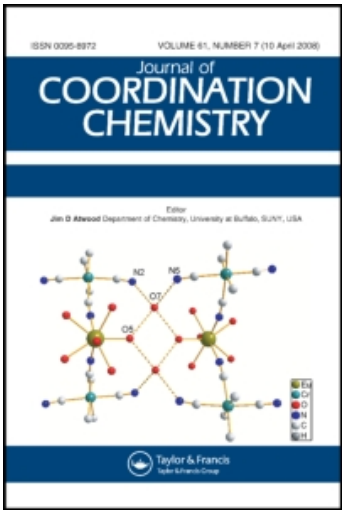

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FORMATION EQUILIBRIA OF COPPER(II) TERNARY COMPLEXES WITH (S)-LEUCINEHYDROXAMIC ACID AND (*R*)- OR (S)-AMINO ACIDS IN AQUEOUS SOLUTION

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FORMATION EQUILIBRIA OF COPPER(II) TERNARY COMPLEXES WITH (*S*)-LEUCINEHYDROXAMIC ACID AND (*R*)- OR (*S*)-AMINO ACIDS IN AQUEOUS SOLUTION

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Solution equilibria of binary copper(II) complexes with (*S*)-leucinehydroxamic acid and of ternary complexes with (*R*)- or (*S*)-amino acids (valine, proline, phenylalanine, tryptophan) were studied by potentiometry and electronic spectrophotometry at $T = 25°C$ and $I = 0.5\,mol\,dm^{-3}$ (KCl). The mixed species [CuLA] and $[CuLH_{-1}A]^-$ ($L^- =$ leucinehydroxamate, $A^- =$ aminoacidate), do not present stereoselectivity, but are strongly stabilized with respect to their parent binary complexes. Possible structures of the ternary complexes are proposed.

Keywords: Aminohydroxamic acids; amino acids; copper(II); ternary complexes; stability constants; potentiometry

INTRODUCTION

In a general project aimed at studying thermodynamic stereoselectivity in the formation of ternary Cu(II) complexes of bidentate chiral ligands with (*R*)- or (*S*)-amino acids we reported results regarding some (*S*)-amino acid amides.[1,2] It was then possible to clarify the role of the stereoselectivity observed in aqueous solution in connection with the mechanism of chiral

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recognition of amino acids in RP-HPLC by (*S*)-amino acid amide/Cu(II) complexes added to the eluent (ligand exchange chromatography).[3] For comparison with the behaviour of the (*S*)-amino acid amides we are now investigating the corresponding ternary Cu(II) complexes of (*S*)-aminohydroxamic acids. These ligands, ($-NH_2$, $-NOH^-$ donors) are analogous to the amino acid amides ($-NH_2$, $-NH^-$ donors) but they have the additional capability of bridging chelation through the carbonyl and deprotonated hydroxamic oxygens, thus forming also dinuclear species[4] with probable effects on stereoselectivity. Moreover, taking into account the possible applications of aminohydroxamic acids in chemotherapy and in chemical modeling of the transport and storage of some metal ions in living organisms,[5] speciation of ternary systems with aminohydroxamic acids and bio-ligands (amino acids, peptides) could help to interpret complicated biological systems. Despite their importance, solution studies on ternary complexes of aminohydroxamic acids reported in the literature are very scarce and only two refer to amino acids.[6–9] As a first approach to the problems of speciation and stereoselectivity of (*S*)-aminohydroxamic acid mixed complexes, we report here the results of a potentiometric and spectrophotometric study in aqueous solution of ternary Cu(II) complexes with (*S*)-leucinehydroxamic acid and (*R*)- or (*S*)-amino acids (valine, proline, phenylalanine, tryptophan).

EXPERIMENTAL

Reagents

(*S*)-Leucinehydroxamic acid (SIGMA), (*R*)- and (*S*)-valine, -phenylalanine, -proline, and -tryptophan (FLUKA) were all high-purity products and used as received. Elemental analyses (C,H,N) of all the ligands gave acceptable results. The ligands were dried *in vacuo* over P_4O_{10} and stock solutions (*ca* 0.02 mol dm^{-3}) were prepared by weight and their titre checked by potentiometric titration with KOH. The solutions were used within 3–4 days. KOH and HCl solutions (*ca* 0.2 mol dm^{-3}) were prepared by diluting concentrated Merck Titrisol ampoules. The concentration of KOH solutions was determined potentiometrically by titration against potassium hydrogen phtalate (Merck, dried at 120°C) and the titre of the HCl solutions was derived from potentiometric titrations with KOH. A stock solution of $CuCl_2 \cdot 2H_2O$ (C.Erba) was prepared and checked for concentration by complexometric titration with EDTA. All solutions were prepared with freshly boiled, doubly distilled water.

Potentiometric Measurements

The titrations were carried out at $T = 25 \pm 0.1°C$ and $I = 0.5\,mol\,dm^{-3}$ (KCl) under an N_2 stream, using $50\,cm^3$ samples. Potentiometric measurements were performed with our automatic apparatus previously described.[1] The Orion Ross 8102SC combined electrode was calibrated in terms of $[H^+]$ by titrating HCl solutions ($0.01\,mol\,dm^{-3}$) in a starting volume of $50\,cm^3$ with standard KOH solutions (*ca* $0.2\,mol\,dm^{-3}$ in $0.5\,mol\,dm^{-3}$ KCl). The PC program BEATRIX,[10] based on the Gran method,[11] was used to calculate V_e, equivalence volume, $E°$, electrodic chain standard potential, and pK_w (13.73(1)).

The protonation constants of (*S*)-Leucinehydroxamic acid, HL, were determined by alkalimetric titration of four samples ($3-5 \times 10^{-3}\,mol\,dm^{-3}$) of the ligand. For the Cu(II)/(*S*)-leucinehydroxamate equilibria, seven titrations were performed: a group of four with ligand/metal ratios from 5 : 1 to 8 : 1 ($C_{Cu} = 0.26-0.40 \times 10^{-3}\,mol\,dm^{-3}$) which covered a pH range between 3 and 11, and a group of three with ligand/metal ratios from 3 : 1 to 10 : 1 ($C_{Cu} = 0.5-1.3 \times 10^{-3}\,mol\,dm^{-3}$) which reached only pH *ca* 7.3 owing to precipitation of $[CuL_2]$. For each of the ternary systems considered, 4–6 titrations were carried out with Cu : L : A ratios 1 : 1 : 1 and 1 : 1 : 2 ($C_{Cu} = 0.3-0.7 \times 10^{-3}\,mol\,dm^{-3}$, HA = amino acid). The pH range explored was between 3 and 11.3.

Spectrophotometric Measurements

Absorption spectra were recorded on a Uvikon 941 Plus Kontron spectrophotometer using matched quarz cells of 5 cm pathlength against $0.5\,mol\,dm^{-3}$ KCl as reference. Solutions were passed from the potentiometric vessel to the spectrophotometric cell, using a peristaltic pump. Eight spectra, at appropriate pH, were recorded between 400 and 800 nm at 2 nm intervals.

Calculations

Stability constants were calculated by the computer program HYPERQUAD[12] which employs the sum of the weighted squares of the residuals between observed and calculated *e.m.f.* values as the optimization function. The weighting of the experimental observations takes into account the errors of both *e.m.f.* and titrant volume that were estimated as 0.2 mV and $0.008\,cm^3$, respectively. Trial values of the $\log\beta$'s of the ternary complexes

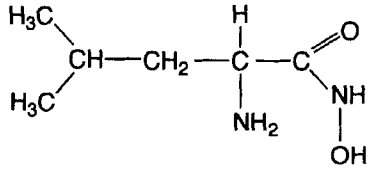
were refined while the constants pertaining ligand protonation and binary Cu(II) complexations were fixed. For each system, the data from different titrations were treated as a unique batch.

RESULTS AND DISCUSSION

Copper(II)/(*S*)-Leucinehydroxamic Acid System

Solution equilibria of Cu^{2+} with several α-aminohydroxamic acids, (HL) were extensively investigated by different techniques (potentiometry, UV-VIS absorption and CD spectrophotometry, EPR) and the well established chemical model consists of $[CuL]^+$, $[Cu_2L_2H_{-1}]^+$, $[CuL_2]$, and $[CuL_2H_{-1}]^-$ species[4]. The amino and the deprotonated hydroxamate nitrogen atoms were suggested to co-ordinate in all these complexes, and X-ray results confirmed this hypothesis in crystals of *trans*-$[CuL_2] \cdot 2H_2O$ for glycine- and α-alanine-hydroxamate.[13,14]

We performed a potentiometric study of the equilibria of (*S*)-leucinehydroxamic acid (2-amino-4-methylpentanehydroxamic acid) (Scheme 1) with H^+ and Cu^{2+} as a check of our preceding work.[15]



SCHEME 1

Experimental data were processed with the HYPERQUAD program[12] and values of the stability constants obtained substantially confirmed those previously reported.[15,16] Results are presented in Table I.

A visible (400–800 nm) spectrophotometric study of the system Cu(II)/(*S*)-leucinehydroxamic acid was also carried out in order to complete our preceding investigation[15] in which the species $[CuL_2H_{-1}]^-$ was not characterized owing to the limited range of pH explored. Spectroscopic data ($A = f(\lambda)$) were processed by the SQUAD program[17] and the molar absorptivities (ε) as a function of λ for the three major species were calculated by using the formation constants obtained by potentiometry and are represented in Figure 1. The λ_{max} (nm) and the corresponding ε ($mol^{-1}\,dm^3\,cm^{-1}$) values obtained ($[Cu_2L_2H_{-1}]^+$, 648(222); $[CuL_2]$, 532(97); $[CuL_2H_{-1}]^-$, 492(123)) are consistent with those reported for

TABLE 1 Logarithms of protonation and Cu(II) complex-formation constants ($\beta_{pqr} = [Cu_pL_qH_r]/[Cu]^p[L]^q[H]^r$) of (*S*)-leucinehydroxamic acid. $T = 25°C$, $I = 0.5\,mol\,dm^{-3}$ (KCl). Standard deviations are given in parentheses

	This work	*Ref.* 15	*Ref.* 16[a]
HL	9.16(1)	9.15(1)	9.10(1)
H_2L^+	16.46(1)	16.42(1)	16.25(1)
s[b]	0.69		
n[b]	299		
$[CuL]^+$	10.46(4)	10.63(5)	10.83(9)
$[Cu_2L_2H_{-1}]^+$	20.37(2)	20.59(2)	21.09(5)
$[CuL_2]$	19.32(1)	19.20(2)	19.51(3)
$[CuL_2H_{-1}]^-$	9.36(3)	9.18(8)	9.98(6)
s[b]	1.99		
n[b]	388		

[a] $I = 0.1\,mol\,dm^{-3}$ ($NaClO_4$). [b] $s = [\sum w_i(E_i^o - E_i^c)^2/(n-m)]^{1/2}$ = sample standard deviation; $w_i = 1/\sigma_i^2$, where σ_i is the expected error on each experimental *e.m.f.* value (E_i^o); n = number of observations; m = number of parameters refined.

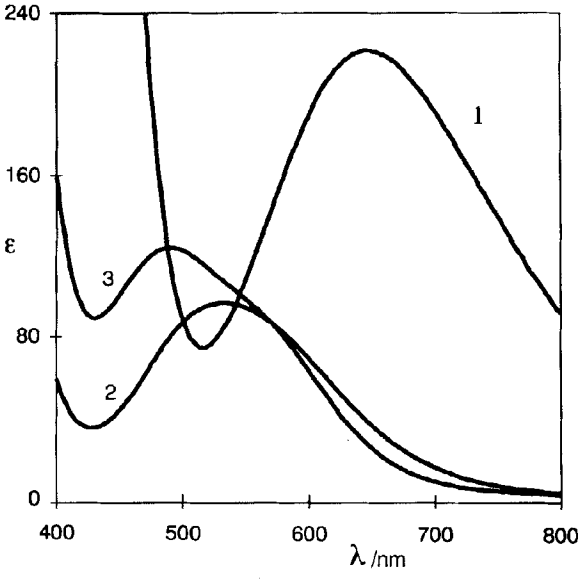
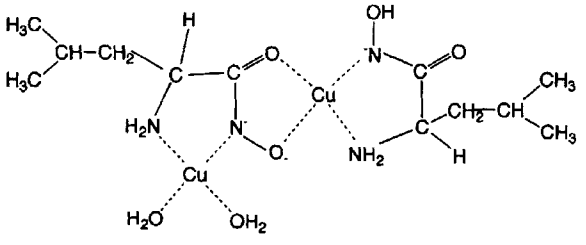


FIGURE 1 Molar absorptivities ($\varepsilon/M^{-1}cm^{-1}$) as a function of λ/nm calculated for the major species of Cu(II)/(*S*)-leucinehydroxamate system; Curve 1: $[Cu_2L_2H_{-1}]^+$; 2: $[CuL_2]$; 3: $[CuL_2H_{-1}]^-$.

various α-aminohydroxamates.[4] Moreover, in agreement with earlier findings for (*S*)-α-alaninehydroxamic acid,[18] a further band with $\lambda_{max} = 344\,nm$ (ε *ca* $1560\,mol^{-1}\,dm^3\,cm^{-1}$) was observed for $[Cu_2L_2H_{-1}]^+$, probably attributable to a charge transfer transition $-NO^-$ (oxygen) → Cu(II).

For the first time, in that work,[18] well documented UV-VIS absorption and CD results supported the coordination mode shown in Scheme 2, instead of a previous proposed hydroxo-bridged dinuclear structure.[15,16]



$[Cu_2L_2H_{-1}]^+$

SCHEME 2

This mixed bonding mode ((*N*,*N*) and (*O*,*O*)) of the hydroxamate mojety was proved by X-ray analysis in the case of copper(II)-β-alaninehydroxamic acid.[19]

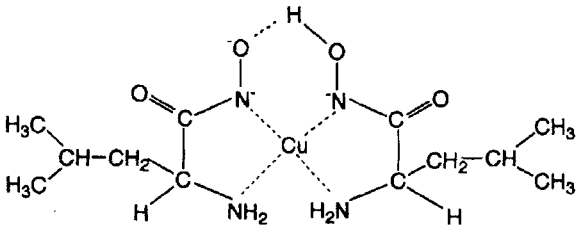
In recent years, there were some controversies about the structure of the complex $[CuL_2H_{-1}]^-$.[4] In fact, the proton released by $[CuL_2]$ above pH *ca* 9 might derive from one of the two *N*-coordinated $-NOH^-$ groups, or from an apical water molecule. In our opinion, it seems reasonable to exclude the hypothesis of the hydroxo-complex mainly on the basis of two arguments. First, the equilibrium constant for the reaction

$$[CuL_2] \rightleftharpoons [CuL_2H_{-1}]^- + H^+$$

is remarkably higher ($\log K = -9.96$) than that reported in the literature[20] for some *bis*-α-aminoamidato copper(II) complexes ($\log K$ *ca* -11.8) where the only possible deprotonation is that of an apical water molecule, *i.e.*,

$$[CuL_2H_{-2}(H_2O)_2] \rightleftharpoons [CuL_2H_{-2}(H_2O)(OH)]^- + H^+$$

(L = (*S*)-amino acid amide of Ala, Val, Pro, Phe). Secondly, according to our spectroscopic data, on going from $[CuL_2]$, with $\lambda_{max} = 532$ nm, to $[CuL_2H_{-1}]^-$, with $\lambda_{max} = 492$ nm, there is a *blue shift* and this supports proton dissociation from one $-NOH$ group with stabilization of the planar arrangement of four nitrogen atoms, possibly assisted by $-O^- \ldots HO-$ hydrogen bonding (Scheme 3).



$[CuL_2H_{-1}]^-$

SCHEME 3

This type of structure was also found for glycinehydroxamic acid in crystals of *cis*-$Na[NiL_2H_{-1}] \cdot 3H_2O$ by X-ray analysis.[21] On the contrary, the formation of a real hydroxo-species from Cu(II) complexes with four equatorial nitrogens by deprotonation of an apical water molecule gives a *red shift*, *e.g.*, 6 nm for the couple $[CuL_2H_{-2}(H_2O)_2]^-/[CuL_2H_{-2}(OH)(H_2O)])^-$, (L = (*S*)-phenylalaninamide)[20] and 49 nm for $[Cu(en)_2(H_2O)_2)]^{2+}/[Cu(en)_2(OH)(H_2O)]^+$ (en = ethylenediamine).[22]

Copper(II)/(*S*)-Leucinehydroxamic Acid/(*R*)- or (*S*)-Amino Acid Ternary Systems

For the potentiometric study of the mixed complexes of Cu^{2+} with (*S*)-leucinehydroxamate and amino acids, HA, two aliphatic, valine and proline, and two aromatic amino acids, phenylalanine and tryptophan, were chosen. Because of the low solubility of the $[CuL_2]$ complex of (*S*)-leucinehydroxamate, experiments with Cu : L : A = 1 : 2 : 1 ratio were excluded and only those with 1 : 1 : 1 and 1 : 1 : 2 ratios were carried out. Protonation and Cu(II) complexation constants of the amino acids used for the calculation of the ternary complexes stabilities were taken from the literature[23] and refer to (*S*)-enantiomers (Table II). With the assumption that in the ternary complexes Cu(II) presents the same coordination number as in its *bis*-complex with (*S*)-leucinehydroxamate, only the mixed species [CuLA] and

TABLE II Literature values[a] for protonation and Cu(II) complex-formation constants ($\log \beta_{pqr}$) of (*S*)-amino acids used in the calculations. $T = 25°C$, $I = 0.5\,mol\,dm^{-3}$

	(S)-Val	*(S)-Pro*	*(S)-Phe*	*(S)-Trp*
HA	9.49(3)	10.41(10)	9.09(4)	9.32(5)
H_2A^+	11.75(2)	12.30(10)	11.26(4)	11.67(5)
$[CuA]^+$	8.09(4)	8.84(2)	7.90(4)	8.25(3)
$[CuA_2]$	14.90(10)	16.36(8)	14.80(10)	15.40(10)

[a] Ref. 23.

TABLE III Formation constants ($\log\beta_{pqrs}$; $\beta_{pqrs}=[Cu_pL_qA_rH_s]/[Cu]^p[L]^q[A]^r[H]^s$) of the ternary Cu(II) complexes of (*S*)-leucinehydroxamate with (*R*)- or (*S*)-amino acids. $T=25°C$ and $I=0.5\,mol\,dm^{-3}$ (KCl). Standard deviations are given in parentheses. L^- = leucinehydroxamate, A^- = aminoacidate

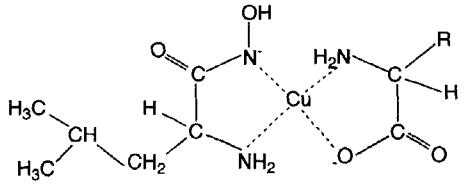
	Val		*Phe*		*Pro*		*Trp*	
	(*R*)	(*S*)	(*R*)	(*S*)	(*R*)	(*S*)	(*R*)	(*S*)
[CuLA]	17.80(7)	17.73(8)	17.77(3)	17.75(3)	19.08(7)	19.00(8)	18.35(3)	18.30(3)
$[CuLH_{-1}A]^-$	7.97(6)	7.88(6)	8.16(2)	8.18(3)	8.11(8)	7.89(10)	8.30(3)	8.25(3)
s^a	2.56	2.61	2.15	1.84	2.37	2.33	2.37	2.54
n^a	282	282	507	301	191	202	337	330

[a] *C.f.* Footnote to Table I.

$[CuLH_{-1}A]^-$ were considered in the calculations, and actually these are the complexes found in the Cu(II)/(*S*)-α-alaninehydroxamate/(*S*)-α-alanine system.[9] The overall formation constants yielding the best fit of the potentiometric data are given in Table III. It clearly appears that no stereoselectivity is present in the formation of the two diastereoisomeric complexes of (*S*)-leucinehydroxamate with each amino acid, the small differences between the two $\log\beta$'s being not significant. This result is in agreement with the behaviour observed with some (*S*)-amino acid amides and the same amino acids considered here.[1] In that case, remarkable stereoselectivity was found only for those diastereoisomeric complexes which contained one ligand with the side-chain residue of proline and the other that of phenylalanine or tryptophan, whereas practically no stereoselectivity appeared when one of the ligands had an aliphatic residue like valine.

A species distribution diagram for the Cu^{2+}/(*S*)-leucinehydroxamate/(*S*)-phenylalanine = 1 : 1 : 2 system is represented in Figure 2. The formation of [CuLA] starts at pH = 6, reaches a maximum concentration of 70% total copper(II) at pH = 8 and then changes into $[CuLH_{-1}A]^-$, which is practically the only species present above pH = 10.5.

With regard to the molecular structures attributable to these two ternary complexes, it is feasible that [CuLA] is *trans*-square planar like *trans*-$[CuL_2]$ (Scheme 4),



[CuLA]

SCHEME 4

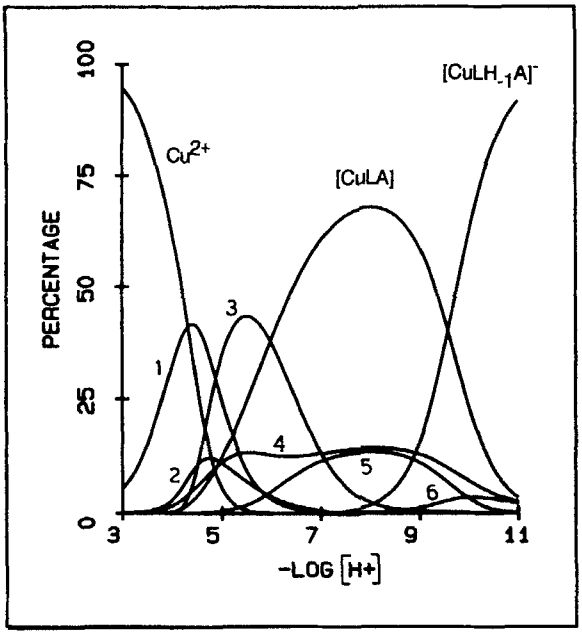
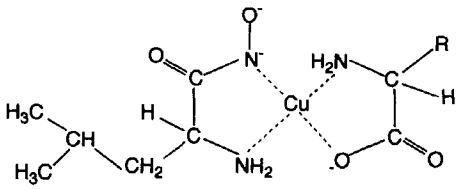


FIGURE 2 Species distribution for the Cu(II)/(*S*)-leucinehydroxamate/(*S*)-phenylalanine 1 : 1 : 2 system, with $C_{Cu} = 0.5 \times 10^{-3}$ mol dm^{-3}; Curve 1: $[CuA]^+$; 2: $[CuL]^+$; 3: $[Cu_2L_2H_{-1}]^+$; 4: $[CuA_2]$; 5: $[CuL_2]$; 6: $[CuL_2H_{-1}]^-$.

whereas it can be concluded that $[CuLH_{-1}A]^-$ is not an hydroxo-complex, *i.e.*, $[CuLA(OH)]^-$, on the basis of the same arguments for $[CuL_2H_{-1}]^-$. In fact, if we consider the equilibrium

$$[CuLA] = [CuLH_{-1}A]^- + H^+$$

we obtain $\log K$ values (−9.6/−10.0) for valine, phenylalanine and tryptophan which are very similar to that calculated (−9.96) for the deprotonation of $[CuL_2]$ and therefore we can suppose the same type of process in both reactions. The proline value, however, is different ($\log K$ *ca* −11), but we cannot give any convincing explanation for this behaviour. Also, the spectroscopic properties of [CuLA] and $[CuLH_{-1}A]^-$ resemble those of the binary species $[CuL_2]$, $[CuL_2H_{-1}]^-$; solutions of the ternary systems where [CuLA] prevails (70%, pH ≃ 8) show λ_{max} *ca* 567 nm and those with the maximum concentration of $[CuLH_{-1}A]^-$ (90%, pH ≃ 11.2) have λ_{max} *ca* 547 nm. Qualitatively, this *blue shift* excludes the hypothesis of OH^- apical coordination. Therefore, the molecular structure of $[CuLH_{-1}A]^-$ is most probably as shown in Scheme 5.



[CuLH$_{-1}$A]$^-$

SCHEME 5

For an estimation of the stability of the ternary complexes with respect to their parent binary complexes, we can use the parameter[24] $\log X$ (the constant for the equilibrium $[CuL_2] + [CuA_2] \rightleftharpoons 2[CuLA]$) for the species [CuLA], but not for $[CuLH_{-1}A]^-$, since $[CuL_2H_{-2}]^{2-}$ is not formed. The calculated $\log X$ values are somewhat larger than expected on a statistical basis (0.6),[25] (*e.g.* (*R*)-valine, 1.38; -proline, 2.48; -phenylalanine, 1.42; -tryptophan, 1.98) and this means that the formation of the mixed complexes is notably favoured.

Acknowledgments

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