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Dependence of an Intramolecular Aromatic-Ring Stacking Interaction in Mixed-Ligand Copper(II) Complexes in Aqueous Solution on the Distance of the Stacking Moiety from the Coordinating Group and the Solid-State Structure of the Ternary Copper(II)–1,10-Phenanthroline–Phenylpropionate Complex[1]

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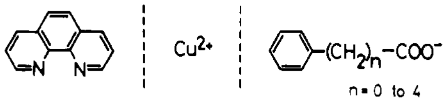
The stability constants of mixed-ligand complexes of the type Cu(phen)(PheCA)$^+$, where phen = 1,10-phenanthroline and PheCA$^-$ = benzoate, 2-phenylacetate, 3-phenylpropionate, 4-phenylbutyrate, and 5-phenylvalerate, have been determined by potentiometric pH titration in aqueous solution and compared with the stabilities of the corresponding ternary complexes formed with formate or acetate. The ternary complexes containing phenylalkanecarboxylates (PheCA$^-$) are significantly more stable because of the intramolecular stacking between the phenyl moiety of the PheCA$^-$ ligands and the phenanthroline molecule. This type of stacking is confirmed by ^{1}H NMR shift measurements of the Zn^{2+}/phen/benzyl alcohol system in water: the stability of the resulting unbridged adduct was determined ($K = 2.2$ M^{-1}). In addition, by measuring the upfield shifts of the Zn^{2+}/phen/2-phenylacetate system, the formation of stacks was also shown and the stability constant determined by potentiometric pH titration was confirmed; similarly, the stability constant of the corresponding Cu^{2+} system was confirmed by UV difference spectrophotometry. The extent of the intramolecular stacking in the ternary Cu^{2+} complexes was calculated; the stacked isomers occur between about 20 and 50%, depending on the number of methylene groups between the phenyl moiety and the coordinated carboxylate groups; the "best fit" is reached with 2-phenylacetate and 3-phenylpropionate. From an aqueous solution of the Cu^{2+}/phen/3-phenylpropionate (PPr$^-$) system crystals of Cu(phen)(PPr)(NO$_3$)·2H$_2$O were isolated and subjected to an X-ray analysis. Crystal data: monoclinic, a = 22.876 (3), b = 12.284 (2), c = 16.320 (6) Å; β = 111.03 (2)°; space group $C2/c$, Z = 8. In the solid state the complex consists of dimeric [Cu$_2$(phen)$_2$(PPr)$_2$(H$_2$O)$_2$]$^{2+}$ cations, NO$_3^-$ anions with a considerable amount of disorder, and H$_2$O molecules hydrogen bonded to the H$_2$O molecules of the dimers. The dimers result from bridging of two Cu(phen)$^{2+}$ units by two carboxylate groups and a phen–phen stack. The Cu–Cu distance is 3.054 Å; antiferromagnetic coupling of the two unpaired electrons on each copper center is evidenced by magnetic susceptibility measurements. Each copper atom has an approximate square-pyramidal coordination geometry consisting of two nitrogen and three oxygen atoms. Aromatic ring–ring interactions are dominated by the "homo" stacks of the phenanthroline ligands within the dimers, but weak *intra*molecular ligand–ligand interactions between the phenyl moiety of PPr$^-$ and an edge of a phenanthroline, both partners being linked to the *same* Cu^{2+}, are also observed, as well as the corresponding *inter*molecular interactions. The solid-state structure and the structures of the complexes in solution are compared and discussed.

Among the intramolecular ligand–ligand interactions occurring in ternary complexes[4,5] the stacking interactions between suitable aromatic moieties of the two-coordinated ligands are especially fascinating. Such intramolecular stacks are formed, e.g., between the indole moiety of tryptophanate and the purine moiety of adenosine 5′-triphosphate,[6,7] and they are known to occur also in a number of other mixed-ligand complexes of biological interest.[8,9] In addition it has been shown[10] that stacking interactions may influence the rate of complex formation.

One of the problems in employing ligands of biological origin in such studies is that the ligand structures can hardly be altered in a systematic way. To overcome this problem we decided to study the ternary complexes indicated in Chart I.[11]

Chart I



The use of the phenylalkanecarboxylate ligands benzoate (Bz$^-$), 2-phenylacetate (PAc$^-$), 3-phenylpropionate (PPr$^-$), 4-phenylbutyrate (PBu$^-$), and 5-phenylvalerate (PVa$^-$) allows a systematic lengthening of the link between the coordinated carboxylate group and the phenyl moiety undergoing possibly an intramolecular stacking with the also coordinated 1,10-phenanthroline (phen).

We have now determined the extent of intramolecular stacking in aqueous solution for the ternary complexes of Chart I. In addition, we isolated crystals from a solution containing Cu^{2+}, phen, and 3-phenylpropionate and subjected these to an X-ray analysis. Previous studies of other ternary M(A)(B) complexes had already revealed for the solid state three main types of stacking:[12] (i) intermolecular stacks between A and B; (ii) intermolecular "homo" stacks between A and A (and/or B and B); (iii) intramolecular stacks[13,14] between A and B

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(1) Part 44 of the series "Ternary Complexes in Solution"; for part 43, see ref 4.

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(11) Abbreviations: A, B, or L, general ligand; Ac$^-$, acetate; Bz$^-$, benzoate; BzOH, benzyl alcohol; CA$^-$, carboxylate ligand; PAc$^-$, 2-phenylacetate; PBu$^-$, 4-phenylbutyrate; phen, 1,10-phenanthroline; PPr$^-$, 3-phenylpropionate; Pr$^-$, propionate; PVa$^-$, 5-phenylvalerate; M, general metal ion. Bz$^-$, PAc$^-$, PPr$^-$, PBu$^-$, and PVa$^-$ are designated as phenylalkanecarboxylates (=PheCA$^-$).

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within M(A)(B). Which of these types is preferred depends on the additional interactions occurring in a crystal lattice;[12] in addition, combinations of the given three types are also possible, e.g., intra- and intermolecular stacks can occur simultaneously.[14]

Experimental Section

Materials. 5-Phenylvaleric acid was synthesized by oxidation of 5-phenylpentan-1-ol with $K_2Cr_2O_7$ in concentrated H_2SO_4 or in basic media with $KMnO_4$.[15] At the end of the reaction the mixture was adjusted to pH 1–2 and extracted several times with diethyl ether. The etheral extract was treated with 2 M NaOH, and this aqueous phase was again adjusted to pH 1–2 and extracted with ether. After evaporation of the ether, the crude product was once recrystallized from petroleum/ether and once from water; mp_{cor} 58.5–59 °C, lit.[16] mp 59–60 °C. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; O, 17.96. Found: C, 73.90; H, 8.01; O, 18.09.

All the other materials were purchased: benzyl alcohol, formic acid, acetic acid, propionic acid, $Cu(ClO_4)_2 \cdot 6H_2O$ (all pro analysi), 2-phenylacetic acid, and 4-phenylbutyric acid (both puriss.) were from Fluka AG, Buchs, Switzerland. Benzoic acid, NaOH (Titrisol), HNO_3, $HClO_4$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, KNO_3, $NaNO_3$, $NaClO_4$, 1,10-phenanthroline monohydrate, potassium hydrogen phthalate, the disodium salt of ethylenediaminetetraacetic acid (all pro analysi), 3-phenylpropionic acid (hydrocinnamic acid) (puriss.), and a 10% tetramethylammonium hydroxide solution were obtained from Merck AG, Darmstadt, Germany.

The titer of the NaOH used for the titrations was determined with potassium hydrogen phthalate; the exact concentrations of the carboxylic acids were measured by titrations with NaOH. The concentrations of the stock solutions of the divalent metal ions were determined with EDTA.

Potentiometric pH Titrations. The pH titrations were carried out with a Metrohm potentiograph E 336 A and a Metrohm macro EA 121 glass electrode. 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.

The acidity constants $K^H_{H(CA)}$ for the carboxylic acids were determined by titrating 50 mL of aqueous 0.2 mM HNO_3 and KNO_3 (I = 0.1; 25 °C) in the presence and absence of 0.6 mM carboxylic acid under N_2 with 1 mL of 0.05 M NaOH. $K^H_{H(CA)}$ was always calculated from at least six independent titrations within the range determined by the lowest point of neutralization reached by the experimental conditions and about 98% neutralization.

The conditions for the determination of the stability constants $K^{Cu}_{Cu(CA)}$ of the binary $Cu(CA)^+$ complexes (I = 0.1; 25 °C) were the same as for the acidity constants, but KNO_3 was partly replaced by 25 mM (sometimes 12.5 mM) $Cu(NO_3)_2$, i.e., the $[CA]:[Cu^{2+}]$ ratio was about 1:42 (or 1:21). The stability constants $K^{Cu}_{Cu(CA)}$ were computed by taking into account the species H^+, H(CA), CA^-, Cu^{2+}, and $Cu(CA)^+$.[17] The individually calculated values for log $K^{Cu}_{Cu(CA)}$ showed no dependence on pH or on the excess of Cu^{2+}.

In the ternary Cu^{2+}/1,10-phenanthroline/carboxylic acid systems, complex formation is practically complete between Cu^{2+} and phen (at pH >2.5). Hence, as shown earlier,[18] each of these systems could also be treated as a binary one by considering the species[17] H^+, H(CA), CA^-, $Cu(phen)^{2+}$, and $Cu(phen)(CA)^+$. The $[CA]:[Cu^{2+}/phen]$ ratio was also about 1:42 (or 1:21), and the properties of the systems were as expected for a "binary" one.

In all Cu^{2+}-containing systems, the data were collected from 5% or 10% complex formation to the beginning of the hydrolysis of Cu_{aq}^{2+} or $Cu(phen)_{aq}^{2+}$, which was evident from the titrations without carboxylic acid. For all systems at least three independent pairs of titration curves were recorded and the results averaged.

Spectrophotometric Measurements. The UV difference spectra were recorded on a Cary 219 (auto-slit, 0.05–3.6 nm; auto base line) for aqueous solutions of the reactants using 1-cm quartz cells: the reference beam contained one cell with Cu^{2+}/phen and a second one with 2-phenylacetic acid; one cell in the sample beam contained the mixed system and the other water. All four cells contained $NaClO_4$ to maintain I at 0.1 M, and the pH was adjusted to 4.00 (25 °C). The experimental details not evident from Figure 3 were described in ref 19.

The apparent stability constant (valid for pH 4.00) was determined by an evaluation at several wavelengths in a way related to the Benesi–Hildebrand method,[20] but by plotting $[PAc]_{tot}/\Delta A$ vs. $[PAc]_{tot}$; in this way all experimental points have about the same weight. The details are described in ref 19. The apparent stability constant, K_{app}, determined in this way, was transformed to the pH-independent constant by taking into account the competition of the proton[21] for PAc^- with eq 1.

$$\log K^{Cu}_{Cu(PAc)} = \log K_{app} + \log (1 + [H^+]/K^H_{H(PAc)}) \qquad (1)$$

^{1}H NMR Spectroscopy. The ^{1}H NMR spectra were recorded on a Varian Anaspect EM-360 spectrometer (60 MHz) at 34 °C in H_2O as solvent, using the center peak of the tetramethylammonium ion triplet as internal reference. However, all chemical shifts were converted to a (trimethylsilyl)propanesulfonate reference by adding 3.174 ppm. The last mentioned reference is not directly usable due to its hydrophobic interaction with Zn^{2+}/phen.[22]

The stability constant of the unbridged adduct between benzyl alcohol (BzOH) (1.64×10^{-2} M) and Zn^{2+}/phen was determined by two independent experiments (an example is shown in Figure 2) in water (I = 0.25–0.50 ($NaNO_3$); 34 °C) at pH 5.20 by measuring the upfield shift of the protons at the phenyl residue in dependence on $[Zn^{2+}/phen]$ = 0.02–0.16 M. The observed upfield shifts were plotted in dependence on the increasing concentration of Zn^{2+}/phen and analyzed with a Hewlett-Packard 9821A or 9538A calculator by a curve-fitting procedure using the equations given in ref 8 and a Newton–Gauss nonlinear least-squares program. In this way the stability constant of the adduct, $K^{Zn(phen)}_{Zn(phen)(BzOH)}$, and the limiting shift, δ_∞, for the complete formation of the complex were obtained.

The apparent stability constant, K_{app}, of the ternary Zn(phen)-$(PAc)^+$ complex at pH 5.20 was obtained in the same way by employing the following concentrations: [PAc] = 1.25×10^{-2} M, $[Zn^{2+}/phen]$ = 1.5×10^{-2} to 8×10^{-2} M (I = 0.25 ($NaNO_3$); 34 °C). K_{app} was transferred into the pH-independent constant, $K^{Zn(phen)}_{Zn(phen)(PAc)}$, with eq 1.

Magnetic Susceptibility Measurements. The magnetic susceptibility of $Cu(phen)(PPr)(NO_3) \cdot 2H_2O$ from 50 to 300 K was measured on a Faraday balance from Oxford Instruments similar to that described by Gardner and Smith[23] with a magnetic field of 1.919 T and at three gradient fields (0.3, 0.5, 0.7 T/cm). A powder sample of 8.48 mg in a cylindrical sample holder formed from aluminum foil was used, suspended on a thin quartz fiber. The data were corrected for diamagnetism with $\chi_g = -0.624 \times 10^{-6}$ cgsu/g (calculated from ref 24).

Collection and Reduction of the X-ray Data. The crystals of $Cu(phen)(PPr)(NO_3) \cdot 2H_2O$ were prepared by dissolving 1 mmol of 3-phenylpropionic acid and 1 mmol of 1,10-phenanthroline in 50 mL of warm water and adjusting with 4 M NaOH to pH 5. To this solution was added 1 mL of 1 M aqueous $Cu(NO_3)_2$ under stirring, and then the pH was adjusted to 3.5–4.0. From this solution the complex crystallized within 1–7 days. Anal. Calcd for $C_{21}H_{21}N_3O_7Cu$: C, 51.38; H, 4.31; N, 8.56; Cu, 12.94. Found: C, 51.35; H, 4.25; N, 8.55; Cu, 12.9.

Preliminary cell dimensions were determined from Weissenberg and precession photographs; subsequently, these values were refined by least squares using 25 reflections centered on an Enraf-Nonius CAD4 diffractometer. A summary of the crystal data is presented in Table I. A possible transformation of the monoclinic unit cell to an orthorhombic pseudocell with a = 16.32 Å, b = 42.70 Å, c = 12.28

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Table I. Crystal Data, Details of Data Collection, and Analysis for $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$

cryst syst	monoclinic
cell const	
a, Å	22.876 (3)
b, Å	12.284 (2)
c, Å	16.320 (6)
β, deg	111.03 (2)
V, $Å^3$	4280.6
syst absences	hkl $(h + k = 2n + 1)$; $h0l$ $(l = 2n + 1)$
space group	$C2/c$
formula units/cell	8
d_{calcd}, g cm^{-3}	1.524
d_{obsd}, g cm^{-3}	1.55
abs coeff (μ), cm^{-1}	10.7
cryst dimens, mm	0.34 × 0.31 × 0.24
radiation (λ, Å)	Mo Kα (0.7107)
2θ limits, deg	1–60
data collcn	ω–2θ scan
no. of reflcns measd (including stds)	7262
no. of unique reflcns	5618
no. of obsd reflcns	2607 ($I > 3\sigma(I)$)
no. of variables	289
function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting scheme	$1/\sigma(F_o^2)$
ignorance factor, p	0.04
R, R_w	0.054, 0.077

Å, and $V = 8561.2$ Å^3 was indicated by the Delaunay reduction program.[25] Since the symmetry requirements for the reflection intensities of this orthorhombic cell however were clearly violated as demonstrated by precession photographs, intensity data were collected with the monoclinic cell given in Table I.

Background counts were measured at both ends, equal at each side to one-fourth of the total scan range of the peak. A variable scan speed (minimum value 1°/min) for the final scan was used for each reflection based on its I and $\sigma(I)$ values resulting from a prescan. The intensities and setting angles of six standard reflections monitored at regular intervals proved that no crystal decomposition or significant change of crystal orientation occurred throughout the entire data collection. The intensities were reduced to F_o by applying corrections for Lorentz, polarization, and background effects but not for absorption.[26]

Solution and Refinement of the Crystal Structure of Cu(phen)(PPr)(NO$_3$)·2H$_2$O. The statistical distribution of normalized structure factors E from a Wilson plot indicated a centric space group. Therefore, the structure determination was started with the assumption of space group $C2/c$. Since direct methods gave no reasonable solution, the structure was solved by conventional heavy-atom techniques. The position of the copper atom was deduced from a Patterson synthesis. Subsequent least-squares, Fourier, and difference Fourier calculations revealed the positions of all non-hydrogen atoms.

A disorder model for the nitrate group had to be chosen to account for the different peaks in the electron density maps. The position of the second water molecule was also affected by some disorder as indicated by its high isotropic thermal motion parameter of $B = 10.8$ Å^2. A disorder model assuming rotational disorder around the threefold axes of the nitrate group using varying occupancy factors did not significantly improve the agreement between F_o's and F_c's. Therefore, the nitrate group was introduced with idealized geometry at its approximate position and refined with anisotropic temperature factors keeping in mind that the resulting bond distances and thermal parameters have no physical significance. In the last cycles of refinement all hydrogen atoms except those of the two water molecules were included at their calculated idealized positions as a fixed contribution to F_c. Four very strong reflections that were obviously affected by secondary extinction were excluded from the refinement.

Results and Discussion

1. Studies in Aqueous Solution. (a) Definitions. The acidity constants (eq 2) of the carboxylic acids (CA) and the stability constants of their binary (eq 3) and ternary Cu^{2+} complexes (eq 4), the latter also involving 1,10-phenanthroline, were determined by potentiometric pH titrations ($I = 0.1$ (KNO_3); 25 °C). The stability of the $Cu(phen)^{2+}$ complex is large,[27]

$$H(CA) \rightleftharpoons H^+ + CA^- \qquad K^{H}_{H(CA)} = [H^+][CA^-]/[H(CA)] \tag{2}$$

$$Cu^{2+} + CA^- \rightleftharpoons Cu(CA)^+ \qquad K^{Cu}_{Cu(CA)} = [Cu(CA)^+]/[Cu^{2+}][CA^-] \tag{3}$$

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

$$K^{Cu(phen)}_{Cu(phen)(CA)} = [Cu(phen)(CA)^+]/[Cu(phen)^{2+}][CA^-] \tag{4}$$

and its formation is practically complete under our experimental conditions (see Experimental Section and ref 18). Hence, the stabilities of the ternary $Cu(phen)(CA)^+$ complexes could directly be determined according to eq 4.

The stability of mixed-ligand complexes is best quantified in relation to the stabilities of their binary parent complexes (eq 5).[5,28] The corresponding equilibrium constant $10^{\Delta \log K}$

$$Cu(phen)^{2+} + Cu(CA)^+ \rightleftharpoons Cu(phen)(CA)^+ + Cu^{2+} \tag{5}$$

is calculated with eq 6, which also shows that the formations of mixed-ligand complexes are cyclic processes.[29,30]

$$\begin{aligned} \Delta \log K &= \log K^{Cu(CA)}_{Cu(CA)(phen)} - \log K^{Cu}_{Cu(phen)} \\ &= \log K^{Cu(phen)}_{Cu(phen)(CA)} - \log K^{Cu}_{Cu(CA)} \end{aligned} \tag{6}$$

In general, eq 5 is expected to be on the left side corresponding to the common rule, $K^{M}_{M(L)} > K^{M(L)}_{M(L)_2}$, as well as to statistical considerations:[28] the first ligand to bind has more possibilities to coordinate at a given metal ion than the second one, etc. Unfortunately, it is difficult to assess statistical values for ternary Cu^{2+} complexes due to the Jahn–Teller distortion of this metal ion, but for the present systems one may estimate[28] $\Delta \log K_{Cu/statist} \simeq -0.5$.

(b) Stabilities of the Binary and Ternary Complexes. Table II contains not only the data for the phenylalkanecarboxylates of Chart I but, for reasons of comparison, also those for formate, acetate (Ac^-), and propionate (Pr^-), because in their ternary $Cu(phen)(CA)^+$ complexes no intramolecular stacking is possible. It is immediately obvious that all the ternary complexes are more stable than expected statistically: $\Delta \log K$ is either close to zero or even *positive*, indicating that equilibrium 5 is partly displaced to the right side. Are these positive values due to an especially low stability of the binary complexes or are the ternary complexes favored? A plot of $\log K^{Cu}_{Cu(CA)}$ vs. $pK^{H}_{H(CA)}$ reveals that for *all* the binary complexes a linear dependence is observed, indicating that the stability of these complexes is determined by the basicity of the carboxylate group of the ligands (Figure 1).

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(25) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius CAD4 SDP programs. This crystallographic computing package is described by: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsfeld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

(26) The intensity data were processed as described in: "SDP User's Guide"; Enraf-Nonius: Delft, Holland, 1982. The raw intensity is given as $I = (K/NPI)(C - 2B)$, where $K = 20.117\times$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The expression for the standard deviation of the intensity corrected for Lorentz–polarization factors is $\sigma(F_o^2) = K(C + 4B)^{1/2}/(NPI)Lp$, where Lp = Lorentz and polarization factors.

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Table II. Negative Logarithms of the Acidity Constants (Eq 2) of Several Carboxylic Acids, Logarithms of the Corresponding Binary $Cu(CA)^+$ (Eq 3) and Ternary $Cu(phen)(CA)^+$ Complexes (Eq 4) in Water (I = 0.1 (KNO_3); 25 °C) and Resulting Values for $\Delta \log K$ (Eq 6)[a]

ligand (CA^-)	n[b]	$pK^H_{H(CA)}$	$\log K^{Cu}_{Cu(CA)}$	$\log K^{Cu(phen)}_{Cu(phen)(CA)}$	$\Delta \log K$
Bz^-	0	4.03 ± 0.01	1.76 ± 0.01	1.84 ± 0.01	0.08 ± 0.01
PAc^-	1	4.12 ± 0.02	1.75 ± 0.04	2.01 ± 0.02	0.26 ± 0.04
PPr^-	2	4.44 ± 0.01	1.87 ± 0.02	2.14 ± 0.01	0.27 ± 0.02
PBu^-	3	4.59 ± 0.01	1.87 ± 0.01	1.99 ± 0.02	0.12 ± 0.02
PVa^-	4	4.65 ± 0.01	1.89 ± 0.01	2.05 ± 0.01	0.16 ± 0.01
$HCOO^-$		3.59 ± 0.02	1.65 ± 0.09	1.61 ± 0.05	−0.04 ± 0.10
Ac^-		4.58 ± 0.02	1.85 ± 0.05	1.84 ± 0.01	−0.01 ± 0.05
Pr^-		4.69 ± 0.01	1.91 ± 0.03	1.93 ± 0.01	0.02 ± 0.03

[a] 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 $\Delta \log K$ were calculated according to the error propagation after Gauss. [b] From Chart I.

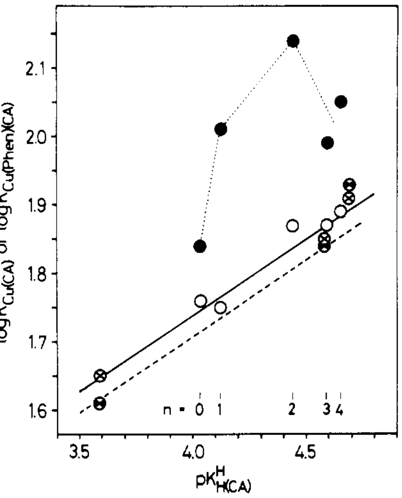

Figure 1. Relation between $\log K^{Cu}_{Cu(CA)}$ or $\log K^{Cu(phen)}_{Cu(phen)(CA)}$ and $pK^H_{H(CA)}$ for the binary complexes, $Cu(CA)^+$ (⊗, ○), or the ternary complexes, $Cu(phen)(CA)^+$ (⊗, ●), with simple carboxylates (⊗, ⊗: $HCOO^-$, Ac^-, Pr^-; from left to right) and the phenylalkanecarboxylates according to Chart I with n = 0–4. The data for the simple carboxylates furnish the reference lines for the binary (full line) and ternary Cu^{2+} complexes (broken line; see text).

The corresponding dependence is also observed for the ternary complexes formed with formate and acetate: within experimental error (Table II) the straight line parallels the one of the binary complexes (Figure 1). The closeness of the two lines, i.e., $\Delta \log K \simeq 0$, indicates a significantly increased stability if comparison is made with the expected statistical basis. This observation corresponds to the well-known fact[5,28,31] that the combination of heteroaromatic N bases and O ligands in ternary complexes that involve also Cu^{2+} or related metal ions leads to an increase in stability that depends on the π-accepting properties of the heteroaromatic N base.[32] The slight displacement toward a higher stability of the point due to propionate results from a weak hydrophobic interaction between the alkyl moiety and the phenanthroline system[33] as discussed recently in detail.[34]

The crucial point of Figure 1 is, however, that all the ternary complexes containing a phenyl moiety are significantly more stable than expected on the basis of carboxylate basicity. This and the fact that the increase in stability depends on the number of methylene groups between the phenyl moiety and the coordinating carboxylate group indicate that intramolecular stacks between the phenyl moiety and the phenanthroline rings are the source of the increased stability.

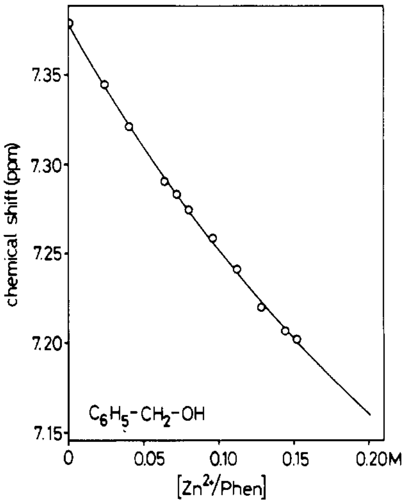

Figure 2. Variation of the chemical shift of the phenyl protons of benzyl alcohol (1.64×10^{-2} M) with increasing concentrations of Zn^{2+}/phen in aqueous solution at pH 5.20 (I = 0.25–0.5 M ($NaNO_3$); 34 °C). The spectra were measured relative to internal $(CH_3)_4N^+$ and converted to values relative to sodium (trimethylsilyl)propanesulfonate by adding 3.174 ppm. The curve shown is the computer-calculated best fit of the experimental data (see Experimental Section).[37]

Indeed, the occurrence of aromatic-ring stacking between such systems has been shown before for the binary adduct between 2,2′-bipyridyl (bpy) and carboxymethyl phenyl sulfide (CPS) ($K^{bpy}_{(bpy)(CPS)} \simeq 2$ M^{-1}; I = 0.15; 34 °C) in 50% aqueous dioxane.[35] In addition, we have now studied by ^1H NMR shift measurements in aqueous solution the stability of the unbridged ternary adduct formed between $Zn(phen)^{2+}$ and benzyl alcohol (BzOH):[36] the expected upfield shifts are observed (Figure 2),[37] and the stability constant, $K^{Zn(phen)}_{Zn(phen)(BzOH)} = 2.2 \pm 0.2$ M^{-1}, is in the expected order.[35,38] Moreover, ^1H NMR shift experiments of the Zn^{2+}/phen/PAc system proved directly the intramolecular stack formation: the expected upfield shifts are observed,[39]

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(31) Sigel, H.; Fischer, B. E.; Prijs, B. *J. Am. Chem. Soc.* **1977**, *99*, 4489–4496.

(32) (a) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945–947. (b) Huber, P. R.; Sigel, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27B*, 1319–1323. (c) Fischer, B. E.; Sigel, H. *Inorg. Chem.* **1979**, *18*, 425–428.

(33) Mitchell, P. R. *J. Chem. Soc., Dalton Trans.* **1979**, 771–776.

(34) Sigel, H. *Angew. Chem.* **1982**, *94*, 421–432; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 389–400.

(35) Farkas, E.; Fischer, B. E.; Griesser, R.; Rheinberger, V. M.; Sigel, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 208–216.

(36) Such a study can only be done with diamagnetic metal ions like Zn^{2+}; with the paramagnetic Cu^{2+} line broadening would occur.[8,22,33]

(37) The chemical shift of free benzyl alcohol, $\delta_0 = 7.379 \pm 0.001$, and chemical shift of the completely formed adduct with $Zn(phen)^{2+}$, $\delta_\infty = 6.670 \pm 0.043$, are given as the averages of two independent experiments. It should be pointed out that the addition of Zn^{2+} alone (i.e., without phen) to BzOH (1.64×10^{-2} M) has practically no influence on the chemical shift of the phenyl protons: 0.15 M $Zn(NO_3)_2$ leads to a very slight *down*field shift (and this shift direction is expected)[35] of 0.004 ppm (clearly, this value is still close to the experimental error).

(38) (a) Naumann, C. F.; Sigel, H. *J. Am. Chem. Soc.* **1974**, *96*, 2750–2756. (b) Mitchell, P. R.; Sigel, H. *J. Am. Chem. Soc.* **1978**, *100*, 1564–1570. (c) Fukuda, Y.; Mitchell, P. R.; Sigel, H. *Helv. Chim. Acta* **1978**, *61*, 638–647.

Table III. Extent of the Intramolecular Phenanthroline–Phenyl Stacks in the Ternary Cu^{2+} Complexes Containing 1,10-Phenanthroline and a Phenylalkanecarboxylate ($PheCA^-$): Intramolecular and Dimensionless Equilibrium Constant K_I and Percentage of the Stacked Isomer $Cu(phen)(PheCA)_{st}^+$ in Aqueous Solution (25 °C; $I = 0.1$ (KNO_3))

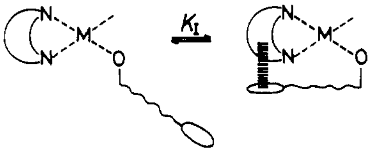
complex	$\Delta \log K$ (eq 6)[a]		$\Delta\Delta \log K$ (eq 10)[c]	K_I (eq 8, 11)[c]	% $Cu(phen)(PheCA)_{st}^+$ (eq 7)[c]
$Cu(phen)(HCOO)^+$	-0.04 ± 0.10	-0.02 ± 0.06[b]			
$Cu(phen)(Ac)^+$	-0.01 ± 0.05				
$Cu(phen)(Bz)^+$	0.08 ± 0.01		0.10 ± 0.01 (0.06)	0.26 ± 0.03 (0.17)	21 ± 2 (11)
$Cu(phen)(PAc)^+$	0.26 ± 0.04		0.28 ± 0.04 (0.07)	0.91 ± 0.18 (0.31)	48 ± 5 (9)
$Cu(phen)(PPr)^+$	0.27 ± 0.02		0.29 ± 0.02 (0.06)	0.95 ± 0.09 (0.27)	49 ± 2 (7)
$Cu(phen)(PBu)^+$	0.12 ± 0.02		0.14 ± 0.02 (0.06)	0.38 ± 0.06 (0.19)	28 ± 3 (10)
$Cu(phen)(PVa)^+$	0.16 ± 0.01		0.18 ± 0.01 (0.06)	0.51 ± 0.04 (0.21)	34 ± 2 (9)

[a] These values and their error ranges (three times the standard error) are from Table I. [b] This value corresponds to $\Delta \log K_{op}$ of eq 10. [c] The error limits given with these data result from the errors of the individual values of $\Delta \log K$. 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 $\Delta \log K$ should be used, because $\Delta \log K_{op}$ is the same for the whole series,[b] and therefore any error in $\Delta \log K_{op}$ will lead to a systematic correction for all values.

and the resulting stability constant, $\log K^{Zn(phen)}_{Zn(phen)(PAc)} = 0.83 \pm 0.27$ ($I = 0.25$ M ($NaNO_3$); 34 °C), is within experimental error (three times the standard deviation) identical with the one measured by potentiometric pH titration: $\log K^{Zn(phen)}_{Zn(phen)(PAc)} = 1.05 \pm 0.03$ ($I = 0.1$ (KNO_3); 25 °C).

The stability constant for the complex between $Cu(phen)^{2+}$ and 2-phenylacetate was in addition determined by UV difference spectrophotometry.[35] The experiments were evaluated by modified[19] Benesi–Hildebrand plots:[20] the data fit straight lines (Figure 3), which proves that only equilibrium 4 occurs and no remarkable amounts of $Cu(phen)(PAc)_2$ are formed, despite the use of excess PAc. Indeed, $\log K^{Cu(phen)}_{Cu(phen)(PAc)} = 1.97 \pm 0.10$ ($I = 0.1$ ($NaClO_4$); 25 °C), calculated from the intercepts of the straight lines in Figure 3 with the x axis,[19] is in excellent agreement with the value determined by potentiometric pH titration: $\log K^{Cu(phen)}_{Cu(phen)(PAc)} = 2.01 \pm 0.02$ ($I = 0.1$ (KNO_3); 25 °C; Table II).

(c) Extent of Intramolecular Stacking in the Ternary Cu(phen)(PheCA)⁺ Complexes. The increased stabilities observed for the $Cu(phen)(PheCA)^+$ complexes are clearly due to an intramolecular stack, but this does not mean that all of the individual ternary complexes exist in this form. In solution there is certainly an intramolecular equilibrium between an "open" and a "stacked" form (eq 7). If the two isomers in eq 7 are designated $Cu(phen)(PheCA)_{op}^+$ and $Cu(phen)(PheCA)_{st}^+$, the dimensionless constant of this intramolecular equilibrium is defined by eq 8. Values of K_I may be calculated



(7)

$$K_I = [Cu(phen)(PheCA)_{st}^+]/[Cu(phen)(PheCA)_{op}^+] \quad (8)$$

from eq 9.[40] The values for $K^{Cu(phen)}_{Cu(phen)(PheCA)_{op}}$ of eq 9a

$$K_I = \frac{K^{Cu(phen)}_{Cu(phen)(PheCA)}}{K^{Cu(phen)}_{Cu(phen)(PheCA)_{op}}} - 1 \quad (9a)$$

$$= \frac{10^{\Delta \log K_{Cu/phen/PheCA}}}{10^{\Delta \log K_{(Cu/phen/PheCA)op}}} - 1 \quad (9b)$$

could be estimated from Figure 1: the acidity constant of a given PheCA ligand and the corresponding point on the reference line of the ternary complexes would furnish an estimate. However, it has become evident[8] that the use of eq 9b is preferable because in the $\Delta \log K$ formulation (eq 6) systematic errors cancel to a large part; hence, the crucial parameter for the calculation of K_I is given by eq 10. Equation 9 may then

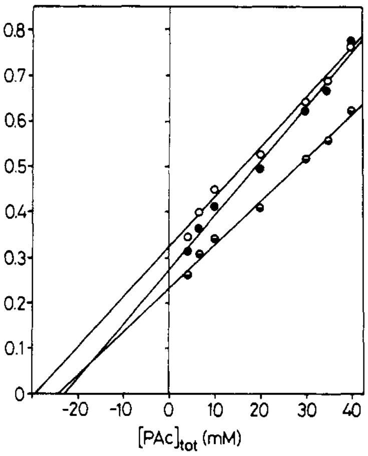


Figure 3. Graphical determination of the apparent stability constant, K_{app}, at pH 4.00 in aqueous solution ($I = 0.1$ ($NaClO_4$); 25 °C) for the reaction between $Cu(phen)^{2+}$ ($[Cu^{2+}] = [phen] = 0.18$ mM) and 2-phenylacetate ($[PAc)_{tot} = 4.17$–40 mM) by plotting $[PAc]_{tot}/\Delta A$ vs. $[PAc]_{tot}$. The difference absorbance, ΔA, was evaluated at 302 vs. 328 nm (●), 308 vs. 356 nm (○), and 302 vs. 384 nm (◒). The straight lines were drawn according to the least-squares method (regression). The intercept with the x axis corresponds to $x_0 = -1/K_{app} = -25.8 \times 10^{-3}$ (in average); the weighted mean of $\log K_{app} = 1.636 \pm 0.047$ (302/328), 1.526 ± 0.035 (308/356), and 1.609 ± 0.035 (302/384) by taking into account eq 1 results in $\log K^{Cu(phen)}_{Cu(phen)(PAc)} = 1.97 \pm 0.10$ (the final error limit corresponds to three times the standard error).

$$\Delta\Delta \log K = \Delta \log K_{Cu/phen/PheCA} - \Delta \log K_{(Cu/phen/PheCA)_{op}} \quad (10)$$

be rewritten as eq 11. Obviously, any experimental error will

$$K_I = 10^{\Delta\Delta \log K} - 1 \quad (11)$$

become the more significant the more similar the two constants forming the difference in eq 10 are. In the present case, the value for $\Delta \log K_{op}$ in eq 10 is obtained by averaging the $\Delta \log K$ values measured for the $Cu^{2+}/phen/HCOO^-$ and $Cu^{2+}/phen/CH_3COO^-$ systems (Table II). Clearly, in $Cu(phen)(HCOO)^+$ no intramolecular interaction can occur, and in $Cu(phen)(CH_3COO)^+$ any hydrophobic interaction with the methyl group, if it occurs at all, will be very small.

The results of the calculations using eq 11 are summarized in Table III. The percentages of the stacked isomers change between about 20 and 50%, and they depend on the number of methylene groups present in the phenylalkanecarboxylates (Chart I): the "best" fit, in the sense that the strongest interaction results, is observed with phenylacetate ($n = 1$) and

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(39) Chemical shift of free 2-phenylacetate at pH 5.20, $\delta_0 = 7.301 \pm 0.003$; chemical shift for the completely formed complex, $Zn(phen)(PAc)^+$, $\delta_\infty = 6.699 \pm 0.083$.

Table IV. Fractional Atomic Coordinates and Equivalent Thermal Parameters (Å²) for $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$[41] (Estimated Standard Deviations in Parentheses)

atom	x	y	z	B_{equiv}
Cu	0.47668 (3)	0.29882 (6)	0.14981 (4)	3.16 (1)
O(91)	0.4144 (2)	0.3885 (4)	0.1743 (3)	4.06 (8)
O(92)	0.4618 (2)	0.4168 (3)	0.3171 (3)	3.92 (9)
O(1)	0.4391 (2)	0.3495 (4)	0.0113 (3)	4.8 (1)
O(2)	0.9810 (4)	0.1114 (5)	0.0749 (4)	10.8 (2)
O(31)	0.1242 (3)	0.1586 (7)	0.4680 (5)	12.4 (2)
O(32)	0.1398 (4)	0.0258 (7)	0.5396 (5)	17.0 (3)
O(33)	0.2394 (4)	0.1539 (11)	0.5561 (6)	21.3 (4)
N(1)	0.5393 (2)	0.1946 (4)	0.1327 (3)	3.28 (9)
N(2)	0.4284 (2)	0.1617 (4)	0.1462 (3)	3.3 (1)
N(3)	0.1659 (4)	0.0968 (10)	0.5276 (5)	13.6 (3)
C(1)	0.2642 (3)	0.3945 (6)	0.2381 (4)	4.3 (1)
C(2)	0.2265 (3)	0.3055 (6)	0.2332 (4)	5.4 (2)
C(3)	0.1993 (4)	0.2503 (6)	0.1560 (5)	5.9 (2)
C(4)	0.2106 (3)	0.2838 (7)	0.0819 (5)	5.3 (2)
C(5)	0.2474 (3)	0.3719 (5)	0.0872 (4)	4.4 (2)
C(6)	0.2755 (2)	0.4284 (5)	0.1643 (4)	3.6 (1)
C(7)	0.3144 (3)	0.5258 (6)	0.1649 (5)	4.9 (1)
C(8)	0.3772 (3)	0.5310 (5)	0.2414 (5)	4.9 (2)
C(9)	0.4216 (2)	0.4372 (5)	0.2438 (4)	3.5 (1)
C(11)	0.5927 (2)	0.2145 (6)	0.1229 (4)	4.2 (1)
C(12)	0.6310 (4)	0.1328 (6)	0.1089 (5)	5.1 (2)
C(13)	0.6119 (2)	0.0262 (7)	0.1059 (4)	5.0 (2)
C(14)	0.5549 (3)	0.0018 (6)	0.1158 (4)	4.2 (1)
C(15)	0.5295 (3)	−0.1058 (6)	0.1123 (4)	5.2 (2)
C(16)	0.4737 (4)	−0.1236 (5)	0.1196 (5)	5.8 (2)
C(17)	0.4368 (3)	−0.0342 (5)	0.1316 (4)	4.3 (1)
C(18)	0.3773 (3)	−0.0456 (5)	0.1364 (5)	5.2 (2)
C(19)	0.3461 (3)	0.0443 (6)	0.1477 (5)	5.4 (2)
C(20)	0.3726 (3)	0.1472 (5)	0.1523 (4)	4.1 (1)
C(21)	0.4603 (3)	0.0713 (4)	0.1359 (4)	3.3 (1)
C(22)	0.5190 (3)	0.0889 (5)	0.1281 (3)	3.4 (1)
H(1)	0.2824	0.4329	0.2932	
H(2)	0.2177	0.2834	0.2843	
H(3)	0.1755	0.1843	0.1539	
H(4)	0.1907	0.2452	0.0270	
H(5)	0.2536	0.3934	0.0354	
H(71)	0.2913	0.5914	0.1676	
H(72)	0.3228	0.5294	0.1117	
H(81)	0.3693	0.5294	0.2956	
H(82)	0.3986	0.5968	0.2397	

phenylpropionate ($n = 2$). This is somewhat surprising because space-filling molecular models indicate that in a square-planar coordination sphere no complete overlaping is possible between the phenyl moiety of PAc^- and the phenanthroline ring system. This indicates that a "good" fit resulting in a strong interaction does not necessarily mean that the two aromatic systems have to overlap completely.

In case of benzoate, the situation is even more critical because the space-filling molecular models indicate that only one edge of the phenyl ring can be arranged above phenanthroline, but for a (hydrophobic) interaction this is enough (vide infra in section 2b). The actual difficulty in reaching a firm conclusion regarding the situation with benzoate is that 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 results compared with those cases in which no conjugation between the phenyl ring and the carboxylate group is possible. Hence, it could be that not the whole stability increase observed for $Cu(phen)(Bz)^+$ is due to an intramolecular interaction; therefore the 21% listed in Table III for the stacked isomer should rather be considered as an upper limit.

Table V. Selected Interatomic Distances (Å) and Angles (deg) in $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$ with Estimated Standard Deviations in Parentheses[41] [a]

(a) Cu Dimer			
Cu–N(1)	2.014 (3)	Cu–O(92')	1.956 (3)
Cu–N(2)	2.004 (4)	Cu–O(1)	2.201 (3)
Cu–O(91)	1.952 (3)	Cu–Cu'	3.054 (1)
N(1)–Cu–N(2)	82.74 (15)	N(2)–Cu–Cu'	90.48 (11)
N(1)–Cu–O(91)	174.09 (15)	O(91)–Cu–O(92')	91.79 (14)
N(1)–Cu–O(92')	91.84 (14)	O(91)–Cu–O(1)	90.32 (15)
N(1)–Cu–O(1)	94.15 (15)	O(91)–Cu–Cu'	77.37 (11)
N(1)–Cu–Cu'	98.98 (10)	O(92')–Cu–O(1)	92.92 (14)
N(2)–Cu–O(91)	92.58 (14)	O(92')–Cu–Cu'	76.36 (11)
N(2)–Cu–O(92')	164.86 (15)	O(1)–Cu–Cu'	163.23 (10)
N(2)–Cu–O(1)	101.53 (15)		
(b) 1,10-Phenanthroline			
N(1)–C(11)	1.311 (5)	C(13)–C(14)	1.404 (7)
N(2)–C(20)	1.327 (5)	C(17)–C(18)	1.398 (7)
N(1)–C(22)	1.372 (6)	C(14)–C(15)	1.437 (7)
N(2)–C(21)	1.371 (5)	C(16)–C(17)	1.441 (8)
C(11)–C(12)	1.403 (7)	C(14)–C(22)	1.405 (6)
C(19)–C(20)	1.393 (7)	C(17)–C(21)	1.395 (6)
C(12)–C(13)	1.376 (8)	C(15)–C(16)	1.341 (8)
C(18)–C(19)	1.363 (8)	C(21)–C(22)	1.412 (6)
C(11)–N(1)–C(22)	118.72 (40)	Cu–N(1)–C(22)	111.49 (13)
C(20)–N(2)–C(21)	117.92 (42)	Cu–N(2)–C(20)	130.19 (14)
Cu–N(1)–C(11)	129.74 (14)	Cu–N(2)–C(21)	111.89 (13)
(c) 3-Phenylpropionate			
phenyl C–C	1.353 (8)-	Cu–O(91)–C(9)	126.29 (15)
	1.388 (8)	Cu'–O(92)–C(9)	128.67 (15)
C(6)–C(7)	1.488 (7)	O(91)–C(9)–O(92)	126.27 (41)
C(7)–C(8)	1.529 (8)		
C(8)–C(9)	1.528 (6)		
C(9)–O(91)	1.241 (6)		
C(9)–O(92)	1.245 (6)		

[a] Primed and unprimed atoms are x, y, z, and $1 - x$, y, $^1/_2 - z$, respectively.

The decreasing percentage of the stacked isomer for the ternary complexes with a chain of the phenylalkanecarboxylate larger than the one of phenylpropionate ($n = 2$) indicates a poorer fit of the stack because either the phenyl moiety will reach beyond the phenanthroline ring system or the methylene groups must be twisted. However, the leveling off to about 30% of a closed isomer in equilibrium 7 indicates also that the methylene groups undergo a hydrophobic interaction with the phenanthroline rings, as is also known from other systems;[34] e.g., $Cu(bpy)(valerate)^+$ exists to about 20% in the closed form in 50% aqueous dioxane ($I = 0.1$ ($NaClO_4$); 25 °C).

However, the observation of a maximal formation degree for the stacked isomer with the phenylalkanecarboxylates having $n = 1$ or 2 proves clearly, that certain structural conditions are necessary for an optimal intramolecular stacking interaction in ternary complexes.

2. Studies in the Solid State. As 3-phenylpropionate undergoes a pronounced intramolecular stacking in the ternary $Cu(phen)(PPr)^+$ complex in aqueous solution, we have grown crystals from this complex in the hope of learning from an X-ray investigation some additional features about the properties involved in the formation of stacks in such systems.

(a) Structural Characterization of the Dimeric $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ Unit. The atomic and isotropic thermal parameters resulting from the crystal structure determination of $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$ are given in Table IV. Selected bond distances and angles are summarized in Table V.[41] The structure consists of dimeric $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ cations, considerably disordered NO_3^- anions, and H_2O molecules hydrogen bonded to the H_2O molecules of the dimers. The dimeric units result through bridge formation between two Cu^{2+} by two carboxylate groups of two 3-phenylpropionates (Figure 4). These dimers are further stabilized by a phen–phen stack between the two 1,10-phenanthroline molecules, each coordinated to a Cu^{2+} in the dimer (vide infra). The coordination around each copper is

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(40) For details see ref 8.

(41) The labeling of the individual atoms is shown in Figures 4 and 5.

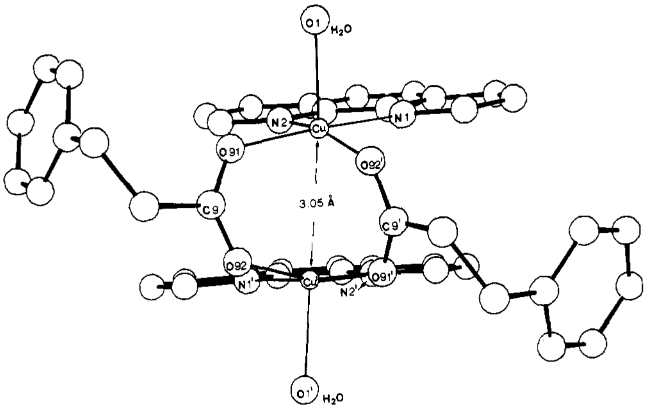

Figure 4. Structure of the dimeric unit $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ in $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$.

approximately square pyramidal by two phen nitrogens and two carboxylate oxygens occupying basal sites and an axial water–oxygen with a bond significantly longer than those of the basal atoms. This arrangement is completed to a distorted octahedron by the adjacent copper atom with a distance of 3.054 Å in the dimer.

Acetate-like bridges in Cu^{2+} dimers are well-known[42,43] and have been first documented in 1953 for copper(II) acetate monohydrate.[44] In most of these structures the two copper atoms are bridged by four carboxylate groups, with two additional ligands L completing a distorted octahedral environment for each copper atom. Cu–Cu distances found for this type of dimers range from 2.565 to 2.886 Å.[42] In the $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ dimer, only two bridging carboxylate groups occur and the Cu–Cu distance is considerably longer (3.054 Å) (vide infra). However, in spite of the longer Cu–Cu distance the total bridge length Cu–O–C–O–Cu′ (6.394 Å) and the O–C–O opening angle (126.3°), as well as the Cu–O–C angles (126.3 and 128.7°), agree with the mean values given by Doedens[42] for fourfold bridged dimeric copper(II) carboxylates.

As expected from the magnetic behavior of similar copper dimers, the magnetic moment of the present compound shows antiferromagnetic coupling of the two unpaired electrons on each copper center. Magnetic moments in units of Bohr magnetons per copper atom at different temperatures (in parentheses) are as follows: 0.83 (50.1 K); 1.41 (111.3 K); 1.662 (295.1 K = 22 °C). These values reflect the generally observed[43] very pronounced temperature dependence of such dimeric compounds for which μ_{eff} at 25 °C is typically about 1.4 μ_B per Cu atom.[43]

In 1,10-phenanthroline the lengths of chemically equivalent bonds coincide within their error limits, although no symmetry is imposed on the ligand by the space group. The variations in the C–N and C–C distances and in the corresponding bond angles follow the pattern observed in the crystal structure of the free molecule[45] as well as in the structures of other phen metal complexes[46,47] or hydrogen-bonded adducts.[48] The bond C(15)–C(16) is the shortest C–C bond in the molecule (1.341 Å), whereas the adjacent C(14)–C(15) with 1.437 Å and C(16)–C(17) with 1.441 Å are significantly longer. Therefore, in accordance with MO calculations[45] 1,10-phenanthroline may be considered as a 2,2′-bipyridyl molecule fused by a C–C bond with predominantly double-bond character.

Table VI. Nonbonding Ring–Ring Interactions (Å) in $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$: Shortest Distances of Atoms from the Least-Squares Plane through the Stacking Molecule or Shortest Atom to Atom Distances[a]

(a) Phenanthroline–Phenanthroline			
Intramolecular[b] (x, y, z to $1-x, y, \frac{1}{2}-z$)			
N(1)	3.269	N(1)–C(20′)	3.412
C(11)	3.271	N(1)–N(2′)	3.438
N(2)	3.352	C(21)–C(21′)	3.508
C(20)	3.403	N(2)–C(22′)	3.555
C(12)	3.470	C(11)–C(20′)	3.561
C(22)	3.486		
Intermolecular (x, y, z to $1-x, -y, -z$)			
C(13)–C(17)	3.631	C(15)–C(22)	3.680
C(12)–C(16)	3.640	C(13)–C(16)	3.693
(b) Phenanthroline–Phenylpropionate			
Intramolecular (x, y, z to x, y, z)			
C(5)–C(20)	3.842	C(4)–C(20)	3.848
Intermolecular (x, y, z to $\frac{1}{2}-x, \frac{1}{2}-y, -z$)			
C(4)–C(20)	3.705	C(5)–C(19)	3.800
Intermolecular (x, y, z to $-\frac{1}{2}+x, \frac{1}{2}+y, z$)			
C(6)–C(13)	3.715	C(1)–C(13)	3.743
C(5)–C(13)	3.738		
(c) Phenylpropionate–Phenylpropionate			
Intermolecular (x, y, z to $\frac{1}{2}-x, \frac{1}{2}-y, -z$)			
C(4)–C(5)	3.755	C(4)–C(4)	3.812

[a] The terms intra- and intermolecular refer here to the dimeric unit $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ as one molecule. [b] See Figure 5. The dihedral angle between the stacking molecules is 9.3.°

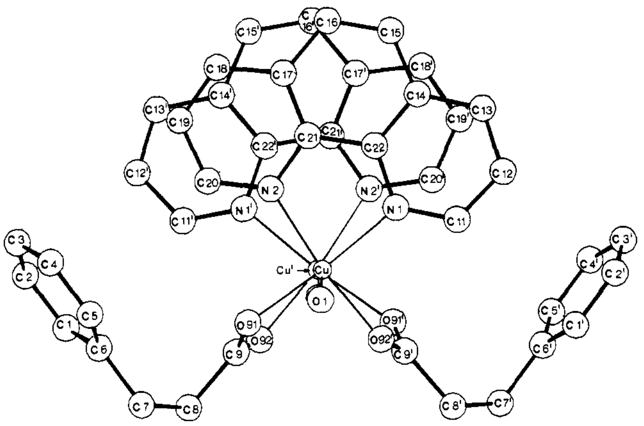

Figure 5. View of the dimeric unit $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ approximately perpendicular to the planes of the two phenanthroline ligands.

The 1,10-phenanthroline molecule as a whole is not perfectly planar but exhibits significant distortion with up to 7σ (0.046 Å) deviations of individual atoms from the least-squares plane. This contrasts with the three individual six-membered rings of the molecule, which show exact planarity with a maximum deviation of 2σ (0.010 Å) of a single atom from the mean planes. The dihedral angles between these mean planes are 1.4, 1.6, and 3.0°. A nonplanarity of phen has also been observed in other structures;[48] the detailed deviations from planarity, however, may vary depending on the special type of intermolecular nonbonding interactions of the molecule.

(b) Intramolecular and Intermolecular Ligand–Ligand Interactions in $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$. The nonbonding

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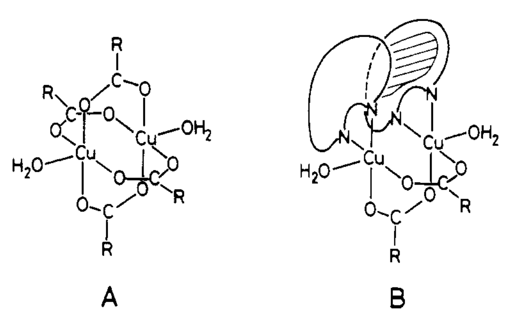

Figure 6. Simplified structures: (A) $[Cu_2(R\text{-}COO)_4(H_2O)_2]$ complexes; (B) the $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ cation. The Cu–Cu distance in (A) ranges from 2.610 to 2.624 Å for R–COO = CH_3COO^-, $^-OOCCH_2CH_2COO^-$, or $o\text{-}BrC_6H_4COO^-$,[42] whereas 3.054 Å results for (B).

ring–ring interactions are summarized in Table VI; they are dominated by a pronounced "homo" stacking between 1,10-phenanthroline molecules bound to two different, but bridged, Cu^{2+} centers (Figure 5). Considering the dimeric cation as one molecule, this interaction represents an intramolecular aromatic-ring stacking. The shortest atom to atom distance within the stacking molecules is 3.41 Å, and the dihedral angle between the two phenanthroline rings amounts to 9.3°. Similar values are found in related stacking complexes, in which the planes of the aromatic moieties are also not exactly parallel to one another.[14c]

From Figure 5 it is evident that there is also some interaction between the phenyl ring of phenylpropionate and the edges of two phenanthroline rings, one of them belonging to the same Cu center, which gives rise to an intra- and an intermolecular interaction as well (Table VI). The coordinated phenylpropionate is bent at C(7) and C(8), resulting in an optimal fit of the phenyl ring between the phenanthroline systems. The dihedral angle between the planes of 1,10-phenanthroline and the interacting phenyl ring of 3-phenylpropionate is 68.8° considering the two ligands coordinated to the same Cu^{2+} center. This is an interesting observation, meaningful also regarding the discussion in section 1c, because it shows that aromatic moieties have not necessarily to be coplanar for an interaction; i.e., a simple hydrophobic interaction is possible in other orientations.

Conclusions

It should probably be emphasized in the present context that no stability constants for any dimer formation in aqueous Cu^{2+}/acetate systems can be found in the literature.[49-51] Similarly, we observed under our experimental conditions no hint for a dimerization of $Cu(phen)(PPr)^+$, or for any of the other complexes studied; all experimental data could perfectly be fitted by assuming only monomeric complex formation. Hence, the dimers observed in the solid state occur in solution, if at all, only in traces.

The observation that the $Cu(phen)(PPr)^+$ complex accommodates different structures in solution and in the solid state is not surprising. The energies involved in the formation of stacks are small[52] and can easily be overplayed by lattice forces. For example, the stability of the unbridged adduct between $Zn(phen)^{2+}$ and benzyl alcohol ($K = 2.2$ M^{-1}; section 1b) corresponds only to $\Delta G° \simeq -2.0$ kJ/mol. The rather remarkable self-stacking tendency of 1,10-phenanthroline in aqueous solution ($K_D = 11.8 \pm 0.9$ M^{-1}; $\Delta G° \simeq -6.1$ kJ/mol)[53,54] is dramatically reduced by the coordination of a metal ion, e.g. Zn^{2+} ($K_D = 0.55 \pm 0.1$ M^{-1}),[53,54] because this leads to a repulsion between the now positively charged $Zn(phen)^{2+}$ units. Partial neutralization of the positive charge at the metal ion in connection with simultaneous bridging by a carboxylate group, as it occurs in the $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ dimers, will facilitate the phen/phen interaction significantly, because now conditions arise that are related to the properties of the metal ion-free phenanthroline system. With this reasoning in mind, it seems indeed not surprising that the Cu^{2+}–carboxylate bridged phen/phen interaction determines the structure in the solid state.

However, the dimeric structure of $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ may be discussed also in relation to the dimeric $[Cu_2(acetate)_4(H_2O)_2]$ and related complexes. They all have a very similar structure, which is indicated in Figure 6A,[42,43,55] and replacement of two bridging carboxylates, i.e. of four O donor atoms, by two 1,10-phenanthroline ligands leads directly to Figure 6B, which represents the structure described in section 2. The considerably larger Cu–Cu distance of 3.054 Å in $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$, compared to other dimeric copper carboxylates (~2.62 Å), is probably not so much due to the existence of only two bridging carboxylate groups, but seems rather the result of the steric constraints imposed on the dimer by the phen–phen stack, because stacking distances below 3.4 Å are hardly observed.[12-14] In fact, the shortest atom to atom distance within the stack of $[Cu_2(phen)_2(PPr)_2(H_2O)_2]^{2+}$ is 3.41 Å, and the two phen systems are oriented in a butterfly-like way with a dihedral angle between the two planes of 9.3°.

One of the most interesting features of the present study are the inter- and the intramolecular ligand–ligand interactions between the phenyl moiety of 3-phenylpropionate and an edge of 1,10-phenanthroline (Figure 5). This structural feature proves that aromatic-ring systems have not necessarily to be arranged in a coplanar fashion for an interaction. This observation corresponds to the hydrophobic interactions detected between aromatic-ring moieties and aliphatic residues in aqueous solution.[8,9] In addition, this result is of importance regarding the discussed intramolecular interactions in the $Cu(phen)(benzoate)^+$ complex (see section 1c), as well as for further studies of this type in aqueous solution.

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Registry No. $[Cu_2(phen)_2(PPr)_2(H_2O)_2](NO_3)_2$, 92011-14-8.

Supplementary Material Available: Listings of anisotropic temperature factors, observed and calculated structure factors, and geometrical characteristics of rings and their least-squares planes and a stereoview of the crystal structure of $Cu(phen)(PPr)(NO_3)\cdot 2H_2O$ within the unit cell (27 pages). Ordering information is given on any current masthead page.

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