Inorganica Chimica Acta, *86* (1984) 145–149

Copper(II) Complexes with Optically Active Diamines. V. Enantioselective Effects in Equally-Paired and Mixed-Ligand Copper(II) Complexes with Diamines

A. A. KURGANOV, T. M. PONOMARYOVA and V. A. DAVANKOV

Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the USSR, 117813 Moscow, U.S.S.R.

Received November 12, 1983

UV- and circular dichroism (CD) spectra of binary (equally-paired) and ternary (mixed-ligand) copper(II) complexes with optically active and racemic 1,2-diaminopropane, 2-(aminomethyl)pyrrolidine and their N-benzyl derivatives were studied. For the first time, enantioselective effects in square-planar copper-diamine complexes were observed.

Differences in the absorption spectra of labile diastereomeric complexes Cu(R,R) and Cu(R,S), containing two ligands of the same or opposite configurations, albeit being sufficient to indicate the non-similarity of the electronic structures of these complexes, are nevertheless insignificant. On the contrary, using CD measurements it was possible to evaluate quantitatively the extent of formation of diastereomeric mixed-ligand complexes $Cu(A_SB_S)$ *and* $Cu(A_SB_R)$ *on mixing two equally-paired complexes* $Cu(A_SA_S)$ *and* $Cu(B_SB_S)$ *or* $Cu(B_RB_R)$*, where* A_S, B_S *and* B_R *stand for diamine ligands of the corresponding configuration. Differences in the free energy of diastereomeric ternary complexes were found to reach levels as high as 5.5 kJ* mol^{-1}.

Probable structures of diastereomeric complexes are considered. The optical activity of complexes is shown to depend mainly on conformational contributions from chiral chelate rings and chiral distortion of the coordination square-plane, with contributions from the asymmetric carbon and nitrogen atoms playing an ancillary role.

Introduction

Enantioselectivity has been defined [1] as the difference in the interaction of one chiral reagent with two enantiomeric forms of the second component of the reaction. This definition distinguishes enantioselective effects from enantiospecific ones, the latter term being reserved for the ability of the chiral reagent to induce new asymmetry in the reaction product. Both enantioselective and enantiospecific effects can be of kinetic and/or thermodynamic nature. The above definitions imply that in reactions involving chiral components, enantioselective and enantiospecific effects can be evaluated separately [1].

Sterical peculiarities of formation of coordination compounds have attracted considerable activity (see reviews [1–3]), enantiospecificity of formation of kinetically inert complexes of Co(III) being the favourite object of investigations for a long period of time. More recently, enantioselectivity effects in kinetically labile complexes of Cu(II), Ni(II), Zn(II) with α-amino acids have focused the greatest part effort in connection with the resolution of racemic compounds using ligand-exchange chromatography technique (see reviews [4, 5]). Contrary to the previously accepted view [2], it has been shown that the enantioselectivity in bis(α-amino acidato)copper(II) complexes is a rather common phenomenon [4, 5]. Enantioselectivity in these systems means that the chiral mono(amino acidato)copper(II) complex distinguishes between the R- and S-configurations of the second amino acid ligand, so that two labile diastereomeric structures formed, Cu(R,R) and Cu(R,S), differ in stabilities and other properties.

Kinetically labile coordination compounds with other types of ligands were given little consideration. Thus, in the case of copper(II) complexes with 1,2-diamines there is only one contribution [6] where a comparative potentiometric titration of Cu(R,R) and Cu(R,S) systems was conducted using 1,2-diaminopropane and 1,2-diaminocyclohexane. It was found that formation of neither meso-structure Cu(R,S) nor of optically-active equally-paired structures Cu(R,R) and Cu(S,S) predominate, and distribution of R- and S-ligands between these three complexes in a racemic system is purely random.

In the present work we discuss the results of studying the copper complexes of 1,2-diaminopropane, 2-(aminomethyl)pyrrolidine and their N-benzyl derivatives conducted in various solvents by UV-spectroscopy and circular dichroism (CD) spectroscopy, which resulted in the first observations of enantioselectivity phenomena in copper-diamine complexes.

0020-1693/84/$3.00

Experimental

1. Synthesis of the initial copper(II) complexes with 1,2-diaminopropane, 2-(aminomethyl)pyrrolidine and their N-benzyl derivatives was as described earlier [7, 8].

2. Absorption spectra of complexes were recorded with a 'Specord UV-VIS' (Zeiss-Jena, GDR) in 1 or 2 cm cells at room temperature and the concentration of the complex of $5 \cdot 10^{-3}$ mol/l.

The CD spectra were obtained with a 'J-20' (JASCO, Japan) in a 1 cm cell at room temperature and solution concentrations of $5 \cdot 10^{-3}$ mol/l.

3. Calculation of CD spectra of individual mixed-ligand complexes and determination of their formation constants were carried out as in [9].

Results and Discussion

Enantioselective effects in labile coordination compounds manifest themselves variously. Thus, on investigating copper(II) complexes with N-alkyl–α-amino acids we found out that some meso- and equally-paired structures are not only different in stability, but their absorption spectra in the visible region are markedly different. Sometimes differences in the colour of solutions of these diastereomeric structures can be observed with a naked eye.

In the case of 1,2-diamines (see Table I) one can also perceive differences in the absorption spectra of complexes formed by racemic and optically active ligands. The differences from 1,2-diaminopropane are not great and manifest themselves only in a slight shift of the absorption maximum of the equally-paired complex to the longwave region in comparison with the racemic complex. Spectral differences increase considerably upon introducing alkyl substituents to the nitrogen atoms of the ligands. Small differences are also observable in the case of complexes with 2-(aminomethyl)pyrrolidine. These effects are, however, of somewhat different nature: while in the case of complexes of 1,2-diaminopropane and its derivatives greater extinction was observed in meso-structures, complexes of 2-(aminomethyl)pyrrolidine and its derivatives were remarkable for more intensely coloured optically-active structures.

The absorption spectra of complexes are known to reflect primarily the structure of the coordination polyheder of the metal ion and to be less sensitive to changes in the ligand structure (if these changes are not related to donating atoms). The shifting of the absorption maximum of the copper(II) complexes with diamines is generally related to a change in coordination of two axial ligands [10] represented in systems considered by solvent molecules or by perchlorate-anions. It can be assumed that the axial ligands in the equally-paired complexes of 1,2-diamines are more closely bound to the Cu(II) atom than are axial ligands of the corresponding meso-complexes. A similar situation was observed with α-amino acid complexes of Cu(II): in the case of complexes with meso-structure Cu(R, S) and trans-configuration of the chelate center, the alkyl substituents at the asymmetrical carbon atoms of the

TABLE I. Position of Absorption Maxima (ν_{max}, kK) and Values of Molar Extinctions (ϵ, mol^{-1} cm^{-1}) for Opticallyactive and Racemic Copper(II) Complexes with 1,2-Diamines.

Complex		CH_3CN		CH_3OH		C_2H_5OH		DMF		H_2O		$PhNO_2$	
		ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ
$[Cu(pn)_2](ClO_4)_2$	RR	18.32	71.5	18.40	62.5	–	–	18.16	69.0	18.24	63.0	18.72*	55.5
	RS	18.40	72.0	18.40	61.5	–	–	18.16	69.0	18.40	61.0	18.96*	55.0
$[Cu(N^1\text{-Bzl-pn})_2](ClO_4)_2$	RR	17.60	120.5	–	–	–	–	17.29	125.5	–	–	18.00	93.0
	RS	17.68	126.5	–	–	–	–	17.25	129.0	–	–	18.00	99.0
$[Cu(N^1,N^2\text{-Bzl}_2\text{–pn})_2](ClO_4)_2$	RR	16.50	270.0	16.97	126.0	16.69	106.0	15.82	207.0	insolub.		17.12	174.0
	RS	16.50	308.5	16.97	139.0	16.69	97.0	16.13	221.0	insolub.		17.12	204.0
$[Cu(amp)_2](ClO_4)_2$	RR	17.92	90.5	18.00	88.0	17.60	92.0	17.56	83.0	17.92	83.0	18.08	90.0
	RS	17.60	88.5	18.20	88.0	17.76	88.0	17.68	81.0	17.92	88.5	18.72	87.0
$[Cu(N^1\text{-Bzl–amp})_2](ClO_4)_2$	RR	17.12	328.0	17.04	156.0	16.80	151.0	16.48	228.0	16.80	118.0	17.28	334.0
	RS	16.96	326.0	17.28	180.0	16.88	180.0	16.32	224.0	16.80	115.0	17.28	302.0
$[Cu(N^2\text{-Bzl–amp})_2](ClO_4)_2$	RR	17.12	162.0	17.44	136.0	16.88	142.0	16.64	142.0	17.12	140.0	17.44	135.0
	RS	17.28	150.0	17.44	128.0	17.04	135.0	16.88	136.0	17.12	124.0	17.68	125.0
$[Cu(N^1,N^2\text{-Me}_2\text{–pn})_2](ClO_4)_2$	RR	17.20	120.0	–	–	17.76	100.0	16.80	102.5	17.04	99.0	–	–
	RS	17.36	116.0	–	–	17.80	102.5	17.04	109.5	17.28	114.5	–	–

*In nitrometane.

ligands are located on both sides of the square-plane of the bis-chelate (Fig. 1) and partially screen off both axial positions of the copper atom. In the equally-paired structures Cu(R,R) and Cu(S,S) these substituents are located on one side of the chelate plane and at least one of the axial positions remains fully open.

In pursuing the comparison with α-amino acid complexes [11] it can be noted that spectral differences in diastereomeric 1,2-diamine complexes are much less pronounced. While amino acid complexes easily lose both axial ligands, 1,2-diamine complexes manifest a strong tendency to preserve the coordination number of six or five of the Cu(II) atom [7, 8]. For this reason their absorption spectra exhibit only a slight dependence upon temperature and the solvent. It is natural that the configuration of the asymmetrical carbon atoms in the ligands will only influence slightly the absorption spectra.

At present one cannot draw a definite conclusion concerning the causes of differences in molar extinctions of meso- and equally-paired structures with similar location of the absorption maxima. In the majority of investigations concerning the absorption spectra of coordination compounds the description can be successfully made in terms of the gallosymmetry of the complexes [10]. From this point of view the optical configuration of the ligand should not influence the absorption spectrum at all. However, we observed this influence both with purely four-coordination structures of α-amino acid complexes and tetragonal structures of Cu(II) complexes with diamines. The differences in extinctions of meso- and equally-paired structures are most likely to be related to small distortions in the structure of their chelate square plain. These distortions were for instance observed on X-ray investigation of copper(II) complexes with N-benzylproline [13] and N-benzylvaline [14].

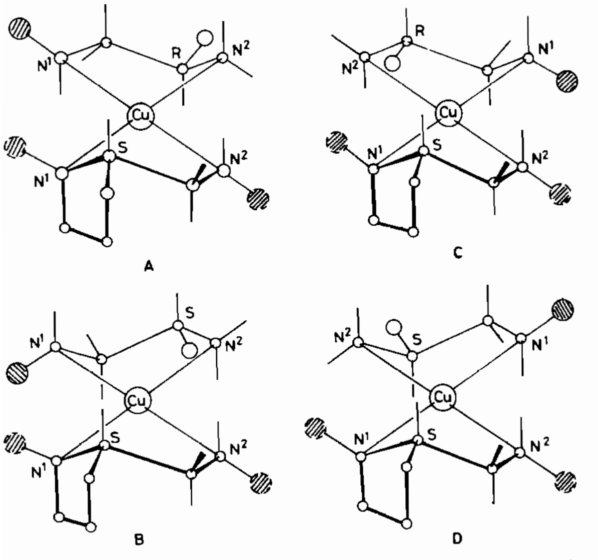

Fig. 1. Possible structures of Cu(II) complexes with (S)-2-(aminomethyl)pyrrolidine and N^1-benzyl–1,2-diaminopropane or their N-benzyl derivatives: A, *trans*-Cu(A_s, B_R); B, *trans*-Cu(A_s, B_s); D, *cis*-Cu(A_s, B_R); D, *cis*-Cu(A_s, B_s).

In general, the differences in absorption spectra of copper complexes with racemic and optically active 1,2-diamines reveal some deviations in the electronic structure of equally-paired and meso-complexes, Cu(R, R) and Cu(R, S). Reliable although purely qualitative information concerning enantioselectivity can also be obtained from electronic spectra of diastereomeric mixed-ligand complexes having two different diamine ligands. The differences observed in electronic spectra of diastereomeric complexes are, however, not sufficient for quantitative calculations of relative stability of these structures. In this case circular dichorism (CD) spectroscopy seems to be a more reliable technique of quantitative study of enantioselectivity.

The calculated CD spectra of individual mixed-ligand copper(II) complexes with a number of 1,2-diamine ligands are shown in Figs. 2–4 by dashed lines. They are estimated according to [9] from the results of CD spectra measurements on equilibrium mixtures of type (1):

$$\mathrm{Cu(A,A)} + \mathrm{Cu(B,B)} \overset{K}{\rightleftharpoons} 2\mathrm{Cu(A,B)} \qquad (1)$$

In our earlier papers [9, 15] we noted that the shape of CD spectra of 1,2-diamine complexes is mostly determined by the conformational contribution of the ligands, with vicinal asymmetric atoms of carbon and nitrogen playing an ancillary role. According to this conclusion the shape of a CD

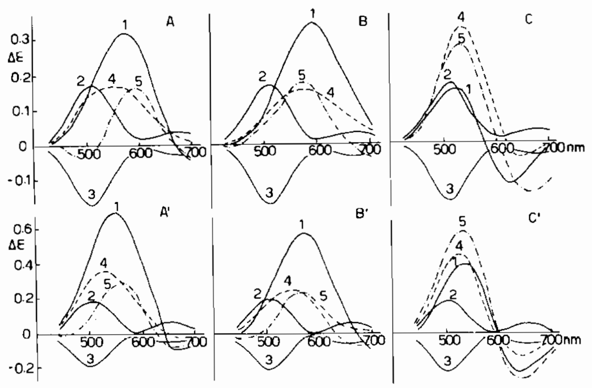

Fig. 2. CD spectra of Cu(II) complexes with (S)-2-(aminomethyl)pyrrolidine or its N-benzyl derivatives and (R)- or (S)-1,2-diaminopropane in acetonitrile (A, B, C) and nitrobenzene (A′, B′, C′). A, A′: 1: $\mathrm{Cu(amp)_2}$, 2: $\mathrm{Cu(R\text{-}pn)_2}$, 3: $\mathrm{Cu(S\text{-}pn)_2}$, 4: Cu(amp)(R-pn), 5: Cu(amp)(S-pn). B, B′: 1: $\mathrm{Cu(N^2\text{-}Bzl{-}amp)_2}$, 2: $\mathrm{Cu(R{-}pn)_2}$, 3: $\mathrm{Cu(S\text{-}pn)_2}$, 4: Cu($N^2$-Bzl–amp)(R-pn), 5: Cu($N^2$-Bzl-amp)(S-pn). C, C′: 1: $\mathrm{Cu(N^1\text{-}Bzl{-}amp)_2}$, 2: $\mathrm{Cu(R\text{-}pn)_2}$, 3: $\mathrm{Cu(S\text{-}pn)_2}$, 4: Cu($N^1$-Bzl–amp)(R-pn), 5: Cu($N^1$-Bzl–amp)(S-pn).

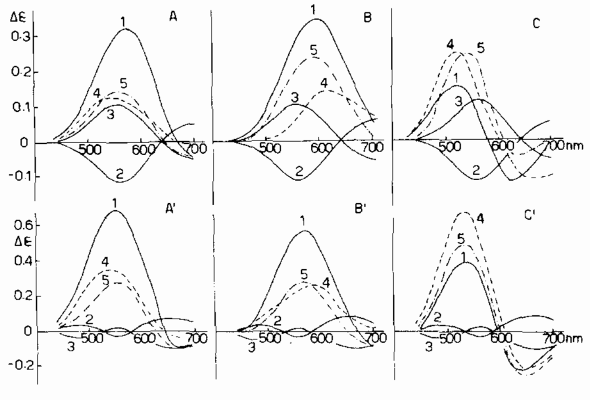

Fig. 3. CD spectra of Cu(II) complexes with (S)-2-(aminomethyl)pyrrolidine or its N-benzyl derivatives and (R)- or (S)-N^1-benzyl–1,2-diaminopropane in acetonitrile (A, B, C) and nitrobenzene (A′, B′, C′). A, A′: 1: Cu(amp)$_2$, 2: Cu(R-N^1-Bzl–pn)$_2$, 3: Cu(S-N^1-Bzl–pn)$_2$, 4: Cu(amp)(R-N^1-Bzl–pn), 5: Cu(amp)(S-N^1-Bzl–pn). B, B′: 1: Cu(N^2-Bzl–amp)$_2$, 2: Cu(R-N^1-Bzl–pn)$_2$, 3: Cu(S-N^1-Bzl–pn)$_2$, 4: Cu-(N^2-Bzl–amp)(R-N^1-Bzl-pn), 5: Cu(N^2-Bzl-amp)(S-N^1-Bzl–pn), C, C′: 1: Cu(N^1-Bzl–amp)$_2$, 2: Cu(R-N^1-Bzl-pn)$_2$, 3: Cu(S-N^1-Bzl–pn)$_2$, 4: Cu(N^1-Bzl–amp)(R-N^1-Bzl–pn), 5: Cu(N^1-Bzl–amp)(S-N^1-Bzl–pn).

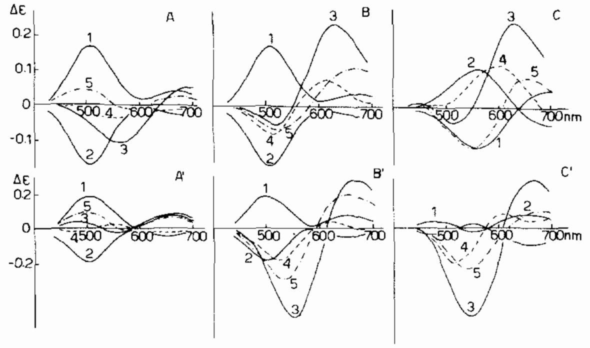

Fig. 4. CD spectra of Cu(II) complexes with 1,2-diaminopropane and its N-benzyl derivatives in acetonitrile (A, B, C) and nitrobenzene (A′, B′, C′). A, A′: 1: Cu(R-pn)$_2$, 2: Cu(S-pn)$_2$, 3: Cu(R-N^1-Bzl–pn)$_2$, 4: Cu(R-pn)(R-N^1-Bzl–pn), 5: Cu(S-pn)(R-N^1-Bzl–pn), B, B′: 1: Cu(R-pn)$_2$, 2: Cu(S-pn)$_2$, 3: Cu(R-N^1,N^2-Bzl$_2$–pn)$_2$, 4: Cu(R-pn)(R-N^1,N^2-Bzl$_2$–pn), 5: Cu(S-pn)(R-N^1,N^2-Bzl$_2$–pn). C, C′: 1: Cu-(R-N^1-Bzl-pn)$_2$, 2: Cu(S-N^1-Bzl–pn)$_2$, 3: Cu(R-N^1,N^2-Bzl$_2$–pn)$_2$, 4: Cu(R-N^1-Bzl–pn)(R-N^1,N^2-Bzl$_2$–pn), 5: Cu(S-N^1-Bzl–pn)(R-N^1,N^2-Bzl$_2$–pn).

spectrum of mixed-ligand complexes involving (S)-2-(aminomethyl)pyrrolidine or its N-derivatives (namely, the cyclic ligands with a fixed conformation and a considerable conformational contribution) is determined by precisely these ligands, while the effect of the configuration and conformation of the second ligand, 1,2-diaminopropane (Fig. 2) or N^1-benzyl-1,2-diaminopropane (Fig. 3), is negligible. A similar dominating role is also observed for the conformationally-rigid N^1,N^2-dibenzyl-1,2-diaminopropane (Fig. 4).

On the other hand, in the case of the mixed-ligand complex Cu(pn)(N^1-Bzl–pn)$^{2+}$ the conformational contributions of both flexible ligands are small and the shape of the CD spectrum is primarily determined by vicinal contributions. Any change in the configuration of these two ligands can be easily observed in the CD spectrum of the mixed-ligand complex (Fig. 4). It is interesting to note that even the change of a solvent in this case strongly influences CD of the mixed-ligand complex, and can result in reversal of the signs of the Cotton effects.

Calculations according to [9] also permit us to evaluate the constant K of formation of mixed-ligand complexes Cu(A, B) for the above mentioned equilibrium process (1). Table II lists the logarithms of these constants for both possible diastereomeric structures of the mixed-ligand complex, Cu(A_S, B_R) and Cu(A_S, B_S).

These data reveal the presence of steric inter-ligand interactions in bis-complexes of N-substituted 1,2-diamines: the equilibrium (1) is considerably shifted to the right if the initial mixture involves a complex of non-substituted diaminopropane as one of its components. Because of the elimination of the interligand tensions in the second initial complex, diaminopropane easily substitutes one of the bulky ligands of the latter to form a less strained mixed-ligand complex. In this case constant K greatly exceeds its theoretical value ($K = 4$, $\log K = 0.602$). The sterically overloaded bis-complexes of benzylated 2-(aminomethyl)pyrrolidine or dibenzyldiaminopropane react with bis(diaminopropane)copper very readily. A similar shifting of the equilibrium towards formation of less overloaded mixed-ligand complexes has been observed earlier [9, 15] making use of non-substituted 1,2-diaminoethane.

Particularly large interligand interactions are characteristic of the Cu(N^1-Bzl-amp)$_2$$^{2+}$ complex. The distortions in the complex structure brought about by these interactions are removed upon substitution of one of its ligands by pn or N^1-Bzl–pn, which is probably the reason for the unexpected growth of the Cotton effects (Fig. 2C and 3C). Similar manifestations were observed earlier [9] by obtaining mixed-ligand complexes with diaminoethane.

The presence of interligand interactions in Cu(II) complexes with substituted 1,2-diamines is the necessary pre-requisite for the thermodynamic enantioselectivity in these complexes i.e. the dependence of stability of complexes on steric configuration of the two ligands involved in their structure [1]. In fact, differences in the free energie of two labile diastereomeric complexes amount to high values, in some cases exceeding 5 kJ mol^{-1} (Table II). The magnitude of enantioselectivity strongly depends on the solvent type. The substitution of acetonitrile

TABLE II. Disproportionation Constants ($\beta = \log K$ for Reaction (1)) and Enantioselectivity $\delta\Delta G = -2.3RT(\beta_{A_SB_S} - \beta_{A_SB_R})$ kJ mol^{-1} of the Formation of Mixed-Ligand Copper(II) Complexes with 1,2-Diamines.

Ligand A	(S) or (R)-pn						(S) or (R)-N^1-Bzl–pn					
	CH_3CN			$PhNO_2$			CH_3CN			$PhNO_2$		
Ligand B	$\beta_{A_SB_S}$**	$\beta_{A_SB_R}$**	$\delta\Delta G$	$\beta_{A_SB_S}$**	$\beta_{A_SB_R}$**	$\delta\Delta G$	$\beta_{A_SB_S}$**	$\beta_{A_SB_R}$**	$\delta\Delta G$	$\beta_{A_SB_S}$**	$\beta_{A_SB_R}$**	$\delta\Delta G$
(R)-N^1-Bzl–pn	0.70	1.25	−3.1	1.43	1.72	−1.6	–	–	–	–	–	–
(R)-N^1,N^2-Bzl_2–pn	1.40	1.42	−0.1	1.70	2.3	−3.4	1.18	0.60	3.3	0.90	0.64	1.8
(S)-amp	0.47	0.98	−2.9	*	*	*	0.57	0.89	−1.8	1.30	1.47	−1.0
(S)-N^1-Bzl–amp	1.81	1.52	1.6	2.3	1.65	3.7	1.07	0.70	2.1	1.06	1.02	0.2
(S)-N^2-Bzl–amp	1.32	2.3	−5.6	2.3	1.46	4.8	*	1.32	*	0.82	1.04	−1.3

*Impossible to calculate, see ref. 9. **$\beta_{A_SB_S} = \beta_{A_RB_R}$ and $\beta_{A_SB_R} = \beta_{A_RB_S}$.

by nitrobenzene can even bring about the reversal of the enantioselectivity sign (Table II). This fact is in a good agreement with the assumed substitution of the axial ligands: in the systems studied the axial positions of the complex are occupied either by acetonitrile molecules or by perchlorate anions. It is evident that the substitution of the axial ligands can alter the whole system of interligand interactions in the coordination sphere and even reverse the sign of enantioselectivity.

It is not possible at present to provide explanations for all the manifestations of enantioselectivity in the systems investigated in this work. In general, the differences in stability of two diastereomeric complexes are brought about by dissimilarities in interligand interactions which occur direct or through axial ligands. The conformational analysis of five-membered chelate rings of diamine ligands suggested that conformations with equatorial disposition of substituents are more preferential [12]. Fig. 1 represents probable structures of mixed-ligand copper(II) complexes with N′-benzyl-1,2-diaminopropane and 2-(aminomethyl)pyrrolidine ligands (or their benzyl derivatives). Taking into account the above mentioned considerations, benzyl groups were drawn in equatorial positions. Only in the case of complexes containing N^1-Bzl-amp is it evident that substituents at the tertiary nitrogen atom should interact with the neighbouring aminogroup of the second ligand. These interactions are minimal if both ligands belong to the same configurational series, which correlates with experimental data listed in Tables I and II.

Moreover, the maximum stability of *cis*-Cu(A_S, B_S)-structure of mixed-ligand Cu(N^1-Bzl–amp)(N^1-Bzl–pn)$^{2+}$ complex in comparison with other three structures represented in Fig. 1 can be substantiated by the same considerations. In fact, this structure (Fig. 1D) appears to be more stable than the diastereomeric complex Cu(A_S, B_R) (Fig. 1, A or C) by 2.14 kJ mol^{-1} when compared in acetonitrile solutions (Table II). However, the enantioselectivity almost vanishes in this system when nitrobenzene is used as the solvent.

To identify interligand interactions responsible for enantioselectivity in other mixed-ligand complexes has proved impossible so far. It is quite likely that X-ray studies now in progress will help to reveal the nature of enantioselective effects in the copper complexes with N-substituted 1,2-diamines.

References

1 V. A. Davankov, A. A. Kurganov and S. V. Rogozhin, *Russ. Chem. Rev., 43,* 764 (1974).

2 R. D. Gillard, *Inorg. Chem. Acta Rev., 1,* 69 (1967); J. H. Dunlop and R. D. Gillard, *Adv. Chem. Radiochem., 9,* 185 (1966).

3 L. D. Pettit and R. J. W. Hefford, in 'Metal Ions in Biological Systems', H. Sigel, *9,* Marcel Dekker, Inc., N.Y. (1979).

4 V. A. Davankov, in 'Adv. in Chromatogr.', J. C. Giddings, E. Grushka, J. Cazes and P. R. Brown, *18,* Marcel Dekker, N.Y. (1980).

5 V. A. Davankov, A. A. Kurganov, A. S. Bochkov, in 'Adv. in Chromatogr.', J. C. Giddings, E. Grushka, J. Cazes and P. R. Brown, *21,* Marcel Dekker, N.Y. (1983).

6 A. T. Advani, D. S. Barnes and L. D. Pettit, *J. Chem. Soc. A,* 2691 (1970).

7 A. A. Kurganov, V. A. Davankov, L. Ya. Zhuchkova and T. M. Ponomaryova, *Inorg. Chim. Acta, 39,* 237 (1980).

8 A. A. Kurganov, T. M. Ponomaryova and V. A. Davankov, *Inorg. Chim. Acta, 45,* L23 (1980).

9 A. A. Kurganov, T. M. Ponomaryova and V. A. Davankov, *Inorg. Chim. Acta, 68,* 51 (1983).

10 A. A. Kurganov and V. A. Davankov, *Inorg. Nucl. Chem. Lett., 12,* 743 (1976).

11 V. A. Davankov and S. V. Rogozhin, A. A. Kurganov, L. Ya. Zhuchkova, *J. Inorg. Nucl. Chem., 37,* 369 (1975).

12 C. J. Hawkins, 'Absolute Configuration of Metal Complexes', N.Y. (1971).

13 G. G. Alexandrov, Yu. T. Struchkov, A. A. Kurganov, S. V. Rogozhin and V. A. Davankov, *Chem. Commun.,* 1328 (1972).

14 V. A. Davankov, S. V. Rogozhin, Yu. T. Struchkov, G. G. Alexandrov and A. A. Kurganov, *J. Inorg. Nucl. Chem., 38,* 631 (1976).

15 A. A. Kurganov, V. A. Davankov, L. Ya. Zhuchkova and T. M. Ponomaryova, *Inorg. Chim. Acta, 39,* 234 (1980).