Ternary Complexes in Solution.[1-3] Influence of Organic Solvents on Intramolecular Aromatic-Ring Stacks in Aqueous Mixed-Ligand Metal Ion Complexes. Opposing Solvent Effects

Helmut Sigel,* Raman Malini-Balakrishnan, and Ulrich K. Häring

Contribution from the Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland. *Received December 20, 1984*

Abstract: The stability constants of mixed-ligand complexes of the type M(phen)(PheCA)$^+$, where M = Cu^{2+} or Zn^{2+}, phen = 1,10-phenanthroline, and PheCA$^-$ = 2-phenylacetate (PAc$^-$) or 3-phenylpropionate (PPr$^-$), have been determined by potentiometric pH titration in aqueous solution, in 30–90% (v/v) ethanol–water and in 10–90% (v/v) dioxane–water, and compared with the stabilities of the corresponding ternary complexes formed with formate or acetate (Ac$^-$). The ternary complexes containing phenylalkanecarboxylates (PheCA$^-$) are significantly more stable due to intramolecular stacking (see below) between the phenyl residue of PheCA$^-$ and the 1,10-phenanthroline molecule. The presence of stacking has also been confirmed by ^{1}H NMR measurements in several aqueous dioxane mixtures for Zn(phen)(PAc)$^+$. The extent of the ligand–ligand interaction in the ternary Cu^{2+} and Zn^{2+} complexes was calculated, and the position of the intramolecular equilibrium between the open and the closed species was determined: the latter occur between about 20 and 60%. There are indications, and these are discussed, that the structure of the closed species may be solvent-dependent: in water, an intramolecular stack is formed, while in the mixed solvents, in addition, probably a series of structurally somewhat different (orientation of the aromatic rings, degrees of solvation and/or coordination number) closed species may occur. As there is at present no way to identify with certainty such different structures, the whole observed stability increase between M(phen)(PheCA)$^+$ and M(phen)(Ac)$^+$ or M(Phen)(HCOO)$^+$ was simply attributed to a (single) so-called "closed" species, which is however possibly a mixture of complexes. The formation degree of the closed species is influenced by the solvent: *addition of some ethanol or dioxane to an aqueous solution favors their formation.* This result is in contrast to the experience made with binary and unbridged ternary stacking adducts: these are *destabilized* by the addition of any ethanol or dioxane. Such a destabilization of the closed species in the ternary complexes occurs only at high concentrations of the organic solvent (usually more than 70%). Evidence is given that the overall stability of the interaction between M^{2+} and PheCA$^-$ is governed by the polarity of the solvent, while the position of the intramolecular equilibrium is influenced by the hydrophobic properties of the solvent molecules. It is also pointed out that a metal ion bridge between components forming a stack or a hydrophobic adduct promotes the formation of this adduct very dramatically. The relevance of the present results with regard to biological systems is discussed, and the high stability of the complex formed between carboxypeptidase A (CPA) and 3-phenylpropionate is explained by a "cooperative mechanism": The accommodation of the phenyl(alkyl) residue of PPr$^-$ in the hydrophobic pocket of CPA enhances not only the complex stability but it decreases also the polarity at the active site, and this promotes then further the interaction between the intrinsic Zn^{2+} and the carboxylate group.

Aromatic-ring stacking is known to facilitate under certain conditions substitution reactions at metal ions,[4] and it is also one type of the important noncovalent interactions occurring in biological systems.[5,6] These aromatic-ring stacks contribute to the stability of nucleic acids and proteins, and they govern to a significant part the interplay between nucleic acids and proteins[7] or between enzymes and nucleotide substrates.[8] Metal ions participate also in these reactions; e.g., DNA and RNA polymerases are metalloenzymes,[9,10] and many nucleotides are active substrates only in the presence of divalent metal ions.[10,11] Consequently, mixed-ligand complexes between nucleotides and amino acids are receiving more and more attention,[12-16] and it has indeed been shown that metal ions are able to promote hydrophobic and stacking interactions between suitable side chains of amino acids and the nucleic base moieties of nucleotides.[17]

Though these last-mentioned mixed-ligand complexes are undoubtedly of great interest, it is rather difficult to study systematic variations in ligand structures on the extent of stacking interactions, e.g., with amino acids or nucleotides. We have therefore turned for the present to more simple model systems which consist of 1,10-phenanthroline, Cu^{2+} or Zn^{2+}, and phenylalkanecarboxylates.[18,19] By employing Cu^{2+} with its tetragonal coordination sphere (i.e., with four nearby donor atoms arranged equatorially around the metal ion with the possibility of one or two more distant axial donors)[20] and Zn^{2+} with its tetrahedral or octahedral structure, by replacing the phenyl residue in the mentioned carboxylates by other aryl moieties, and by varying the number of methylene groups between the coordinating carboxylate group and the phenyl ring undergoing stacking, one can learn much about the optimal conditions for the formation of

(1) This is part 48 of the series; for parts 47 and 46, see ref 2 and 3.
(2) Tribolet, R.; Malini-Balakrishnan, R.; Sigel, H. *J. Chem. Soc., Dalton Trans.*, in press.
(3) Sigel, H.; Tribolet, R.; Scheller, K. H. *Inorg. Chim. Acta* **1985**, *100*, 151-164.
(4) (a) Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, *1002*-1004. (b) Margerum, D. W. *A.C.S. Symp. Ser.* **1982**, *No. 198*, 3-38.
(5) Frieden, E. *J. Chem. Educ.* **1975**, *52*, 754-761.
(6) Scheraga, H. A. *Acc. Chem. Res.* **1979**, *12*, 7-14.
(7) Hélène, C.; Lancelot, G. *Prog. Biophys. Mol. Biol.* **1982**, *39*, 1-68.
(8) (a) Vašák, M.; Nagayama, K.; Wüthrich, K.; Mertens, M. L.; Kägi, J. H. R. *Biochemistry* **1979**, *18*, 5050-5055. (b) Jallon, J. M.; Risler, Y.; Schneider, C.; Thiery, J. M. *FEBS Lett.* **1973**, *31*, 251-255. (c) Yoshino, H.; Morita, F.; Yagi, K. *J. Biochem. (Tokyo)* **1972**, *72*, 1227-1236.
(9) (a) Slater, J. P.; Mildvan, A. S.; Loeb, L. A. *Biochem. Biophys. Res. Commun.* **1971**, *44*, 37-43. (b) Scrutton, M. C.; Wu, C. W.; Goldthwait, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 2497-2501. (c) Regarding Zn^{2+} in *Escherichia coli* DNA polymerase I see: Graham, D. R.; Sigman, D. S. *Inorg. Chem.* **1984**, *23*, 4188-4191.
(10) (a) Eichhorn, G. L. *Met. Ions Biol. Syst.* **1980**, *10*, 1-21. (b) Wu, F. Y.-H.; Wu, C.-W. *Met. Ions Biol. Syst.* **1983**, *15*, 157-192.
(11) (a) Cooperman, B. S. *Met. Ions Biol. Syst.* **1976**, *5*, 79-126. (b) Marzilli, L. G. *Prog. Inorg.* Chem. **1977**, *23*, 255-378. (c) Mildvan, A. S. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1979**, *49*, 103-126.
(12) (a) Naumann, C. F.; Sigel, H. *FEBS Lett.* **1974**, *47*, 122-124. (b) Sigel, H.; Naumann, C. F. *J. Am. Chem. Soc.* **1976**, *98*, 730-739. (c) Mitchell, P. R.; Prijs, B.; Sigel, H. *Helv. Chim. Acta* **1979**, *62*, 1723-1735.
(13) Sigel, H. In "Coordination Chemistry-20"; Banerjea, D., Ed.; Pergamon Press (IUPAC): Oxford and New York, 1980; pp 27-45.
(14) Saha, N.; Sigel, H. *J. Am. Chem. Soc.* **1982**, *104*, 4100-4105.
(15) (a) Vestues, P. I.; Martin, R. B. *Inorg. Chim. Acta* **1981**, *55*, 99-101. (b) Basosi, R.; Gaggelli, E.; Tiezzi, E. *J. Chem. Res., Synop.* **1977**, 278-279.
(16) (a) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1983**, 1271-1278. (b) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1984**, 1651-1658.
(17) Sigel, H.; Fischer, B. E.; Farkas, E. *Inorg. Chem.* **1983**, *22*, 925-934.
(18) Dubler, E.; Häring, U. K.; Scheller, K. H.; Baltzer, P.; Sigel, H. *Inorg. Chem.* **1984**, *23*, 3785-3792.
(19) Malini-Balakrishnan, R.; Scheller, K. H.; Häring, U. K.; Tribolet, R.; Sigel, H. *Inorg. Chem.* **1985**, *24*, 2067-2076.
(20) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385-426.

0002-7863/85/1507-5137$01.50/0

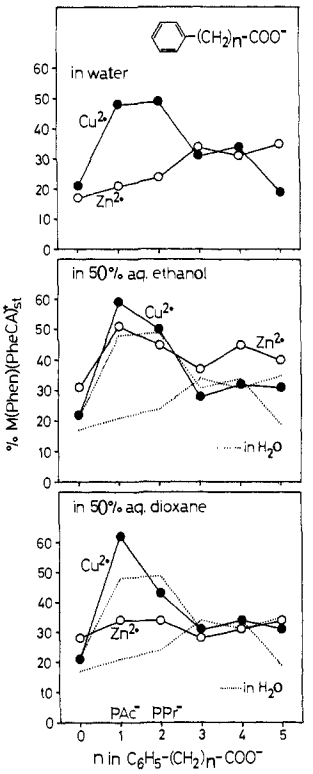


Figure 1. Dependence of the formation degree of the intramolecularly closed species in ternary M(phen)(PheCA)$^+$ complexes (eq 1) of Cu^{2+} (●) and Zn^{2+} (○) in water (top), 50% (v/v) aqueous ethanol (middle), and 50% (v/v) aqueous dioxane (bottom) on the number of methylene groups present in phenylalkanecarboxylates (the formula is shown in the upper right-hand corner). The situation in water is repeated by dotted lines in the middle and lower parts to facilitate comparisons. The data are taken from Tables III and IV of ref 19 (I = 0.1; 25 °C). The average error of the plotted percentages is ±4 (*3 times* the standard error; for details see ref 19). Note, here and in Figures 4 and 7–9, %M(phen)-(PheCA)$_{cl}^+$ is based on [M(phen)(PheCA)$^+$]$_{tot}$ = 100%.

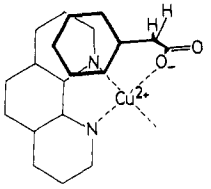
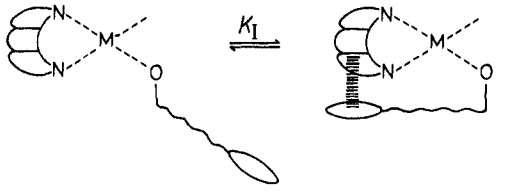


Figure 2. Possible (schematic) structure of a stacked isomer of M(phe)(PAc)$^+$ in solution.

intramolecular stacks in ternary complexes.[19]

A part of these previous results is summarized in Figure 1 and a schematic structure of one of these stacked M(phen)(PheCA)$^+$ complexes[21] in aqueous solution is shown in Figure 2. It is evident from Figure 1 that an intramolecular equilibrium exists between an "open" and a "closed" form, i.e., M(phen)(PheCA)$_{op}^+$ and M(phen)(PheCA)$_{cl}^+$ (for details see ref 22):



(1)

$$K_I = [M(phen)(PheCA)_{cl}^+]/[M(phen)(PheCA)_{op}^+] \quad (2)$$

$$= \frac{10^{\Delta \log K_{(M/phen/PheCA)}}}{10^{\Delta \log K_{(M/phen/PhenCA)op}}} - 1 \quad (3)$$

The constants $10^{\Delta \log K_M}$ refer to equilibrium 4, and they are cal-

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

culated with eq 5[23] on the basis of eq 6 and 7. The intramolecular

$$\Delta \log K_M = \log K^{M(phen)}_{M(phen)(CA)} - \log K^M_{M(CA)} \quad (5)$$

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

$$K^M_{M(CA)} = [M(CA)^+]/[M^{2+}][CA^-] \quad (6)$$

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

$$K^{M(Phen)}_{M(Phen)(CA)} = [M(phen)(CA)^+]/[M(phen)^{2+}][CA^-] \quad (7)$$

and dimensionless equilibrium constant K_I (eq 1 and 2) may now be calculated (eq 3) by using for $\Delta \log K_{(M/phen/PheCA)}$ the value of $\Delta \log K_M$ (eq 5) determined for a given M^{2+}/phen/PheCA system and for $\Delta \log K_{(M/phen/PheCA)_{op}}$ the average of the $\Delta \log K_M$ values measured for the corresponding M^{2+}/phen/formate or acetate systems, in which no (or at least no significant) intramolecular ligand–ligand interactions occur.[19]

Based on potentiometric pH titrations, we have recently determined the necessary stability constants (eq 6 and 7) for several systems and calculated the values of K_I (eq 2), and from these, the percentages for M(phen)(PheCA)$_{cl}^+$ were obtained.[19] Two of the previous observations are important for the present context (Figure 1): (i) The "best fit", in the sense that the strongest intramolecular interaction arises, is clearly obtained with 2-phenylacetate (Figure 2) and, though usually somewhat less pronounced, with 3-phenylpropionate. (ii) The influence of the solvents is very surprising: addition of ethanol or dioxane to an aqueous solution apparently favors under certain conditions the stability of these ternary complexes (see middle and bottom parts of Figure 1). This latter point is interesting because the addition of organic solvents, like ethanol or dioxane, to an aqueous solution containing binary and unbridged stacking adducts reduces the stability of such adducts significantly.[2,24-26] The mentioned point ii warrants therefore further studies, and we have now carried out these by taking into account the results summarized in point i.

A more detailed consideration of the indicated problem seems of general interest, because one expects that solvent polarity is reduced on the surface of proteins and in the active-site cavities of enzymes;[27] in fact, there is good evidence that the equivalent solution dielectric constant is indeed reduced in such cavities.[28] Clearly, if this should also mean that stacking and hydrophobic interactions are not significantly affected, i.e., are not strongly decreasing, this would provide a much better understanding why, e.g., 3-phenylpropionate and related substances are such excellent inhibitors of carboxypeptidase A.[29,30] We have therefore determined the stability of the mixed-ligand complexes composed of Cu^{2+} or Zn^{2+}, 1,10-phenanthroline (phen), and 2-phenylacetate

(21) Abbreviations: Ac$^-$, acetate; ATP^{4-}, adenosine 5′-triphosphate; BzOH, benzyl alcohol; CA$^-$, carboxylate ligand; CPA, carboxypeptidase A; Leu$^-$, L-leucinate; M^{2+}, general divalent metal ion; MOPAc$^-$, 2-(*p*-methoxyphenyl)acetate; PAc$^-$, 2-phenylacetate; PheCA$^-$, phenylalkanecarboxylates, like PAc$^-$ or PPr$^-$; phen, 1,10-phenanthroline; PPr$^-$, 3-phenylpropionate; UTP^{4-}, uridine 5′-triphosphate.

(22) Fischer, B. E.; Sigel, H. *J. Am. Chem. Soc.* **1980**, *102*, 2998–3008.

(23) Usually the difference of eq 5 is referred to as $\Delta \log K_M$; only in those cases where further identification is needed are additional subscripts given, like $\Delta \log K_{(M/phen/PheCA)}$.

(24) Farzami, B.; Mariam, Y. H.; Jordan, F. *Biochemistry* **1977**, *16*, 1105–1110.

(25) Connors, K. A.; Sun, S.-r. *J. Am. Chem. Soc.* **1971**, *93*, 7239–7244.

(26) (a) Granot, J. *J. Am. Chem. Soc.* **1978**, *100*, 6745–6749. (b) Fornili, S. L.; Sgroi, G.; Izzo, V. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1085–1090.

(27) (a) Vallee, B. L.; Williams, R. J. P. *Chem. Br.* **1968**, *4*, 397–402. (b) Rees, D. C. *J. Mol. Biol.* **1980**, *141*, 323–326.

(28) Sigel, H.; Martin, R. B.; Tribolet, R.; Häring, U. K.; Malini-Balakrishnan, R. *Eur. J. Biochem.*, in press.

(29) Bunting, J. W.; Myers, C. D. *Can. J. Chem.* **1973**, *51*, 2639–2649.

(30) Bertini, I.; Luchinat, C. *Met. Ions Biol. Syst.* **1983**, *15*, 101–156.

Table I. Stability Constants (eq 10) of Some Stacking Adducts and Influence of Dioxane (D) or Ethanol (E) by Addition to an Aqueous Solution (W) on the Stability of These Adducts[a]

adduct of	method	°C	solvent	%E or %D	mol fract	$K^{(A)}_{(A)(B)}$, M^{-1}	ref
$Zn(Phen)^{2+}$/BzOH	^1H NMR	34	W (I = 0.25–0.5, $NaNO_3$)	0	0	2.2 ± 0.2	18
	^1H NMR	34	D/W (I = 0.25–1.3, $NaNO_3$)	50 (v/v)	0.175	0.42 ± 0.09	
	^1H NMR	34	D/W (I = 0.25–0.6, $NaNO_3$)	80 (v/v)	0.459	<0.1	
trans-cinnamate methyl	several[c]	25	D/W (I = 0.3, KCl)[d]	0.81 (w/w)	0.0017	19.2	25
ester/1,3-dimethylxanthine[b]	several[c]	25	D/W (I = 0.3, KCl)[d]	40.47 (w/w)	0.139	5.3	25
tryptophan/thiamin chloride	UV	30	W (I = 1.0; pH 5.0)	0	0	4.4	24
	UV	30	E/W (I = 1.0; pH 5.0)	50 (v/v)	0.237	0.74	24

[a] The range of error is *3 times* the standard deviation. [b] 1,3-Dimethylxanthine = theophylline. [c] Spectral, solubility, and kinetic techniques.[25] [d] pH 6.6, phosphate buffer.

(PAc^-) or 3-phenylpropionate (PPr^-) in dependence on the amount of ethanol or dioxane added to an aqueous solution containing the mentioned reactants.

Experimental Section

Materials. The carboxylate ligands and all other materials were the same as used in ref 18 and 19. The stock solutions were also prepared as described.[18]

Potentiometric pH Titrations. The potentiometric pH titrations were carried out under a nitrogen atmosphere as described (I = 0.1; 25 °C).[18,19] 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.[31-33] The concentrations used[18,28] in the potentiometric titrations and the determination of the equilibrium constants, including their calculation, was done as before.[18] This means always that a pair of titration curves obtained by titrating corresponding solutions in the presence and absence of ligand was evaluated; in other words, the titration curve of the strong acid (HNO_3 or $HClO_4$) was not calculated but each time determined experimentally.

In all solutions for the potentiometric titrations, the ionic strength was adjusted to I = 0.1. At the beginning of the project, we had used for this adjustment $NaClO_4$, but this salt required time-consuming "reactivation" treatments of the electrodes and was therefore replaced by KNO_3 as an inert salt. Unfortunately, in 80% and 90% aqueous dioxane, KNO_3 is not enough soluble and therefore we had to change to $NaNO_3$. However, for several of the systems, we have checked that the kind of inert salt used has no influence on the results (cf. Table III).

^1H NMR Spectroscopy. The ^1H NMR spectra were recorded on a Varian Anaspect EM-360 spectrometer (60 MHz) at 34 °C, using the center peak of the tetramethylammonium ion triplet as internal reference. However, all chemical shifts were converted to a 3(trimethylsilyl)-propanesulfonate reference by adding the shift differences between the two references, which were determined in separate experiments for all solvent mixtures. (Trimethylsilyl)propanesulfonate is not directly usable as reference due to its hydrophobic interaction with Zn^{2+}/phen.[34]

The experiments with the Zn^{2+}/phen/BzOH and PAc systems were carried out as described[18] at pH 5.20 (see Tables I and IV). The observed upfield shifts were plotted in dependence on the increasing concentration of Zn^{2+}/phen (Figure 3) and analyzed with a Hewlett-Packard 9825A calculator (connected with a plotter 7470A) by a curve-fit procedure using a Newton-Gauss nonlinear least-squares program. The calculation was based on the definition given in eq 8 for the observed chemical shift

$$\delta_{obsd} = \frac{\delta_{PAc}([PAc^-] + [H(PAc)]) + \delta_{Zn(phen)(PAc)}[Zn(phen)(PAc)^+]}{[PAc]_{tot}} \quad (8)$$

(δ_{obsd}) and the mass action law (see also ref 22); the chemical shift and the apparent stability constant, K_{app}, for the ternary $Zn(phen)(PAc)^+$ complex were obtained. This apparent stability constant is valid only at pH 5.20 and had to be transformed to the pH-independent constant (Table IV) by taking into account the competition of the proton[35] for PAc^- with eq 9.

$$\log K^{Zn(phen)}_{Zn(phen)(PAc)} = \log K_{app} + \log (1 + [H^+]/K^H_{H(PAc)}) \quad (9)$$

Results and Discussion

1. Influence of Organic Solvents on the Stability of Binary and Unbridged Ternary Stacking Adducts. The stability of binary adducts consisting of purely organic moieties is decreased by the addition of ethanol or dioxane to an aqueous solution of the corresponding species.[2,24,25] To see if the incorporation of a charge by a coordinated metal ion alters these observations, we have determined by ^1H NMR shift experiments the influence of increasing amounts of dioxane on the stability of the stack formed between Zn(1,10-phenanthroline)$^{2+}$ and benzyl alcohol (BzOH); i.e., we have measured in several solvent mixtures the position of equilibrium 10a, which may in a more general form also be written

$$Zn(phen)^{2+} + BzOH \rightleftharpoons [Zn(phen)](BzOH)^{2+} \quad (10a)$$

as eq 10b.

$$A + B \rightleftharpoons (A)(B) \quad (10b)$$

$$K^{(A)}_{(A)(B)} = [(A)(B)]/[A][B]$$

Binary stacking adducts between a phenyl residue and the aromatic-ring systems of 1,10-phenanthroline or 2,2′-bipyridyl have been observed before.[19,36] The upfield shifts expected upon stack formation according to equilibrium 10a were now also observed.[37] The results of the NMR experiments are listed in Table I together with some other representative stacking adducts.[24,25,38]

It is evident that the metal-ion containing ternary but unbridged stacking adduct (eq 10a) shows the same properties upon addition of an organic solvent as the binary metal-free stacks: increasing amounts of organic solvents like dioxane or ethanol are clearly *destabilizing* unbridged stacks.

(31) Agrawal, Y. K. *Talanta* **1973**, *20*, 1354–1356.
(32) Bates, R. G. "Determination of pH: Theory and Practice"; Wiley: New York, London, Sydney, and Toronto, 1973; pp 243–249.
(33) (a) Gelsema, W. J.; de Ligny, C. L.; Blijleven, H. A. *Recl. Trav. Chim Pays-Bas* **1967**, *86*, 852–864. (b) Cookson, R. F. *Chem. Rev.* **1974**, *74*, 5–28. See p 11.
(34) Mitchell, P. R.; Sigel, H. *Angew. Chem.* **1976**, *88*, 585–586; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 548.
(35) Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201–208.
(36) Farkas, E.; Fischer, B. E.; Griesser, R.; Rheinberger, V. M.; Sigel, H. *Z. Naturforsch., B* **1979**, *34B*, 208–216.
(37) The experimental data for the measurements in aqueous solution and their evaluation are shown in Figure 2 of ref 18; the present measurements in mixed solvents were carried out correspondingly. In this earlier study,[18] it has also been shown that addition of $Zn(NO_3)_2$ to a solution of BzOH does not practically alter the position of the chemical shifts, though there are indications that a slight *downfield* shift may occur (see footnote 37 in ref 18). At first sight, the upfield shift in aqueous solution ($\Delta\delta$ 0.71 ± 0.13 ppm)[18] seems to be similar to that determined now in 50% (v/v) dioxane–water ($\Delta\delta$ 0.70 ± 0.38 ppm), but in conclusions, care should be exercised because (i) the error limits are large and (ii) examples are known for binary stacks for which $\Delta\delta$ increases (Table 1 of ref 2) with increasing dioxane concentrations, as well as those where it decreases (Table 2 of ref 2).
(38) It may be mentioned that the metal-free binary (phen)(BzOH) adduct is possibly somewhat more stable than the unbridged but ternary adduct, [Zn(phen)](BzOH)$^{2+}$, studied here ($K^{[Zn(phen)]}_{[Zn(phen)](BzOH)}$ = 2.2 ± 0.2 M^{-1}; Table I). This is indicated from the stability of the structurally similar (phen)-[2-(*p*-methoxyphenyl)acetate] adduct which was determined[19] in water by spectrophotometric measurements ($K^{(phen)}_{(phen)(MOPAc)}$ = 6.3 ± 2.9 M^{-1}; I = 0.25, $NaClO_4$; 25 °C) and in 25% (v/v) methanol–water (corresponding to a mole fraction of 0.148) by ^1H NMR shift measurements ($K^{(phen)}_{(phen)(MOPAc)}$ = 4.4 ± 0.4 M^{-1}; I = 1.0, $N(CH_3)_4NO_3$; 34 °C). This indicates a difference in the stability constants by a factor of about 2–3. The following results[12c] are also of interest in this connection: $K^{[Zn(phen)]}_{[Zn(phen)](adenosine)}$ = 14.1 ± 3.1 M^{-1} (in D_2O by ^1H NMR; I = 0.1–0.36, $NaNO_3$; 27 °C), $K^{(phen)}_{(phen)(adenosine)}$ = 21.4 ± 2.5 M^{-1} (in H_2O by UV spectrophotometry; I = 0.1, $NaClO_4$; 25 °C), and $K^{(phen)}_{(phen)(ATP)}$ = 28.2 ± 4.7 M^{-1} (in D_2O by ^1H NMR; I = 0.1, $NaNO_3$; 27 °C); hence, (phen)(adenosine) is by a factor of about 2 more stable than [Zn(phen)]-(adenosine)$^{2+}$. Together, all these results may be taken as a hint that the coordination of Zn^{2+} to phen reduces somewhat the stacking properties of the phen-ring system, possibly due to the hydration shell of the coordinated metal ion.

Table II. Negative Logarithms of the Acidity Constants[a] of Several Carboxylic Acids and Logarithms of the Corresponding Binary $M(CA)^+$ (eq 6) and Ternary $M(phen)(CA)^+$ Complexes (eq 7) in Dependence on the Amount of Ethanol Added to Water and on the Resulting Dielectric Constant (I = 0.1; 25 °C)[a-c]

CA^-	% (v/v) ethanol	mol fract	ϵ[c]	$pK^H_{H(CA)}$	log $K^{Cu}_{Cu(CA)}$	log $K^{Cu(phen)}_{Cu(phen)(CA)}$	Δlog K_{Cu}	log $K^{Zn}_{Zn(CA)}$	log $K^{Zn(phen)}_{Zn(phen)(CA)}$	Δlog K_{Zn}
$HCOO^-$	0	0	78.5	3.59 ± 0.02	1.65 ± 0.09	1.61 ± 0.05	−0.04 ± 0.10	1.07 ± 0.05	0.90 ± 0.04	−0.17 ± 0.06
	30	0.117	63.7	3.90 ± 0.02	1.97 ± 0.02	1.97 ± 0.02	0.00 ± 0.03	1.12 ± 0.04	1.08 ± 0.04	−0.04 ± 0.06
	50	0.237	52.1	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
	60	0.318	46.1	4.55 ± 0.01	2.41 ± 0.01	2.41 ± 0.02	0.00 ± 0.02	1.69 ± 0.02	1.58 ± 0.01	−0.11 ± 0.02
	70	0.420	40.8	4.82 ± 0.01	2.65 ± 0.02	2.68 ± 0.02	0.03 ± 0.03	1.92 ± 0.01	1.81 ± 0.02	−0.11 ± 0.02
	90	0.736	29.1	5.36 ± 0.01	3.34 ± 0.02	3.33 ± 0.01	−0.01 ± 0.02	2.62 ± 0.02	2.43 ± 0.02	−0.19 ± 0.03
Ac^-	0	0	78.5	4.58 ± 0.02	1.85 ± 0.05	1.84 ± 0.01	−0.01 ± 0.05	1.11 ± 0.02	0.90 ± 0.02	−0.21 ± 0.03
	30	0.117	63.7	5.06 ± 0.01	2.33 ± 0.01	2.37 ± 0.01	0.04 ± 0.01	1.46 ± 0.01	1.36 ± 0.01	−0.10 ± 0.01
	50	0.237	52.1	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
	60	0.318	46.1	5.78 ± 0.01	2.92 ± 0.01	2.96 ± 0.01	0.04 ± 0.01	2.07 ± 0.01	1.96 ± 0.01	−0.11 ± 0.01
	70	0.420	40.8	6.08 ± 0.01	3.22 ± 0.01	3.25 ± 0.01	0.03 ± 0.01	2.38 ± 0.01	2.25 ± 0.01	−0.13 ± 0.01
	90	0.736	29.1	6.73 ± 0.02	4.07 ± 0.03	4.08 ± 0.01	0.01 ± 0.03	3.35 ± 0.02	3.10 ± 0.02	−0.25 ± 0.03
PAc^-	0	0	78.5	4.12 ± 0.02	1.75 ± 0.04	2.01 ± 0.02	0.26 ± 0.04	1.14 ± 0.03	1.05 ± 0.03	−0.09 ± 0.04
	30	0.117	63.7	4.80 ± 0.01	2.20 ± 0.01	2.60 ± 0.01	0.40 ± 0.01	1.36 ± 0.02	1.51 ± 0.02	0.15 ± 0.03
	50	0.237	52.1	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
	60	0.318	46.1	5.63 ± 0.01	2.85 ± 0.01	3.31 ± 0.01	0.46 ± 0.01	2.04 ± 0.01	2.17 ± 0.01	0.13 ± 0.01
	70	0.420	40.8	5.92 ± 0.01	3.13 ± 0.01	3.59 ± 0.02	0.46 ± 0.02	2.34 ± 0.01	2.44 ± 0.01	0.10 ± 0.01
	90	0.736	29.1	6.47 ± 0.02	4.02 ± 0.02	4.40 ± 0.03	0.38 ± 0.04	3.29 ± 0.02	3.20 ± 0.01	−0.09 ± 0.02
PPr^-	0	0	78.5	4.45 ± 0.02	1.87 ± 0.02	2.14 ± 0.01	0.27 ± 0.02	1.14 ± 0.04	1.07 ± 0.02	−0.07 ± 0.04
	30	0.117	63.7	5.16 ± 0.01	2.27 ± 0.01	2.65 ± 0.01	0.38 ± 0.01	1.47 ± 0.02	1.64 ± 0.01	0.17 ± 0.02
	50	0.237	52.1	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
	60	0.318	46.1	5.93 ± 0.01	2.95 ± 0.01	3.25 ± 0.01	0.30 ± 0.01	2.12 ± 0.01	2.23 ± 0.01	0.11 ± 0.01
	70	0.420	40.8	6.23 ± 0.01	3.24 ± 0.01	3.52 ± 0.01	0.28 ± 0.01	2.41 ± 0.01	2.47 ± 0.01	0.06 ± 0.01
	90	0.736	29.1	6.80 ± 0.01	4.19 ± 0.02	4.37 ± 0.02	0.18 ± 0.03	3.43 ± 0.01	3.31 ± 0.02	−0.12 ± 0.02

[a] The errors given are *3 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 Δ log K_M were calculated according to the error propagation after Gauss. The acidity constants are defined as $K^H_{H(CA)} = (H^+)[CA^-]/[H(CA)]$. [b] I = 0.1 was adjusted in water with KNO_3 and in all water/ethanol mixtures with $NaNO_3$. The entries for water and 50% aqueous ethanol are from ref 19; the values of the acidity constants of H(CA) and of the stability constants of the binary $M(CA)^+$ complexes are for formate and acetate the same as those given in ref 28. [c] The dielectric constants for the ethanol/water mixtures are interpolated from the data given in Table XII of ref 39.

2. Stability of Ternary $M(phen)(CA)^+$ Complexes in Several Solvents. To be able to evaluate the position of the intramolecular equilibrium 1 and to see to which extent the formation degree of the closed species in the ternary complexes formed between $M(phen)^{2+}$ and 2-phenylacetate (PAc^-; Figure 2) or 3-phenylpropionate (PPr^-) depends on the addition of ethanol or dioxane to an aqueous solution of the reactants, it was necessary to measure also the stability of the corresponding complexes containing formate or acetate (Ac^-).

The equilibrium constants (eq 6 and 7) were determined by potentiometric pH titrations. The results obtained for several ethanol/water mixtures are listed in Table II together with the dielectric constants[39] for these solvents. The constants measured for the dioxane/water mixtures are given in Table III, again with the corresponding dielectric constants.[40]

The stability constants of te $M(phen)(PAc)^+$ complexes in water[18] and in 50% aqueous dioxane[19] determined earlier by UV difference spectrophotometry agree excellently with the constants obtained from the potentiometric pH titrations. To have a further independent check of the measured constants and especially a *direct* proof for the formation of intramolecular stacks, we have recorded the ^1H NMR spectra for the Zn^{2+}/phen/PAc system in water and in aqueous solutions containing up to 80% dioxane. The variation of the chemical shift of the phenyl protons of PAc with increasing concentrations of Zn^{2+}/phen is shown in Figure 3 for the six solvents employed, and the results of the calculations are summarized in Table IV.

The most important point from the ^1H NMR shift measurements is that in *all* solvents used, *upfield* shifts are observed, and this proves[12c,17,22] that the stacked isomer of equilibrium 1 occurs to a remarkable extent under all these conditions. The agreement

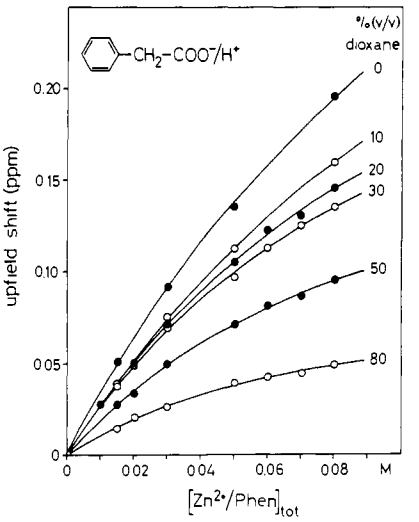


Figure 3. Variation of the upfield shift of the resonance of the phenyl protons of 2-phenylacetate (1.25×10^{-2} M) in dependence on $[Zn^{2+}$/phen] at pH 5.20 (for $pK^H_{H(PAc)}$, see Table IV) in several water/dioxane mixtures as solvent (I = 0.25, $NaNO_3$; 34 °C). The curves shown are computer-calculated best fits of the experimental data (see Experimental Section). The resulting chemical shifts and the corresponding stability constants for $Zn(phen)(PAc)^+$ are listed in Table IV.

between the constants determined for $Zn(phen)(PAc)^+$ by the ^1H NMR shift measurements and by the potentiometric pH titrations (see Table IV) is good, considering the higher temperature and the larger ionic strength which had to be used in the NMR experiments.

3. Influence of the Solvent on the Formation Degree of the Closed Species in the Ternary $M(phen)(PheCA)^+$ Complexes. The results of the ^1H NMR experiments (Figure 3; Table IV) prove that intramolecular stacks are formed in the ternary complexes (Figure 2), but these data give little or no information about the

(39) Åkerlöf, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125–4139.
(40) (a) Åkerlöf, G.; Short, O. A. *J. Am. Chem. Soc.* **1936**, *58*, 1241–1243. (b) Critchfield, F. E.; Gibson, J. A., Jr.; Hall, J. L. *J. Am. Chem. Soc.* **1953**, *75*, 1991–1992. (c) Åkerlöf, G.; Short, O. A. *J. Am. Chem. Soc.* **1953**, *75*, 6357.

Table III. Negative Logarithms of the Acidity Constants[a] of Several Carboxylic Acids and Logarithms of the Corresponding Binary $M(CA)^+$ (eq 6) and Ternary $M(phen)(CA)^+$ Complexes (eq 7) in Dependence on the Amount of Dioxane Added to Water and on the Resulting Dielectric Constant (I = 0.1; 25 °C)[a-c]

CA^-	% (v/v) dioxane	mol fract	ϵ[c]	$pK^H_{H(CA)}$	log $K^{Cu}_{Cu(CA)}$	log $K^{Cu(phen)}_{Cu(phen)(CA)}$	Δlog K_{Cu}	log $K^{Zn}_{Zn(CA)}$	log $K^{Zn(phen)}_{Zn(phen)(CA)}$	Δlog K_{Zn}
$HCOO^-$	0	0	78.5	3.59 ± 0.02	1.65 ± 0.09	1.61 ± 0.05	−0.04 ± 0.10	1.07 ± 0.05	0.90 ± 0.04	−0.17 ± 0.06
	10	0.023	70.1	3.71 ± 0.01	1.79 ± 0.03	1.73 ± 0.01	−0.06 ± 0.03			
	30	0.083	52.7	4.14 ± 0.02	2.20 ± 0.01	2.19 ± 0.01	−0.01 ± 0.01	1.24 ± 0.02	1.10 ± 0.03	−0.14 ± 0.04
	50	0.175	35.2	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
	60	0.241	26.6	5.15 ± 0.01	3.15 ± 0.01	3.16 ± 0.01	0.01 ± 0.01			
	70	0.331	18.6	5.52 ± 0.01	3.50 ± 0.01	3.50 ± 0.01	0.00 ± 0.01			
	80	0.459	11.6	5.73 ± 0.01	3.67 ± 0.01	3.55 ± 0.02	−0.12 ± 0.02	2.73 ± 0.01	2.67 ± 0.01	−0.06 ± 0.01
	90	0.656	6.0	6.12 ± 0.01	3.85 ± 0.01	3.74 ± 0.01	−0.11 ± 0.01	2.97 ± 0.01	2.83 ± 0.01	−0.14 ± 0.01
Ac^-	0	0	78.5	4.58 ± 0.02	1.85 ± 0.05	1.84 ± 0.01	−0.01 ± 0.05	1.11 ± 0.02	0.90 ± 0.02	−0.21 ± 0.03
	10	0.023	70.1	4.79 ± 0.01	2.05 ± 0.02	2.09 ± 0.01	0.04 ± 0.02			
	30	0.083	52.7	5.31 ± 0.01	2.61 ± 0.01	2.63 ± 0.01	0.02 ± 0.01	1.62 ± 0.01	1.50 ± 0.01	−0.12 ± 0.01
	50	0.175	35.2	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
	60	0.241	26.6	6.43 ± 0.01	3.72 ± 0.01	3.76 ± 0.01	0.04 ± 0.01			
	70	0.331	18.6	6.84 ± 0.01	4.09 ± 0.01	4.14 ± 0.01	0.05 ± 0.01			
	80	0.459	11.6	7.08 ± 0.01	4.32 ± 0.01	4.21 ± 0.02	−0.11 ± 0.02	3.22 ± 0.01	3.22 ± 0.01	0.00 ± 0.01
	90	0.656	6.0	7.49 ± 0.01	4.66 ± 0.04	4.56 ± 0.02	−0.10 ± 0.04	3.45 ± 0.06	3.39 ± 0.02	−0.06 ± 0.06
PAc^-	0	0	78.5	4.12 ± 0.02	1.75 ± 0.04	2.01 ± 0.02	0.26 ± 0.04	1.14 ± 0.03	1.05 ± 0.03	−0.09 ± 0.04
	10	0.023	70.1	4.39 ± 0.01	1.94 ± 0.01	2.26 ± 0.01	0.32 ± 0.01			
	30	0.083	52.7	5.09 ± 0.02	2.50 ± 0.01	2.87 ± 0.01	0.37 ± 0.01	1.55 ± 0.01	1.64 ± 0.01	0.09 ± 0.01
	50	0.175	35.2	5.88 ± 0.01	3.22 ± 0.02	3.68 ± 0.04	0.46 ± 0.04	2.26 ± 0.02	2.29 ± 0.01	0.03 ± 0.02
	60	0.241	26.6	6.38 ± 0.02	3.66 ± 0.02	4.13 ± 0.01	0.47 ± 0.02			
	70	0.331	18.6	6.81 ± 0.01	4.10 ± 0.01	4.54 ± 0.01	0.44 ± 0.01			
	80	0.459	11.6	7.07 ± 0.01	4.29 ± 0.04	4.62 ± 0.01	0.33 ± 0.04	3.21 ± 0.02	3.38 ± 0.01	0.17 ± 0.02
	90	0.656	6.0	7.42 ± 0.01	4.69 ± 0.02	4.87 ± 0.01	0.18 ± 0.02	3.56 ± 0.05	3.54 ± 0.02	−0.02 ± 0.05
PPr^-	0	0	78.5	4.45 ± 0.02	1.87 ± 0.02	2.14 ± 0.01	0.27 ± 0.02	1.14 ± 0.04	1.07 ± 0.02	−0.07 ± 0.04
	30	0.083	52.7	5.41 ± 0.01	2.49 ± 0.01	2.83 ± 0.01	0.34 ± 0.01	1.62 ± 0.01	1.76 ± 0.01	0.14 ± 0.01
	50	0.175	35.2	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
	80	0.459	11.6	7.36 ± 0.01	4.32 ± 0.03	4.42 ± 0.01	0.10 ± 0.03	3.16 ± 0.03	3.23 ± 0.03	0.07 ± 0.04

[a] See footnote *a* in Table II. [b] I = 0.1 was adjusted in 50% dioxane with $NaClO_4$ and in 80% and 90% dioxane with $NaNO_3$; for all other solutions KNO_3 was used. In the case of 30% dioxane I = 0.1 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. The entries for water and 50% aqueous dioxane are from ref 19; the values of the acidity constants of H(CA) and of the stability constants of the binary $M(CA)^+$ complexes are for formate and acetate the same as those given in ref 28. [c] The dielectric constants for the dioxane/water mixtures are from ref 40.

Table IV. Chemical Shift, $\delta_{PAc/H(PAc)}$, of the Signal due to the Protons in the Phenyl Moiety of PAc and of Its $Zn(phen)(PAc)^+$ Complex, $\delta_{Zn(phen)(PAc)}$, Together with the Corresponding Upfield Shift $\Delta\delta$ (ppm) in Several H_2O/Dioxane Mixtures at pH 5.20 (I = 0.25, $NaNO_3$; 34 °C).[a] The Logarithm of the Apparent Stability Constant of the Ternary Complex, log K_{app}, as Calculated from These ^1H NMR Experiments (Figure 3) Is also Given Together with the pH-Independent Stability Constant, log $K^{Zn(phen)}_{Zn(phen)(PAc)}$ (eq 9).[a,b] Corresponding Values from the Potentiometric pH Titrations (I = 0.1, 25 °C) Are Given for Comparison[a]

% (v/v) dioxane	$\delta_{PAC/H(PAc)}$	$\delta_{Zn(phen)(PAc)}$	$\Delta\delta$	log K_{app}	$pK^H_{H(PAc)}$[c]	log $K^{Zn(phen)}_{Zn(phen)(PAc)}$ ^1H NMR[b]	log $K^{Zn(phen)}_{Zn(phen)(PAc)}$ pH titr[c]
0	7.301 ± 0.008	6.70 ± 0.25	0.60 ± 0.25	0.79 ± 0.27	4.12 ± 0.02	0.8 ± 0.3	1.05 ± 0.03
10	7.292 ± 0.005	6.80 ± 0.17	0.49 ± 0.17	0.80 ± 0.23	4.39 ± 0.01	0.9 ± 0.2	1.20 ± 0.05[d]
20	7.283 ± 0.005	6.92 ± 0.09	0.36 ± 0.09	0.95 ± 0.18	4.70 ± 0.03[d]	1.1 ± 0.2	1.38 ± 0.05[d]
30	7.280 ± 0.005	6.974 ± 0.069	0.306 ± 0.069	1.02 ± 0.18	5.09 ± 0.02	1.3 ± 0.2	1.64 ± 0.01
50	7.268 ± 0.003	7.067 ± 0.036	0.201 ± 0.036	1.08 ± 0.15	5.88 ± 0.01	1.9 ± 0.2	2.29 ± 0.01
80	7.245 ± 0.003	7.154 ± 0.024	0.091 ± 0.024	1.22 ± 0.25	7.07 ± 0.01	3.1 ± 0.3	3.38 ± 0.01

[a] The errors given are *3 times* the standard deviations. [b] Calculated with eq 9, and the $pK^H_{H(PAc)}$ values given in this table. [c] Values from Table III (I = 0.1; 25 °C). It may be mentioned that the influence of some variation in temperature (25–35 °C) and ionic strength (0.1–1.0 M) on the acidity constants of carboxylic acids is small (i.e., within 0.02 log unit);[41] hence, the use of the above acidity constants in the calculations with eq 9 is justified. [d] Interpolated value (see as examples the figures in ref 28); the error is estimated.

position of the intramolecular equilibrium between an opened and a stacked isomer (eq 1). However, with eq 3 and the experimental data collected in Tables II and III, one may calculate intramolecular equilibrium constants K_I (eq 1–3) and percentages of the closed species formed in the different systems by assuming that the stability increase between the $M(phen)(PheCA)^+$ and the $M(phen)(HCOO^-$ or $Ac^-)^+$ complexes is solely due to an intramolecular ligand–ligand interaction, a problem to be further addressed in section 7. The results of these calculations are listed for the solvent mixtures containing ethanol or dioxane in Tables V and VI, respectively.

The percentages for equilibrium 1 of the closed species in dependence on the mole fractions of ethanol or dioxane are plotted in Figure 4 for the ternary $M(phen)(PAc)^+$ and $M(phen)(PPr)^+$ complexes. It is evident that the addition of (some) ethanol or dioxane *favors* the formation degree of the closed species. This formation degree reaches a relatively broad maximum for all the complex systems. Only in solutions which contain more than about 70% ethanol or dioxane does the concentration of the closed species decrease, though it may still be of the order found in aqueous solution.

It should be emphasized that this rather general description given in the preceding paragraph holds for all four ternary complexes considered here (Figure 4), despite the fact that the absolute formation degrees of the closed species differ due to the different coordination geometries of Cu^{2+} and Zn^{2+} and due to the different structures of 2-phenylacetate and 3-phenylpropionate. Furthermore, the described result contrasts strongly with the general experience made with binary and unbridged ternary stacking adducts (section 1): in this case, addition of the same amount of dioxane, e.g., to an aqueous solution of $Zn(phen)^{2+}$/BzOH will *reduce* the concentration of the stacked adduct by a factor of about

Table V. Extent of the Closed Species Formed in the Ternary Complexes Containing Cu^{2+} or Zn^{2+}, 1,10-Phenanthroline (phen), and 2-Phenylacetate or 3-Phenylpropionate ($PheCA^-$) in Dependence on the Amount of Ethanol Added to Water: Intramolecular and Dimensionless Equilibrium Constant K_I and Percentage of the Closed Species $M(phen)(PheCA)_{cl}^+$ in Different Solvents at I = 0.1 and 25 °C

no.	complex	% (v/v) ethanol	$\Delta \log K_M$ (eq 5)[a]	$\Delta \log K_{op}$ (eq 5)[b]	$\Delta\Delta \log K$[c]	K_I (eq 2, 3)[c]	$\%M(phen)(PheCA)_{cl}^+$ (eq 1)[c]
1	$Cu(phen)(PAc)^+$	0	0.26 ± 0.04	−0.02 ± 0.06	0.28 ± 0.04 (0.07)	0.91 ± 0.20 (0.32)	48 ± 5 (9)
2		30	0.40 ± 0.01	0.02 ± 0.02	0.38 ± 0.01 (0.02)	1.40 ± 0.08 (0.12)	58 ± 1 (2)
3		50	0.47 ± 0.02	0.08 ± 0.02	0.39 ± 0.02 (0.03)	1.45 ± 0.13 (0.19)	59 ± 2 (3)
4		60	0.46 ± 0.01	0.02 ± 0.01	0.44 ± 0.01 (0.02)	1.75 ± 0.09 (0.12)	64 ± 1 (2)
5		70	0.46 ± 0.02	0.03 ± 0.01	0.43 ± 0.02 (0.03)	1.69 ± 0.14 (0.17)	63 ± 2 (2)
6		90	0.38 ± 0.04	0.00 ± 0.02	0.38 ± 0.04 (0.04)	1.40 ± 0.20 (0.23)	58 ± 3 (4)
7	$Zn(phen)(PAc)^+$	0	−0.09 ± 0.04	−0.19 ± 0.04	0.10 ± 0.04 (0.05)	0.26 ± 0.12 (0.16)	21 ± 8 (10)
8		30	0.15 ± 0.03	−0.07 ± 0.03	0.22 ± 0.03 (0.04)	0.66 ± 0.11 (0.16)	40 ± 4 (6)
9		50	0.23 ± 0.02	−0.08 ± 0.03	0.31 ± 0.02 (0.04)	1.04 ± 0.11 (0.17)	51 ± 3 (4)
10		60	0.13 ± 0.01	−0.11 ± 0.01	0.24 ± 0.01 (0.02)	0.74 ± 0.06 (0.08)	42 ± 2 (3)
11		70	0.10 ± 0.01	−0.12 ± 0.01	0.22 ± 0.01 (0.02)	0.66 ± 0.05 (0.07)	40 ± 2 (3)
12		90	−0.09 ± 0.02	−0.22 ± 0.02	0.13 ± 0.02 (0.03)	0.35 ± 0.07 (0.09)	26 ± 4 (5)
13	$Cu(phen)(PPr)^+$	0	0.27 ± 0.02	−0.02 ± 0.06	0.29 ± 0.02 (0.06)	0.95 ± 0.10 (0.28)	49 ± 3 (7)
14		30	0.38 ± 0.01	0.02 ± 0.02	0.36 ± 0.01 (0.02)	1.29 ± 0.07 (0.11)	56 ± 1 (2)
15		50	0.38 ± 0.01	0.08 ± 0.02	0.30 ± 0.01 (0.03)	1.00 ± 0.06 (0.13)	50 ± 2 (3)
16		60	0.30 ± 0.01	0.02 ± 0.01	0.28 ± 0.01 (0.02)	0.91 ± 0.06 (0.08)	48 ± 2 (2)
17		70	0.28 ± 0.01	0.03 ± 0.02	0.25 ± 0.01 (0.02)	0.78 ± 0.06 (0.09)	44 ± 2 (3)
18		90	0.18 ± 0.03	0.00 ± 0.02	0.18 ± 0.03 (0.03)	0.51 ± 0.10 (0.12)	34 ± 4 (5)
19	$Zn(phen)(PPr)^+$	0	−0.07 ± 0.04	−0.19 ± 0.04	0.12 ± 0.04 (0.06)	0.32 ± 0.14 (0.17)	24 ± 8 (10)
20		30	0.17 ± 0.02	−0.07 ± 0.03	0.24 ± 0.02 (0.04)	0.74 ± 0.09 (0.15)	43 ± 3 (5)
21		50	0.18 ± 0.01	−0.08 ± 0.03	0.26 ± 0.01 (0.03)	0.82 ± 0.06 (0.13)	45 ± 2 (4)
22		60	0.11 ± 0.01	−0.11 ± 0.01	0.22 ± 0.01 (0.02)	0.66 ± 0.05 (0.07)	40 ± 2 (3)
23		70	0.06 ± 0.01	−0.12 ± 0.01	0.18 ± 0.01 (0.02)	0.51 ± 0.05 (0.07)	34 ± 2 (3)
24		90	−0.12 ± 0.02	−0.22 ± 0.02	0.10 ± 0.02 (0.03)	0.26 ± 0.06 (0.09)	21 ± 4 (5)

[a] These values and their error ranges (*3 times* the standard error) are from Table II. [b] These values for $\Delta \log K_{op}$ are the averages of $\Delta \log K_M$ determined from $HCOO^-$ and Ac^- in each individual solvent (see Table II). [c] The error limits given with these data ($\Delta\Delta \log K = \Delta \log K_M - \Delta \log K_{op}$; see ref 18, 19, and 22) result from 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. For internal comparisons, e.g., between the complexes containing PAc^- or PPr^- in the *same* solvent, the errors based only on the individual $\Delta \log K_M$ value are more appropriate, because $\Delta \log K_{op}$ has then the same value and therefore any error in $\Delta \log K_{op}$ will influence the result in the same (systematic) way. Regarding the meaning of the formula, $M(phen)(PheCA)_{cl}^+$, and the possible formation of closed complexes with somewhat different structures, see the discussion in section 7.

Table VI. Extent of the Closed Species Formed in the Ternary Complexes Containing Cu^{2+} or Zn^{2+}, 1,10-Phenanthroline (phen), and 2-Phenylacetate or 3-Phenylpropionate ($PheCA^-$) in Dependence on the Amount of Dioxane Added to Water: Intramolecular and Dimensionless Equilibrium Constant K_I and Percentage of the Closed Species $M(phen)(PheCA)_{cl}^+$ in Different Solvents at I = 0.1 and 25 °C.

no.	complex	% (v/v) dioxane	$\Delta \log K_M$ (eq 5)[a]	$\Delta \log K_{op}$ (eq 5)[b]	$\Delta\Delta \log K$[c]	K_I (eq 2, 3)[c]	$\%M(phen)(PheCA)_{cl}^+$ (eq 1)[c]
1	$Cu(phen)(PAc)^+$	0	0.26 ± 0.04	−0.02 ± 0.06	0.28 ± 0.04 (0.07)	0.91 ± 0.20 (0.32)	48 ± 5 (9)
2		10	0.32 ± 0.01	−0.01 ± 0.02	0.33 ± 0.01 (0.02)	1.14 ± 0.07 (0.12)	53 ± 2 (3)
3		30	0.37 ± 0.01	0.01 ± 0.01	0.36 ± 0.01 (0.02)	1.29 ± 0.07 (0.09)	56 ± 1 (2)
4		50	0.46 ± 0.04	0.04 ± 0.02	0.42 ± 0.04 (0.05)	1.63 ± 0.27 (0.29)	62 ± 4 (4)
5		60	0.47 ± 0.02	0.03 ± 0.01	0.44 ± 0.02 (0.02)	1.75 ± 0.14 (0.16)	64 ± 2 (2)
6		70	0.44 ± 0.01	0.03 ± 0.01	0.41 ± 0.01 (0.02)	1.57 ± 0.08 (0.10)	61 ± 1 (2)
7		80	0.33 ± 0.04	−0.11 ± 0.02	0.44 ± 0.04 (0.04)	1.75 ± 0.26 (0.28)	64 ± 3 (4)
8		90	0.18 ± 0.02	−0.10 ± 0.02	0.28 ± 0.02 (0.03)	0.91 ± 0.10 (0.14)	48 ± 3 (4)
9	$Zn(phen)(PAc)^+$	0	−0.09 ± 0.04	−0.19 ± 0.04	0.10 ± 0.04 (0.05)	0.26 ± 0.12 (0.16)	21 ± 8 (10)
10		30	0.09 ± 0.01	−0.13 ± 0.02	0.22 ± 0.01 (0.02)	0.66 ± 0.05 (0.09)	40 ± 2 (3)
11		50	0.03 ± 0.02	−0.15 ± 0.01	0.18 ± 0.02 (0.03)	0.51 ± 0.08 (0.10)	34 ± 3 (4)
12		80	0.17 ± 0.02	−0.03 ± 0.01	0.20 ± 0.02 (0.02)	0.58 ± 0.08 (0.09)	37 ± 3 (4)
13		90	−0.02 ± 0.05	−0.10 ± 0.03	0.08 ± 0.05 (0.06)	0.20 ± 0.15 (0.17)	17 ± 10 (12)
14	$Cu(phen)(PPr)^+$	0	0.27 ± 0.02	−0.02 ± 0.06	0.29 ± 0.02 (0.06)	0.95 ± 0.10 (0.28)	49 ± 3 (7)
15		30	0.34 ± 0.01	0.01 ± 0.01	0.33 ± 0.01 (0.02)	1.14 ± 0.07 (0.09)	53 ± 2 (2)
16		50	0.28 ± 0.02	0.04 ± 0.02	0.24 ± 0.02 (0.03)	0.74 ± 0.09 (0.11)	43 ± 3 (4)
17		80	0.10 ± 0.03	−0.11 ± 0.02	0.21 ± 0.03 (0.04)	0.62 ± 0.12 (0.13)	38 ± 4 (5)
18	$Zn(phen)(PPr)^+$	0	−0.07 ± 0.04	−0.19 ± 0.04	0.12 ± 0.04 (0.06)	0.32 ± 0.14 (0.17)	24 ± 8 (10)
19		30	0.14 ± 0.01	−0.13 ± 0.02	0.27 ± 0.01 (0.02)	0.86 ± 0.06 (0.10)	46 ± 2 (3)
20		50	0.03 ± 0.01	−0.15 ± 0.01	0.18 ± 0.01 (0.02)	0.51 ± 0.05 (0.07)	34 ± 2 (3)
21		80	0.07 ± 0.04	−0.03 ± 0.01	0.10 ± 0.04 (0.04)	0.26 ± 0.12 (0.13)	21 ± 8 (8)

[a–c] These footnotes are the same as those given in Table V, but the data for $\Delta \log K_M$ and $\Delta \log K_{op}$ are based on Table III.

1/5; in 80% dioxane solutions, the differences are even more drastic (cf. the results of Table I with those shown in Figure 4).

4. Why Do Certain Amounts of Ethanol or Dioxane Favor the Intramolecularly Closed Species in $M(phen)(PheCA)^+$ Complexes? In the case of unbridged stacking adducts, increasing amounts of ethanol or dioxane clearly *weaken* the stacking tendency (section 1). This result is easily rationalized as the addition of these organic solvents leads to a solvation of the aromatic-ring systems by the alkyl parts of the solvent molecules. Hence, this "hydrophobic" solvation competes with the formation of the unbridged stacks and thus reduces their formation degree.

The influence of organic solvents on the formation degree of the closed species in the $M(phen)(PheCA)^+$ complexes is obviously more complicated (Figure 4). There is the unexpected result that

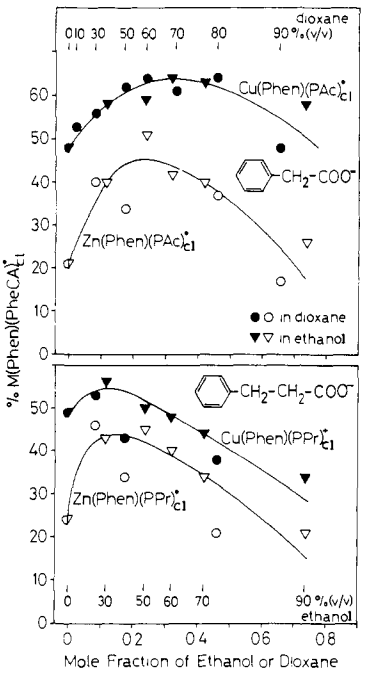


Figure 4. Formation degree of the intramolecularly closed species (eq 1) in ternary M(phen)(PAc)$^+$ (top) and M(phen)(PPr)$^+$ (bottom) complexes of Cu^{2+} (●, ▼) and Zn^{2+} (○, ▽) in dependence on the mole fractions of ethanol (▼, ▽) or dioxane (●, ○); the second solvent component is always water. The data are taken from Tables II, III, V, and VI (I = 0.1; 25 °C).

some ethanol or dioxane *favors* the intramolecular interaction (eq 1), and only at high concentrations of the organic solvent does inhibition occur. Hence, there must be at least two opposing solvent effects; to be able to evaluate these at least approximately, first some finer details have to be considered in sections 5–7.

5. Polarity of the Solvent Governs the Overall Stability of the Complexes. The size of the dielectric constant, i.e., the polarity of the solvent, is important, if the overall affinity of phenylalkanecarboxylates toward metal ions is considered; this affinity is to a first approximation also for the ternary M(phen)(PheCA)$^+$ complexes determined by the charge interaction between M^{2+} and the carboxylate group. This is nicely seen in Figure 5, where as an example the logarithms of the stability constants of the binary M(PAc)$^+$ and ternary M(phen)(PAc)$^+$ complexes are plotted vs. the mole fractions of ethanol or dioxane:[42] for a given complex, studied in the two series of solvent mixtures, *different* lines or curves are obtained. Indeed, the dielectric constant decreases more strongly by the addition of dioxane (see Tables II and III), and the solvating properties toward charged species are also expected to be poorer for dioxane than for ethanol, in accord herewith dioxane favors the overall stability of M(PAc)$^+$ or M(phen)(PAc)$^+$ more than does ethanol; the corresponding arguments are of course also valid for the ionization of the carboxylic acid residue, which is reflected in the increasing values for $pK^H_{H(PAc)}$ (see top of Figure 5).

Actually Figure 5 indicates that there exists a relation or even a kind of parallelism between the acidity of 2-phenylacetic acid and the stability of the 2-phenylacetate complexes for the several solvent mixtures. Indeed, plots of the values for log $K^M_{M(CA)}$ vs. $pK^H_{H(CA)}$ for 2-phenylacetate, and also for formate as a further example, result in straight lines (Figure 6). Furthermore, it is evident from Figure 6 that for a given M^{2+}/CA system, all the data fit well on the same straight line,[43] i.e., independent of the

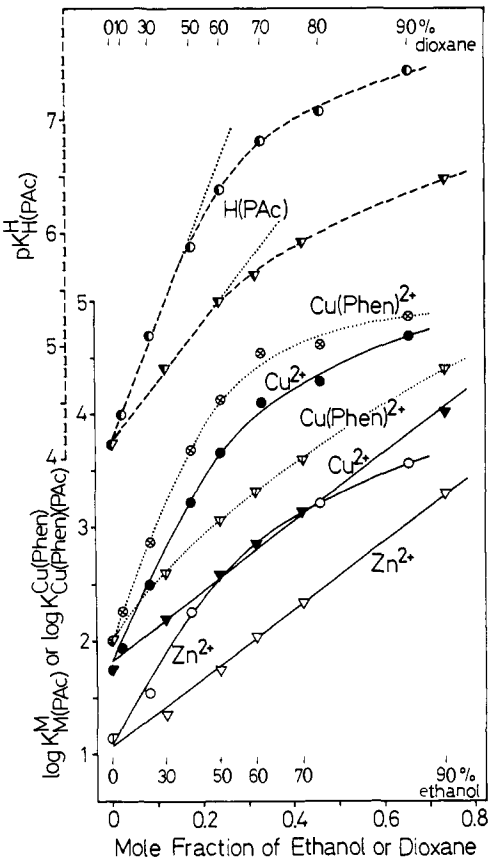


Figure 5. Negative logarithms (broken lines) of the acidity constants of 2-phenylacetic acid, $pK^H_{H(PAc)}$ (◐, ▼), and logarithms (full or dotted lines; lower part) of the stability constants of the Cu^{2+} (●, ▼) and Zn^{2+} (○, ▽) 1:1 complexes with 2-phenylacetate (PAc^-), log $K^M_{M(PAc)}$, or the ternary Cu(phen)(PAc)$^+$ complexes, log $K^{Cu(phen)}_{Cu(phen)(PAc)}$ (⊗, ▼), in dependence on the mole fractions of ethanol (▼, ▼, ▽, ▽) or dioxane (◐, ●, ⊗, ○);[42] the second solvent component is always water. The dotted lines in the upper part indicate extensions corresponding to straight lines. The data are taken from Tables II and III. For Cu(PAc)$^+$ (▼) and Zn(PAc)$^+$ (▽) in ethanol for the slope of the regression line, it holds: m_{Cu} = 3.05 ± 0.10 (±1σ) and m_{Zn} = 3.00 ± 0.09.

solvent used for the measurements. Clearly, in the whole range from 0% to 90% aqueous/organic solvent mixtures, the stability of the binary M(CA)$^+$ complexes increases steadily. In other words, with decreasing solvent polarity, the affinity of R–COO^- for M^{2+} increases as one would expect on the basis of a simple Coulomb consideration.[28] The same holds for the ternary M(phen)(HCOO)$^+$ and M(phen)(Ac)$^+$ complexes; the experimental data still fit well on straight lines (not shown). However, in corresponding plots for M(phen)(PheCA)$^+$, the lines show "breaks"; in other words, there is no satisfactory linear relation anymore between log $K^{M(phen)}_{M(phen)(PheCA)}$ and $pK^H_{H(PheCA)}$. This deviation is tentatively also seen in Figure 5, if the curves for Cu(phen)(PAc)$^+$ and Cu(PAc)$^+$ are compared:[42] the curvature of the lines due to the ternary systems is clearly more pronounced, which is the result of the additional intramolecular interaction in the M(phen)(PheCA)$^+$ complexes.

6. Intramolecular Ligand–Ligand Interaction and "Hydrophobicity" of the Solvent vs. Solvent Polarity. In Figure 4, the percentage of the closed species of the M(phen)(PAc)$^+$ and M(phen)(PPr)$^+$ complexes is plotted in dependence on the mole fraction of the organic solvent. It is evident, though it was in no way predictable, that the data obtained for the same mole fractions

(41) (a) Sillén, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*. (b) Sillén, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc., Suppl. 1* **1971**, *No. 25*. (c) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York and London, 1977; Vol. 3.

(42) The data for Zn(phen)(PAc)$^+$ are not shown in Figure 5 for reasons of clarity, but the properties of Zn(phen)(PAc)$^+$ in the series of the two solvent mixtures correspond to those seen for Cu(phen)(PAc)$^+$.

(43) The only exceptions are the data measured in 90% aqueous ethanol (see also ref 28); in these cases, the addition of ethanol promotes the stability of the complexes more than the basicity of the carboxylate group, i.e., the corresponding points are somewhat above the reference lines. It should be emphasized, however, that these deviations are real and not due to experimental errors; this is also evident from Figure 5 where the data measured in 90% ethanol fit excellently into the general picture.

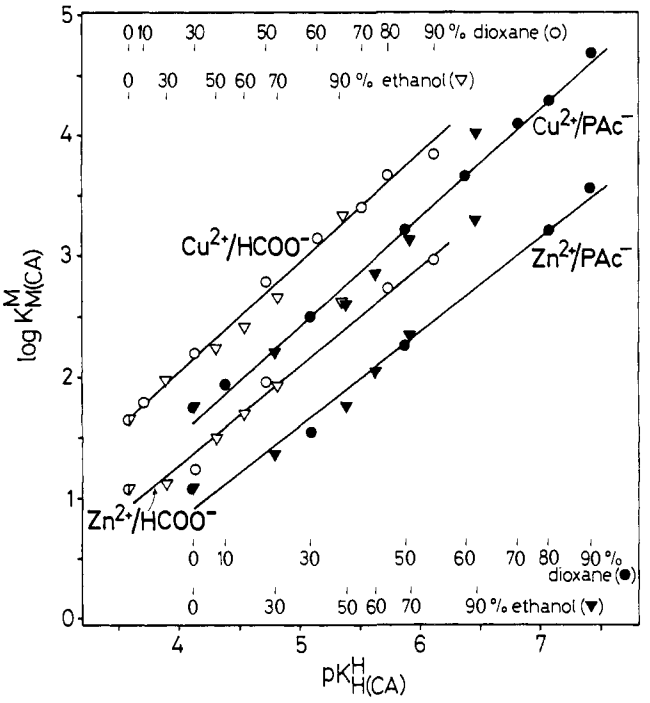


Figure 6. Relationship between log $K^{M}_{M(CA)}$ (eq 6) and $pK^{H}_{H(CA)}$ for the $M(HCOO)^+$ (○, ▽) and $M(PAc)^+$ (●, ▼) complexes of Tables II and III (I = 0.1; 25 °C) resulting from the addition of increasing amounts of ethanol, (▽, ▼) or dioxane (○, ●) to the solvent. The slopes of the straight (regression) lines are $m_{Cu/HCOO}$ = 0.908 ± 0.033 (±1σ) (○, ▽) [in ethanol (▽) alone, 0.783 ± 0.035; in dioxane (○) alone; 0.901 ± 0.029], $m_{Zn/HCOO}$ = 0.818 ± 0.039 (○, ▽) [in ethanol (▽) alone, 0.727 ± 0.077; in dioxane (○) alone, 0.799 ± 0.059], $m_{Cu/PAc}$ = 0.902 ± 0.028 (●, ▼) [in ethanol (▼) alone, 0.753 ± 0.044; in dioxane (●) alone, 0.888 ± 0.015], and $m_{Zn/PAc}$ = 0.776 ± 0.041 (●, ▼) [in ethanol (▼) alone, 0.660 ± 0.094; in dioxane (●) alone, 0.753 ± 0.052]. The values due to 90% ethanol are off the straight lines and were therefore not considered in the calculations of the slopes (see ref 43).

of ethanol or dioxane fit to a first approximation for each complex on a single curve (see also below and Figure 8). A similar, but somewhat less informative, picture is obtained (not shown), if the percentage of $M(phen)(PheCA)_{cl}^+$ is plotted vs. the percentage of ethanol or dioxane present in the aqueous/mixed solvent; considering the percentages of dioxane and ethanol, given in the insertions at the top and bottom of Figure 4, this is not surprising.

It is helpful to compare the results of Figure 4 with those of Figure 7, where the percentage of $M(phen)(PheCA)_{cl}^+$ is plotted vs. the dielectric constant of the several solvent mixtures. It is evident that it would be more difficult to fit the values measured in aqueous ethanol and dioxane solutions for a given $M(phen)(PheCA)^+$ complex on the same curve.

The reason for these observations is most probably that the percentage of the closed species is determined to a significant part by the solvating properties of ethanol and dioxane toward aromatic-ring systems. Indeed, as both organic solvents contain the structural dimethylene unit ($-CH_2-CH_2-$), one may expect similar solvating properties toward aromatic rings. As the same mole fraction means that the same number of ethanol or dioxane molecules are present, the results seen in Figures 4 and 7 are not surprising under this view. However, 1,4-dioxane contains two dimethylene units, and, as already indicated, the solvating properties are expected to be quite similar for such a unit in ethanol or in dioxane; hence, the latter solvent is expected to be about twice as efficient in solvating aromatic residues than ethanol.[44] We have therefore also plotted the percentages of the closed species

(44) Clearly, the factor of 2 is probably somewhat too large because there are steric restrictions in dioxane which will not always allow a simultaneous participation of both dimethylene units in a solvating process; therefore a factor of about 1.5 might actually be more appropriate. However, with such a factor, the fits of the data would still be quite similar to those of Figure 8.

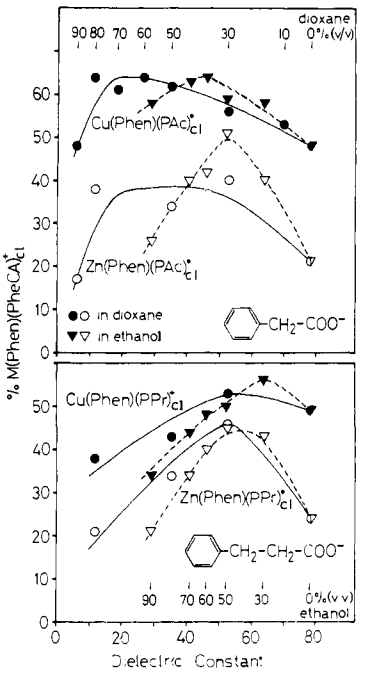


Figure 7. Formation degree of the intramolecular aromatic-ring stack (eq 1) in ternary $M(phen)(PAc)^+$ (top) and $M(phen)(PPr)^+$ (bottom) complexes of Cu^{2+} (●, ▼) and Zn^{2+} (○, ▽) in dependence on the variation of the dielectric constant resulting from the addition of ethanol (▼, ▽) or dioxane (●, ○) to water; the data are from Tables II, III, V, and VI (I = 0.1; 25 °C).

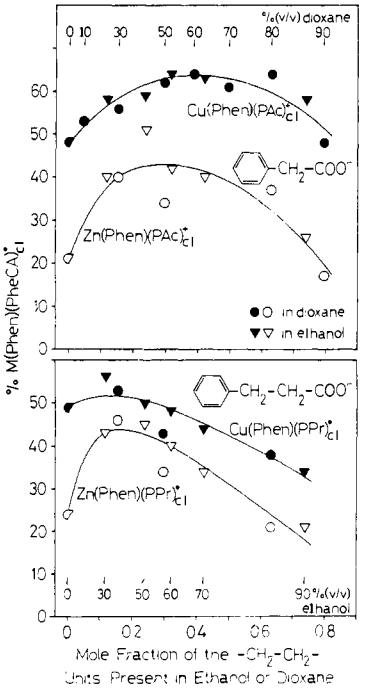


Figure 8. Formation degree of the intramolecular aromatic-ring stack (eq 1) in ternary $M(phen)(PAc)^+$ (top) and $M(phen)(PPr)^+$ (bottom) complexes of Cu^{2+} (●, ▼) and Zn^{2+} (○, ▽) in dependence on the mole fractions of ethanol (▼, ▽) or dioxane (●, ○) based on the number of dimethylene units ($-CH_2-CH_2-$) present in these solvent molecules (see text in section 6); the second solvent component is always water (Tables V and VI; I = 0.1; 25 °C). Note, the mole fractions for ethanol are the same as in Figure 4, but those for dioxane are different, because there are two dimethylene units in each dioxane molecule.[44]

(eq 1) in dependence on the mole fractions of the dimethylene units present in ethanol or dioxane. It is evident from Figure 8 that now the data of both kinds of solvent mixtures fit excellently (with ±8%), i.e., even better than in Figure 4, on a single curve for a given ternary complex.

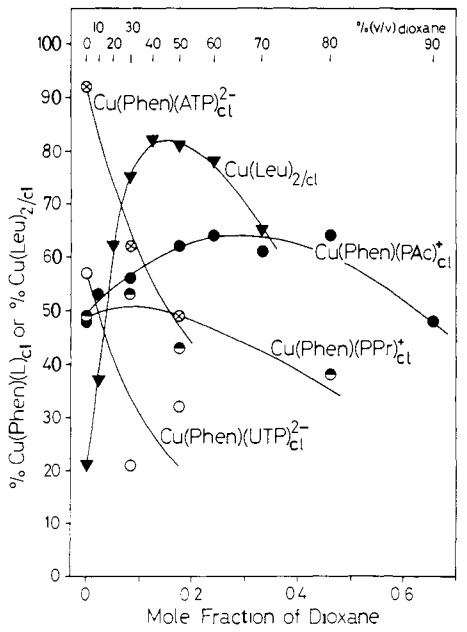


Figure 9. Formation degree of the intramolecularly closed species (eq 1) in the ternary Cu(phen)(L) complexes, where L = PAc$^-$ (●, Table VI), PPr$^-$ (◓, Table VI), ATP^{4-} (⊗, ref 2),[21] or UTP^{4-} (○, ref 2: these values are estimates, but the trend shown is certain), and in the binary Cu(Leu)$_2$ complex (▼, ref 3: here, an intramolecular hydrophobic isopropyl–isopropyl interaction is possible; see also the general discussion in Section 7) in dependence on the mole fractions of dioxane; the second solvent component is water (I = 0.1; 25 °C).

7. Is There Besides a Stacked Isomer a Further "Closed" Complex in the M(phen)(PheCA)$^+$ Systems? By looking on the results summarized in Figure 8, it is tempting to postulate in addition to the two complexes indicated in equilibrium 1 a *third* species, which should also somehow be "closed". This would allow an easy interpretation of the data giving species both rising and falling as organic solvent is added, thereby accounting for the maxima. The concentration of such species could be calculated in a way similar to the treatment offered by Mariam and Martin[45a] for isomeric equilibria in nucleotide–metal ion complexes.

In the present case, it is tempting to describe this additional "closed" species as one having a metal ion–aromatic ring interaction, because with increasing organic solvent the aqueous hydration shell of the metal ion is expected to be reduced, and this might then favor such an interaction. However, for Cu^{2+} and Zn^{2+}, no hint for a metal ion–aromatic ring interaction could be discovered (for a detailed discussion, see ref 3),[19,28] and what is more important: the promotion of closed species by addition of certain amounts of organic solvents seems a general phenomenon, apparently independent of the kind of metal ion (Figure 8), and not only valid for systems with aromatic rings but also for those with aliphatic residues as is evident from the results plotted in Figure 9 for the Cu^{2+}/L-leucinate system;[3] the formation degree of Cu(Leu)$_{2/closed}$ follows also a "bell-shaped" curve. Evidently, a Cu^{2+}–isopropyl interaction can hardly be postulated, a conclusion in agreement with the recent observations of Kim and Martin[45b] made at (dipeptide)Pd^{II}(amine) complexes. These authors concluded for the order of decreasing interaction energies the following: phenyl–aromatic > phenyl–propyl (or larger alkyl residue) > ... > Pd–aromatic ≫ Pd–aliphatic ~ 0. Hence, a third complex with an intramolecular metal ion–aliphatic or –aromatic interaction cannot be the cause for the "bell-shaped" curves.

What other possibilities remain then for the postulation of a third species? There appear to be two, which are closely connected: (i) Hydrophobic solvation of the intramolecular stacks via the ethylene groups of the organic solvent molecules could lead to stacks with a somewhat different geometry, i.e., different orientations of the aromatic rings as well as altered distances between these rings, even partial intercalation of the organic solvent molecules appears as possible;[46] this would then also account for the influence of the solvent on the extent of the ^{1}H NMR upfield shifts ($\Delta\delta$).[47] (ii) Addition of the organic solvents will most probably reduce the size of the aqueous hydration shell of the metal ion in M(phen)(PheCA)$^+$, and this could even lead to a reduction of the coordination number of the metal ion. It should be noted that this suggestion applies to species in which the aromatic (or aliphatic) residues still "feel" each others presence, because any solvent effects occurring in the completely open isomer are expected to cancel as we are evaluating our results on the basis of the constants measured for M(phen)(HCOO)$^+$ and M(phen)(Ac)$^+$.

It is evident that the "third" species described above in i and ii would still be a complex with a ligand–ligand interaction, though structurally (somewhat) different from that of the stacked complex occurring in aqueous solution (Figure 2). In addition, having points i and ii in mind, it becomes apparent that in the mixed solvents, probably a whole series of closed (or stacked) species is present, which differ in their number of solvating molecules and possibly even in the coordination number of their metal ions. The consequence of this is that it becomes useless to try to attribute a distinct structure to the so-called "third" species; these are best classified simply also as "closed" complexes, which brings us back to the consideration of equilibrium 1. However, one should be aware that "closed" species, at least for the mixed solvents, may mean a series of ternary complexes all having an intramolecular ligand–ligand interaction but somewhat different structures (orientation of the aromatic rings, degrees of solvation[46] and/or coordination numbers).

One might view this situation also by saying that the aromatic stack or the aliphatic intramolecular adduct originally present in water possibly acts as germ to attract the organic solvent molecules and to form a micelle-like hydrophobic environment close to the metal ion. It is evident that this and the above description is a hypothesis; there are at present only indirect hints for it but no experimental proofs. However, at the same time, one should point out that at least to some extent, simple stacks (Figure 2) appear still to be present in agreement with the NMR results (Figure 3; Table IV), and studies in 50% (v/v) dioxane–water showed[19] that the stability increase measured for the ternary M(phen)(PheCA)$^+$ complexes depends on the size of the aromatic residue (e.g., phenyl vs. naphthyl) and, more important, is also influenced by substituents altering the electron density in the phenyl moiety and thus its charge-transfer properties.

All these considerations should be kept in mind when one analyzes the results of Tables V and VI (or Figures 8–10). The whole increase in stability which is quantified by $\Delta\Delta$ log K (column 6 in Tables V and VI) is here attributed by using eq 3 to M(phen)(PheCA)$_{cl}^+$; this complex is probably only in water a well-defined stack, while in the mixed solvents it may be a mixture of species.

8. Opposing Solvent Effects Determine the Formation Degree of the Closed Species in M(phen)(PheCA)$^+$. In trying to answer the question raised in section 4 by taking into account the considerations of sections 5–7, we believe that the results summarized in Figure(s) 8 (and 9) may be explained in the following way.

(i). In accord with the observations for the binary M(CA)$^+$ complexes, the *overall* stability of the ternary complexes formed

(45) (a) Mariam, Y. H.; Martin, R. B. *Inorg. Chim. Acta* **1979**, *35*, 23–28. (b) Kim, S.-H.; Martin, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 1707–1712.

(46) (a) Theoretical studies[46b,c] of hydrophobic interactions in aqueous solution support the idea that the hydrophobic effect can act over longer distances (than originally expected) via solvent-separated associations involving alkyl groups or aromatic-ring systems. It is shown[46b] that "long-range interactions corresponding to solvent-separated structures are important". This raises, for example, the possibility[46b] that "the equilibrium structures of nucleotide bases in aqueous solution exist to some significant extent in stacked solvent-separated forms" (for related experimental studies in water–dioxane mixtures see ref 2). (b) Ravishankar, G.; Beveridge, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 2565–2566. (c) See list of references cited in ref 46b.

(47) For a detailed analysis of the chemical shifts (Table IV), it would be necessary to determine in independent experiments also the exact influence on the shift position of the proton and of Zn^{2+} alone; for these latter interactions (small), downfield shifts are expected (see also footnote 37 and for studies on related systems ref 48a).

between $M(phen)^{2+}$ and the negatively charged phenylalkanecarboxylates is favored due to the decrease in polarity in aqueous/organic solvent mixtures, compared with a purely aqueous solution (section 5; Figure 5).

(ii). However, the explanation for the favored formation of metal ion-bridged "stacks" in certain (low and medium ratio) organic solvent/water mixtures has to focus on the intramolecular equilibrium 1, the position of which is *independent* on the total concentration of $M(phen)^+$ and $PheCA^-$. Hence, the explanation can only be that under certain conditions, the closed species of $M(phen)(PheCA)^+$ are further stabilized; this could occur in at least three ways (or in combinations thereof): (a) through a preferred hydrophobic solvation of the stacks initially present in aqueous solution by the organic solvent molecules, (b) the micelle-like hydrophobic environment (section 7) close to the metal ion could reduce the *effective* dielectric constant at the metal ion and consequently the M^{2+}/O^- binding would be stabilized,[28,49] and (c) through a facilitated reduction of the coordination number of the metal ion also, an enhanced complex stability could result.[50] Hence, it is suggested that due to these effects operating only in more or less closed species (see section 7), these are favored; consequently, the completely open isomers (at the left in eq 1) appear as less attractive for a hydrophobic solvation by the organic solvent molecules.

(iii). Clearly, the bridging metal ion must be the cause for the apparent inhibition of the hydrophobic solvation of the aromatic residues by the organic solvent molecules in the open isomers, because in the *unbridged* stacking adducts (section 1) the individual aromatic moieties are preferably solvated and stack formation is then inhibited (section 4). If the metal ion, i.e., probably more precisely its aqueous solvation shell in $M(phen)(PheCA)^+$,[51] is the cause for a reduced solvation of the open isomer by the organic solvent molecules, then this solvation should become easier again with increasing distance of the aromatic moieties from the metal ion center. This assumption is at least tentatively confirmed by some additional results also summarized in Figure 9: for $Cu(phen)(ATP)_{cl}^{2-}$ and $Cu(phen)(UTP)_{cl}^{2-}$, no bell-shaped curve is observed.[2,52,53] Hence, the results of Figure 9 suggest that the disappearance of the bell-shaped property, i.e., the promotion of the closed species (section 7), by the addition of (small amounts of) organic solvents is a process which depends on the distance between the groups undergoing the intramolecular ligand–ligand interaction and those groups coordinating to the metal ion. This distance increases in the series $M(phen)(PAc)^+ > M(phen)(PPr)^+ \gg M(phen)(ATP)^{2-} \sim M(phen)(UTP)^{2-}$.

(iv). Finally, at high concentrations of the organic solvent, the metal ion/carboxylate interaction in the $M(phen)(PheCA)^+$ complexes is still further favored (point i), but the aqueous hydration shell of the bridging metal ion in the open isomer is now so reduced in size that the individual aromatic-ring systems (or the alkyl residues) are now also easily solvated by the organic solvent molecules and consequently the formation of the intramolecular closed species (or the formation of the micelle-like hydrophobic environments at the metal ion) is inhibited (or no longer perferred) and therefore the effects discussed in points (ii) and (iii) are eliminated. Hence, e.g., the stability of $M(phen)(PheCA)^+$ corresponds now to that of $M(phen)(HCOO)^+$ or $M(phen)(Ac)^+$.

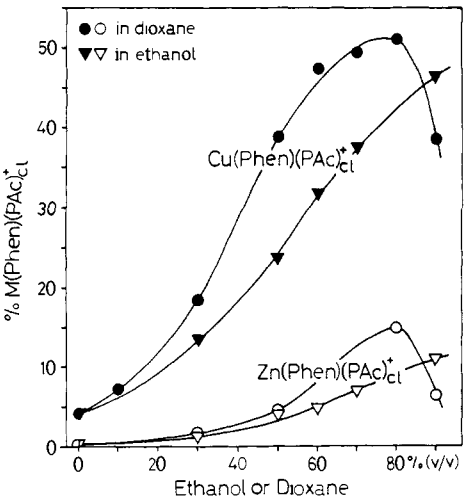


Figure 10. Concentration of $M(phen)(PAc)_{cl}^+$, expressed as percentage of $[M^{2+}]_{tot} = 100\%$ ($[M^{2+}]_{tot} = [phen]_{tot} = [PAc]_{tot} = 10^{-3}$ M), for the Cu^{2+} (●, ▼) and Zn^{2+} (○, ▽) systems at pH 7 in dependence on the percentage of ethanol (▼, ▽) or dioxane (●, ○) present in the aqueous solvent mixture.[54] The concentration of the species was calculated with the constants listed in Tables II, III, V, and VI ($I = 0.1$; 25 °C).

One could summarize the situation by saying that in water, the aqueous hydration shell of the bridging metal ion is large, hindering the solvation of the open isomer by the organic solvent molecules, and that this aqueous shell is possibly already somewhat reduced in size in the closed species, favoring a preferred solvation of the intramolecular (and themselves already hydrophobic) adduct, leading thus to an increased formation degree of these closed complexes (section 7) due to the reasons given in ii. At high concentrations of the organic solvents, there are enough of these molecules present to separate the aromatic moieties and to enforce their individual solvation despite the presence of the metal ion bridge (which has now certainly also a much smaller hydration shell), thus favoring the open isomer. However, it is evident that more experimental material and studies of related systems are needed before a more final explanation, also regarding the possible structural alterations discussed in section 7, can be given.

9. Relation between Formation of the Closed Species and Absolute Concentration. The "bell-shaped" effect of Figures 4, 8, and 9, which characterizes the formation degree of the closed species (eq 1), is indirectly coupled with the increasing overall stability of the ternary complexes (eq 7) as is evident from Figure 5. These coupled properties have a dramatic effect on the *actual* concentration of the closed species present in solutions: considering, e.g., $Zn(phen)(PAc)^+$ at pH 7 and at reactant concentrations of 10^{-2} M, one calculates with the constants of Tables III and VI, relative to the *total* reactant concentration, that in water, 2% exist as $Zn(phen)(PAc)_{cl}^+$, in 50% aqueous dioxane 16%, and in 80% aqueous dioxane 27%.[54] These results have to be compared with

(48) (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.

(49) This would be quite an effective mechanism; see Figure 11 and the corresponding discussion in the General Conclusions section.

(50) The possibility that a change in coordination number is an important factor for the $M(phen)(PheCA)^+$ complexes seems not too attractive, because one would expect that Cu^{2+} and Zn^{2+} change their coordination number at different organic solvent/water ratios, but in fact, the properties of the Cu^{2+} and Zn^{2+} complexes parallel each other rather well (Figure 8). More of a parallelism is expected, however, if the stability increase occurs via an alteration of the effective dielectric constant.[49]

(51) That the aqueous solvation shell of a metal ion may have an influence on the stacking properties of a system is also indicated by the results summarized in footnote 38.

(52) The extent of stacking in $Cu(phen)(UTP)^{2-}$ is smaller than in $Cu(phen)(ATP)^{2-}$, because the pyrimidine moiety of UTP^{4-} is a much smaller aromatic residue compared with the purine portion of ATP^{4-}.[2]

(53) It must be pointed out that also for $M(phen)(ATP)^{2-}$ and $M(phen)(UTP)^{2-}$, the metal ion bridge favors intramolecular stack formation between the phenanthroline rings and the (relatively far distant) purine or pyrimidine residues; e.g., $Cu(phen)(ATP)_{cl}^{2-}$ decreases *only* by a factor of about $^1/_2$ by going from water to 50% (v/v) dioxane–water (Figure 9), while the stability of the binary $(phen)(ATP)^{4-}$ adduct[2] decreases by a factor of about $^1/_{20}$.

(54) It should be noted that the above calculations were carried out for pH 7 to allow a unified view about the influence of the solvent composition on the formation of the closed species under conditions where the competition between H^+ and M^{2+} for binding at the carboxylate group of PAc^- is small. Any hydroxocomplex formation which occurs to a different extent at pH 7 in these solvent mixtures with Zn^{2+} or Cu^{2+} systems has not been considered in the calculations, as this would add a further factor which has primarily nothing to do with the intended comparisons. There are also many metal ions, like Mg^{2+}, Ni^{2+}, or Cd^{2+}, which form no hydroxocomplexes at pH 7 but which are able to form bridged adducts between organic residues. It should be emphasized that the experiments on which our results and calculations are based were carried out, of course, under conditions where no hydroxocomplex formation occurs.

the corresponding calculations for the unbridged [Zn(phen)]-(BzOH)$^{2+}$ stack (Table I), i.e., with 2% stack in water, 0.4% in 50% dioxane, and less than 0.1% in 80% dioxane, and then the promoting effect of the metal ion bridge becomes very evident by itself.

At this point, it should be emphasized once more that the formation of metal-ion-bridged adducts is favored by the addition of (some) ethanol or dioxane (Figures 4, 8, and 9). However, this is true not only if the intramolecular equilibrium 1 is considered; it is even more true, if the absolute concentrations of a closed species are examined: Figure 10 shows the formation of M(phen)(PAc)$_{cl}^{+}$ in 10^{-3} M reactant solutions at pH 7 in dependence on the percentage of the organic solvent present in the solvent mixture.[54] It is evident that even in 90% aqueous ethanol or dioxane, the concentration of the closed species (see section 7) of M(phen)(PAc)$^{+}$ is still larger than in water. Moreover, the corresponding unbridged stack occurs in its highest concentration in water (section 1), where it is only about 2×10^{-6} M, which corresponds to 0.2% of the total reactants concentration. All this is certainly of importance with regard to biological systems because related metal-ion-bridged adducts are now well-known: e.g., by nucleotides and amino acids in aqueous solution, stacks are formed.[17]

General Conclusions

It seems rewarding to consider the properties of the individual groups characterized in this study somewhat more in detail to obtain some further insight into events occurring in nature. The carboxylate residue, e.g., present in proteins, is an important ligating group for metal ions,[35] and the phenyl ring, e.g., present in phenylalanine, is able to participate in stacking interactions as we have seen in this and previous studies.[18,19,22] The corresponding properties have been described for the indole residue of tryptophan and the imidazole ring in histidine,[19,22] and similar observations have also been made for aliphatic residues, which are able to undergo hydrophobic interactions in mixed-ligand complexes.[3,17,22] All this agrees with the recognized[5-7] importance of hydrophobic and stacking interactions in systems of biological origin. However, the interplay between these interactions and the coordination of metal ions is only at the brink of recognition.[17,22,48]

An observation of interest in this connection is that 3-phenylpropionate and related carboxylate ligands are excellent inhibitors of carboxypeptidase A (CPA).[29,30] Recently, in different connection, we have estimated[28] the equivalent solution dielectric constant in the active-site cavity of CPA as approximately 70. Assuming that the affinity of acetate toward Zn^{2+} in the active-site cavity of CPA is governed solely[55] by the decreased polarity, this estimation is duplicated by the arrow inserted in Figure 11, where log $K^{M}_{M(Ac)}$ and p$K^{H}_{H(Ac)}$ are plotted in dependence on the dielectric constant. Hence, the equivalent solution (or effective) dielectric constant in the active-site cavity of CPA corresponds about to that of an aqueous solution containing approximately 10% dioxane or about 15% ethanol.

For the present context, it is important only to note that the affinity of acetate toward the intrinsic Zn^{2+} of CPA (log $K^{(CPA-Zn)}_{(CPA-Zn)(Ac)}$ = 1.3; I = 0.2; 25 °C)[29] is about 0.2 log unit larger than toward Zn_{aq}^{2+} (log $K^{Zn}_{Zn(Ac)}$ = 1.11; I = 0.1; 25 °C; see Table II). This fact is crucial because it allows us to estimate the affinity of 3-phenylpropionate toward CPA under the assumption that only the coordination tendency of the carboxylate group toward the intrinsic Zn^{2+} governs the situation: i.e., log $K^{(CPA-Zn)}_{(CPA-Zn)(PPr)/estimate}$ = 1.14 (Table II) + 0.2 ≃ 1.34. However, this value is by 2.4 log units too low, if compared with the measured constant, log $K^{(CPA-Zn)}_{(CPA-Zn)(PPr)}$ = 3.77 (I = 0.2; 25 °C);[29] hence, additional interactions must be present which are responsible for this stability increase.

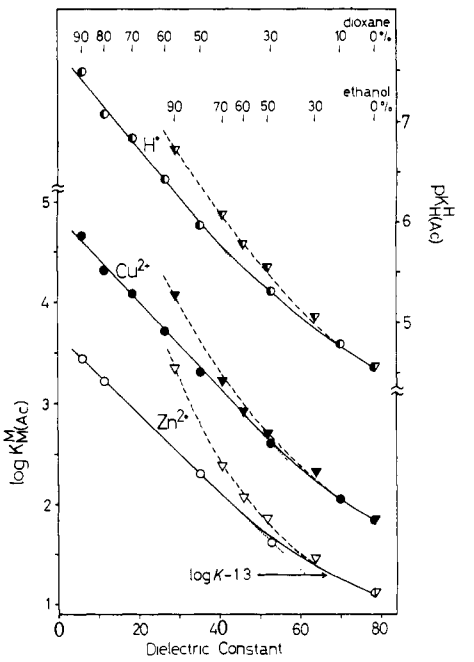


Figure 11. Negative logarithms of the acidity constants, p$K^{H}_{H(Ac)}$, of acetic acid (◐, ▽) and logarithms of the stability constants, log $K^{M}_{M(Ac)}$ (eq 6), of the Cu^{2+} (●, ▼) and Zn^{2+} (○, ▽) 1:1 complexes with acetate in dependence on the variation of the dielectric constant resulting from the addition of dioxane (full lines) or ethanol (broken lines) to water; the data are from Tables II and III (I = 0.1; 25 °C). The dotted line parts indicate extensions corresponding to straight lines. The constant inserted at the bottom part is the stability constant for the complex between carboxypeptidase A and acetate, log $K^{(CPA-Zn)}_{(CPA-Zn)(Ac)}$ = 1.3;[29] this value marks the approximate equivalent solution dielectric constant[28] of the active-site cavity in CPA.

Indeed, it has been suggested earlier[29,30] that aliphatic or aromatic residues of such carboxylate ligands, like 3-phenylpropionate, can conveniently be accommodated in a hydrophobic pocket in the active-site region. However, to explain a stability increase of 2.4 log units seems hardly possible in this simple way: in the most favored cases of the present study, the stability increase due to intramolecular ligand–ligand interactions corresponds only to 0.4 log unit. Certainly, this value corresponds to an interaction which occurs only from *one* side (i.e., phenyl to phenanthroline) and not with a two-sited pocket, but even if we take this into account by a further factor of 10 (which means to stretch the matter quite far), we have left unexplained still about 1.0 log unit.

We believe that this additional increase in stability can be explained by a "cooperative mechanism" which functions in the following way: the carboxylate group coordinates to the intrinsic Zn^{2+} in the active-site cavity and the "bulky" residue of the carboxylate undergoes a hydrophobic/stacking interaction with the hydrophobic pocket also present in the active-site region. This latter interaction with the "bulky" moiety of the carboxylate ligand influences also the polarity in the active site, i.e., it initiates a further decrease of the equivalent solution dielectric constant, and this of course strengthens then in turn the carboxylate/Zn^{2+} interaction. From Figure 11, it is evident that a reduction of the dielectric constant from about 70 to about 40 would lead to an additional stability increase of about 1.0 log unit. An equivalent solution dielectric constant close to about 40,[56] created in this way, is of a very reasonable order and close to the recent[28] estimate of 35 made for the active-site cavity of bovine carbonic anhydrase.

The indicated "cooperative mechanism" is able to explain the high stability of many metalloenzyme/substrate or inhibitor adducts.[57] Furthermore, for those metalloenzymes which catalyze

(55) The influence of the reduced coordination number of Zn^{2+} in CPA and several other effects influencing the coordination tendency of the metal ion are evaluated in detail in ref 28; all these effects are small and cancel out to a first approximation.

(56) An equivalent solution dielectric constant of about 40 would correspond to an aqueous solution containing approximately 40% dioxane or 70% ethanol (see Tables II and III and Figure 11).

transfer reactions of polar groups (e.g., of phosphate residues), the release of the products from the active site would automatically be initiated, because as soon as the link between the polar group and the hydrophobic site is broken, the distance between them will (at least slightly) increase and the cooperativity will disappear. In this way, the active site would become accessible for another substrate molecule, and a perpetual turnover would be guaranteed.

(57) (a) A similar "cooperative mechanism" between hydrogen-bonding and hydrophobic interactions has very recently been suggested[57b] for the complexes formed by peptides and the glycopeptide antibiotics, vancomycin and ristocetin. It was concluded "that addition of a hydrophobic group not only allows hydrophobic bonding but also strengthens existing hydrogen bonds" and that the "increased hydrogen bond strength can be an important factor in determining the overall binding energy". (b) Williamson, M. P.; Williams, D. H. *Eur. J. Biochem.* **1984**, *138*, 345-348.

Acknowledgment. The computer was made available by the Rechenzentrum der Universität Basel (Univac 1100/81). This support, a research grant from the Swiss National Science Foundation, and a fellowship to U.K.H. from the Stipendienfonds der Basler Chemischen Industrie are gratefully acknowledged.

Registry No. BzOH, 100-51-6; ethanol, 64-17-5; dioxane, 123-91-1.

Catalytic Photochemical Dehydrogenation of Organic Substrates by Polyoxometalates

Craig L. Hill* and Donald A. Bouchard

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322.
Received December 3, 1984

Abstract: The photochemical behavior of the polyoxometalates based on W, Mo, V, Nb, and Ta in the presence of water or one of a variety of organic substrates including alcohols, amides, ethers, aldehydes, carboxylic acids, nitriles, ketones, and ureas is examined. Irradiation of the charge-transfer bands of polyoxometalates dissolved in organic media at 25 °C leads in most cases to the oxidation of the organic substrate and reduction of the polyoxometalate. The polyoxometalates fall into three categories defined by their thermal and photochemical redox chemistry in the presence of organic substrates. Type I complexes exemplified by those of Nb and Ta do not appear to photooxidize any organic substrate upon irradiation. Type II complexes, exemplified by decavanadate and most heteropoly- and isopolymolybdates, and type III complexes, exemplified by most heteropoly- and isopolytungstates, do oxidize a wide range of organic substrates upon irradiation. Reoxidation of the reduced forms of the type II complexes either by reaction with O_2 or by evolution of H_2 is kinetically or thermodynamically unfavorable; reoxidation of the reduced forms of the type III complexes either by reaction with O_2 or by evolution of H_2 is not. Several factors affecting the quantum yields for production of reduced polyoxometalates are outlined, and the energetic features regarding hydrogen evolution are discussed. The infrared, electronic, ^{31}P NMR, ^{183}W NMR, and ^{17}O NMR spectral properties of α-$H_3PW_{12}O_{40}\cdot 6H_2O$, **1**, and other polyoxometalates remain the same before and after catalytic photochemical dehydrogenation of representative alcohol, ether, or amide substrates. These results indicate that little if any polyoxometalate decomposition occurs during the photoredox chemistry. Interactions between organic substrates and polyoxometalates have profound effects on the electronic structure of the polyoxometalates. The charge-transfer transitions of polyoxometalate **1** display different sensitivities to medium in the low-energy ($\lambda > 300$ nm) vs. the high-energy region of the ultraviolet–visible spectral range. The highest sensitivities of the quantum yields for photoredox chemistry involving organic substrates and **1** to medium are observed in the low-energy or absorption tail region of the spectrum. One possible model explaining the wavelength dependence of the absorption and photochemical action spectra is discussed. A general mechanism in agreement with all the experimental data is proposed for organic substrate oxidation and the effective capture of light energy in these polyoxometalate–organic substrate systems.

Polyoxometalates or polyoxoanions have been known for well over a century, yet it has been only in the last few years that scientific interest in these materials began to increase dramatically.[2,3] Two reasons for the recent surge in popularity of polyoxometalate chemistry are that only recently have many of the potential applications for these materials become well defined and the analytical methodology for adequately characterizing these complex molecules become well developed.[2,4-10] Since 1977, polyoxometalates and, in particular, heteropoly acids have received increasing attention as reagents or catalysts for redox processes involving organic substrates.[11-14] Most of these polyoxo-

(1) Some of the preliminary research on this chemistry was executed at the University of California, Berkeley, by C.L.H. Approximately 60% of this work was presented at the Joint NSF-CNRS Polyoxoanion Workshop, St. Lambert des Bois, France, July 11-13, 1983, and written up in the proceedings of that meeting.

(2) The most recent and definitive review on polyoxometalates: Pope, M. T. In "Heteropoly and Isopoly Oxometalates"; Springer-Verlag: Berlin, 1983.

(3) Other reviews: (a) Weakley, T. J. R. *Struct. Bonding (Berlin)* **1974** *18*, 131. (b) Tsigdinos, G. *Top. Curr. Chem.* **1978**, *76*, 1. (c) Evans, H. T., Jr. *Perspect. Struct. Chem.* **1971**, 4, 1; (d) Kepert, D. L. *Prog. Inorg. Chem.* **1962**, *4*, 199. (e) Tytko, T.-H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239.

(4) The application of $^{17}O_6$ NMR largely by Klemperer and co-workers[5] and ^{183}W NMR by the groups of Baker,[6] Brevard, and Schimpf,[7] Finke,[8] and Domaille[9] to polyoxometalates is noteworthy as is the very recent report of fast atom bombardment mass spectrometry (FABMS) for polyoxometalate characterization by Finke, Suslick, and co-workers.[10]

(5) Filowitz, M.; Ho, R. K. C.; Kelmperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93 and references therein.

(6) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384 and references cited therein.

(7) Brevard, C.; Schmipf, R.; Tourne, G.; Tourne, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059.

(8) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587.

(9) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677.

(10) Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750.

(11) Trost, B. M.; Masuyama, Y. *Tetrahedron Lett.* **1984**, 173.

(12) (a) Davison, S. F.; Mann, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1223. (b) Urabe, K.; Kimura, F.; Izumi, Y. 7th International Congress on Catalysis, Tokyo, 1980, Part B, p 1418. (c) Ogawa, H.; Fujinami, H.; Taya, K.; Teratani, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1274. (d) Mateev, K. I. *Kinet. Katal.* **1977**, *18*, 716. (e) Rudenkov, A. I.; Mennenga, G. U.; Rachkovskaya, L. N.; Mateev, K. I.; Kozhevnikov, I. V. *Ibid.* **1977**, *18*, 758. (f) Pachkovskaya, L. N.; Mateev, K. I.; Il'inich, G. N.; Eremenko, N. K. *Ibid.* **1977**, *18*, 854. (g) Taraban'ko, V. E.; Kozhevnikov, I. V.; Mateev, K. I. *Ibid.* **1978**, *19*, 937. (h) Kozhevnikov, I. V.; Taraban'ko, V. E.; Mateev, K. I. *Ibid.* **1980**, *21*, 679, 685. (i) Mennenga, G. U.; Rudenkov, A. I.; Mateev, K. I.; Kozhevnikov. I. V. *React. Kinet. Catal. Lett.* **1976**, *5*, 401. (j) Rochkovskaya, L. N.; Mateev, K. I.; Rudenkov, A. I.; Mennenga, G. U. *Ibid.* **1977**, *6*, 73. (k) Taraban'ko, V. E.; Kozhevnikov, I. V.; Mateev, K. I. *Ibid.* **1978**, *8*, 77.

0002-7863/85/1507-5148$01.50/0