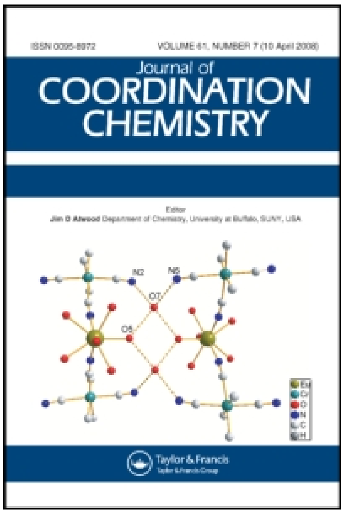

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COMPLEX FORMATION IN COPPER(II) TERNARY SYSTEMS INVOLVING POLYAMINES AND DIAMINOCARBOXYLATES STUDIED BY POTENTIOMETRIC AND SPECTROSCOPIC TECHNIQUES

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COMPLEX FORMATION IN COPPER(II) TERNARY SYSTEMS INVOLVING POLYAMINES AND DIAMINOCARBOXYLATES STUDIED BY POTENTIOMETRIC AND SPECTROSCOPIC TECHNIQUES

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Potentiometric and spectroscopic methods were used to study complex formation in ternary Cu(II) systems with the ligands *en, tn, Put, dien, 2,3-tri, 3,3-tri, Spd, dapa* and *daba*. Mixed complexes, Cu/diamine/triamine, formed in aqueous solution are characterized by 5N-type coordination, with four atoms coordinating equatorially and one at an axial position. An exception is the complex Cu(Put)(3,3-tri) in which 4N coordination was detected. A relatively low tendency to form mixed complexes was found for Cu/triamine/triamine systems, where formation of only the Cu (dien)(Spd) compound was found. The complexing character of *daba* molecules proves diversified and dependent on the type of the second ligand it forms the complex with. In Cu/daba/diamine compounds, coordination of the 3N1O type (with a 1N1O fragment from daba) was observed. In the Cu/daba/triamine complexes one nitrogen atom of the diaminocarboxylate is involved in coordination at an equatorial position and the second at an axial position (5N coordination). A *dapa* ligand is not so diversified and its two amino groups coordinate equatorially (2N), yielding chromophore 4N in complexes with diamines (probably with weak interaction of an oxygen atom) and 5N with triamines. Spermidine also reveals different coordination properties, depending on the second ligand. In complexes with diamines, the interactions involve 3 nitrogen atoms from *Spd* but only two in complexes with triamines. Following the process of formation of mixed copper(II) complexes it was found that with increasing pH, in the triamine/diamine and triamine/diaminocarboxylate systems, the anchoring ligand is the triamine, while in the diamine/diaminocarboxylate systems, *dapa* or *daba* are first to react and only then does the diamine join the complex.

Keywords: copper(II); polyamines; diaminocarboxylates; complexes; stability; mode of coordination

INTRODUCTION

Aliphatic polyamines (PA, biogenic amines), mainly putrescine, $NH_2(CH_2)_4NH_2$, spermidine, $NH_2(CH_2)_3NH\ (CH_2)_4NH_2$ and spermine, $NH_2(CH_2)_3\,NH(CH_2)_4$

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$NH (CH_2)_3 NH_2$, are natural components of living organisms and play an important role in many biological processes.[1–9] The widespread presence of PAs, a marked increase of their concentration in young cells and a change in the concentration level in tumor tissues has stimulated intense interest in this group of compounds.[1,10,11] At physiological pH, polyamines occur in protonated, cationic form and as such they interact with negative fragments of other biomolecules, *i.e.*, amino acids, proteins and phospholipids. Of particular importance is the affinity of PAs for DNA, RNA and ribosomes and their effect on the biosynthesis of proteins and nucleic acids.[8,12] Reactions of PAs with nucleic acids determine their role in genetic information transfer. The nature of these processes is conditioned by both the charge and structure of the polyamines and the resultant interactions lead to structural changes on a few levels of organization[13–23] (to the early 1990s about a thousand research reports concerning processes involving polyamines have appeared). The sometimes suggested model assuming only electrostatic reactions does not account for the high selectivity of some of them. Moreover, the centres of PA interactions with other bioligands constitute potential coordination sites of metal ions present in living cells. Thus, these metal ions should be treated as factors interfering with interactions in biological fluids. On the other hand, if it assumed that metal ions form stable complexes with nucleic acids,[24] polyamines may be treated as the interfering factor. The mechanism of interactions of metal ions on the molecular level has not been fully recognized. In recent studies of binary systems of Cu(II) ions with a series of polyamines[25] we have found, that 4 nitrogen atoms (square-planar coordination) or 5 nitrogen atoms with one of them at an axial position mostly are involved in coordination.

It should be remembered that living cells usually contain different biogenic amines and other bioligands (*e.g.*, aminoacids). The present paper reports investigations on complexation of Cu(II) in ternary systems involving polyamines and diaminocarboxylates. Besides determination of the thermodynamic stabilities of the compounds, an attempt has been made to establish the coordination mode of the complexes in aqueous systems and to continue analysis of the controversial problem of donor atom binding at axial positions.

EXPERIMENTAL

The monohydrochloride of *DL*-2,3-diaminopropionic acid (*dapa*; Aldrich) and the dihydrochloride of *DL*-2,4-diamino-*n*-butyric acid (*daba*; Sigma) were used as received. Hydrochlorides of the amines ethylenediamine (*en*), 1,3-

diaminopropane (*tn*), 1,4-diaminobutane (putrescine, *Put*), diethylenetriamine (*dien, 2,2-tri*), 1,6-diamino-4-azahexane (*2,3-tri*), 1,7-diamino-4-azaheptane (*3,3-tri*), 1,8-diamino-4-azaoctane (spermidine, *Spd*) were obtained from amines (Sigma) by neutralizing them with two or three equivalents of HCl. They were crystallized from water-methanol solutions. All hydrochlorides were subjected to analysed and results (%N, %C, %H) were in agreement with the theoretically calculated values (±0.5%). $Cu(ClO_4)_2$ was prepared according to the previously described method.[26] Concentration of Cu(II) ions in solution was determined by complexometric titration.[26] Stock solutions of the ligands were made by solving appropriate portions in water. Potentiometric titrations were carried out at ionic strength $\mu = 0.1$ (KNO_3) under argon, using as titrant CO_2-free, 0.25668 M NaOH. The measuring vessel was thermostatted at 20 (± 0.1)°C. For potentiometric measurements, a DTS 800 Multi-Titration System, (Radiometer) was used with calomel (K4040) and glass (G2040C) electrodes after previous calibration in terms of hydrogen ion concentration.[27]

Stability constants of complexes were calculated using the SUPERQUAD computer program,[28] and the distribution of complex forms by the HALTAFAL program.[29] Electronic spectra were recorded using a Shimadzu UV 160 spectrometer, at identical concentrations of metal ions as in the potentiometric studies (0.003 M) and at the same mol ratio of components, $M:L:L' = 1:1:1$. EPR spectra were recorded using an SE/X 2547 Radiopan spectrometer. Measurements were carried out at 77K for water and water-methanol solutions.

RESULTS AND DISCUSSION

The ligands under study are shown below.

$NH_2-CH_2-CH_2-NH_2$ **en** $CH_2(NH_2)\ CH\ (NH_2)\ COO^-$ **dapa**
$NH_2-CH_2-CH_2-CH_2-NH_2$ **tn** $CH_2(NH_2)\ CH_2\ CH(NH_2)\ COO^-$ **daba**
$NH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$ **Put**
$NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2$ **dien**
$NH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-NH_2$ **2,3 tri**
$NH_2-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-NH_2$ **3,3 tri**
$NH_2-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-CH_2-NH_2$ **Spd**

Overall stability constants of mixed complexes are given in Table I. For the sake of comparison, the values of stability constants of binary complexes also are given.

TABLE I Overall stability constants of complexes

*Binary complexes**	*logβ*	*Ternary complexes*	*logβ*
Cu(en)	10.78(08)	Cu(Put)(dien)	20.42(12)
$Cu(en)_2$	19.88(08)	Cu(Put)(3,3-tri)	16.64(14)
		Cu(en)(dien)	21.15(15)
Cu(tn)	9.68(12)	Cu(en)(2,3-tri)	20.81(06)
$Cu(tn)_2$	16.79(26)	Cu(H)(en)(3,3-tri)	30.34(08)
$Cu(tn)_3$	21.66(32)	Cu(en)(3,3-tri)	22.71(08)
CuHtn	15.78(14)	Cu(en)(3,3-tri)(OH)	2.51(11)
		Cu(H)(en)(Spd)	29.70(10)
Cu(Put)	8.62(13)	Cu(en)(Spd)	21.30(12)
$Cu(Put)_2$	13.40(18)	Cu(en)(Spd)(OH)	11.70(13)
CuHPut	15.83(17)	Cu(tn)(2,3-tri)	20.25(10)
$Cu(Put)_2OH$	0.065(06)	Cu(H)(tn)(Spd)	27.75(09)
		Cu(tn)(Spd)	19.12(09)
Cu(dien)	16.18(07)	Cu(tn)(Spd)(OH)	9.57(09)
$Cu(dien)_2$	21.30(08)	Cu(tn)(dien)	20.64(10)
		Cu(tn)(en)	18.61(10)
Cu(2,3-tri)	16.76(02)	Cu(Spd)(dien)	21.00(14)
$Cu(2,3\text{-tri})_2$	20.59(04)	Cu(Spd)(dien)(OH)	10.58(17)
$Cu(2,3\text{-tri})(OH)_2$	−3.63(05)	$Cu(H)_2(3,3\text{-tri})(tn)$	36.59(06)
		Cu(H)(3,3-tri)(tn)	27.94(07)
Cu(3 3-tri)	13.71(03)		
$Cu(3,3\text{-tri})_2$	18.48(24)	Cu(dapa)(dien)	21.09(07)
CuH(3,3-tri)	18.87(18)	Cu(dapa)(2,3-tri)	20.45(10)
Cu(3,3-tri)(OH)	3.14(05)	Cu(H)(dapa)(en)	25.39(02)
		$CuH_2(dapa)(3,3\text{-tri})$	34.91(08)
Cu(Spd)	11.70(06)	CuH(dapa)(3,3-tri)	27.54(18)
$Cu(Spd)_2$	17.13(12)	$CuH_3(dapa)(Spd)$	42.71(03)
CuHSpd	18.91(07)	$CuH_2(dapa)(Spd)$	35.36(06)
Cu(Spd)(OH)	2.90(11)	CuH(dapa)(Spd)	27.61(05)
$Cu(Spd)_2(OH)$	6.72(12)	Cu(dapa)(Spd)	17.31(11)
		Cu(daba)(dien)	20.13(08)
Cu(dapa)	11.54(10)	Cu(daba)(dien)(OH)	9.43(11)
$Cu(dapa)_2$	19.13(06)	Cu(daba)(2,3-tri)	19.59(14)
CuHdapa	15.48(08)	$CuH_4(daba)(Spd)$	49.68(05)
$CuH_2(dapa)_2$	29.82(05)	$CuH_2(daba)(Spd)$	35.99(09)
$CuH(dapa)_2$	25.05(07)	CuH(daba)(Spd)	27.64(07)
		Cu(daba)(Spd)	17.28(11)
Cu(daba)	11.28(05)	$CuH_2(dapa)(tn)$	32.42(04)
$Cu(daba)_2$	17.24(07)	CuH(dapa)(tn)	25.72(08)
CuHdaba	16.76(05)	Cu(dapa)(tn)	18.67(16)
$CuH(daba)_2$	25.47(06)	Cu(daba)(tn)	18.75(12)

* Values from [25,31,35]

In a few systems (mainly those containing putrescine with thermodynamically unfavourable 7-membered rings), due to precipitation of hydroxo complexes, it was not possible to perform the potentiometric measurements. Examples of the calculated distributions of the formed species is shown in Figure 1.

Mixed-ligand complexes of the MLL′ type are formed at pH *ca* 7–8. Binary complexes form from a pH of about 3–4.[25] It is characteristic that the biogenic amine spermidine and its analogue, *3,3-tri* (which also occurs in living organisms)

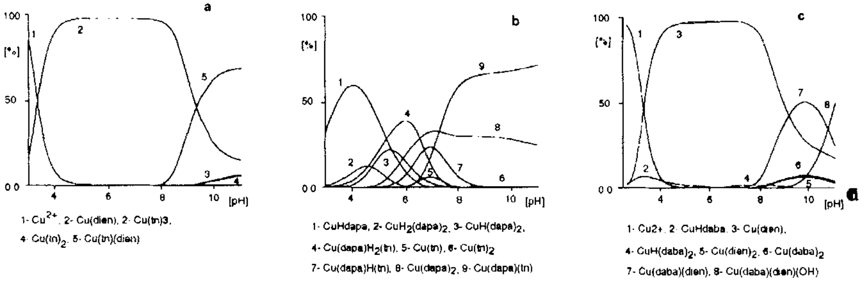

FIGURE 1 Distribution diagrams for the systems (a) Cu/tn/dien, (b) Cu/dapa/tn, (c) Cu/daba/dien

the only ligands which form several types of mixed-ligand complexes in ternary systems with other biomolecules. Using the determined log β, equilibrium constants for complex formation were calculated (Table II).

Though the ligands involved are relatively simple, for the number of binary complexes, the coordination mode in solution has not been univocally established yet (in particular for complexes of the ML_2 or ML_3 type, including important compounds of *Spd*). The results suggest, however, that most characteristic are structures with four nitrogen atoms coordinated equatorially with, in some of them, one (less often two) atom(s) at axial position(s).[25] Comparative analysis of the results of equilibrium studies and the results of electronic and EPR measurements have been employed to evaluate the tendency of particular ligands to form mixed-ligand species as well as to determine the coordination mode of these species.

TABLE II Equilibrium constants for ternary complex formation $ML + L' \rightleftarrows MLL'$ in Cu(II)/polyamine/polyamine systems

Cr	*Reaction*	*log*$K^{L'}$ Cu*LL'*
1	Cu(en) + en ⇄ $Cu(en)_2$	9.10
2	Cu (en) + tn ⇄ Cu(en)(tn)	7.83
3	Cu(en) + dien ⇄ Cu(en)(dien)	10.37
4	Cu(en) + 2,3-tri ⇄ Cu(en)(2,3-tri)	10.03
5	Cu(en) + 3,3-tri ⇄ Cu(en)(3,3-tri)	11.93
6	Cu(en) + Spd ⇄ Cu(en)(Spd)	10.52
7	Cu(tn) + en ⇄ Cu(tn)(en)	8.93
8	Cu(tn) + tn ⇄ $Cu(tn)_2$	7.11
9	Cu(tn) + dien ⇄ Cu(tn)(dien)	10.96
10	Cu(tn) + 2,3-tri ⇄ Cu(tn)(2,3-ti)	10.57
11	Cu(tn) + Spd ⇄ Cu(tn)(Spd)	9.44
12	Cu(dien) + dien ⇄ $Cu(dien)_2$	5.12
13	Cu(dien) + Spd ⇄ Cu(dien)(Spd)	4.82
14	Cu(dien) + Put ⇄ Cu(dien)(Put)	4.24
15	Cu(3,3-tri) + Put ⇄ Cu(3,3-tri)(Put)	2.93

Mixed Ligand Complexes in the Cu(II)/Diamine/Polyamine Systems

It follows from our findings (the results of equilibrium and spectroscopic studies[25]) for binary complexes, that complexes of the ML type containing *en* and *dien* include, respectively, the chromophores 2N and 3N where all donor atoms of the ligands are involved in coordination. In a ternary complex, Cu(en)(tn), coordination of both amines leads to formation of chromophore 4N and a square-planar structure, which is indicated by comparison of both the values of stability constants of the parent complexes with the stability constant of the mixed ones (Table I) and of the *d-d* band positions of particular compounds in binary and ternary complexes (Table III) as well as by analysis of EPR parameters (Table IV). On the basis of the data from the distribution curves, it was possible to establish the optimum conditions for the spectroscopic measurements, *i.e.*, the range of pH with the highest concentration of the investigated species whose spectrum was to be recorded. As regards EPR studies, it is known that in complexes with only σ bonding, the value of $g_{\parallel}$ depends very clearly on the number of donor atoms and also on the type of the formed ring. For example, the relation can be seen by comparing $g_{\parallel}$ values for $Cu(en)_2$, $Cu(tn)_2$ and $Cu(Put)_2$ or comparing values for Cu(en)Spd and Cu(tn)Spd complexes (Table IV). For systems of Cu(II) with polyamines the complex species with two nitrogen atoms involved in coordination have $g_{\parallel}$ about 2.28, those with three atoms have a value about 2.23 and those with four atoms about 2.20–2.22. The complexes formed in the studied systems are species with d_{x2-y2} ground state and the differences in $g_{\parallel}$ should be explained in terms of equatorial ligand field.[30] Some additional information was also taken from $A_{\parallel}$ values. It is observed that the value is usually higher for complexes with more nitrogen atoms coordinated in the equatorial plane, but a decrease in value can be observed for complexes with a nitrogen atom located in an axial position.[30]

TABLE III Electronic spectrum absorption data for the ternary systems

Complex	*pH*	λ_{max}*[nm]*
Cu(tn)(en)	9–11	555
Cu(en)(dien)	10	627
Cu(en)(2,3-tri)	10	585
Cu(en)H(3,3-tri)	6.5	600
Cu(en)(3,3-tri)	9	600
Cu(en)(3,3-tri)(OH)	11	585
Cu(en)H(Spd)	7.5	594
Cu(en)(Spd)	9	580
Cu(en)(Spd)(OH)	11	565
Cu(tn)(dien)	11	619
Cu(tn)(2,3-tri)	10	592
Cu(tn)H(Spd)	8	600
Cu(tn)(Spd)	9	592

TABLE III (*Continued*)

Complex	*pH*	λ_{max}*[nm]*
Cu(tn)(Spd)(OH)	11	581
Cu(Put)(dien)	11	594
Cu(Put)(3,3-tri)	11	590
Cu(dien)(Spd)	10	602
Cu(dapa)(dien)	10	630
Cu(dapa)(2,3-tri)	10	587
Cu(dapa)H_3(Spd)	6	622
Cu(dapa)H(Spd)	9	570
Cu(dapa)H_2(tn)	6	608
Cu(dapa)(tn)	10	560
Cu(daba)(tn)	10	600
Cu(daba)(dien)	9.5	630
Cu(daba)(dien)(OH)	11	627
Cu(daba)H_4(Spd)	5	700
Cu(daba)H(Spd)	9.5	608
Cu(daba)(Spd)	11	602

TABLE IV EPR data for copper(II)-polyamine(diaminocarboxylate) complexes

System	*pH*	*Molar ratio*	*Complex*	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}[10^{-4}\text{cm}^{-1}]$
Cu				2.412	2.085	2.199	135
Cu/en	4.6	1:2	ML	2.281	2.072	2.142	182
	10–11	1:2	ML_2	2.209	2.053	2.106	200
Cu/tn	6.9	1:2	ML	2.286	2.062	2.139	180
	8.6–10	1:2	ML_2	2.217	2.053	2.109	205
Cu/put	10	1:6	ML_2	2.214	2.051	2.107	200
Cu/dien	3.2–10.2	1:2	ML	2.231	2.064	2.117	192
	10.3	1:6	ML_2	2.214	2.050	2.106	186
Cu/2,3-tri	3.3–7.5	1:2	ML	2.237	2.050	2.115	183
	9–11.3	1:2	ML_2	2.215	2.056	2.111	190
Cu/3,3-tri	6.6	1:2	ML	2.251	2.055	2.123	163.5
	10	1:2	ML_2	2.228	2.051	2.112	189.5
Cu/spd	8–10.3	1:2	ML_2	2.208	2.057	2.112	198
Cu/daba		1:2	ML_2	2.226	2.051	2.111	201
Cu/en/tn	10.3	1:1:1	MLL’	2.207	2.056	2.108	206
Cu/en/spd	8.9	1:1:1	MLL’	2.205	2.058	2.108	201
Cu/en/3,3-tri	8.9	1:1:1	MLL’	2.207	2.045	2.100	204
Cu/tn/spd	9.1	1:1:1	MLL’	2.213	2.057	2.110	200
Cu/tn/daba	10.4	1:1:1	MLL’	2.239	2.051	2.115	191
Cu/put/dien	10.5	1:1:1	MLL’	2.194	2.048	2.098	198
Cu/daba/spd	9.5	1:1:1	MLL’	2.222	2.052	2.110	193
	11.5	1:1:1	MLL’	2.222	2.050	2.109	194

By comparing the equilibrium constants of formation of ternary complexes with ethylenediamine as the first ligand (Table II), it is seen that addition of *tn* another *en* corresponds to a clearly lower value of logK than is observed for the formation of analogous complexes with triamines. This suggests interaction of 3 nitrogen atoms from *dien, 2,3-tri* or *3,3-tri* with metal ions, or, in other words, coordination of the 5N type. This bears on the position of electronic absorption bands for the complexes (Table III); λ_{max} of the parent complex of $Cu(en)_2$ is equal to 550 nm,[25] while for Cu(en) (triamine) a red shift by *ca* 50 nm is observed as a result of involvement of a donor atom at an axial position. Although λ_{max} of about 600 nm corresponds also to a 3N chromophore, the value of $g_{\parallel}$ excludes coordination with only 3 nitrogen atoms (Table IV).

Similar results apply to systems with 1,3-diaminopropane (*tn*). Equilibrium constants of formation of mixed complexes, Cu(II)/tn/terdentate ligand, are two orders of magnitude higher than for the Cu(II)/tn/bidentate ligand systems. This is indicative of involvement of an additional donor atom and of 5N coordination (the fifth nitrogen atom from a trifunctional amine at an axial position) and is in agreement with conclusions drawn from analysis of spectroscopic data as well as with observations concerning quantitative dependencies of equilibrium constants on the number and type of the rings formed.[32] For Cu(en)(tn) it was found that λ_{max} = 555nm, while for Cu(tn)Spd, Cu(tn)(dien) and Cu(tn)(2,3-tri) the band is red-shifted respectively by *ca* 40, 60 and 40 nm (Table III).

In mixed complexes of triamines containing putrescine as the second ligand, due to the relatively low complexing ability of *Put*, the anchoring ligand is the triamine which constitutes the chromophore 3N. As follows from comparison of equilibrium constants and the overall stability constants for Cu(3,3-tri)Put with analogous constants for Cu(dien)Put (Tables I and II) as well as from the spectroscopic data (Table III), the potentially bidentatne *Put* forms a mixed ligand complex Cu(3,3-tri)Put with 4N coordination (only 1 donor atom from *Put*) and this is the only example of this type of chromophore among the examined ternary systems. The monofunctional character of *Put* was observed previously in binary systems.[31, 33] In the Cu(dien)Put complexes all nitrogen atoms are involved in coordination.

Application of the parameter proposed by Sigel[34] $\Delta\log K_{TER} = \log\beta_{CuLL'} - \log\beta_{CuL} - \log\beta_{CuL}$ suggests (Table V) that in a series of ternary complexes of Cu(II) in the diamine/polyamine systems the coordination tendency and the values of the Sigel parameters are the highest when a trifunctional ligand forms a system of two 6-membered rings (or unexpectedly 6- and 7-membered), but unfavourable when at least one of the rings of the second ligand is five-membered. (It should be remembered that in all the studied systems the 5N chromophore is dominant).

TABLE V Values of $\Delta\log K_{TER}$ for ternary systems

Complex	$\Delta\log K_{TER}$
Cu(en)(tn)	−1.85
Cu(en)(3,3-tri)	−1.58

TABLE V *(Continued)*

Complex	$\Delta logK_{TER}$
Cu(en)(Spd)	-1.18
Cu(en)(dien)	-5.81
Cu(en)(2,3-tri)	-6.74
Cu(tn)(Spd)	-2.26
Cu(tn)(dien)	-5.22
Cu(tn)(2,3-tri)	-6.19
CuPut(dien)	-4.38
CuPut(3,3-tri)	-5.49
Cu(dapa)(tn)	-2.55
Cu(daba)(tn)	-2.21

Of the values presented in Table V, only the one for complex Cu(3,3-tri)Put did not satisfy the dependencies proposed above concerning the stability of ternary compounds (low value of $\Delta logK_{TER}$), though *3,3-tri* forms six-membered rings. This, however, clearly confirms the suggestion that the complex is characterized by a different coordination mode (4N type).

It is interesting that unlike in the binary systems where *Spd* favours square-planar coordination (type 4N) leaving the axial position unoccupied (which is important in catalytic reactions involving such a molecule), in ternary systems one of the donor atoms of spermidine in the complex Cu(diamine)Spd occupies a position outside the equatorial plane.

Mixed Ligand Complexes in the Cu(II)/Triamine/Triamine Systems

Unlike the ternary systems involving diamines, in the series of the studied systems containing two triamines, mixed-ligand complexes are formed only in the system Cu/dien/Spd (at detectable concentrations). The value λ_{max} = 602 nm and the overall stability constant for the Cu(dien)Spd complex relative to that for complexes with coordination 4N[25] indicate that the most probable structure is one with one donor atom in an axial position. The above results are in line with the general tendency that, in ternary systems, compounds with 5N coordination are dominant. Two triamines have six donor atoms in total, so a nitrogen atom from one - $(CH_2)_xNH_2$ group is not involved in coordination and, additionally, a side chain is responsible for steric bulkiness. For systems where no mixed complexes were reported to occur, the accuracy of computer analysis was corroborated by comparing the computer simulated titration curves (obtained for the model in which ternary complexes were not included) with the experimental ones (Figure 2). Good agreement of the two curves testifies to the correctness of the procedure of model selection.[36]

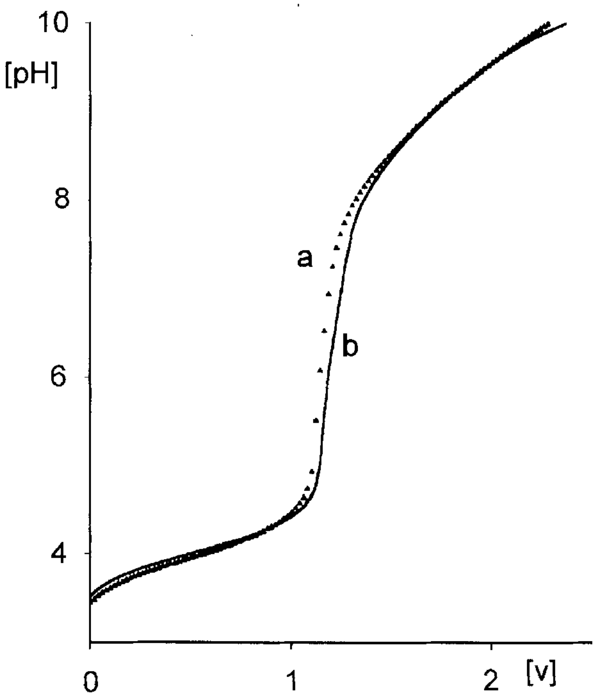

FIGURE 2 Simulated (b) and experimental (a) curve for the system Cu(II)/dien/2,3-tri (addition of a mixed complex to the model diminishes the agreement between the curves).

Mixed-Ligand Complexes in the Systems Cu(II)/Polyamine/Diaminocarboxylate

Stability and equilibrium constants of mixed complexes are presented in Tables I and VI.

TABLE VI Equilibrium constants for ternary complex formation ML + L' ⇄ MLL' in Cu(II)/polyamine/diaminocarboxylate systems

	Reaction	*logK*$^{L'}$ Cu*LL'*
1	Cu(daba) + H(en) ⇄ Cu(daba)H(en)	3.70
2	Cu(daba) + H(tn) ⇄ Cu(daba)H(tn)	3.48
3	Cu(dapa) + tn ⇄ Cu(dapa)(tn)	7.13
4	Cu(daba) + tn ⇄ Cu(daba)(tn)	7.42
5	Cu(dien) + dapa ⇄ Cu(dien)(dapa)	4.91
6	Cu(dien) + daba ⇄ Cu(dien)(daba)	3.95
7	Cu(2, 3-tri) + dapa ⇄ Cu(dapa)(2,3-tri)	3.69
8	Cu(2, 3-tri) + daba ⇄ Cu(2,3-tri)(daba)	2.83

TABLE VI (*Continued*)

	Reaction	*log*$K^{L'}$ Cu*LL'*
9	Cu(Spd) +dapa ⇄ Cu(Spd)(dapa)	5.61
10	Cu(Spd) +daba ⇄ Cu(Spd)(daba)	5.58
11	Cu(dapa) + Spd ⇄ Cu(dapa)(Spd)	5.77
12	Cu(daba) + HSpd ⇄ Cu(daba)H(Spd)	5.39
13	Cu(daba) + Spd ⇄ Cu(daba)(Spd)	6.00

Results of studies on parent complexes of these anions show[25] that glycine-like coordination in ML is probable and the *d-d* bands as well as the sequence of increasing stability constants of the complexes *gly<en<dapa and gly<tn<daba* indicates involvement of the 2N1O group in coordination. However, as follows from the equilibrium studies, the involvement of the oxygen atom is relatively weak. Moreover, differences in the coordination character between *daba* and *dapa* were found. In the case of *daba* in ML_2 there is mixed coordination with chromophores 2N1O and 1N1O (two different chromophores from two molecules of the same ligand). The complex $Cu(dapa)_2$, has all nitrogen atoms located in the plane with coordination 4N (probably with some contribution of the oxygen atom). The differences between *daba* and *dapa* are also found for the interactions of diaminocarboxylate anions with Pd(II).[37]

Taking into account the results of studies on binary systems, it can be assumed that in ternary complexes Cu/diaminocarboxylate/diamine the anchoring ligand is *dapa* (or *daba*), which is supported by the distribution presented in Figure 1b. Lower basicities of NH_2 groups from diaminocarboxylate anions in comparson to NH_2 groups from polyamines facilitate complex formation at lower pH. Similar values of thermodynamic parameters of the protonated complexes Cu(dapa)H(en) and Cu(dapa)H(tn) (Tables I and VI) provide evidence of an identical mode of coordination (chromophore 3N1O) involving nitrogen atoms of diaminocarboxylate anion and polyamine as well as an oxygen atom from *dapa* (or *daba*). Equilibrium constants for ternary copper complexes MLL′ of *tn* and *dapa* (or *daba*) in comparison to those of protonated complexes MLHL′ (Table VI, equations 1–4) are significantly higher, which indicates that coordination in MLL′ involves a greater number of donor atoms. However, in the system with *dapa*, 4 nitrogen atoms are located at equatorial positions and one oxygen atom at an axial position, whereas in the system with *daba*, coordination of the 3N1O type (with one of the nitrogen atoms out of the coordination sphere) occurs, as can be clearly concluded from equlibrium, electronic and EPR data. The difference in character of the two diaminocarboxylate anions is analogous to their parent complexes of the ML_2 type.

A different picture of complexation applies to the Cu/diaminocarboxylate/triamine system. Parent complexes of triamines are characterized by significantly greater stability than the analogous *dapa* or *daba* compounds and therefore it is the amines that should be treated as anchoring ligands, but only those forming 5/5 or 5/6 ring systems (spermidine with a 6/7 ring system behaves differently). Sequence of complexation from the distribution diagram (Figure 1c) confirms the above model. The coordination mode in the system Cu/diaminocarboxylate with *dien* or *2,3-tri* is different than in the case of diamine, as evidenced by values of stability constants of ternary complexes and by the position of the *d-d* bands. Triamine occupies three coordination sites in the equatorial plane, leaving only one donor site for a nitrogen atom from *dapa* (or *daba*). Localization of the second nitrogen atom of the diaminocarboxylic anion at an axial position is responsible for the observed red shift [*e.g.*, relative to Cu(dapa)(tn)], particularly noticeable in the system with *dien* (Table III). On the other hand, two clearly different absorption bands correspond to two *Spd* complexes, Cu(dapa)H(Spd) and Cu(daba)H(Spd), though the values of stability constants for the two compounds are almost identical (Table I and III). These results coupled with the information obtained from studies on binary systems suggest that in the protonated *dapa* complex square-planar 4N coordination probably occurs, while in the *daba* complex coordination is 3N1O, as supported by EPR parameters (Table IV).

In acidic media, an adduct Cu(daba)H_4(Spd) is formed. The presence of a similar compound was reported in the system with Pd (II)[38] and in the system Cu(II)/spermine/ATP.[39] Increase in pH leads to deprotonation of ligands and involvement of two donor atoms of Spd into the inert coordination sphere [complex Cu(daba)H(Spd)], which is accompanied by a shift of the *d-d* band from about 700 to about 600 nm. Further deprotonation with formation of Cu(daba)(Spd) complex does not change the coordination mode, as evidenced by the position of the absorption bands (Table III), similar values of equilibrium constants for the reactions Cu (daba) + HSpd $\rightleftarrows$ Cu (daba) H (Spd) and Cu (daba) + Spd $\rightleftarrows$ Cu(daba)(Spd) (Table VI, reactions 12 and 13), as well as by the identical EPR spectra obtained in the range of occurrence of both species (Figure 3).

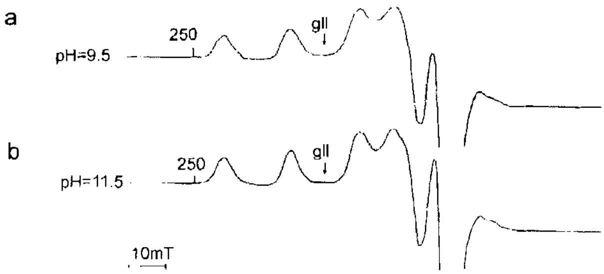

FIGURE 3 EPR spectra of (a) Cu(daba)H(Spd) and (b) Cu(daba)(Spd) complexes.

On the basis of the above results, especially the values of equilibrium constants (Table II and VI) it may be claimed that in the ternary complexes Cu(II)/dapa (or daba)/Spd, spermidine coordinates in such a way that two nitrogen atoms are involved, as in the systems Cu(II)/triamine/Spd. This is different to the Cu(II)/diamine/Spd systems where all spermidine donor atoms take part in coordination.

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References

[1] J. Jänne, H. Pösö and A. Raina, *Biochim. Biophys. Acta*, **473**, 241 (1978).
[2] C.W. Tabor and H. Tabor, *Ann. Rev. Biochem.*, **45**, 285 (1976).
[3] O.P. Shukla, *J. Sci. Ind. Res. India*, **49**, 263 (1990).
[4] U. Bachran, *Function of Naturally Occuring Polyamines*, (Academic Press, N.Y., 1973).
[5] *Progress in Polyamine Research*, V. Zappia and A.E. Pegg (eds.), (Plenum Press, New York, 1988).
[6] L. Lomozik, *Wiadomosci Chemiczne*, **48**, 339 (1994).
[7] L. Lomozik, *Metal Complexes with Polyamines*, in *Handbook of Metal-Ligand Interactions in Biological Fluids*, G. Berthon (ed.), (Marcel Dekker, N.Y., 1995), V. I, p. 686.
[8] A. Raina and J. Jänne, *Med. Biol.*, **53**, 121 (1975).
[9] F. Schuber, *Biochem. J.*, **260**, 1 (1989).
[10] J. Jänne, L. Alhonen and P. Leinonen, *Ann. Med.*, **23**, 241 (1991).
[11] H.G. Williams-Ashman and Z.N. Canellakis, *Perspect. Biol. Med.*, **22**, 421 (1979).
[12] C.W. Tabor and H. Tabor, *Ann. Rev. Biochem.*, **53**, 749 (1984).
[13] M.D. Bratek-Wiewiorowska, M. Alejska, M. Figlerowicz, J. Barciszewski, M. Wiewiorowski, M. Jaskolski, W. Zielenkiewicz, A. Zielenkiewicz and M. Kaminski, *Pure Appl. Chem.*, **59**, 407 (1987).
[14] W.H. Braunlin, T.J. Strick and M.T. Record, Jr., *Biopolymers*, **21**, 1301 (1982).
[15] D.E. Wemmer, K.S. Srivenugopal, B.R. Reid and D.R. Morris, *J. Mol. Biol.*, **185**, 457 (1985).
[16] C.N. Nakai and W. Glinsmann, *Biochemistry*, **16**, 5636 (1977).
[17] P.M. Vertino, R.J. Bergeron, P.F. Cavanaugh and C.W. Porter, *Biopolymers*, **26**, 691 (1987).
[18] B.G. Feuerstein, N. Pattabiraman and L.J. Marton, *Nucleic Acids Res.*, **18**, 1271 (1990).
[19] G.E. Plum, P.G. Arscott and V.A. Bloomfield, *Biopolymers*, **30**, 631 (1990).
[20] T.J. Thomas and R.P. Messner, *J. Mol. Biol.*, **201**, 463 (1988).
[21] E. Rowatt and R.J.P. Williams, *J. Inorg. Biochem.*, **46**, 87 (1992).
[22] K.A. Marx and T.C. Reynolds, *Int. J. Biol. Macromol.*, **11**, 241 (1989).
[23] T.J. Thomas, U.B. Gunnia and T. Thomas, *J. Biol. Chem.*, **266**, 6137 (1991).
[24] G.L. Eichhorn, *Complexes of Polynucleotides and Nucleic Acids*, in *Inorganic Biochemistry*, G.L. Eichhorn. (ed.), (Elsevier, Amsterdam, 1973), V. **2**, p. 1210.
[25] L. Lomozik, L. Bolewski and R. Bregier-Jarzebowska, *Polish. J. Chem.*, **69**, 197 (1995).
[26] L. Lomozik, *Monatsh. Chem.*, **115**, 261 (1984).
[27] M.H. Irving, M.G. Miles and L.D. Pettit, *Anal. Chim. Acta*, **38**, 475 (1967).
[28] P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1195 (1985).
[29] N. Ingri, W. Kakolowicz, L. Sillen and B. Warnqvist, *Talanta*, **14**, 1261 (1967).
[30] R. Barbucci and M.J.M. Campbell, *Inorg. Chim. Acta*, **16**, 113 (1976).
[31] L. Lomozik and A. Gasowska, *Monatsh. Chem.*, **124**, 109 (1993).
[32] D.M. Templeton and B. Sarkar, *Can. J. Chem.*, **63**, 3122 (1985).

[33] L. Lomozik and A. Wojciechowska, *Polyhedron*, **8**, 2645 (1989).
[34] H. Sigel, *Coordination Chemistry-20*, D. Banerjea, (ed.), (Pergamon Press, Oxford, 1980), p. 27.
[35] A. Wojciechowska, L. Bolewski and L. Lomozik, *Monatsh. Chem.*, **122**, 131 (1991).
[36] L. Lomozik, M. Jaskolski and A. Wojciechowska, *Polish J. Chem.*, **65**, 1795 (1991).
[37] L. Lomozik and L. Bolewski, to be published.
[38] L. Lomozik, A. Odani and O. Yamauchi, *Inorg. Chim. Acta*, **291**, 107 (1994).
[39] M.L. Antonelli, V. Carunchio, E. Cernia and R. Purello, *J. Inorg. Biochem.*, **37**, 201 (1989).