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# Copper(II) Complexes with Optically Active Diamines. III.[+] The Complexes of 2-(Aminomethyl)-pyrrolidine and its N-benzyl Derivatives: Synthesis, Properties and Circular Dichroism Spectra

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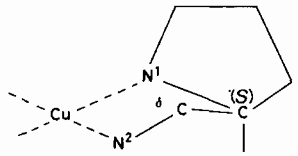
In previous communications [1, 2] we examined the properties of copper(II) complexes with N-alkyl derivatives of 1,2-diaminopropane and, when studying their circular dichroism (CD) spectra, stressed the important role of conformational contributions to the optical activity of the complexes. The vicinal contributions of asymmetric nitrogen and carbon atoms in these complexes are, in our view, of secondary importance, provided the complex contains two or more N-substituents. This statement could not, however, be regarded as proven conclusively, because the configurations of nitrogen atoms in the compounds studied had not been unambiguously fixed. We therefore thought it expedient to study copper(II) complexes with cyclic diamines, particularly with (S)-2-(aminomethyl)pyrrolidine, where, with the chelation of copper ion, the (S)-configuration of the nitrogen atom ($N^1$) in the pyrrolidine cycle is unambiguously determined by the (S)-configuration of the asymmetrical carbon atom:



## Results and Discussion

The properties of copper(II) complexes with (S)-2-(aminomethyl)pyrrolidine and its $N^1$- and $N^2$-monobenzyl derivatives are shown in Table I. It is seen from the table that in solvents with a high permittivity and good solvating capacity the complexes behave as 2:1 electrolytes, whereas in poorly solvating media (*e.g.*, nitrobenzene) they practically do not dissociate. Previously [1] we explained the latter fact by the fixation of counterions in the axial positions of the positively charged diamine complexes dissolved in non-coordinated solvents. Due to the preservation of the coordination number of the copper ion and the electronic configuration of the complex in all media, the impact of the solvent on the absorption spectra of the 2-(aminomethyl)pyrrolidine complexes is not great and is similar to that observed by us for the majority of 1,2-diaminoethane and 1,2-diaminopropane derivatives [1].

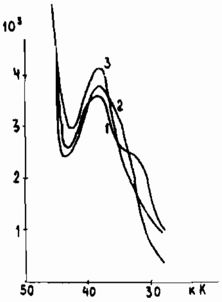


Fig. 1. Absorption spectra of copper(II) complex with $N^1$-benzyl(S)-2-(aminomethyl)pyrrolidine in different solvents: 1) methanol, 2) water, 3) ethanol.

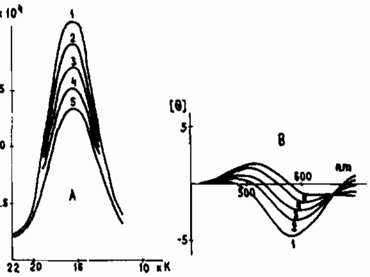


Fig. 2. Temperature dependence of absorption spectrum (A) and circular dichroism spectrum (B) of copper(II) complex with $N^1$-benzyl(S)-2-(aminomethyl)pyrrolidine dissolved in dimethylformamide: 1) 25°, 2) 35°, 3) 45°, 4) 55°, 5) 65 °C.

However, certain peculiarities in absorption spectra observed by us in the copper complexes with $N^1$,$N^2$-dibenzyl derivatives of 1,2-diaminoethane and 1,2-diaminopropane are observed in the present series for the $N^1$-benzyl-2-(aminomethyl)pyrrolidine complex. We see that in methanol it displays (Fig. 1) an additional absorption band in the near UV, and the temperature dependence of absorption spectra, very slight in all the other complexes studied, is sharply expressed (Fig. 2) for this compound in dimethylformamide.

Circular dichroism spectra of complexes of the unsubstituted (S)-2-(aminomethyl)pyrrolidine and its $N^2$-benzyl derivative are very similar (Figs. 3A and 3B) and show in the region of d–d transitions one

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[+] Part II: *cf.* [2].

TABLE I. Analytical and Spectral Data.

| Complex | Analysis % Cu | | Electric conductivity $\lambda_o \times 10^{-3}$ (ohm$^{-1}$ cm$^2$ mol$^{-1}$) | | | | | | Position of maximum ($\lambda_{max}$, kK) and molar extinction ($\epsilon$ mol$^{-1}$ cm$^{-1}$ l) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | calc. | found | $H_2O$ | MeOH | EtOH | MeCN | DMF | $PhNO_2$ | $H_2O$ | MeOH | EtOH | MeCN | DMF | $PhN_2O$ |
| $Cu(amp)_2(ClO_4)_2$ | 13.8 | 14.2 | 184 | 89 | 27 | 215 | 97 | 13 | 17.68<br>(88) | 18.00<br>(83) | 17.68<br>(85) | 17.52<br>(85) | 17.52<br>(83) | 18.16<br>(94) |
| $Cu(N^1\text{-Bzl-amp})_2\cdot(ClO_4)_2$ | 9.9 | 9.6 | 149.8 | 119 | 38 | 198 | 87 | 13 | 16.80<br>(112) | 17.12<br>(152) | 16.80<br>(144) | 16.96<br>(328) | 16.56<br>(228) | 17.36<br>(332) |
| $Cu(N^2\text{-Bzl-amp})_2\cdot(ClO_4)_2$ | 9.9 | 9.9 | 154.5 | – | 27.5 | 78 | 87.3 | 6.6 | 17.04<br>(140) | 17.36<br>(132) | 16.80<br>(142) | 16.96<br>(158) | 16.64<br>(142) | 17.36<br>(132) |

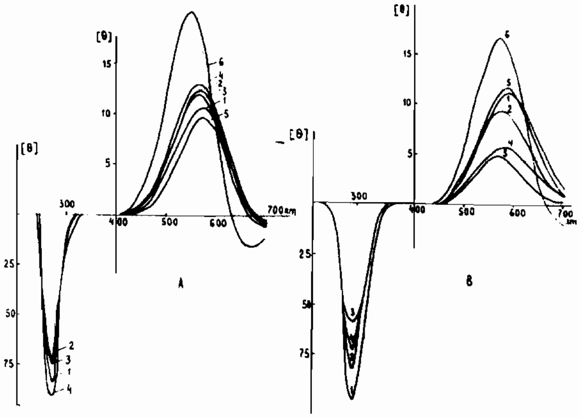

Fig. 3. Circular dichroism spectra of copper(II) complexes with (S)-2-(aminomethyl)pyrrolidine (A) and (S)-2-(benzylaminomethyl)pyrrolidine (B) in different solvents: 1) acetonitrile, 2) water, 3) methanol, 4) ethanol, 5) dimethylformamide, 6) nitrobenzene.

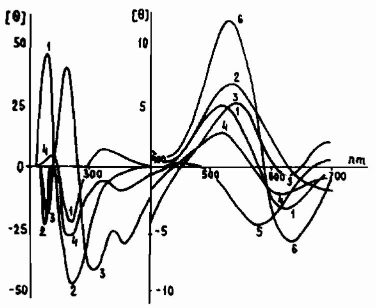

Fig. 4. Circular dichroism spectra of copper(II) complex with $N^1$-benzyl-(S)-2-(aminomethyl)pyrrolidine in different solvents: 1) acetonitrile, 2) water, 3) methanol, 4) ethanol, 5) dimethylformamide, 6) nitrobenzene.

positive band at *ca.* 550 nm (and a weak additional negative component at *ca.* 700 nm which is more expressed in nitrobenzene). An important observation is that the insertion of the benzyl substituent to the $N^2$ atom causing the appearance of a new asymmetrical atom in the chelate cycle does not change significantly the CD spectrum of the complex. Obviously, the vicinal contribution of this new asymmetric atom is small as compared to other contributions, particuarly that of the chiral chelate conformation.

The presence of the heterocyclic structure in the ligands studied in this work must restrict the set of available conformations for the chelate cycle and, therefore, make relatively constant its conformational contribution to the circular dichroism spectra. Supposing the equatorial arrangement of the substituent at the chiral carbon atom of the (S)-configuration, we arrive at the δ-conformation of the puckered chelate ring. This type of chiral distortion should manifest itself in the positive sign of the main CD-band (Fig. 3). This is in accordance with the λ-assignment of the chelate conformation in the N-substituted (R)-1,2-diaminopropane complexes, the main CD band of which in the region of 500–550 nm was definitely negative [2].

Again, the Cu(II) complex with N$^1$-benzyl derivative of (S)-2-(aminomethyl)pyrrolidine displays some peculiar features in the CD spectra (Fig. 4). Here, the negative component is shifted from 700 nm to 620–640 nm and is observed not only in nitrobenzene, but also in such solvents as acetonitrile and ethanol. In dimethylformamide, the circular dichroism spectrum of this complex is completely reversed as compared with the spectra shown in Fig. 3: the band at 580 nm has a negative sign and the band in the region of 700 nm is positive. However, with rising temperature (Fig. 2) the CD spectrum undergoes a sharp change and already at 65 °C acquires the form characteristic of other solvents (Fig. 4), where the effect of temperature is, generally speaking, not strongly expressed. In methanol, in the region of d–d transitions, the copper(II) complex with N$^1$-benzyl-(S)-2-(aminomethyl)pyrrolidine has three bands with the +, –, + system of signs, and in the UV region an additional negative band appears at 360 nm. The presence of a definite isodichroic point on the set of CD-curves registered at different temperatures (Fig. 2) could be explained in terms of structural isomerisation of the complex. However, the evaluation of structures involved in this process requires further investigations. Here, the parallels to the unidentified copper complexes of N$^1$,N$^2$-dibenzyl derivatives of 1,2-diaminopropane and 1,2-diaminoethane [1, 2] should be mentioned once again.

## Experimental

### *Synthesis of Ligands*

#### *(S)-2-(Aminomethyl)pyrrolidine* [4]

33 g of L-proline amide obtained by a standard method [3] were added by portions to a suspension of 16.6 g of lithiumaluminium hydride in 650 ml of dry tetrahydrofuran and boiled whilst being stirred for 30 hours. The excess of lithiumaluminium hydride was then decomposed by adding 32.3 ml of water. The precipitated salts were separated boiled for 2 hours with 150 ml of THF and filtered off. The flow of HCl was passed through the combined filtrates to convert the amine into hydrochloride, and the solvent was then distilled off with the help of a rotary evaporator. Tablets of potassium hydrate were added to the remaining viscous oil, and the isolated amine extracted 4 times by 150 ml of diethyl ether. The combined ether extracts were dried over KOH, the ether was evaporated and the residue distilled at 72–76 °C and 20 torr; yield 37.6 g (65% of theoretical). A completely anhydrous product was obtained after boiling and distilling the amine over metallic sodium. $[\alpha]_D^{20}$ = +16.8° (c = 1.021 g dl$^{-1}$, ethanol), $[\alpha]_{436}^{20}$ = +31.14° (c = 1.021 g dl$^{-1}$, ethanol).

#### *(S)-2-(Benzylaminomethyl)pyrrolidine*

5.5 ml of benzaldehyde was added with cooling to 5 g of (S)-2-(aminomethyl)pyrrolidine in 50 ml of abs. benzene, and the mixture was boiled until 1.0 ml of water was distilled off. Benzene was then evaporated, the residue dissolved in methanol and transferred into a vessel for hydrogenation. The hydrogenation was conducted at atmospheric pressure and room temperature in the presence of 3 g of 5% palladium on coal until the termination of hydrogen absorption (about 1.3 1). The catalyst was then filtered off, the solution concentrated by evaporation and the residue distilled in vacuum at 90–92 °C and 2 × 10$^{-3}$ torr. Yield 5.5 g (58% of theoretical). Calculated for $C_{12}H_{18}N_2$: C = 75.8, H = 9.5, N = 14.7. Found: C = 75.6, H = 9.45, N = 14.75. $[\alpha]_{436}^{20}$ = +27.7 (c = 0.0902 g dl$^{-1}$, ethanol).

#### *N$^1$-Benzyl-(S)-2-(aminomethyl)pyrrolidine*

To the Schiff base obtained in 50 ml of benzene from 5 g of (S)-2-(aminomethyl)pyrrolidine and 5.5 g of benzaldehyde, as described in item 2, 14 g of benzyl chloride and 70 ml of 10% aqueous solution of KOH were added dropwise during 1 hour at boiling point, after which the mixture was boiled for another 1 hour. The organic layer was then separated, washed three times with water, and the benzene was distilled off in vacuum. Into the remaining oil 60 ml of 6 *M* hydrochloric acid and 250 ml of alcohol were poured, and the mixture was boiled for 30 min to remove the protecting benzylidene groups. The benzaldehyde formed was extracted with benzene, the aqueous layer concentrated by 2/3, potassium hydrate tablets were added to it, and the amine was extracted 4 times by 150 ml of diethyl ether. Combined ether extracts were dried over KOH, the ether was evaporated, and the residue distilled in vacuum at 84–88 °C and 6 × 10$^{-2}$ torr. Yield 5.45 g (57.4% of theoretical) $[\alpha]_{436}^{20}$ = –135.05 (c = 0.0991 g dl$^{-1}$, ethanol). Calculated for $C_{12}H_{18}N_2$: C = 75.8, H = 9.5, N = 14.7. Found: C = 75.55, H = 9.56, N = 14.95.

### *Synthesis of Complexes*

The complexes were prepared by mixing alcoholic solutions of $Cu(ClO)_4 \cdot 6H_2O$ and the corresponding amine, taken at stoichiometric ratios. The precipitated complex was filtered off and recrystallized from alcohol which contained a small quantity of acetonitrile. Analyses of the compounds obtained are given in Table I.

### *Investigation of the Complexes*

Electric conductivity of solutions of complexes was determined with the help of OP-208 ('Radelkis', Hung.) conductometer at concentration 5 X $10^{-3}$–1 X $10^{-3}$ *M* and temperature 22 °C.

Absorption spectra of the complexes were obtained on a double-beam automatic spectrophotometer, 'Spekord' (Zeis–Jena, DDR), in a thermostatted cell 2 cm thick (visible region) or 0.1 cm thick (UV region). The concentration of complexes, when measured in the visible region, amounted to 5 X $10^{-3}$–2.5 X $10^{-3}$ *M*, in the UV region 5 X $10^{-4}$ *M*. Temperature 25 °C, except for the specially indicated cases.

Circular dichroism spectra of the complexes were obtained on an automatic spectropolarimeter, 'J-20' (JASCO, Japan), in thermostatted cells 1 cm thick at concentration 5 X $10^{-3}$ *M* (for visible region) or 0.1 cm thick at concentration 5 X $10^{-4}$ (for UV region). Temperature 25 °C, except for the specially indicated cases.

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