Copper(II) Complexes with Optically Active Diamines.
II*. The Effect of Solvent, Temperature and Alkyl Substituents at Nitrogen Atoms on Circular Dichroism Spectra of Copper(II) Equally-paired and Mixed-ligand Complexes with (R)-1,2-Diaminopropane

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Circular dichroism (CD) spectra have been evaluated for copper(II) equally-paired and mixed-ligand complexes with different 1,2-diamines (R-pn, en and their N-benzyl and N-methyl derivatives) in solvents differing in the ability to coordinate in the axial positions. CD spectra of all the studied complexes contain two main bands at 500–550 and ca. 650 nm. The insertion of two or more substituents into the amino groups of the complex makes the sign of the 500–550 nm component negative. A similar, though weaker, effect is caused by an increase in the solvent polarity, higher band resolution being observed at lower temperature. These regularities are explained in terms of assumption of the dominant role of conformaional contribution to the overall CD spectrum of complexes containing two or more subsituents at amino groups.

For the copper(II) complex with (R)-N¹,N²-dibenzyl-1,2-diaminopropane, the structure formed is shown to be different from that of all the other complexes studied.

Introduction

Having carried out a comprehensive study [1–3] of circular dichroism (CD) spectra of copper(II) complexes with N-alkyl-α-aminoacids we came to the conclusion that the dominant role in their CD spectra belongs to the conformational effect, while the vicinal contributions of asymmetrical C- and N-atoms play a subordinate role. For diamine complexes one can also expect that conformational effects will make the principal contribution to the CD spectrum since, according to conformational calculations [4], chelate diamine rings have a much more puckered structure in comparison with the aminocarboxylate chelate rings. The information on CD spectra of Cu(II) complexes with diamines is,
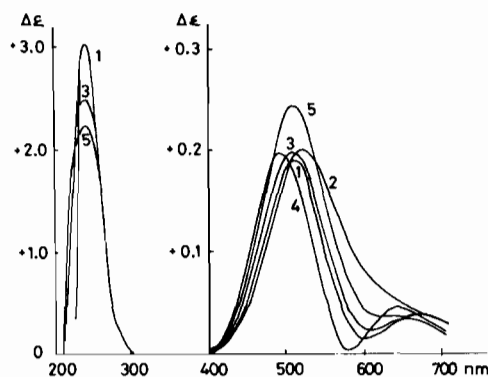
*Part I: see ref. [10].

Fig. 1. Circular dichroism spectra of $((R)\text{-pn})_2Cu(ClO_4)_2$ at 25 °C in different solvents: 1) acetonitrile, 2) dimethylformamide, 3) water, 4) nitrobenzene, 5) methanol.
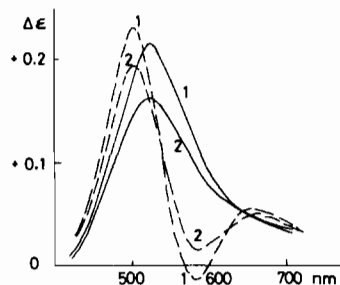

Fig. 2. Temperature dependence of the circular dichroism spectra of $((R)\text{-pn})_2Cu(ClO_4)_2$ in dimethylformamide (———) and nitrobenzene (-------): 1) 15 °C, 2) 75 °C.

however, more limited and often of contradictory nature. In earlier works [5, 6] copper(II) complex with (R)-1,2-diaminopropane was found to have two positive bands (at 508 and 660 nm) in its CD spectrum, whereas in [7] only one positive band was reported at 515 nm. In papers [8, 9] however, which also appeared in 1972, it was again communicated that the CD spectra of Cu(II) complexes with diamines (including 1,2-diaminopropane) have two

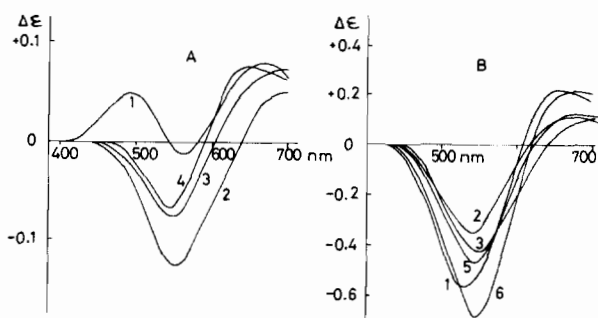Fig. 3. Circular dichroism spectra of copper(II) complexes with (R)-N^1-benzyl-1,2-diaminopropane (A) and (R)-N^1,N^2-dimethyl-1,2-diaminopropane (B) at 25 °C in different solvents: 1) nitrobenzene, 2) water, 3) dimethylformamide, 4) methanol, 5) acetonitrile, 6) tetrahydrofuran.

bands (at 500–525 and 665 nm) between which, with the help of Gaussian analysis, a third negative component was identified at ca. 590 nm.

To clear up these discrepancies, as well as to study the effect of solvent and temperature on the CD spectra of Cu(II) complexes with various N-substituted diamines, we have carried out investigations the results of which are presented below.

Results and Discussion

CD spectra of the bis-[(R)-1,2-diaminopropane]-copper(II) perchlorate in different solvents are shown in Fig. 1. The spectrum consists of two positive bands at 500–530 nm and ca. 650 nm, but on rising the temperature (Fig. 2) or passing over to well coordinated solvents (methanol) their resolution is less distinct. On the contrary, with decreasing temperature, in a poorly coordinated solvent (nitrobenzene) one can observe the appearance of a third band at 585 nm (Fig. 2), with a negative sign, which was predicted by calculations of the Japanese authors [8, 9].

It should be noted, however, that the similarity of the spectrum dependence on the solvent type and the temperature, and the presence of isodichroic points in the studied temperature range of 15–75 °C can be indicative of an equilibrium existing between two isomeric forms of a complex (possibly, conformers).

The insertion of a benzyl radical to the N^1 atom of (R)-1,2-diaminopropane results in the reversal of the sign of the main short-wave band of the complex dissolved in polar, well coordinated solvents, whereas in nitrobenzene only a decrease in the intensity of this positive band is observed (Fig. 3A). The long-wave band for this as well as other complexes preserves its positive sign in all the solvents.

The presence of substituents at each of the two nitrogen atoms in the molecule of (R)-1,2-diaminopropane stabilises the negative sign of the short-wave band, so that for the (R)-N^1,N^2-dimethyl-1,2-diaminopropane complex the CD spectra (Fig. 3B) in all solvents turn out to be approximately the same.

The temperature dependence of CD spectra of all the complexes studied coincides with that of the 1,2-diaminopropane complex: an increase in temperature causes a decrease in intensity of both bands.

When one compares the studied CD spectra of copper(II) complexes of N-alkylated 1,2-diaminopropane with those for copper(II) complexes with N-alkyl-α-aminoacids, the structures of diamine complexes are seen to be less susceptible to the solvent or the temperature, but the insertion of substituents to nitrogen atoms exerts a similar substantial effect in both the aminoacid and 1,2-diamine complexes.

Since, as previously shown by us [10], the coordination number of the metal ion does not change with the insertion of substituents to nitrogen atoms of diamine complexes, all the changes in their CD spectra are determined by variations in the vicinal contributions of asymmetric carbon and nitrogen atoms and the conformation contributions of distorted chelate rings. To deal with the gradual insertion of asymmetrical centers into the complex molecule and make it easier to separate the above kinds of contributions, we evaluated from experimental data the CD of mixed-ligand complexes where the Cu(II) ion is coordinated with two different 1,2-diamine ligands, one of them being optically inactive.

The 1,2-diaminopropane molecule and the 1,2-diaminoethane molecule are the ligands in the simplest chiral complex of copper(II) with 1,2-diamines. The CD spectrum of this compound, shown in Fig. 4, is determined by the vicinal contribution of the asymmetrical C atom and the contributions of chiral conformations of chelate rings. This spectrum represents exactly one 'half' of the CD spectrum of copper(II) bis-complex with 1,2-diaminopropane, which means that the ethylenediamine ring does not make any conformational contribution. This fact indicates that no appreciable interactions between ligands are taking place in the molecules of [Cu(R-pn)(en)]$^{2+}$ and [Cu(R-pn)$_2$]$^{2+}$, and the chirality of the conformation of the pn chelate rings is determined solely by the configuration of its assymetrical C atoms. The difference between the λ (equatorial position of CH$_3$ group) and the δ (axial position of CH$_3$ group) conformations of the R-pn chelate ring is known to be less than 1 kcal/mol [4, 11] and, therefore, the above CD spectra characterize an equilibrium mixture of complexes with λ and δ conformations of chelate rings.
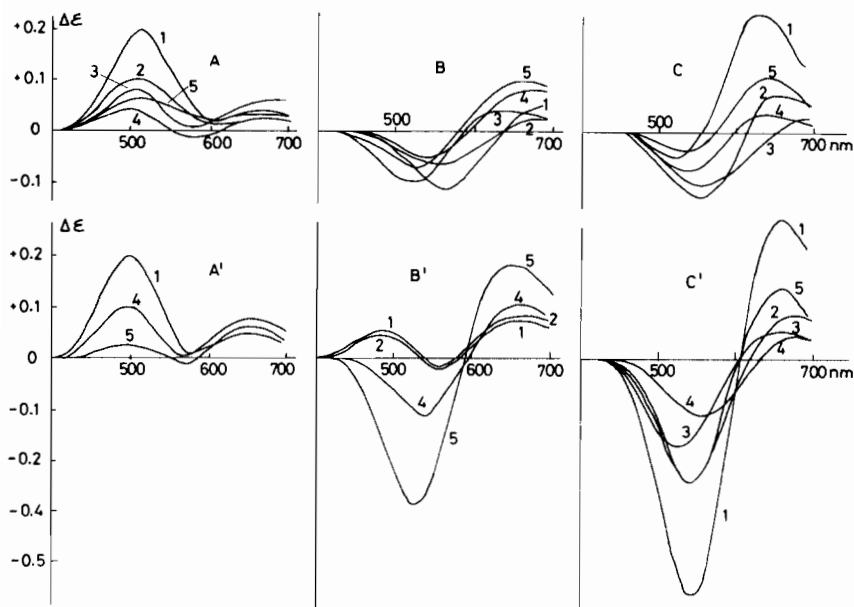
Fig. 4. Circular dichroism spectra of copper(II) complexes with (R)-1,2-diaminopropane and ethylenediamine and their N-benzyl derivatives in acetonitrile (A, B, C) and nitrobenzene (A', B', C'). A,A': Complexes having none or one N-benzyl radical: 1. Cu(pn)$_2$, 2. Cu(pn)(en), 3. Cu(N^1-Bzlpn)(en), 4. Cu(pn)(N^1-Bzlpn), 5. Cu(pn)(Bzlen). B,B': Complexes having two N-benzyl radicals: 1. Cu(N^1-Bzlpn)$_2$, 2. Cu(N^1-Bzlpn)(Bzlen), 3. Cu(N^1,N^2-Bzl$_2$pn)(en), 4. Cu(pn)(N^1,N^2-Bzl$_2$en), 5. Cu(pn)(N^1,N^2-Bzl$_2$pn). C,C': Complexes having three or more N-benzyl radicals: 1. Cu(N^1, N^2-Bzl$_2$pn)$_2$, 2. Cu(N^1-Bzlpn)(N^1,N^2-Bzl$_2$pn), 3. Cu(N^1-Bzlpn)(N^1,N^2-Bzlen), 4. Cu(N^1,N^2-Bzl$_2$pn)(Bzlen), 5. Cu(N^1,N^2-Bzl$_2$pn)(N^1,N^2-Bzl$_2$en).
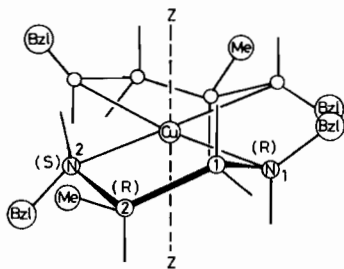
Fig. 5. Possible structure of the complex [Cu(N^1,N^2-Bzl$_2$-R-pn)$_2$]$^{2+}$ with the λ chelate ring conformations.

The appearance of a benzyl substituent at the N^1 nitrogen atom of the 1,2-diaminopropane ligand first of all gives rise to a new asymmetrical center. The minimum non-bonded interactions in the five-membered chelate ring will be obviously associated with the equatorial arrangement of the benzyl radical, *i.e.*, R configuration of the N^1 atom and λ conformation of the ring (Fig. 5). One can also expect the benzyl group insertion to increase and stabilize the λ-chiral deformation of the chelate ring, which ensures the equatorial arrangement of both its substituents. The appearance of the vicinal contribution

of the N^1 atom and an increase in the conformational contribution to the CD spectrum of the [Cu(pn)(N^1-Bzlpn)]$^{2+}$ complex jointly result in a negative band appearing between the two normal bands at 510 and 680 nm (Fig. 4A).

It should be noted that a similar trend was observed in the CD spectrum of the [Cu(R-pn)$_2$]$^{2+}$ complex with a decrease in solution temperature; here it could only be caused by the change in the ratio between δ and λ conformations in favor of the latter.

Insertion of a second benzyl radical into the R-pn molecule accounts for a new vicinal contribution from the N^2 nitrogen, which should not differ significantly from that of N^1. At this stage, however, the final fixation of the chelate ring λ conformation takes place, ensuring the equatorial arrangement of all the three substituents (Fig. 5). In the CD spectrum of the [Cu(Bzl$_2$-R-pn)(en)] complex sharp changes are observed: instead of a positive short-wave band a negative band appears in the region of 540 nm (Fig. 4B). It is quite obvious that at this point the conformational contribution starts playing the dominant role. Now the substitution of the ethylenediamine ligand by R-pn, and then by N^1-Bzl-R-pn, no longer changes the overall shape of the spectrum (Fig. 4B, C), *i.e.*, neither the vicinal contribution of a

TABLE 1. Equilibrium Constants K of Formation of the Mixed-ligand Complexes [CuAB] from the Equally-paired Complexes [CuA$_2$] and [CuB$_2$]

CuA$_2$ \ CuB$_2$	In Acetonitrile					
	Cu(en)$_2$	Cu(Bzlen)$_2$	Cu(Bzl$_2$en)$_2$	Cu(pn)$_2$	Cu(Bzlpn)$_2$	Cu(Bzl$_2$pn)$_2$
Cu(pn)$_2$	a	4	50	--	5	25
Cu(Bzlpn)$_2$	8	a	15	5	–	15
Cu(Bzl$_2$pn)$_2$	19	7	4	25	15	–

CuA$_2$ \ CuB$_2$	In Nitrobenzene					
	Cu(en)$_2$	Cu(Bzlen)$_2$	Cu(Bzl$_2$en)$_2$	Cu(pn)$_2$	Cu(Bzlpn)$_2$	Cu(Bzl$_2$pn)$_2$
Cu(pn)$_2$	–	2	25	--	27	50
Cu(Bzlpn)$_2$	–	a	5	27	--	9
Cu(Bzl$_2$pn)$_2$	–	6	a	50	9	–

[a]See Experimental.

second asymmetrical carbon nor that of new asymmetrical nitrogens can compete with the conformational contribution (vicinal contribution of the carbon atoms exerts an unambiguous effect only on the intensity of the positive long-wave band in the CD spectrum).

Extremely interesting is the fact that all the complexes containing 2 or 3 benzyl radicals have similar CD spectra, irrespective of whether the substituents are located in the ethylenediamine or the propylenediamine ligand or are distributed between them. This means that the presence of two benzyl radicals in the molecule of a complex is sufficient to fix both chelate rings in the λ conformation. And, indeed, if, e.g., in the [Cu(R-pn)(Bzl$_2$en)]$^{2+}$ or [Cu(Bzl$_2$-R-pn)(en)]$^{2+}$ complexes the ethylenediamine rings were not preferably in λ conformation, we should have observed substantial differences in their CD spectra in the 540 nm region as compared to that of the [Cu(Bzl$_2$-R-pn)(R-pn)]$^{2+}$ complex, where both rings are in λ conformation. In fact, the differences between these spectra are not great and, therefore, the en and Bzl$_2$en rings in these complexes make conformational contributions of almost the same magnitude as those of R-pn and Bzl$_2$-R-pn. The possibility of such a restriction of the conformational freedom of one ligand, caused by steric interactions with another ligand, was also revealed by the Japanese authors [12] for the [Pd(Me$_4$-R-pn)(en)]$^{2+}$ complex with the help of CD and PMR spectroscopy. In our case, the ligand interaction manifests itself for a sterically much less overloaded diamine. The cause of this, most probably, lies in the Cu atom having a smaller radius than the Pd atom which should, naturally, result in a higher mutual effect of ligands. At the same time, the CD spectrum of the [Cu(R-pn)(Bzlen)]$^{2+}$ complex is almost identical

to that of [Cu(R-pn)(en)]$^{2+}$ and, therefore, the presence of only one N atom substituent is not sufficient for the ligand interactions to result in the fixation of the λ conformation of rings and an unambiguous configuration of the asymmetric nitrogen atom.

The above discussed CD spectra summarized in Fig. 4A–C were obtained for complexes dissolved in acetonitrile where they behave as 2:1 electrolytes [10]. Taking into account the high coordinative capacity of the solvent one can assume that the axial positions of the complexes are occupied by acetonitrile molecules. Fig. 4 A'–C' shows CD spectra of the same complexes in a poorly coordinating solvent – nitrobenzene (in this series mixed-ligand complexes are missing with an unsubstituted ethylenediamine as one of the ligands, because of the insolubility of the starting [Cu(en)$_2$]$^{2+}$ complex in nitrobenzene). All the other complexes in nitrobenzene solution behave as non-electrolytes, which indicates that stable ionic pairs are formed between the complex cation and the ClO$_4^-$ anions occupying its axial positions [10]. Such structures must be more polarized (the Cu^{2+}–ClO$_4^-$ bond is basically ionic) and we observe in the CD spectra a certain increase in intensity of transitions. But on the whole the nature of CD spectra variations in nitrobenzene taking place with a gradual insertion of benzyl substituents confirms the conclusions arrived at above for spectra of complexes in acetonitrile: when 2–3 benzyl substituents are present in the complex both the chelate rings are fixed in the λ conformation and the conformational contribution begins to determine the CD spectral shape.

Finally, it is worth mentioning that [Cu(Bzl$_2$-R-pn)$_2$]$^{2+}$ and [Cu(Bzl$_2$-R-pn)(Bzl$_2$en)]$^{2+}$ complexes with four benzyl radicals possess an abnormally

intense positive band in the long-wave region of the CD spectrum (Figs. 4C and C′). Ligand interactions in these complexes are probably so great that they cause some additional structure distortions which clearly manifest themselves in the CD spectra. These interactions apparently destabilize the $[Cu(Bzl_2\text{-}R\text{-}pn)_2]^{2+}$ and $[Cu(Bzl_2en)_2]^{2+}$ complexes, as indicated by the high values of formation constants of mixed-ligand complexes where one of these huge ligands is replaced by molecules of en or pn (see Table I). The results obtained on studying CD spectra coincide with the earlier conclusion [10] that (R)-N^1,N^2-dibenzyl-1,2-diaminopropane forms copper(II) complexes differing in structure from that of other complexes of this series as well as from binuclear complexes of the $[Cu_2(Me_4en)_2(OH)_2](ClO_4)_2$ type.

Experimental

Synthesis and properties of the bis(1,2-diamine)-copper(II) perchlorate complexes have already been described [10].

Solvents used in the work were purified in accordance with the standard techniques [13].

CD spectra were recorded on JASCO J-20 dichrograph (Japan) in a thermostatted 1 cm cell at 25 ± 0.1 °C (except for the data in Fig. 2). Concentration of complexes when recorded in the visible region was 5×10^{-3} m/l, in the UV region 10^{-4}–10^{-5} m/l.

For the evaluation of the CD spectrum of a mixed-ligand complex a series of 11 solutions was prepared, where the initial equally-paired $[CuA_2]$ and $[CuB_2]$ complexes were mixed in different ratios at a constant overall molar concentration. Following the procedure previously proposed by us [14], the CD spectra of mixtures were used to calculate the equilibrium constant K (see Table I) of the mixed complexes formation

$$[CuA_2] + [CuB_2] \underset{\longleftarrow}{\overset{K}{\longrightarrow}} 2[CuAB]$$
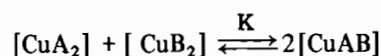
(in case of statistical distribution of complexes K = 4) and the CD spectrum of the individual $[CuAB]$ complex. In few cases (marked in the Table with *) it was impossible to calculate the value of K [14], so that the CD spectrum of the mixed-ligand complex was supposed to be equal to the half-sum of the CD spectra of the two initial complexes.

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