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Copper(II) Complexes with Optically Active Diamines. IV. Between-ligand Interactions in Mixed-ligand Copper(II) Complexes containing (S)-2-(Aminomethyl)-pyrrolidine, Ethylenediamine, 1,2-Diaminopropane and their N-Benzyl Derivatives

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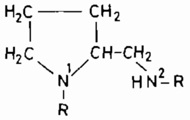
In this paper we present the results of studies of circular dichroism (CD) spectra of acetonitrile or nitrobenzene solutions of mixed-ligand copper(II) complexes containing in various combinations (S)-2-(aminomethyl)-pyrrolidine, 1,2-diaminoethane, (R)-1,2-diaminopropane, and their N-benzyl derivatives. As has been demonstrated, the shape of CD spectra is mainly determined by the conformational contributions of the chelate rings, while the vicinal contributions of asymmetric nitrogen and carbon play only a minor role. CD spectra of complexes containing N^1-benzyl-2-(aminomethyl)-pyrrolidine or N^1, N^2-dibenzyl-1,2-diaminopropane clearly visualize between ligand interactions. The latter decrease the stability of complexes, which follows from determinating the constants of formation of mixed-ligand complexes from the initial equally-paired complexes. In sterically overloaded complexes, CD spectra are strongly sensitive to the ligands (which may change with the change of the solvent) coordinated in the axial positions.

Introduction

In the series of our previous works, we studied the chiroptical properties of equally-paired and mixed-ligand complexes of copper(II) containing (R)-1,2-diaminopropane and its N-alkyl derivatives [1, 2]. As follows logically from our investigations, the conformational contribution to the net optical activity of the complex dominates the spectrum, whereas the vicinal contributions from asymmetric nitrogen and carbon are small. However, our deduction cannot be experimentally proved due to an indeterminate configuration of the nitrogen atoms in N-alkyl-1,2-diaminopropane ligand, which become asymmetric while coordinating with Cu(II). We therefore prepared Cu(II) complexes containing (S)-2-(aminomethyl)-pyrrolidine and its N-benzyl derivatives [3], wherein the heterocyclic nitrogen configuration is strictly defined.



R = H, $-C_6H_5$

While analyzing mixed complexes of these ligands with 1,2-diaminoethane, 1,2-diaminopropane, and their N-benzyl derivatives, we may trace the change in the optical activity of the complexes at successive introduction to their structure of various centers of chirality.

Experimental

The synthesis of perchlorates of bis copper(II) complexes containing diamines of the general formula $[CuA_2](ClO_4)_2$ has been described by us earlier [1, 3]. The analytical data refer to the same sources.

CD spectra in the region 400–700 nm were recorded on a spectropolarimeter "J-20 Jasco" (Japan) in a 1 cm cell at room temperature and a concentration of 5×10^{-3} *M*.

To obtain a CD spectrum of mixed-ligand complex [CuAB], we recorded a series of spectra of 11 solutions containing the initial equally-paired complexes $[CuA_2]$ and $[CuB_2]$ in various concentrations, while preserving the net concentration constant. The mixture attains the following equilibrium:

$$[CuA_2] + [CuB_2] \overset{K}{\rightleftharpoons} 2[CuAB],$$

where

$$K = \frac{[CuAB]^2}{[CuA_2]\,[CuB_2]}$$ is the equilibrium constant.

The ellipticity of a series of solutions can be described by the linearized equation [4]:

$$-\frac{A\cdot B}{\alpha^2} = -\frac{1}{\Delta}\cdot\frac{A+B}{\alpha} + \frac{K-4}{K}\cdot\frac{1}{\Delta^2} \qquad (1)$$

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where A and B are the initial concentrations of equally-paired complexes [CuA_2] and [CuB_2], respectively;

$$\alpha = \theta/l - \theta_{CuA_2} \cdot A - \theta_{CuB_2} \cdot B$$

$$\Delta = 2\theta_{CuAB} - \theta_{CuA_2} - \theta_{CuB_2}$$

θ_{CuAB}, θ_{CuA_2}, θ_{CuB_2} are molar ellipticities of mixed-ligand and equally-paired complexes, respectively; l is the length of the cell; and θ is the measured ellipticity of the solution. Coefficients $1/\Delta$ and $(K-4)/K \cdot 1/\Delta^2$ in eqn. (1) and then θ_{CuAB} and K were found by using the least squares method. This allows the net spectrum of the mixed-ligand complex [CuAB] to be calculated.

The calculation cannot be carried out when $\Delta = 0$, *i.e.* when the spectrum of the mixed-ligand complex constitutes a half-sum of the spectra of the initial complexes. The value of K in this case cannot be computed from CD spectra.

The exact value of K cannot be calculated when it exceeds 200, since the concentration of at least one of the initial components approaches zero (within the accuracy of the method).

The spectrum of a mixed-ligand complex [CuAB], however, may be computed with a sufficient accuracy from circular dichroism of the mixture wherein the concentration of one component, [CuA_2], so exceeds the concentration of the other, [CuB_2], that all ligands B may be considered incorporated into the mixed complex [CuAB].

Results and Discussion

Figures 1 and 2 present CD spectra of bis complexes of copper containing (S)-2-(aminomethyl)-pyrrolidine, $[Cu(amp)_2]^{2+}$, and its N^1- and N^2-benzyl derivatives, $[Cu(N^1Bzlamp)_2]^{2+}$ and $[Cu(N^2Bzlamp)_2]^{2+}$ (the spectra were recorded in acetonitrile and nitrobenzene) and also calculated CD spectra of mixed-ligand structures containing all possible combinations of these ligands and 1,2-diaminoethane (en), (R)-1,2-diaminopropane (pn), and their benzyl derivatives.

While analyzing the CD spectra, the first thing that attracted our attention was the similarity of spectra of $[Cu(amp)_2]^{2+}$ and $[Cu(N^2Bzlamp)_2]^{2+}$ complexes and the sharp distinction of the spectral characteristics of the complex $[Cu(N^1Bzlamp)_2]^{2+}$. We shall start with the first two complexes and mixed-ligand structures formed by ligands amp and N^2Bzlamp.

The simplest chiral complexes of these ligands are structures $[Cu(amp)(en)]^{2+}$ and $[Cu(N^2Bzlamp)(en)]^{2+}$ incorporating 1,2-diaminoethane molecule as the second ligand. As the experiment shows, CD spectra of these complexes in acetonitrile are the halved spectra of the initial bis complexes $[Cu(amp)_2]^{2+}$ and $[Cu(N^2Bzlamp)_2]^{2+}$. This unambiguously testifies (i) that in equally-paired bis complexes each of the ligands give the same (independent of the other ligand) contribution to the optical activity of the complex; (ii) in mixed-ligand complexes, the ethylenediamine chelate ring is optically inactive; and (iii) in equally-paired and mixed-ligand complexes, no pronounced between ligand interactions capable of altering the chelate ring conformation and causing change in the conformational contributions to the optical activity of the complexes are observed.

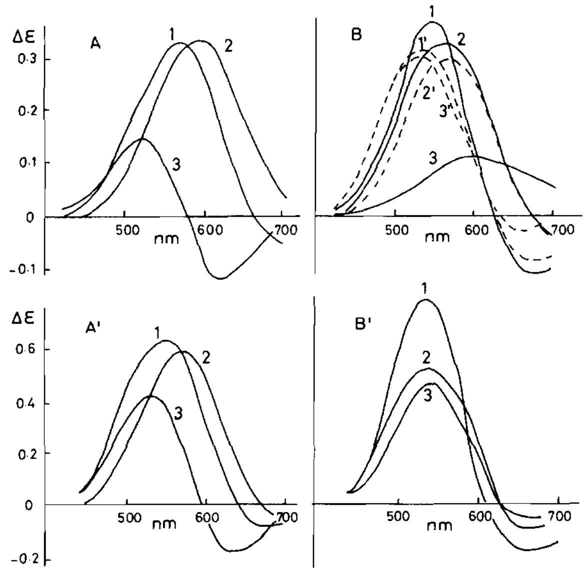

Fig. 1. CD spectra of Cu(II) complexes containing (S)-2-(aminomethyl)-pyrrolidine and its N-benzyl derivatives taken in acetonitrile (A, B) and nitrobenzene (A', B').
A,A': 1 - $[Cu(amp)_2]^{2+}$, 2 - $[Cu(N^2Bzlamp)_2]^{2+}$, 3 - $[Cu(N^1Bzlamp)_2]^{2+}$.
B,B': - 1,1' $[Cu(amp)(N^1Bzlamp)]^{2+}$, 2,2' $[Cu(amp)(N^2Bzlamp)]^{2+}$, 3,3' $[Cu(N^1Bzlamp)(N^2Bzlamp)]^{2+}$.
——— recorded spectra. – – – – calculated spectra.

As follows from the above, the additivity holds almost precisely in the given systems, and the CD spectrum of the mixed-ligand complex, $[Cu(amp)(N^2Bzlamp)]^{2+}$, coincides sufficiently enough with the sum of spectra of complexes $[Cu(amp)(en)]^{2+}$ and $[Cu(N^2Bzlamp)(en)]^{2+}$ (see Fig. 1B).

While analyzing the CD spectra (Fig. 2), our attention was arrested by a remarkable similarity of spectra in the following series of mixed-ligand complexes: $[Cu(amp)(en)]^{2+}$, $[Cu(amp)(Bzlen)]^{2+}$, $[Cu(amp)(Bzl_2en)]^{2+}$, $[Cu(amp)(pn)]^{2+}$, $[Cu(amp)(N^1Bzlpn)]^{2+}$, $[Cu(N^2Bzlamp)(en)]^{2+}$, $[Cu(N^2Bzlamp)(Bzlen)]^{2+}$, $[Cu(N^2Bzlamp)(Bzl_2en)]^{2+}$, $[Cu(N^2Bzlamp)(pn)]^{2+}$, $[Cu(N^2Bzlamp)(N^1Bzlpn)]^{2+}$.

From this similarity a number of important deductions can be drawn:

(i) the vicinal contribution of asymmetric carbon of (R)-1,2-diaminopropane and its benzyl derivatives is small as compared to the net optical activity of their complexes;

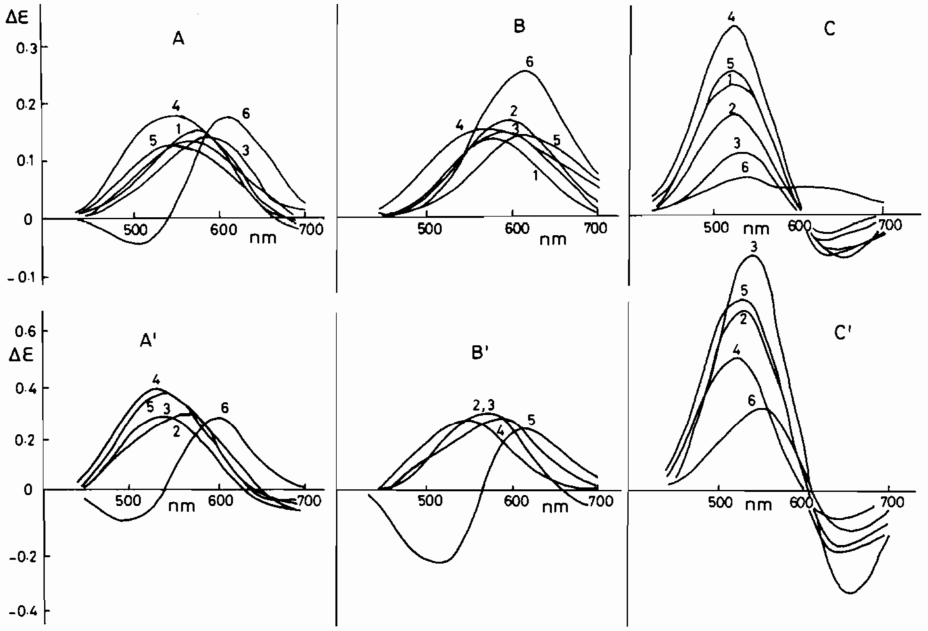

Fig. 2. CD spectra of mixed-ligand complexes taken in acetonitrile (A, B, C) and nitrobenzene (A′, B′, C′).
A,A′: 1 - $[Cu(amp)(en)]^{2+}$, 2 - $[Cu(amp)(Bzlen)]^{2+}$, 3 - $[Cu(amp)(Bzl_2en)]^{2+}$, 4 - $[Cu(amp)(pn)]^{2+}$, 5 - $[Cu(amp)(N^1Bzlpn)]^{2+}$, 6 - $[Cu(amp)(Bzl_2pn)]^{2+}$.
B,B′: 1 - $[Cu(N^2Bzlamp)(en)]^{2+}$, 2 - $[Cu(N^2Bzlamp)(Bzlen)]^{2+}$, 3 - $[Cu(N^2Bzlamp)(Bzl_2en)]^{2+}$, 4 - $[Cu(N^2Bzlamp)(pn)]^{2+}$, 5 - $[Cu(N^2Bzlamp)(N^1Bzlpn)]^{2+}$, 6 - $[Cu(N^2Bzlamp)(Bzl_2pn)]^{2+}$.
C,C′: 1 - $[Cu(N^1Bzlamp)(en)]^{2+}$, 2 - $[Cu(N^1Bzlamp)(Bzlen)]^{2+}$, 3 - $[Cu(N^1Bzlamp)(Bzl_2en)]^{2+}$, 4 - $[Cu(N^1Bzlamp)(pn)]^{2+}$, 5 - $[Cu(N^1Bzlamp)(N^1Bzlpn)]^{2+}$, 6 - $[Cu(N^1Bzlamp)(Bzl_2pn)]^{2+}$.

(ii) the vicinal contributions of asymmetric nitrogens bearing benzyl substitutents in Bzlen, Bzl_2en, N^1Bzlpn, and $N^2Bzlamp$ ligands do not dominate the spectrum either (the coordination of benzyl-substituted amino groups not invariably proceeds enantiospecifically);
(iii) in the mixed-ligand complexes, the conformation of chelate rings en, Bzlen, Bzl_2en, pn, and N^1Bzlpn is hardly unique, which points to their weak interaction with the second ring; and (iv) optical activity of the complexes is determined by the conformational contribution of the chelate ring amp which is chirally skewed and rigidly fixed owing to its bicyclic structure.

These conclusions agree well with the dominating role of the conformational contributions from chelate rings en and pn provided their chiral conformation be fixed by between ligand interactions [2].

Now we shall pass on to considering complexes containing $N^1Bzlamp$. Substituting one of such ligands in the bis-complex $[Cu(N^1Bzlamp)_2]^{2+}$ by optically inactive en leads to a sharp increase in optical activity, though this substitution should change neither vicinal contributions from asymmetric carbon and nitrogen, nor conformational contributions from the chiral chelate ring. It is quite obvious that in the initial equally-paired complex, two $N^1Bzlamp$ ligands intensively interact. In this ligand, two substituents on nitrogen leave the plane of the chelate ring, which drastically limits a set of conformations accessible for the second ligand. Between ligand interactions in the bis complex $[Cu(N^1Bzlamp)_2]^{2+}$ may also hinder the coordination of acetonitrile molecules or perchlorate anions in the axial positions of the square-planar complex, or lead to a tetrahedral distortion of the chelate node structure.

In mixed-ligand complexes of N^1-benzyl-2-(aminomethyl)-pyrrolidine also containing Bzlen, Bzl_2en, pn, N^1Bzlpn, or Bzl_2pn, the conformations of the ligands may be limited or variously distorted so that the additivity does not hold (Fig. 2). CD spectra (Fig. 1) demonstrate that complex $[Cu(N^1Bzlamp)(N^2Bzlamp)]^{2+}$ exhibits especially pronounced between ligand interactions.

Along with $N^1Bzlamp$, Bzl_2pn holds a unique position (Fig. 2) among the ligands discussed in this paper: asymmetric carbon probably dictates a strictly determinate configuration to the coordinating nitrogen atoms. Therefore, this ligand can escape interaction with the second ligand to a lesser degree than, for example, Bzl_2en, and in mixed-ligand complexes of Bzl_2pn, the additivity scheme does not act.

Nevertheless, the CD spectrum of a mixed-ligand complex containing two sterically overloaded ligands may sometimes approach a half-sum of the spectra of

TABLE I. Formation Constants β = logK of Mixed-ligand Complexes $[CuAB]^{2+}$ Prepared from $[CuA_2]^{2+}$ and $[CuB_2]^{2+}$.

A	(S)-amp		N^{1}Bzl amp		N^{2}Bzl amp	
B	CH_3CN	$PhNO_2$	CH_3CN	$PhNO_2$	CH_3CN	$PhNO_2$
en	[a]	[b]	>2.3	[b]	[a]	[b]
Bzl-en	[a]	1.172	1.807	1.137	[a]	[a]
N^1, N^2-Bzl$_2$-en	1.799	1.531	1.785	−0.338	[a]	[a]
(R)-pn	0.984	[a]	1.524	1.645	>2.3	1.460
N^{1}Bzl-pn	0.893	1.468	0.699	1.022	1.322	1.041
N^1, N^2-Bzl$_2$-pn	1.861	1.806	[a]	0.004	[a]	0.934
(S)-amp			0.486	0.830	1.845	0.937
N^1-Bzl-amp	0.486	0.830			1.176	[a]
N^2-Bzl-amp	1.845	0.937	1.176	a		

[a] Not calculated, see text. [b] The initial complex $[Cu(en)_2](ClO_4)_2$ is insoluble in nitrobenzene.

two initial equally-paired complexes. This pertains, for instance, to the spectra of [Cu(N^{1}Bzlamp)(Bzl$_2$pn)]$^{2+}$ taken in acetonitrile and nitrobenzene, and of [Cu(N^{1}Bzlamp)(N^{2}Bzlamp)]$^{2+}$ recorded in nitrobenzene. In mixed-ligand complexes, each ligand probably limits a conformational set of the other ligand to the same extent as it occurred in the initial equally-paired complexes.

This conforms well with the data on the constants of formation of mixed-ligand complexes from two symmetric structures (Table I). When in the initial equally-paired or resulting mixed-ligand complexes no pronounced steric interactions occur or they preserve at the same level, the formation constant approaches a statistical value logK = 0.6. If the formation of mixed-ligand complex eliminates between ligand interactions, taking place at least in one of the initial equally-paired complexes, the value of the formation constant exceeds logK = 0.6. On the contrary, when ligands in the mixed complex interact more appreciably than in the initial complexes, the formation constant is under the statistical value. In such a way behave complexes [Cu(N^{1}Bzlamp)(Bzl$_2$pn)]$^{2+}$ and [Cu(N^{1}Bzlamp)(Bzl$_2$en)]$^{2+}$ in nitrobenzene.

In conclusion, we would like to comment on the effect of solvents on CD spectra of complexes. Substituting nitrobenzene for acetonitrile in structures characterized by weak between ligand interactions does not change the shape of the spectrum but only increases the intensity of the Cotton effects. This should be attributed, as noted earlier [2], to a greater polarization of the complex molecules in nitrobenzene since in this noncoordinating solvent the axial positions of the Cu(II) ion are occupied by perchlorate anions bonded mainly ionically with the metal atom. However, for sterically overloaded complexes containing N^{1}Bzlamp or Bzl$_2$pn ligands, the spectra of the mixed-ligand complexes in nitrobenzene considerably differ from those taken in acetonitrile. The change of the axial ligand may considerably influence the nature of between ligand interactions in these structures leading to a change in the conformational contributions of the main ligands to optical activity of the complex.

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