyAc^-$, 1-pyrroleacetate; $TMOPAc^-$, 2-(3,4,5-trimethoxyphenyl)acetate. For the structures of the carboxylate ligands see Charts I–III.

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tween the carboxylate and the phenyl residues.

This previous study[1] has now been extended to all ligands of Chart I, and instead of the use of only Cu^{2+} with its tetragonal coordination sphere allowing four equatorial and nearby donor atoms and possibly one or two more distant axial donors, Zn^{2+} was also employed. With Zn^{2+} having a tetrahedral or octahedral geometry, additional ligand arrangements become possible, and this is indeed reflected in the stability of the ternary complexes. All the ternary M^{2+}/phen/PheCA$^-$ systems were studied not only in aqueous solution but also in 50% (v/v) aqueous ethanol and 50% (v/v) aqueous dioxane: in different solvents the optimal stacking interaction is observed with different ligand combinations.

To learn more about the nature of the stacking interactions, the size of the aromatic residue of the carboxylate ligands was varied; i.e., pyrrole, phenyl, indole, and naphthyl moieties were employed, and the electron density in the phenyl ring of 2-phenylacetate was altered by methoxy and nitro substituents. These studies were carried out in 50% (v/v) aqueous dioxane, as in this solvent the parent ligand 2-phenylacetate shows an especially pronounced stacking interaction.

Experimental Section

Synthesis of Ligands. 6-Phenylcaproic acid was synthesized by converting 5-phenylpentan-1-ol with hydrobromic acid into 1-bromo-5-phenylpentane (yield 69%);[7] this was reacted in diethyl ether with Mg to the Grignard reagent, which was treated with dry ice (CO_2) and then hydrolyzed.[8] The carboxylic acid was isolated (yield 90%) as described for 5-phenylvaleric acid,[1] and recrystallized several times from petroleum ether; mp_{cor} 18–19 °C, lit.[9] mp 10–11 °C. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; O, 16.64. Found: C, 74.91; H, 8.46; O, 16.63.

1-Pyrroleacetic acid was synthesized similarly as described.[10] First potassium pyrrole was prepared[10] in 300 mL of xylene, and at the end of the reaction about half of the xylene was removed under reduced pressure. Then the mixture was treated dropwise for 1.5 h with ethyl chloroacetate; after the reaction had ceased, the mixture was kept for 0.5 h at 90 °C. Ethyl 1-pyrroleacetate was isolated (yield 28%) and hydrolyzed to 1-pyrroleacetic acid[10] (yield 63%). The substance was recrystallized three times from petroleum ether (80–100 °C); mp_{cor} 91–92 °C, lit.[10] mp 91 °C. Anal. Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.19; O, 25.57. Found: C, 57.61; H, 5.71; N, 11.11; O, 25.68.

Other Materials. 3-Indolepropionic acid, 2-(*p*-methoxyphenyl)acetic acid (both puriss.), 2-(3,4,5-trimethoxyphenyl)acetic acid (pract.; used only after several recrystallizations), 2-(*p*-nitrophenyl)acetic acid, 2-(α-naphthyl)acetic acid, and 2-(β-naphthyl)acetic acid (all purum) were from Fluka AG, Buchs, Switzerland. 3-Indoleacetic acid (purum), ethanol (absolute; pro analysi), and 1,4-dioxane (extra pure) were obtained from Merck AG, Darmstadt, West Germany, and zinc perchlorate was purchased from K and K Laboratories, Cleveland, OH. All other reagents were the same as used earlier;[1] the stock solutions were prepared as described.[1]

Measurements. The potentiometric pH titrations were carried out at 25 °C and an ionic strength (I) of 0.1 M under a nitrogen atmosphere with Metrohm potentiographs (Models E 336A and E 536) and Metrohm macro glass electrodes (Model EA 121). The buffers (pH 4.64 and 7.00) used for calibration were also from Metrohm AG, Herisau, Switzerland. The direct pH-meter readings were used in the calculations for the acidity constants; no "corrections" were applied for the change in solvent from water to aqueous dioxane or ethanol.[11-13] The determination and calculation of the equilibrium constants[14] was carried out as described recently.[1]

The spectrophotometric measurements were done with a Varian Techtron spectrophotometer (Model 635) connected to Honeywell (Model 196) or Walz & Walz (Model 1100) recorders. The ^1H NMR spectra were recorded on a Varian Anaspect EM-360 spectrometer (60 MHz). All experimental details and the evaluation of the experiments correspond to the recently described procedures.[1]

Results and Discussion

1. Stability of Unbridged Binary Stacking Adducts. One aim of this study was to use not only water as solvent but also aqueous ethanol and dioxane mixtures. As it is well-known that addition of these organic solvents to an aqueous solution reduces the stability of simple unbridged stacks,[15] we determined at first the stability of the adduct between 1,10-phenanthroline (phen) and 2-(*p*-methoxyphenyl)acetate (MOPAc$^-$) in 50% (v/v) aqueous dioxane. MOPAc$^-$ was selected as a representative of the phenylalkanecarboxylates used in this study (see Chart III in part 10); the formation of similar binary adducts in water had already been established.[1]

The position of equilibrium 1a was determined[1] by UV-difference spectrophotometry in 50% (v/v) aqueous dioxane, which corresponds to the mole fraction 0.175 of dioxane, at pH 8.1, where MOPAc$^-$ exists as the anion ($pK^H_{H(MOPAc)} = 5.96$; see Table VI).

$$\text{phen} + \text{MOPAc}^- \rightleftharpoons (\text{phen})(\text{MOPAc})^- \quad (1a)$$

$$K^{phen}_{(phen)(MOPAc)} = [(phen)(MOPAc)^-]/[phen][MOPAc^-] \quad (1b)$$

In the experiments the concentration of MOPAc$^-$ was varied and the result, $K^{phen}_{(phen)(MOPAc)} = 6.3 \pm 2.9\ M^{-1}$ (I = 0.25 M ($NaClO_4$), 25 °C), demonstrates that under these conditions stacking adducts are actually formed. This is confirmed by ^1H NMR measurements: increasing amounts of phen added to MOPAc$^-$ at pH 8.1 in 25% (v/v) aqueous methanol (mole fraction 0.148) led to upfield shifts of the resonances due to the phenyl protons of MOPAc$^-$; evaluation[1,16] of the data gave $K^{phen}_{(phen)(MOPAc)} = 4.4 \pm 0.4\ M^{-1}$ (I = 1.0 M ($N(CH_3)_4NO_3$), 34 °C).

These stability constants are of the same order as those determined earlier[16] in 50% (v/v) aqueous dioxane (I = 0.1 M ($NaClO_4$), 25 °C) for the binary stacks between 2,2′-bipyridyl and 3-phenylpropionate ($K^{bpy}_{(bpy)(PPr)} \approx 7.9\ M^{-1}$) or carboxymethyl phenyl sulfide ($K^{bpy}_{(bpy)(PSAc)} \simeq 8\ M^{-1}$). It should be emphasized that the calculated stability constants are not the main result of all these measurements, but rather that they prove that the phenyl moiety of phenylalkanecarboxylates may form stacks with the aromatic-ring systems of phen and bpy.

2. Stability of Metal Ion Complexes and Definition of Constants. On the basis of the results described in part 1 one could expect that intramolecular stacking interactions are also possible in mixed-ligand complexes containing phen and the phenylalkanecarboxylates of Chart I. Therefore, we have measured by potentiometric pH titrations the stability constants of the corresponding binary and ternary complexes of Cu^{2+} and Zn^{2+} in water, as well as in 50% (v/v) aqueous ethanol or dioxane (mole fractions 0.237 and 0.175, respectively). The equilibrium constants are listed in Table I, together with the corresponding constants for formate, acetate, and partly also propionate. The equilibrium constants involving the carboxylates (CA$^-$) are defined as

$$H(CA) \rightleftharpoons CA^- + H^+ \quad (2a)$$

$$K^H_{H(CA)} = [H^+][CA^-]/[H(CA)] \quad (2b)$$

$$M^{2+} + CA^- \rightleftharpoons M(CA)^+ \quad (3a)$$

$$K^M_{M(CA)} = [M(CA)^+]/[M^{2+}][CA^-] \quad (3b)$$

$$M(phen)^{2+} + CA^- \rightleftharpoons M(phen)(CA)^+ \quad (4a)$$

$$K^{M(phen)}_{M(phen)(CA)} = [M(phen)(CA)^+]/[M(phen)^{2+}][CA^-] \quad (4b)$$

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Table I. Negative Logarithms of the Acidity Constants (Eq 2) of Several Carboxylic Acids and Logarithms of the Corresponding Binary $M(CA)^+$ (Eq 3) and Ternary $M(phen)(CA)^+$ Complexes (Eq 4) in Water, 50% (v/v) Aqueous Ethanol (Corresponding to a Mole Fraction of 0.237), and 50% (v/v) Aqueous Dioxane (Mole Fraction 0.175) at I = 0.1 M and 25 °C[a]

ligand CA^-	n of Chart I	$pK^H_{H(CA)}$	$\log K^{Cu}_{Cu(CA)}$	$\log K^{Cu(phen)}_{Cu(phen)(CA)}$	$\Delta \log K_{Cu}$	$\log K^{Zn}_{Zn(CA)}$	$\log K^{Zn(phen)}_{Zn(phen)(CA)}$	$\Delta \log K_{Zn}$
				In Water[b]				
$HCOO^-$		3.59 ± 0.02[c]	1.65 ± 0.09[c]	1.61 ± 0.05[c]	−0.04 ± 0.10	1.07 ± 0.05	0.90 ± 0.04	−0.17 ± 0.06
Ac^-		4.58 ± 0.02[c]	1.85 ± 0.05[c]	1.84 ± 0.01[c]	−0.01 ± 0.05	1.11 ± 0.02	0.90 ± 0.02	−0.21 ± 0.03
Pr^-		4.69 ± 0.01[c]	1.91 ± 0.03[c]	1.93 ± 0.01[c]	0.02 ± 0.03			
Bz^-	0	4.03 ± 0.02	1.76 ± 0.01[c]	1.84 ± 0.01[c]	0.08 ± 0.01	1.06 ± 0.05	0.95 ± 0.03	−0.11 ± 0.06
PAc^-	1	4.12 ± 0.02[c]	1.75 ± 0.04[c]	2.01 ± 0.02[c]	0.26 ± 0.04	1.14 ± 0.03	1.05 ± 0.03	−0.09 ± 0.04
PPr^-	2	4.45 ± 0.02	1.87 ± 0.02[c]	2.14 ± 0.01[c]	0.27 ± 0.02	1.14 ± 0.04	1.07 ± 0.02	−0.07 ± 0.04
PBu^-	3	4.59 ± 0.01[c]	1.82 ± 0.05	1.96 ± 0.04	0.14 ± 0.06	1.09 ± 0.04	1.08 ± 0.04	−0.01 ± 0.06
PVa^-	4	4.65 ± 0.01[c]	1.89 ± 0.01[c]	2.05 ± 0.01[c]	0.16 ± 0.01	1.13 ± 0.05	1.10 ± 0.03	−0.03 ± 0.06
PCa^-	5	4.68 ± 0.01	1.84 ± 0.04	1.91 ± 0.02	0.07 ± 0.04			~0.0[f]
				In 50% Ethanol[d]				
$HCOO^-$		4.31 ± 0.01	2.24 ± 0.03	2.31 ± 0.03	0.07 ± 0.04	1.49 ± 0.03	1.38 ± 0.04	−0.11 ± 0.05
Ac^-		5.55 ± 0.01	2.70 ± 0.01	2.78 ± 0.02	0.08 ± 0.02	1.86 ± 0.01	1.81 ± 0.02	−0.05 ± 0.02
Bz^-	0	5.41 ± 0.01	2.63 ± 0.01	2.82 ± 0.01	0.19 ± 0.01	1.80 ± 0.01	1.88 ± 0.01	0.08 ± 0.01
PAc^-	1	5.39 ± 0.01	2.59 ± 0.02	3.06 ± 0.01	0.47 ± 0.02	1.75 ± 0.02	1.98 ± 0.01	0.23 ± 0.02
PPr^-	2	5.70 ± 0.01	2.70 ± 0.01	3.08 ± 0.01	0.38 ± 0.01	1.88 ± 0.01	2.06 ± 0.01	0.18 ± 0.01
PBu^-	3	5.88 ± 0.01	2.77 ± 0.01	2.99 ± 0.01	0.22 ± 0.01	1.91 ± 0.01	2.03 ± 0.01	0.12 ± 0.01
PVa^-	4	5.93 ± 0.01	2.78 ± 0.02	3.03 ± 0.01	0.25 ± 0.02	1.91 ± 0.03	2.09 ± 0.01	0.18 ± 0.03
PCa^-	5	5.98 ± 0.01	2.80 ± 0.01	3.04 ± 0.01	0.24 ± 0.01	1.96 ± 0.01	2.10 ± 0.01	0.14 ± 0.01
				In 50% Dioxane[e]				
$HCOO^-$		4.73 ± 0.02	2.79 ± 0.02	2.82 ± 0.02	0.03 ± 0.03	1.96 ± 0.01	1.82 ± 0.02	−0.14 ± 0.02
Ac^-		5.97 ± 0.01	3.31 ± 0.02	3.35 ± 0.01	0.04 ± 0.02	2.31 ± 0.01	2.15 ± 0.01	−0.16 ± 0.01
Bz^-	0	5.76 ± 0.01	3.24 ± 0.02	3.38 ± 0.02	0.14 ± 0.03	2.27 ± 0.02	2.26 ± 0.01	−0.01 ± 0.02
PAc^-	1	5.88 ± 0.01	3.22 ± 0.02	3.68 ± 0.04	0.46 ± 0.04	2.26 ± 0.02	2.29 ± 0.02	0.03 ± 0.03
PPr^-	2	6.18 ± 0.01	3.36 ± 0.01	3.64 ± 0.02	0.28 ± 0.02	2.36 ± 0.01	2.39 ± 0.01	0.03 ● 0.01
PBu^-	3	6.36 ± 0.01	3.44 ± 0.02	3.64 ± 0.02	0.20 ± 0.03	2.46 ± 0.01	2.45 ± 0.01	−0.01 ± 0.01
PVa^-	4	6.43 ± 0.01	3.48 ± 0.01	3.70 ± 0.01	0.22 ± 0.01	2.49 ± 0.01	2.50 ± 0.01	0.01 ± 0.01
PCa^-	5	6.44 ± 0.01	3.48 ± 0.01	3.68 ± 0.01	0.20 ± 0.02	2.47 ± 0.01	2.50 ± 0.01	0.03 ± 0.01

[a] The resulting values for $\Delta \log K_M$ (eq 6) are also listed. The errors given are *three times* the standard error of the mean value or the sum of the probable systematic errors, whichever is larger. The values of the error limits for $\Delta \log K_M$ were calculated according to the error propagation after Gauss. [b] I = 0.1 M was adjusted with KNO_3, but for PCa^- $NaNO_3$ was used. For PBu^- I = 0.1 M was adjusted in some experiments with KNO_3 and in others with $NaNO_3$; no significant difference between the results was observed, and the above values are the average of all experiments. [c] From ref 1. [d] I = 0.1 M was adjusted with $NaNO_3$. [e] I = 0.1 M was adjusted with $NaClO_4$. [f] This value is only an estimate; see comment in the legend for Figure 3.

Table II. Comparison of the Logarithms of the Stability Constants of Several $M(phen)(CA)^+$ Complexes (Eq 4) As Determined by UV-Difference Spectrophotometry (I = 0.1 M ($NaClO_4$), 25 °C) or Potentiometric pH Titrations (Tables I and VI; I = 0.1 M, 25 °C)[a]

complex	% (v/v) dioxane	$\log K^{M(phen)}_{M(phen)(CA)}$ UV	pH titr
$Cu(phen)(PAc)^+$	0	1.97 ± 0.10[b]	2.01 ± 0.02
$Cu(phen)(PAc)^+$	50	3.70 ± 0.09	3.68 ± 0.04
$Zn(phen)(PAc)^+$	50	2.23 ± 0.09	2.29 ± 0.02
$Cu(phen)(MOPAc)^+$	50	3.79 ± 0.10	3.78 ± 0.03
$Zn(phen)(MOPAc)^+$	50	2.32 ± 0.10	2.35 ± 0.01

[a] The errors given are three times the standard deviations. [b] From ref 1.

To check the reliability of the measured constants, we determined the stability of some mixed-ligand complexes containing 2-phenylacetate (PAc^-) or 2-(*p*-methoxyphenyl)acetate ($MOPAc^-$; see part 10) also by UV-difference spectrophotometry.[1,16] It is gratifying to see (Table II) that the two completely independent determinations are in excellent agreement.

3. Some Conclusions from the Stability of the Complexes. For a series of structurally related ligands it is expected[17,18] that plots of $\log K^M_{M(L)}$ against $pK^H_{H(L)}$ result in straight lines. This is indeed the case for the binary complexes in all three solvents if $\log K^M_{M(CA)}$ is plotted vs. $pK^H_{H(CA)}$;[19] an example is shown in Figure 1 for the Cu^{2+} and Zn^{2+} systems in aqueous solution. In the mixed solvents the fit is even better[19] as the stability of the binary complexes is somewhat larger and therefore the experimental error smaller (Table I). But still, in aqueous solution the values of the Cu^{2+} and Zn^{2+} complexes with formate, acetate, propionate, and

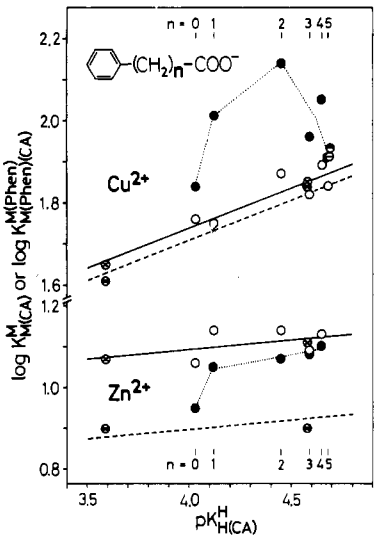

Figure 1. Relationship between $\log K^M_{M(CA)}$ or $\log K^{M(phen)}_{M(phen)(CA)}$ and $pK^H_{H(CA)}$ in aqueous solution for the binary complexes, $M(CA)^+$ (⊗, ⊖, ○), or the ternary complexes, $M(phen)(CA)^+$ (⊛, ⊜, ●), with *simple* carboxylates [$HCOO^-$, Ac^- (⊗, ⊛) and Pr^- (⊖, ⊜), from left to right] and the *phenyl*alkanecarboxylates (see formula above) with n = 0–5 (○, ●). The data are from Table I, and those of the binary complexes fit on straight lines (*solid* lines; regression m_{Cu} = 0.192 ± 0.028, m_{Zn} = 0.046 ± 0.032); the reference lines for the ternary complexes (*broken* lines) are drawn with the corresponding slopes but only through the points of $HCOO^-$ and Ac^- (see text).

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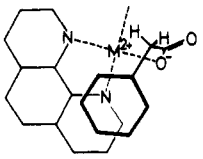


Figure 2. Possible (schematic) structure of M(phen)(PAc)$^+$ for the isomer with the intramolecular stack between the phenyl residue of 2-phenylacetate and the aromatic-ring system of 1,10-phenanthroline.

all phenylalkanecarboxylates (Chart I) fit within ±0.04 log unit on the two corresponding straight lines. This fit of the binary phenylalkanecarboxylate complexes shows that there is no significant Cu^{2+}- or Zn^{2+}/aromatic-ring interaction as was recently discovered by Kim and Martin[20] for several Pd^{2+} complexes in aqueous solution.

Figure 1 shows also that the ternary complexes behave completely differently: only the values for Cu(phen)(CA)$^+$ and Zn(phen)(CA)$^+$ with formate and acetate fit within experimental error on straight lines (broken lines) parallel to the reference lines of the binary complexes (solid lines). Already the point due to Cu(phen)(Pr)$^+$ is significantly above the corresponding broken line (upper part of Figure 1). Hence, this ternary complex is more stable than expected on the basis of the basicity of the carboxylate group of propionate; this means that an extra stabilization within the ternary complex must occur. In fact, this extra stabilization may be attributed to intramolecular hydrophobic ligand/ligand interactions between the alkyl chain of propionate and the aromatic-ring system of phen. This interpretation is in accord with the observations in related systems[21,22] and also with ^{1}H NMR shift studies,[23] which prove such hydrophobic interactions for Zn(phen)(Pr)$^+$ and similar complexes.[24]

The important conclusion is that M(phen)(HCOO)$^+$ and M(phen)(Ac)$^+$ are representative for ternary complexes resulting from the coordination of a carboxylate group to M(phen)$^{2+}$. All the ternary complexes of the phenylalkanecarboxylates of Chart I are significantly more stable than expected on the basis of their carboxylate basicity (see Figure 1); this indicates the formation of intramolecular stacks between the phenyl moiety and the aromatic-ring systems of phen. More importantly, the increase in stability for M(phen)(PheCA)$^+$ obviously depends on the number of methylene groups between the phenyl residue and the coordinating carboxylate group, and this is convincing evidence that intramolecular stacks are indeed its source. A simplified structure for such a stacked species is shown in Figure 2.

An additional direct proof for the formation of intramolecular stacks follows from the observed upfield shifts in the ^{1}H NMR spectra of the Zn^{2+}/phen/PAc$^-$ system in aqueous solution[1] and in 50% aqueous dioxane.[25] Moreover, the stability constants calculated from these experiments for Zn(phen)(PAc)$^+$ agree with those measured by potentiometric pH titrations.

4. Quantification of the Stability of the Ternary M(phen)(CA)$^+$ Complexes Relative to That of Their Binary Parent Complexes. The relative stability of mixed-ligand complexes toward their parent complexes is best quantified by considering equilibrium 5a.[4,26] Both sides of this equilibrium contain species of the same

$$M(phen)^{2+} + M(CA)^+ \rightleftharpoons M(phen)(CA)^+ + M^{2+} \quad (5a)$$

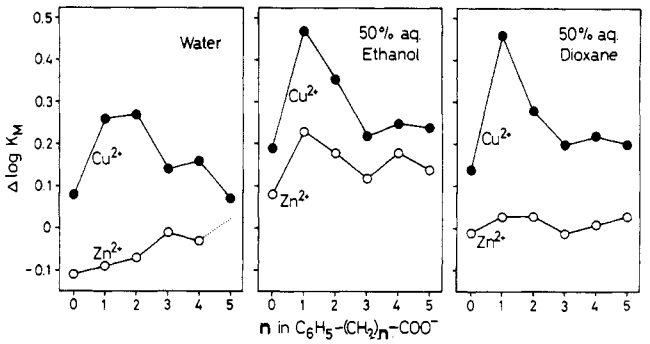


Figure 3. Dependence of the values for Δ log K_M (from Table I), which reflect the relative stabilities of the ternary M(phen)(PheCA)$^+$ complexes, in different solvents on the number of methylene groups present in the phenylalkanecarboxylates (see Chart I) between the coordinating carboxylate group and the phenyl residue participating in the intramolecular stack. The dotted-line portion for the Zn^{2+} complexes in the left part of the figure (water) reflects uncertainty: we had difficulties in determining reliable and reproducible values for log $K^{Zn}{}_{Zn(PCa)}$ and log $K^{Zn(phen)}{}_{Zn(phen)(PCa)}$, but the corresponding value for Δ log K_{Zn} (eq 6) appears to be close to zero (i.e. between 0 and +0.1 log unit). In any case, the value is not strongly negative.

charge type, minimizing any electrostatic contribution to the corresponding equilibrium constant, which is defined by eq 5b and

$$10^{\Delta \log K_M} = \frac{[M(phen)(CA)^+][M^{2+}]}{[M(phen)^{2+}][M(CA)^+]} \quad (5b)$$

calculated with eq 6. In general, equilibrium 5a is expected[1,4,26]

$$\Delta \log K_M = \log K^{M(phen)}{}_{M(phen)(CA)} - \log K^{M}{}_{M(CA)}$$
$$= \log K^{M(CA)}{}_{M(CA)(phen)} - \log K^{M}{}_{M(phen)} \quad (6)$$

to be on its left side with negative values for Δ log K_M. Indeed, for the coordination of a bidentate ligand followed by a monodentate ligand in a regular octahedral (oh) coordination sphere statistical considerations[26] indicate that Δ log K_{oh} = log (4:1/6:1) = −0.18; assuming Zn^{2+} has not an octahedral but rather a tetrahedral (th) coordination sphere in these ternary complexes, then it holds that Δ log K_{th} = log (2:1/4:1) = −0.3. For the tetragonal or Jahn-Teller-distorted octahedral coordination sphere of Cu^{2+} a statistical value is more difficult to assess, but on the basis of previously advanced arguments[26] one may for the present estimate Δ log $K_{Cu(statist)} \simeq -0.5$.

The stabilities of M(phen)(HCOO)$^+$ and M(phen)(Ac)$^+$ (Table I) are governed by the basicity of the carboxylate group and *not* by intramolecular ligand/ligand interactions (part 3); the Δ log K_M values vary between about −0.2 to +0.1 log unit. Hence, in comparison with the statistical expectation an increased stability is observed; this result corresponds to the well-known fact that the combination of heteroaromatic N bases and O ligands in ternary complexes with Cu^{2+} or Zn^{2+} and related metal ions leads to an increased stability.[4,26-28] The important conclusion is the following: the evaluation of the stacking intensity in the ternary M(phen)(PheCA)$^+$ complexes has to be done in relation to the Δ log K_M values of the corresponding formate and acetate complexes (see part 6).

5. Influence of Ligand Structure, Metal Ion Coordination Sphere, and Solvents on the Extent of the Stability Increase of M(phen)(PheCA)$^+$ Complexes. Since we shall restrict ourselves for the present to *relative* comparisons of the series within the same solvent, a deduction of the Δ log K_M values due to the

(20) Kim, S.-H.; Martin, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 1707–1712.
(21) (a) Sigel, H. *Angew. Chem.* **1982**, *94*, 421–432; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 389–400. (b) Sigel, H. *Experientia* **1981**, *37*, 789–798.
(22) Sigel, H.; Tribolet, R.; Scheller, K. H. *Inorg. Chim. Acta* **1985**, *100*, 151–164.
(23) Mitchell, P. R. *J. Chem. Soc., Dalton Trans.* **1979**, 771–776.
(24) (a) The value Δ log K_{Cu} = 0.17 (for the definition see eq 6 in part 4) determined[24b] for the Cu^{2+}/bpy/2-cyclohexylacetate system in aqueous solution indicates also that hydrophobic ligand–ligand interactions occur in the corresponding ternary complex, because the expected value without any ligand–ligand interaction would be Δ log $K_{Cu} \simeq 0.0$ (see e.g. Tables I and VI). In fact, for 50% aqueous dioxane as solvent we have proved[22] the hydrophobic interaction in the complex mentioned. (b) John, E. *Microchem. J.* **1981**, *26*, 174–180.
(25) Sigel, H.; Malini-Balakrishnan, R.; Häring, U. K. *J. Am. Chem. Soc.*, in press.
(26) Sigel, H. *Angew. Chem.* **1975**, *87*, 391–400; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394–402.
(27) Sigel, H.; Fischer, B. E.; Prijs, B. *J. Am. Chem. Soc.* **1977**, *99*, 4489–4496.
(28) (a) Banerjea, D.; Kaden, T. A.; Sigel, H. *Inorg. Chem.* **1981**, *20*, 2586–2590. (b) Saha, N.; Sigel, H. *J. Am. Chem. Soc.* **1982**, *104*, 4100–4105.

formate and acetate complexes (part 4) from the values due to the M(phen)(PheCA)$^+$ complexes is unnecessary as this would only lead to a constant variation within a series.

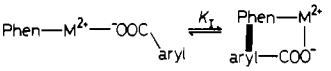
To facilitate these *relative* comparisons, the $\Delta \log K_M$ values for the M(phen)(PheCA)$^+$ complexes of Table I are plotted in Figure 3 in dependence on the number of methylene groups between the phenyl residue and the coordinating carboxylate group (see Chart I). The following conclusions are evident:

(1) The ligand structure, i.e. the distance between the coordinating carboxylate group and the phenyl residue undergoing stacking, influences the stability of the Cu(phen)(PheCA)$^+$ complexes: overall, the "best" fit in the sense that the strongest interaction results is evidently obtained with 2-phenylacetate ($n = 1$). This is somewhat surprising because space-filling molecular models indicate that in a square-planar coordination sphere no complete overlapping is possible between the phenyl moiety and the phen ring system (Figure 2). This result indicates that a "good" fit leading to a strong interaction does not necessarily mean that the two aromatic systems have to overlap completely; this is in accord with observations in the solid state, where the aromatic rings are also often shifted toward each other (e.g., ref 1, 29, and 30). With benzoate ($n = 0$) no real overlap in Cu(phen)(Bz)$^+$ is possible (see part 7), while the lower stability of the Cu^{2+} complexes with the longer phenylalkanecarboxylates ($n \geq 3$) indicates that also no ideal fit is obtained; i.e., the phenyl residue will reach beyond the phen ring system, or the methylene groups must be twisted (see also point 2).

(2) The geometry of the coordination sphere of the metal ion also has a crucial influence on the formation of intramolecular stacks as is evident from the data obtained for aqueous solution (left part in Figure 3): Cu^{2+} and Zn^{2+} complexes differ significantly. The tetrahedral or octahedral coordination sphere of Zn^{2+} allows already with benzoate ($n = 0$) a stacking interaction, which is then increasingly supported by an additional hydrophobic interaction between the methylene groups ($n \geq 1$) and the phen ring system. Due to this hydrophobic interaction, which becomes dominating with larger alkyl chains, $\Delta \log K_M$ levels off at $n \geq 3$. It appears that the coordination sphere of Zn^{2+} is able to accommodate any of the PheCA$^-$ ligands such that some intramolecular interaction results, and therefore, no special ligand structure is significantly favored. This situation corresponds to the Cu(phen)(PheCA)$^+$ complexes with $n \geq 3$ in which hydrophobic ligand/ligand interactions are certainly also of importance.

(3) The influence of the solvent, originating in different solvation properties, is also evident from Figure 3. In aqueous solution the intramolecular stacking tendency is about the same in Cu(phen)(PAc)$^+$ ($n = 1$) and Cu(phen)(PPr)$^+$ ($n = 2$), but addition of ethanol or dioxane favors Cu(phen)(PAc)$^+$ considerably. Even more striking is the different influence of water and 50% aqueous ethanol on the properties of the Cu(phen)(PheCA)$^+$ and Zn(phen)(PheCA)$^+$ complexes: there is a pronounced parallelism between the two series of complexes in the ethanolic solution, but not in water. Dioxane appears to have the same influence as ethanol on the Cu^{2+} complexes, but a smaller one on the Zn^{2+} complexes. Consequently all Zn^{2+} complexes have about the same values for $\Delta \log K_{Zn}$ in 50% aqueous dioxane, while they differ for water and 50% aqueous ethanol. One has to conclude that different organic solvents influence the intramolecular stacking tendency differently; this includes in certain complexes even a promotion of the intramolecular ligand–ligand interaction (see part 6).

6. Intramolecular Equilibria: Extent of the Formation Degree of the Intramolecular Stack in the Ternary M(phen)(PheCA)$^+$ Complexes. The facts discussed in parts 3 and 5 prove only that stacks exist, but not to which extent. For example, the influence of the different solvents on the values of $\Delta \log K_M$ (Figure 3) indicates already that the formation degree of stacks can vary. Hence, there is certainly an intramolecular equilibrium in solution between an "opened" and a "stacked" form, i.e. between the isomers as indicated in equilibrium 7a. If these two isomers are



(7a)

designated as M(phen)(ArCA)$^+_{op}$ and M(phen)(ArCA)$^+_{st}$, the dimensionless constant of this equilibrium is defined by eq 7b.

$$K_I = [M(phen)(ArCA)^+_{st}]/[M(phen)(ArCA)^+_{op}] \quad (7b)$$

Values of K_I may be calculated from eq 8.[3] The values of

$$K_I = \frac{K^{M(phen)}_{M(phen)(ArCA)}}{K^{M(phen)}_{M(phen)(ArCA)_{op}}} - 1 \quad (8a)$$

$$= \frac{10^{\Delta \log K(M/phen/ArCA)}}{10^{\Delta \log K(M/phen/ArCA)_{op}}} - 1 \quad (8b)$$

$K^{M(phen)}_{M(phen)(ArCA)}$ are known (eq 4), and those of $K^{M(phen)}_{M(phen)(ArCA)_{op}}$ could be estimated according to Figure 1: the acidity constant of a given ArCA$^-$ ligand allows one to read from the intercept with the reference line the stability constant expected for a simple carboxylate coordination.

However, experience shows[3] that the use of the $\Delta \log K_M$ formulation (eq 8b) is preferable because systematic errors cancel to a large part. The values due to $\Delta \log K(M/phen/ArCA)$ are known; they correspond to those calculated from eq 6. There is also no problem regarding $\Delta \log K(M/phen/ArCA)_{op}$: this value is certainly well represented by those determined for M(phen)(HCOO)$^+$ and M(phen)(Ac)$^+$. Clearly, in M(phen)(HCOO)$^+$ no intramolecular interaction is possible and in M(phen)(Ac)$^+$ an interaction with the methyl group, if it occurs at all, is small and insignificant (Figure 1; parts 3 and 4). Hence, $\Delta \log K(M/phen/ArCA)_{op}$ is obtained by averaging the $\Delta \log K_M$ values measured for the M/phen/HCOO$^-$ and M/phen/Ac$^-$ systems (Table I).

The crucial parameter for calculating K_I (eq 8b) is the difference given by eq 9. Equation 8b may now be rewritten as eq 10. Obviously, any experimental error will be the more significant

$$\Delta\Delta \log K = \Delta \log K(M/phen/ArCA) - \Delta \log K(M/phen/ArCA)_{op} \quad (9)$$

$$K_I = 10^{\Delta\Delta \log K} - 1 \quad (10)$$

the smaller the difference in eq 9 is. The results of the calculations using eq 10 and the constants listed in Table I for the phenylalkanecarboxylates are summarized in Tables III and IV for the ternary Cu^{2+} and Zn^{2+} complexes, respectively. These tables contain in addition results that refer to complexes of other arylalkanecarboxylates (entries 25–41); these will be discussed in parts 7–10.

A comparison of the data given in Tables III and IV confirms all the conclusions of part 5, but from the present quantitative evaluation some additional features become evident: The percentage of the closed isomer is always relatively similar for a given phenylalkanecarboxylate in the Cu(phen)(PheCA)$^+$ and Zn(phen)(PheCA)$^+$ complexes in 50% aqueous ethanol (entries 11–16), while there are distinct differences for the M(phen)(PAc)$^+$ and M(phen)(PPr)$^+$ complexes in water (entries 4 and 5) and 50% aqueous dioxane (entries 20 and 21); i.e., the percentage of the stacked isomer is in both solvents larger for the Cu^{2+} than for the Zn^{2+} complexes. The highest formation degree is reached with about 60% for Cu(phen)(PAc)$^+$ in 50% aqueous ethanol or dioxane; in other words, the addition of ethanol (entry 12) or dioxane (entry 20) to water (entry 4) promotes the formation of the intramolecular stack. This result is very surprising and warrants further studies,[25] because the stability of unbridged binary stacking adducts (like those described in part 1) is decreased by the addition of ethanol or dioxane.[15,25]

(29) (a) Åoki, K. *J. Am. Chem. Soc.* **1978**, *100*, 7106–7108. (b) Orioli, P.; Cini, R.; Donati, D.; Mangani, S. *J. Am. Chem. Soc.* **1981**, *103*, 4446–4452.
(30) Ishida, T.; Shibata, M.; Fujii, K.; Inoue, M. *Biochemistry* **1983**, *22*, 3571–3581.

Table III. Extent of the Intramolecular Aromatic-Ring Stacks (See E.g. Figure 2) in Ternary Cu^{2+} Complexes Containing 1,10-Phenanthroline or 2,2'-Bipyridyl (A) and an Arylalkanecarboxylate ($ArCA^-$): Intramolecular and Dimensionless Equilibrium Constant K_I and Percentage of the Stacked Isomer $Cu(A)(ArCA)^+_{st}$ in Water, 50% (v/v) Aqueous Ethanol, and 50% (v/v) Aqueous Dioxane ($I = 0.1$, 25 °C)

no.	complex	$\Delta \log K_{Cu}$ (eq 6)[a]	$\Delta\Delta \log K$ (eq 9)[c]	K_I (eq 7, 10)[c]	% $Cu(A)(ArCA)^+_{st}$ (eq 7a)[c]
		In Water			
1	Cu(phen)(HCOO)$^+$	−0.04 ± 0.10 } −0.02 ± 0.06[b]			
2	Cu(phen)(Ac)$^+$	−0.01 ± 0.05 }			
3	Cu(phen)(Bz)$^+$	0.08 ± 0.01	0.10 ± 0.01 (0.06)	0.26 ± 0.04 (0.17)	21 ± 3 (11)
4	Cu(phen)(PAc)$^+$	0.26 ± 0.04	0.28 ± 0.04 (0.07)	0.91 ± 0.20 (0.32)	48 ± 5 (9)
5	Cu(phen)(PPr)$^+$	0.27 ± 0.02	0.29 ± 0.02 (0.06)	0.95 ± 0.10 (0.28)	49 ± 3 (7)
6	Cu(phen)(PBu)$^+$	0.14 ± 0.06	0.16 ± 0.06 (0.09)	0.45 ± 0.21 (0.29)	31 ± 10 (14)
7	Cu(phen)(PVa)$^+$	0.16 ± 0.01	0.18 ± 0.01 (0.06)	0.51 ± 0.05 (0.21)	34 ± 2 (9)
8	Cu(phen)(PCa)$^+$	0.07 ± 0.04	0.09 ± 0.04 (0.07)	0.23 ± 0.13 (0.21)	19 ± 8 (14)
		In 50% Ethanol			
9	Cu(phen)(HCOO)$^+$	0.07 ± 0.04 } 0.08 ± 0.02[b]			
10	Cu(phen)(Ac)$^+$	0.08 ± 0.02 }			
11	Cu(phen)(Bz)$^+$	0.19 ± 0.01	0.11 ± 0.01 (0.03)	0.29 ± 0.04 (0.08)	22 ± 3 (5)
12	Cu(phen)(PAc)$^+$	0.47 ± 0.02	0.39 ± 0.02 (0.03)	1.45 ± 0.13 (0.19)	59 ± 2 (3)
13	Cu(phen)(PPr)$^+$	0.38 ± 0.01	0.30 ± 0.01 (0.03)	1.00 ± 0.06 (0.13)	50 ± 2 (3)
14	Cu(phen)(PBu)$^+$	0.22 ± 0.01	0.14 ± 0.01 (0.03)	0.38 ± 0.04 (0.09)	28 ± 2 (5)
15	Cu(phen)(PVa)$^+$	0.25 ± 0.02	0.17 ± 0.02 (0.03)	0.48 ± 0.08 (0.11)	32 ± 3 (5)
16	Cu(phen)(PCa)$^+$	0.24 ± 0.01	0.16 ± 0.01 (0.03)	0.45 ± 0.05 (0.09)	31 ± 2 (4)
		In 50% Dioxane			
17	Cu(phen)(HCOO)$^+$	0.03 ± 0.03 } 0.04 ± 0.02[b]			
18	Cu(phen)(Ac)$^+$	0.04 ± 0.02 }			
19	Cu(phen)(Bz)$^+$	0.14 ± 0.03	0.10 ± 0.03 (0.03)	0.26 ± 0.08 (0.10)	21 ± 5 (6)
20	Cu(phen)(PAc)$^+$	0.46 ± 0.04	0.42 ± 0.04 (0.05)	1.63 ± 0.27 (0.29)	62 ± 4 (4)
21	Cu(phen)(PPr)$^+$	0.28 ± 0.02	0.24 ± 0.02 (0.03)	0.74 ± 0.09 (0.11)	43 ± 3 (4)
22	Cu(phen)(PBu)$^+$	0.20 ± 0.03	0.16 ± 0.03 (0.03)	0.45 ± 0.09 (0.11)	31 ± 5 (5)
23	Cu(phen)(PVa)$^+$	0.22 ± 0.01	0.18 ± 0.01 (0.02)	0.51 ± 0.05 (0.08)	34 ± 2 (3)
24	Cu(phen)(PCa)$^+$	0.20 ± 0.02	0.16 ± 0.02 (0.03)	0.45 ± 0.07 (0.10)	31 ± 4 (5)
25	Cu(phen)(α-NAc)$^+$	0.68 ± 0.02	0.64 ± 0.02 (0.03)	3.37 ± 0.22 (0.29)	77 ± 1 (2)
26	Cu(phen)(β-NAc)$^+$	0.70 ± 0.04	0.66 ± 0.04 (0.04)	3.57 ± 0.38 (0.42)	78 ± 2 (2)
27	Cu(phen)(IAc)$^+$	0.69 ± 0.05	0.65 ± 0.05 (0.06)	3.47 ± 0.55 (0.58)	78 ± 3 (3)
28	Cu(phen)(IPr)$^+$	0.36 ± 0.03	0.32 ± 0.03 (0.03)	1.09 ± 0.14 (0.16)	52 ± 3 (4)
29	Cu(phen)(PyAc)$^+$	0.34 ± 0.01	0.30 ± 0.01 (0.02)	1.00 ± 0.06 (0.11)	50 ± 2 (3)
30	Cu(phen)(NPAc)$^+$	0.26 ± 0.03	0.22 ± 0.03 (0.03)	0.66 ± 0.11 (0.13)	40 ± 4 (5)
31	Cu(phen)(MOPAc)$^+$	0.50 ± 0.04	0.46 ± 0.04 (0.04)	1.88 ± 0.24 (0.27)	65 ± 3 (3)
32	Cu(phen)(TMOPAc)$^+$	0.50 ± 0.02	0.46 ± 0.02 (0.03)	1.88 ± 0.15 (0.19)	65 ± 2 (2)
33	Cu(bpy)(HCOO)$^+$	0.04 } 0.10[b]			
34	Cu(bpy)(Ac)$^+$	0.15 }			
35	Cu(bpy)(PPr)$^+$	0.38	0.28	0.91 ± 0.22[d]	48 ± 6[d]
36	Cu(bpy)(PSAc)$^+$	0.64	0.54	2.47 ± 0.40[d]	71 ± 3[d]
37	Cu(bpy)(MPSAc)$^+$	0.60	0.50	2.16 ± 0.36[d]	68 ± 4[d]
38	Cu(bpy)(NPSAc)$^+$	0.36	0.26	0.82 ± 0.21[d]	45 ± 6[d]
39	Cu(bpy)(Bz)$^+$	0.28	0.18	0.51 ± 0.17[d]	34 ± 8[d]
40	Cu(bpy)(MBz)$^+$	0.22	0.12	0.32 ± 0.15[d]	24 ± 9[d]
41	Cu(bpy)(NBz)$^+$	0.12	0.02	0.05 ± 0.12[d]	≤15[d]

[a] These values and their error ranges (*three times* the standard error) are from Tables I (entries 1–24), V (entries 25–29), and VI (entries 30–41). [b] This value corresponds to $\Delta \log K_{op}$ of eq 8b and 9. [c] The error limits given with these data correspond to the errors of the individual values of $\Delta \log K_M$. The error limits in parentheses include also the error in $\Delta \log K_{op}$; these error limits should be used in external comparisons. However, for internal comparisons the errors based only on the individual $\Delta \log K_M$ values should be used, because $\Delta \log K_{op}$ is the same for a whole series of data,[b] and therefore any error in $\Delta \log K_{op}$ will lead to a systematic correction for all these values. [d] These errors are estimates and correspond to an error of ±0.05 log unit in $\Delta\Delta \log K$.

Another interesting observation along the same line is the remarkable independence from the solvent of the percentage for $M(phen)(PheCA)^+_{st}$ with 4-phenylbutyrate (entries 6, 14 and 22 in Tables III and IV), 5-phenylvalerate (entries 7, 15, and 23), and 6-phenylcaproate (entries 8, 16, and 24). Moreover, the percentage of the closed isomer for all these complexes is throughout close to about 33%; i.e., this value is not only rather independent from the solvent but also from the kind of metal ion and the structure of the phenylalkanecarboxylate. In other words, with at least three methylene groups between the coordinating carboxylate group and the phenyl residue the ligand is flexible enough to adapt itself to the conditions created by the geometry of the coordination sphere of the metal ion.

7. The Special Case of Benzoate as Ligand. From all the ligands studied, benzoate is the only one in which the phenyl ring is directly bound to the carboxylate group and this could alter the electronic density of the binding site in such a way that a somewhat higher stability of the complexes results compared with those cases in which no conjugation between the phenyl ring and the carboxylate group is possible. Though an increased stability of the $Cu(phen)(Bz)^+$ and $Zn(phen)(Bz)^+$ complexes is observed in all three solvents (entries 3, 11, and 19 in Tables III and IV), space-filling molecular models indicate that stack formation is possible in a tetrahedral or octahedral coordination sphere (Zn^{2+}), but not in a tetragonal arrangement of the ligands (Cu^{2+}). In fact, in the latter case only one edge of the phenyl ring can be arranged above phenanthroline, though this would be enough for a hydrophobic interaction (vide infra).

This leads to the following question: Is the increased stability of $M(phen)(Bz)^+$ due to electronic effects of the phenyl ring at the carboxylate group or due to intramolecular ligand/ligand interactions? Though no final answer can yet be given, the sum

Table IV. Extent of the Intramolecular Aromatic-Ring Stacks (See E.g. Figure 2) in Ternary Zn^{2+} Complexes Containing 1,10-Phenanthroline or 2,2'-Bipyridyl (A) and an Arylalkanecarboxylate ($ArCA^-$): Intramolecular and Dimensionless Equilibrium Constant K_I and Percentage of the Stacked Isomer $Zn(A)(ArCA)^+_{st}$ in Water, 50% (v/v) Aqueous Ethanol, and 50% (v/v) Aqueous Dioxane ($I = 0.1$, 25 °C)

no.	complex	$\Delta \log K_{Zn}$ (eq 6)[a]	$\Delta\Delta \log K$ (eq 9)[c]	K_I (eq 7, 10)[c]	% $Zn(A)(ArCA)^+_{st}$ (eq 7a)[c]
			In Water		
1	$Zn(phen)(HCOO)^+$	-0.17 ± 0.06	-0.19 ± 0.04[b]		
2	$Zn(phen)(Ac)^+$	-0.21 ± 0.03			
3	$Zn(phen)(Bz)^+$	-0.11 ± 0.06	0.08 ± 0.06 (0.07)	0.20 ± 0.16 (0.19)	17 ± 11 (13)
4	$Zn(phen)(PAc)^+$	-0.09 ± 0.04	0.10 ± 0.04 (0.05)	0.26 ± 0.12 (0.16)	21 ± 8 (10)
5	$Zn(phen)(PPr)^+$	-0.07 ± 0.04	0.12 ± 0.04 (0.06)	0.32 ± 0.14 (0.17)	24 ± 8 (10)
6	$Zn(phen)(PBu)^+$	-0.01 ± 0.06	0.18 ± 0.06 (0.07)	0.51 ± 0.20 (0.23)	34 ± 9 (10)
7	$Zn(phen)(PVa)^+$	-0.03 ± 0.06	0.16 ± 0.06 (0.07)	0.45 ± 0.19 (0.23)	31 ± 9 (11)
8	$Zn(phen)(PCa)^+$	~0.0[e]			~35
			In 50% Ethanol		
9	$Zn(phen)(HCOO)^+$	-0.11 ± 0.05	-0.08 ± 0.03[b]		
10	$Zn(phen)(Ac)^+$	-0.05 ± 0.02			
11	$Zn(phen)(Bz)^+$	0.08 ± 0.01	0.16 ± 0.01 (0.03)	0.45 ± 0.05 (0.10)	31 ± 2 (5)
12	$Zn(phen)(PAc)^+$	0.23 ± 0.02	0.31 ± 0.02 (0.04)	1.04 ± 0.11 (0.17)	51 ± 3 (4)
13	$Zn(phen)(PPr)^+$	0.18 ± 0.01	0.26 ± 0.01 (0.03)	0.82 ± 0.06 (0.13)	45 ± 2 (4)
14	$Zn(phen)(PBu)^+$	0.12 ± 0.01	0.20 ± 0.01 (0.03)	0.58 ± 0.05 (0.11)	37 ± 2 (4)
15	$Zn(phen)(PVa)^+$	0.18 ± 0.03	0.26 ± 0.03 (0.04)	0.82 ± 0.13 (0.18)	45 ± 4 (5)
16	$Zn(phen)(PCa)^+$	0.14 ± 0.01	0.22 ± 0.01 (0.03)	0.66 ± 0.05 (0.12)	40 ± 2 (4)
			In 50% Dioxane		
17	$Zn(phen)(HCOO)^+$	-0.14 ± 0.02	-0.15 ± 0.01[b]		
18	$Zn(phen)(Ac)^+$	-0.16 ± 0.01			
19	$Zn(phen)(Bz)^+$	-0.01 ± 0.02	0.14 ± 0.02 (0.03)	0.38 ± 0.07 (0.08)	28 ± 4 (4)
20	$Zn(phen)(PAc)^+$	0.03 ± 0.03	0.18 ± 0.03 (0.03)	0.51 ± 0.10 (0.11)	34 ± 4 (5)
21	$Zn(phen)(PPr)^+$	0.03 ± 0.01	0.18 ± 0.01 (0.02)	0.51 ± 0.05 (0.07)	34 ± 2 (3)
22	$Zn(phen)(PBu)^+$	-0.01 ± 0.01	0.14 ± 0.01 (0.02)	0.38 ± 0.04 (0.06)	28 ± 2 (3)
23	$Zn(phen)(PVa)^+$	0.01 ± 0.01	0.16 ± 0.01 (0.02)	0.45 ± 0.05 (0.06)	31 ± 2 (3)
24	$Zn(phen)(PCa)^+$	0.03 ± 0.01	0.18 ± 0.01 (0.02)	0.51 ± 0.05 (0.07)	34 ± 2 (3)
25	$Zn(phen)(\alpha\text{-NAc})^+$	0.29 ± 0.01	0.44 ± 0.01 (0.02)	1.75 ± 0.09 (0.12)	64 ± 1 (2)
26	$Zn(phen)(\beta\text{-NAc})^+$	0.14 ± 0.02	0.29 ± 0.02 (0.03)	0.95 ± 0.10 (0.12)	49 ± 3 (3)
27	$Zn(phen)(IAc)^+$	0.24 ± 0.01	0.39 ± 0.01 (0.02)	1.45 ± 0.08 (0.11)	59 ± 1 (2)
28	$Zn(phen)(IPr)^+$	0.11 ± 0.03	0.26 ± 0.03 (0.03)	0.82 ± 0.12 (0.13)	45 ± 4 (4)
29	$Zn(phen)(PyAc)^+$	-0.07 ± 0.01	0.08 ± 0.01 (0.02)	0.20 ± 0.04 (0.05)	17 ± 3 (4)
30	$Zn(phen)(NPAc)^+$	0.07 ± 0.02	0.22 ± 0.02 (0.03)	0.66 ± 0.09 (0.10)	40 ± 3 (4)
31	$Zn(phen)(MOPAc)^+$	0.07 ± 0.02	0.22 ± 0.02 (0.03)	0.66 ± 0.09 (0.10)	40 ± 3 (4)
32	$Zn(phen)(TMOPAc)^+$	0.12 ± 0.03	0.27 ± 0.03 (0.03)	0.86 ± 0.12 (0.13)	46 ± 3 (4)
33	$Zn(bpy)(HCOO)^+$	-0.14	-0.12[b]		
34	$Zn(bpy)(Ac)^+$	-0.11			
35	$Zn(bpy)(PPr)^+$	0.11	0.23	0.70 ± 0.20[d]	41 ± 7[d]
36	$Zn(bpy)(PSAc)^+$	0.16	0.28	0.91 ± 0.22[d]	48 ± 6[d]
37	$Zn(bpy)(MPSAc)^+$	0.18	0.30	1.00 ± 0.23[d]	50 ± 6[d]
38	$Zn(bpy)(NPSAc)^+$	0.13	0.25	0.78 ± 0.20[d]	44 ± 6[d]
39	$Zn(bpy)(Bz)^+$	0.05	0.17	0.48 ± 0.17[d]	32 ± 8[d]
40	$Zn(bpy)(MBz)^+$	0.05	0.17	0.48 ± 0.17[d]	32 ± 8[d]
41	$Zn(bpy)(NBz)^+$	0.03	0.15	0.41 ± 0.16[d]	29 ± 8[d]

[a-d] These footnotes are the same as those given in Table III. The above entry numbers are also the same as those used for the corresponding Cu^{2+} complexes in Table III. [e] Estimate; see comment in the legend for Figure 3.

of all the following points indicates strongly that also in the $M(phen)(Bz)^+$ complexes on intramolecular ligand/ligand interaction occurs:

(1) The points given by the stability constants of the binary $M(Bz)^+$ complexes and the acidity constants of H(Bz) fall within experimental error in all three solvents on the reference line furnished by the other carboxylates of Chart I (Figure 1 and ref 19). Hence, there is no increased stability, and this indicates that there is no special electronic effect due to the conjugation between the phenyl ring and the carboxylate group, which is only felt by the metal ion, but not by the proton. It is difficult to see why this should be different in the mixed-ligand complexes.

(2) If the intramolecular interaction in $Cu(phen)(Bz)^+$ occurs only via an edge of the phenyl ring of benzoate, substitution in the para position should for steric reasons disturb this interaction. Indeed, from entries 39–41 in Table III, which refer to 2,2'-bipyridyl complexes, it is evident that a methyl substituent reduces the stability of the ternary complex somewhat and that a nitro substituent, as one would expect, does so considerably more. The influence of these para substituents in benzoate on the stability of the Zn^{2+} complexes is much less pronounced (entries 39–41 in Table IV); a result that is also expected due to the different geometry of the coordination sphere. If the influence of the nitro group would occur via the phenyl ring on the carboxylate group, the Zn^{2+} complexes should be affected to about the same extent as the Cu^{2+} complexes.

(3) From X-ray studies it is known[1,31] that in the solid state hydrophobic interactions between an edge of a phenyl ring and another aromatic-ring system are possible; this means, in addition, that aromatic moieties do not necessarily have to be in a coplanar arrangement for an interaction: a simple hydrophobic interaction is possible in other orientations.

8. Influence of the Size of the Aromatic-Ring System on the Stability of the Intramolecular Stack. To see how the size of the aryl residue of the carboxylate ligand influences the stacking tendency, we have studied the binary and ternary Cu^{2+} and Zn^{2+}

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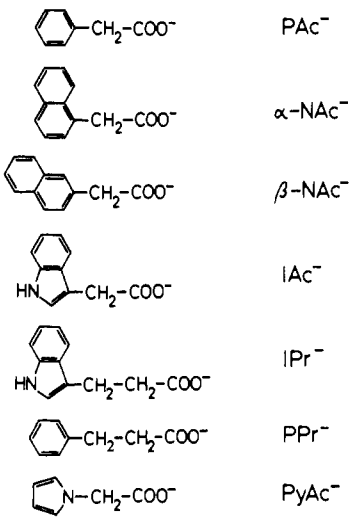
Table V. Influence of the Size of the Aromatic Residue of the Carboxylic Acid on the Extent of the Stacking Interaction in the Ternary $M(phen)(CA)^+$ Complex As Reflected in the Values for $\Delta \log K_M$ (Eq 6): Negative Logarithms of the Acidity Constants (Eq 2) of Several Carboxylic Acids and the Logarithms of the Corresponding Binary $M(CA)^+$ (Eq 3) and Ternary $M(phen)(CA)^+$ Complexes (Eq 4) in 50% (v/v) Aqueous Dioxane as Solvent (I = 0.1 M, and 25 °C)[a]

no.	CA^-	$pK^H_{H(CA)}$	$\log K^{Cu}_{Cu(CA)}$	$\log K^{Cu(phen)}_{Cu(phen)(CA)}$	$\Delta \log K_{Cu}$	$\log K^{Zn}_{Zn(CA)}$	$\log K^{Zn(phen)}_{Zn(phen)(CA)}$	$\Delta \log K_{Zn}$
1	$HCOO^-$	4.73 ± 0.02	2.79 ± 0.02	2.82 ± 0.02	0.03 ± 0.03	1.96 ± 0.01	1.82 ± 0.02	−0.14 ± 0.02
2	Ac^-	5.97 ± 0.01	3.31 ± 0.02	3.35 ± 0.01	0.04 ± 0.02	2.31 ± 0.01	2.15 ± 0.01	−0.16 ± 0.01
3	PAc^-	5.88 ± 0.01	3.22 ± 0.02	3.68 ± 0.04	0.46 ± 0.04	2.26 ± 0.02	2.29 ± 0.02	0.03 ± 0.03
4	α-NAc^-	6.06 ± 0.02	3.23 ± 0.02	3.91 ± 0.01	0.68 ± 0.02	2.33 ± 0.01	2.62 ± 0.01	0.29 ± 0.01
5	β-NAc^-	5.92 ± 0.01	3.20 ± 0.02	3.90 ± 0.03	0.70 ± 0.04	2.31 ± 0.02	2.45 ± 0.01	0.14 ± 0.02
6	IAc^-	6.38 ± 0.02	3.44 ± 0.05	4.13 ± 0.02	0.69 ± 0.05	2.48 ± 0.01	2.72 ± 0.01	0.24 ± 0.01
7	IPr^-	6.45 ± 0.01	3.43 ± 0.02	3.79 ± 0.02	0.36 ± 0.03	2.52 ± 0.02	2.63 ± 0.02	0.11 ± 0.03
8	PPr^-	6.18 ± 0.01	3.36 ± 0.01	3.64 ± 0.02	0.28 ± 0.02	2.36 ± 0.01	2.39 ± 0.01	0.03 ± 0.01
9	$PyAc^-$	4.75 ± 0.01	2.73 ± 0.01	3.07 ± 0.01	0.34 ± 0.01	1.92 ± 0.01	1.85 ± 0.01	−0.07 ± 0.01

[a] Regarding the error limits, see footnote *a* in Table I. I = 0.1 M was adjusted with $NaClO_4$ (entries 1–3, 5 and 8), $NaNO_3$ (entry 9), or KNO_3 (entries 4, 6, and 7). Entries 1–3 and 8 are from Table I.

Chart II



complexes of the arylalkanecarboxylates shown in Chart II. The corresponding equilibrium constants are given in Table V, and the evaluations regarding the intramolecular equilibria are summarized in entries 25–29 of Tables III and IV.

$Cu(phen)(PAc)^+$ is especially well suited for a high formation degree of the intramolecular stack, and its different properties compared with those of $Zn(phen)(PAc)^+$ are especially evident in 50% aqueous dioxane (Figure 3; Tables III and IV). Therefore, this solvent was selected and the phenyl residue of 2-phenylacetate (PAc^-) was replaced by a naphthyl residue, leading to 2-(α-naphthyl)acetate (α-NAc^-) and 2-(β-naphthyl)acetate (β-NAc^-) as ligands (Chart II, top).

Replacement of PAc^- in $Cu(phen)(PAc)^+$ and $Zn(phen)(PAc)^+$ by α-NAc^- increases $\Delta \log K_M$ by 0.22 and 0.26 log unit, respectively (cf. entries 3 and 4 in Table V); i.e., the stability increase is within experimental error the same and the formation degree of the intramolecular stack reaches now a remarkable 77 and 64%, respectively (entry 25 in Tables III and IV). Hence, α-NAc^- can be equally well accommodated in the ternary complexes of both metal ions; this is different with β-NAc^-. In $Cu(phen)(\beta\text{-}NAc)^+$ the steric conditions evidently still allow an optimal fit of the naphthyl residue on the phen ring system: $\Delta \log K_{Cu}$ increases again by 0.24 log unit (cf. entries 3 and 5 in Table V). In $Zn(phen)(\beta\text{-}NAc)^+$ (entry 5 in Table V) the additional stability increase amounts only to 0.11 log unit, and this probably indicates that the β-naphthyl residue reaches beyond the aromatic phen system.

9. Intramolecular Stacking Interactions with Aromatic Residues of Biological Interest. The phenyl residue is a part of the amino acid phenylalanine and is well able to form stacks with other suitable aromatic systems as we have seen in the preceding sections. In fact, there is evidence for phenylalaninate and the related tyrosinate as well that the phenyl ring is able to participate in ternary amino acid complexes in intramolecular hydrophobic and stacking interactions.[3,22]

Another aromatic-ring system of biological interest and with a size comparable to that of the naphthyl residue is the indole moiety. This group is a part of the amino acid tryptophan and plays an important role in stacking interactions with nucleotides and derivatives.[2,5,30] Therefore, we have included in our studies 3-indoleacetate (IAc^-), which has steric requirements similar to those of 2-(α-naphthyl)acetate (Chart II). Indeed, the formation degrees of the intramolecular stacks are quite similar (entries 25 and 27 in Tables III and IV) for the two Cu^{2+} complexes (78 and 77%) as well as for the two Zn^{2+} complexes (59 and 64%), and the replacement of PAc^- by IAc^- in $M(phen)(PAc)^+$ results in an increase of the $\Delta \log K_M$ values by 0.23 and 0.21 log unit for the Cu^{2+} and Zn^{2+} complexes (entries 3 and 6 in Table V); this result corresponds closely to that obtained with α-NAc^-.

By comparing 2-phenylacetate (PAc^-) and 3-phenylpropionate (PPr^-), we have seen (Figure 3) that the increase of the alkyl part, i.e. the addition of one methylene group, decreases the stacking intensity in 50% aqueous dioxane considerably. The same is observed with 3-indoleacetate (IAc^-) and 3-indolepropionate (IPr^-; Chart II) (cf. entries 6 and 7 in Table V); the latter ligand differs from tryptophan only by the absence of the α-amino group.[32] However, the IPr^- complexes of Cu^{2+} and Zn^{2+} show again analogous properties: replacement of PPr^- in $M(phen)(PPr)^+$ by IPr^- leads still to an additional increase in $\Delta \log K_M$, though only by 0.08 log unit (entries 7 and 8 in Table V), which corresponds to a further increase in the formation degree of about 10% (entries 21 and 28 in Tables III and IV); hence, the stacked isomer reaches 52% for $Cu(phen)(IPr)^+$ and 45% for $Zn(phen)(IPr)^+$.

The imidazole residue of histidine is another aromatic ring system that may undergo stacking with nucleotides and their derivatives.[33,34] However, to obtain a quantitative insight into the stacking properties of the five-membered imidazole ring in the presence of metal ions is a difficult matter, though some data exist.[3] The difficulty is that the pyridine-like nitrogen of the imidazole ring has a rather pronounced tendency to coordinate metal ions,[28] and this reaction interferes easily with the formation of stacks or, at least, makes their detection more difficult. To overcome this problem, we selected another aromatic five-membered ring as a model system, namely a pyrrole derivative: 1-pyrroleacetate ($PyAc^-$) can coordinate to metal ions only via the

(32) (a) There is no doubt that an indole/aromatic-ring stacking contributes also to the stability of Cu(bpy or phen)(tryptophanate)$^+$ complexes in contrast to a recent conclusion "that the charge transfer interaction...may not contribute to the positive $\Delta \log K$ values".[32b] It must further be pointed out that small or partial aromatic-ring overlaps as they may occur in Cu(phen)(phenylalaninate)$^+$ are strong enough to be reflected in the stability of the complexes (see also part 7 and ref 22). (b) Bhattacharya, P. K.; Patel, V. K. *J. Indian Chem. Soc.* **1982**, *59*, 1244–1246.

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Table VI. Indirect Evidence for a Charge Transfer within the Stack of the Ternary $M(A)(CA)^+$ Complexes As Indicated by the Values for Δ log K_M (Eq 6): Negative Logarithms of the Acidity Constants (Eq 2) of Several Carboxylic Acids and Logarithms of the Corresponding Binary $M(CA)^+$ (Eq 3) and Ternary $M(A)(CA)^+$ Complexes (Eq 4) in 50% (v/v) Aqueous Dioxane as Solvent (I = 0.1 ($NaClO_4$), 25 °C)[a]

no.	A	CA^-	$pK^H_{H(CA)}$	log $K^{Cu}_{Cu(CA)}$	log $K^{Cu(A)}_{Cu(A)(CA)}$	Δ log K_{Cu}	log $K_{Zn(CA)}$	log $K^{Zn(A)}_{Zn(A)(CA)}$	Δ log K_{Zn}
1	phen	$HCOO^-$	4.73 ± 0.02	2.79 ± 0.02	2.82 ± 0.02	0.03 ± 0.03	1.96 ± 0.01	1.82 ± 0.02	−0.14 ± 0.02
2	phen	Ac^-	5.97 ± 0.01	3.31 ± 0.02	3.35 ± 0.01	0.04 ± 0.02	2.31 ± 0.01	2.15 ± 0.01	−0.16 ± 0.01
3	phen	PAc^-	5.88 ± 0.01	3.22 ± 0.02	3.68 ± 0.04	0.46 ± 0.04	2.26 ± 0.02	2.29 ± 0.02	0.03 ± 0.03
4	phen	$NPAc^-$	5.27 ± 0.01	2.93 ± 0.02	3.19 ± 0.02	0.26 ± 0.03	2.01 ± 0.02	2.08 ± 0.01	0.07 ● 0.02
5	phen	$MOPAc^-$	5.96 ± 0.01	3.28 ± 0.02	3.78 ± 0.03	0.50 ± 0.04	2.28 ± 0.02	2.35 ± 0.01	0.07 ± 0.02
6	phen	$TMOPAc^-$	5.78 ± 0.01	3.13 ± 0.01	3.63 ± 0.02	0.50 ± 0.02	2.21 ± 0.02	2.33 ± 0.02	0.12 ± 0.03
7	bpy	$HCOO^-$	4.75 ± 0.01	2.80	2.84	0.04	1.97	1.83	−0.14
8	bpy	Ac^-	6.01 ± 0.01	3.36	3.51	0.15	2.32	2.21	−0.11
9	bpy	PPr^-	6.17 ± 0.01	3.37	3.75	0.38	2.39	2.50	0.11
10	bpy	$PSAc^-$	5.05 ± 0.01	2.89	3.53	0.64	2.04	2.20	0.16
11	bpy	$MPSAc^-$	5.17 ± 0.01	3.01	3.61	0.60	2.04	2.22	0.18
12	bpy	$NPSAc^-$	4.54 ± 0.02	2.59	2.95	0.36	1.78	1.91	0.13
13	bpy	Bz^-	5.79 ± 0.01	3.30	3.58	0.28	2.35	2.40	0.05
14	bpy	MBz^-	6.02 ± 0.01	3.44	3.66	0.22	2.43	2.48	0.05
15	bpy	NBz^-	4.64 ± 0.01	2.76	2.88	0.12	1.83	1.86	0.03

[a] Regarding the given error limits, see footnote *a* in Table I; in those cases where no error limit is given with the stability constants, the reproducibility was ±0.05 log unit or better. Entries 1–3 are from Table I and 7–15 from the literature: ref 38 (entries 7, 8 and 13–15), ref 16 (entries 9–11), and ref 14b (entry 12).

carboxylate group and resembles closely, aside from the aromatic ring, 2-phenylacetate (PAc^-) (Chart II).

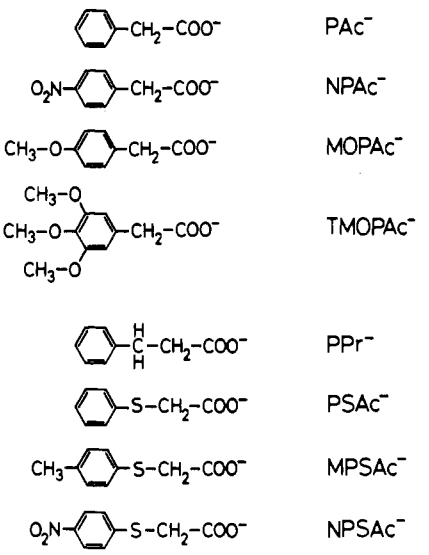
The stacking properties of $PyAc^-$ and PAc^- may therefore be compared: Replacement of PAc^- in $M(phen)(PAc)^+$ by $PyAc^-$ reduces Δ log K_M of the Cu^{2+} and Zn^{2+} complexes in 50% aqueous dioxane by 0.12 and 0.10 log unit (entries 3 and 9 in Table V); i.e., the geometry of the coordination sphere of the metal ion has no significant influence on the extent of the decrease in stacking, and this suggests that the decrease is governed by the reduction of the ring size. However, it should be emphasized that of Zn(phen)$(PyAc)^+$ and Cu(phen)$(PyAc)^+$ still about 17 and 50%, respectively, exist in the stacked form (entry 29 in Tables III and IV).

To a first approximation one may certainly assume that the stacking tendency of an imidazole residue will be similar to that described here for the pyrrole group. Hence, one may conclude that the tendency to form intramolecular stacks in ternary complexes decreases for the following amino acid residues in the series indole > phenyl > imidazole.

10. Evidence for Charge-Transfer Interactions in Intramolecular Stacks. The formation of stacking adducts is usually connected with π/π interactions between the aromatic systems forming the stack. These π/π interactions are often signaled by the appearance of new bands in the UV/visible spectrum due to charge-transfer transitions,[35,36] though stacks without a detectable charge-transfer absorption may also be formed.[37] However, in the present study such absorption bands have been used to determine the stability of binary stacks formed between 2-(*p*-methoxyphenyl)acetate and 1,10-phenanthroline (part 1) or carboxymethyl phenyl sulfide and 2,2′-bipyridyl.[16]

As in a charge transfer one of the aromatic systems acts as electron donor and the other as acceptor, one may hope to influence the stability of the corresponding adduct by introducing electron-withdrawing or electron-donating substituents. By taking care that no substituents with a remarkable affinity toward metal ions were chosen, we selected the arylalkanecarboxylates shown in Chart III to study the influence of substituents, which alter the electron density. The constants of the binary $M(ArCA)^+$ and ternary $M(phen)(ArCA)^+$ complexes containing the phenylacetate derivatives and Cu^{2+} or Zn^{2+} were measured; the values for the lower four carboxylates of Chart III and their ternary complexes

Chart III



with 2,2′-bipyridyl were taken from our earlier work.[16] The equilibrium constants for all these systems in 50% aqueous dioxane are listed in Table VI; the evaluations regarding intramolecular equilibrium 7a are given in entries 30–38 of Tables III and IV. For the Zn/phen/NPac and -MOPAc systems the formation of the stacked isomer has also directly been proven by ^1H NMR shift experiments: the expected *upfield* shifts are observed ($\Delta\delta \simeq 0.2$ ppm).

Evidently, substitution of an electron-withdrawing nitro group into the para position of 2-phenylacetate lowers the value for Δ log K_{Cu} considerably (compare entries 3 and 4 in Table VI); the same observation is made with carboxymethyl phenyl sulfide ($PSAc^-$) and its nitro derivative (entries 10 and 12 in Table VI). In both nitro-substituted Cu^{2+}-bridged stacks the formation degree is reduced by about 20% (cf. entry 20 with 30, and entry 36 with 38, in Table III). The influence of the (weakly) electron-donating substituents, i.e. methyl and methoxy, is rather small; the only significant influence occurs if the methylene group next to the phenyl ring in 3-phenylpropionate (PPr^-) is replaced by a sulfur atom, which leads to carboxylatomethyl phenyl sulfide ($PSAc^-$; see Chart III) and a significant promotion of the stacking degree (Tables III and VI). It should be emphasized that the sulfur atoms in the ligands of entries 10–12 in Table VI (and entries 36–38 in Tables III and IV) do *not* participate in complex formation, as was shown earlier.[16]

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The results indicated in the last paragraph for the Cu^{2+} systems seem to hold also for those with Zn^{2+} as far as this can be judged, because the observed differences are smaller. This seems to be generally true for Zn^{2+} complexes in 50% aqueous dioxane (Figure 3), but a further possible reason for this apparently different behavior could be the weaker interaction between the π systems of 1,10-phenanthroline or 2,2′-bipyridyl and Zn^{2+} with its d^{10} electron configuration; in the case of Cu^{2+}, phen and bpy act as π acceptors.[39]

Overall it appears that the aryl residues of the ligands in Chart III presumably act as electron donors and 1,10-phenanthroline and 2,2′-bipyridyl are acceptors in the π/π interactions within the intramolecular stacks.

General Conclusions

That organic molecules with two aromatic-ring systems which are linked together by an aliphatic chain may favor in solution a folded configuration is well-known and has been shown, e.g., for a series of 2-arylethyl *p*-toluenesulfonates[37] and many other molecules allowing an intramolecular aryl/aryl interaction.[40,41] It is also known that the distance between the aromatic residues has an influence on the properties of such aryl/aryl molecules: e.g., the pyrene–$(CH_2)_n$–pyrene systems were studied for a large number of *n* values, and it was observed that the intramolecular interaction was most pronounced for $n = 3$.[42,43]

The spacing of two aromatic-ring moieties by a trimethylene bridge has been well exploited.[44] For example, in aqueous solution interactions are observable between bridged nucleic acid bases, like 9-substituted adenine or guanine, or 1-substituted cytosine, thymine, or uracil residues.[44] The trimethylene bridge is probably most suitable because it is the shortest link allowing a stacked arrangement of the aromatic planes with a distance of about 3.4 Å; this distance has often been observed in the solid state[1,29,30,45] between aromatic-ring systems.

It is interesting to view the present results in connection with the above observations. The highest formation degree of the intramolecular stack is obtained in the ternary $M(phen)(PAc)^+$ and (usually to a somewhat smaller extent) $M(phen)(PPr)^+$ complexes (Figure 3; Tables III and IV). This means that the following atoms form the link between the aromatic moieties (Figure 2): one M^{2+}, one O, and two (or three) C. Hence, the most suitable linking chain contains in the case of ternary metal ion complexes in total four (or five) atoms, in contrast to the three C atoms observed for the alkyl link in pure organic molecules. This difference is understandable, because the metal ion coordinates to 1,10-phenanthroline in the plane of the aromatic-ring system (Figure 2) and contributes little (Zn^{2+}) or nothing (Cu^{2+}) to shorten the link of the aryl residue that forms the stack. Thus, overall the situation is comparable in metal ion bridged and purely alkyl-linked stacking adducts.

A remarkable property that seems to be connected with the participation of a metal ion in the formation of the stack is indicated by the results of Tables III and IV: addition of ethanol or dioxane to an aqueous solution may promote the formation degree of an intramolecular stack. This observation is interesting and warrants further studies,[25] because the experience[15] with (purely organic) unbridged binary stacks is that addition of ethanol or dioxane inhibits stacking.

Another point of general interest is the influence of the geometry of the coordination sphere of the bridging metal ion on the extent of stacking. The metal ion may impose certain steric restrictions and influence thus the orientation of the coordinated ligating groups that carry the aromatic moieties forming the intramolecular stack. This type of orientation could be important, e.g., in metalloenzyme/substrate interactions.

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Registry No. Ethanol, 64-17-5; dioxane, 123-91-1.

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Contribution from the Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

^{13}C NMR Study of Nickel(II) Amino Carboxylate Binding†

R. F. EVILIA

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The ^{13}C NMR spectra of a variety of nickel(II) amino carboxylate complexes are reported and analyzed. The spectra are interpreted to indicate that the solution structure of $Ni(EDTA)^{2-}$ is approximately 32% pentadentate at probe ambient temperature (~28 °C) with rapid (lifetime <3 μs) pentadentate ⇌ hexadentate equilibrium. The solution structure of $Ni(PDTA)^{2-}$ is found to be 17% pentadentate, with only the in-plane acetate on the side opposite the methyl involved in the equilibrium. No evidence for any pentadentate CYDTA is found. The thermodynamic properties of the hexadentate ⇌ pentadentate equilibria of EDTA and PDTA are found to be $\Delta H = -14.2$ kJ mol^{-1}, $\Delta S = -58.5$ J mol^{-1} K^{-1} and $\Delta H = -9.2$ kJ mol^{-1}, $\Delta S = -43$ J mol^{-1} K^{-1}, respectively. These values lead to the conclusion that the mole fraction of either form of the complex is a sensitive function of temperature when the temperature is close to normal ambient conditions. At low temperature, the pentadentate form predominates, and at high temperature, the hexadentate form predominates. The temperature and ionic strength dependence of the equilibrium are believed to be responsible for the large number of contradictory conclusions regarding the coordination of EDTA.

Introduction

The question of whether EDTA functions as a hexadentate or pentadentate ligand has been studied by a wide variety of investigators utilizing an equally wide variety of techniques.[1-13] The conclusions of many of these studies have, however, been con-

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