

Copper(II) Complexes with Optically Active Diamines. I. Synthesis and Properties of Copper(II) Complexes with N-Benzyl and N-Methyl Derivatives of 1,2-Diaminopropane

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The paper describes the synthesis of N-derivatives of (R)-1,2-diaminopropane and the results of investigations on the electrical conductivity, magnetic susceptibility and absorption spectra of their complexes with copper. As distinct from α -amino acid complexes, where the insertion of N-alkyl substituents results in their structure being changed from distorted octahedral to four-coordinate square-planar, diamine complexes invariably preserve their distorted octahedral structure with the introduction of up to two substituents in the ligand molecule, and in the case of more overloaded ligands binuclear complexes are formed. Even in solvents with poor coordinative capacity no four-coordinate structures could be detected, which has been explained by the coordination of anions in the axial positions of the positively charged complexes.

Introduction

When studying copper(II) complexes with N-alkyl- α -amino acids [1, 2] we found a strong dependence of their absorption spectra on the degree of the ligand amino group substitution, solvent type and solution temperature. This dependence was explained in terms of existence of an equilibrium between the usual distorted octahedral form of complexes and the four-coordinate square-planar form resulting from steric hindrance of axial positions. For 1,2-diamine complexes, thermochromic behavior was observed in case of N,N-diethylethylenediamine in solid state [3-5], where it was thoroughly studied by Paoletti, Fabrizzi *et al.* [6-8]. No information, however, is given in literature on the thermochromic behavior of copper(II) complexes with diamines in solution and, besides, the available data refer mainly to 1,2-diaminoethane derivatives.

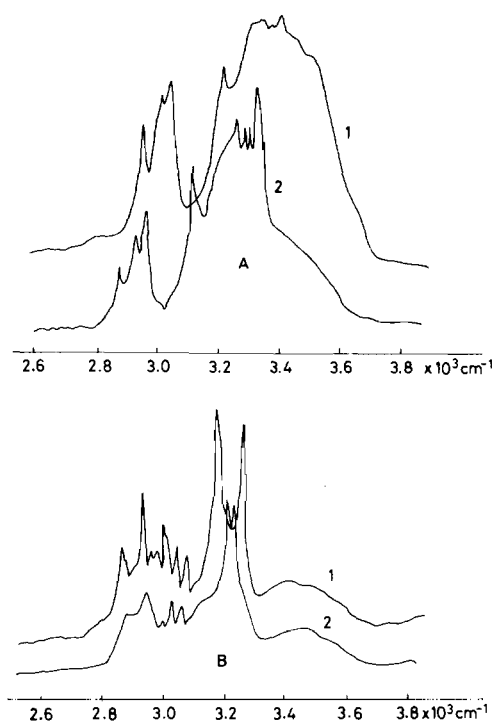


Fig. 1. IR spectra of copper(II) complexes with (R)-1,2-diaminopropane (A) and N¹,N²-dibenzyl-1,2-diaminoethane (B) before (1) and after (2) removing the solvate molecules.

In this paper we present the results of investigating the copper(II) complexes with N-methyl and N-benzyl derivatives of (R)-1,2-diaminopropane and 1,2-diaminoethane in non-aqueous media, as well as the data on synthesis of these compounds.

Results and Discussion

All the complexes isolated in crystalline form (see Table I) contained no solvent molecules except the

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TABLE I. Properties of Copper(II) Complexes with Derivatives of en and (R)-pn.

Complex	Analysis		Electrical conductivity $10^3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$					λ_{max} , ($\epsilon \text{ mol}^{-1} \text{ cm}^{-1}$)					μ (B.M.)	
	Cu	N	H ₂ O	CH ₃ OH	CH ₃ CN	DMFA	THF	PhNO ₂	sol.	PhNO ₂	CH ₃ OH	CH ₃ CN		DMFA
Cu(en) ₂ (ClO ₄) ₂	16.60	14.64	232	85	124	101	insol	insol	537	530	540	552	570	
	16.31	14.4								(52)	(55)	(61)	(71)	
Cu(Bzlen) ₂ ·(ClO ₄) ₂	11.29	9.95	180	65	205	86	0.12	2.0	545	558	562	568	582	
	11.4	9.8								(106)	(120)	(126)	(128)	
Cu(N ¹ , N ² -Bzl ₂ en) ₂ ·(ClO ₄) ₂	8.78	7.75	insol	131	137	116	insol	7.3	555	582	563	578	595	
	8.5	7.8								(105)	(90)	(136)	(134)	
Cu ₂ (Me ₄ en) ₂ (OH) ₂ (ClO ₄) ₂	21.44	9.46	182	118	276	121	insol	61	—	555	582	578	642	
	21.2	9.6								(129)	(115)	(125)	(131)	
Cu(pn) ₂ (ClO ₄) ₂	15.47	13.60	200	82	182	119	insol	7.3	535	535	543	555	552	
	15.6	13.9								(59)	(62)	(71)	(71)	
Cu(N ¹ -Bzlpn) ₂ (ClO ₄) ₂	10.75	9.48	203	80.9	148	100	0.2	6.48	550	555	565	568	578	
	10.2	9.0								(93)	(116)	(121)	(125)	
Cu(N ¹ , N ² -Bzl ₂ pn) ₂ ·(ClO ₄) ₂	8.24	7.27	insol	94	153	95	0.3	9.0	592	584	589	606	632	
	7.7	7.6								(174)	(126)	(270)	(204)	
Cu ₂ (Me ₄ pn) ₂ (OH) ₂ (ClO ₄) ₂	20.05	9.03	162	120	252	115	0.85	16	—	568	595	598	578	
	19.9	9.2								(166)	(148)	(146)	(162)	
Cu(N ¹ , N ² -Me ₂ pn) ₂ (ClO ₄) ₂	13.6	12.0	162	67	187	88	0.3	7.2	558	565	578	582	595	
	14.2	12.2								(102)	(103)	(119)	(104)	

^a above the line, calculated value; under the line, found value.^b In MeOH.^c In CH₃CN.

complexes of 1,2-diaminopropane and N^1,N^2 -dibenzyl-1,2-diaminoethane which contained 4.5 molecules of water and one toluene molecule, respectively. In both these cases the solvate molecules are not securely retained and are removed with drying, which results in substantial changes in the IR spectrum of the complex with 1,2-diaminopropane in the 3600–3000 cm^{-1} region, but only in slight changes in the IR spectrum of the N^1,N^2 -dibenzyl-1,2-diaminoethane complex (Fig. 1). After drying both these compounds acquire a violet coloration, characteristic of copper complexes with diamines, and display their absorption maximum in the diffuse reflection spectrum at 535 and 555 nm, respectively. As seen from the data in Table I, there is a close analogy in spectral properties, electrical conductivity of solutions and magnetic susceptibility of the corresponding complexes of 1,2-diaminopropane and 1,2-diaminoethane.

With the increasing size and number of substituents at nitrogen atoms, the maximum in the diffuse reflection spectra is shifted towards longer wavelengths, this shift being more pronounced for 1,2-diaminopropane complexes. A similar picture is also observed in the spectra of complexes in solution. This shift of absorption maximum towards longer wavelengths is somewhat unexpected since, with the growth of steric interactions in the molecule of a complex, one would anticipate the coordination of axial ligands to weaken and, therefore, the absorption maximum to shift towards shorter wavelengths, as is the case with the complexes of N -alkyl- α -amino acids [2]. A hypsochromic shift in the absorption spectrum of copper(II) complexes with 1,2-diamines is also observed with an increase in solution temperature (Fig. 2A), which, again, is contrary to the behavior of amino acid complexes.

When one compares the changes in the spectra for the complexes of N -derivatives of 1,2-diamines with similar dependences for the complexes of N -alkyl- α -amino acids, the first thing that should be noted is the smaller sensitivity of the absorption spectra of 1,2-diamine complexes to the factors studied (degree of substitution, temperature, solvent). Thus, changing the solvent for the bis(N -benzyl- L -prolinato) copper(II) results in the absorption maximum being shifted by 100 nm (from 490 nm in CHCl_3 to 590 nm in MeOH), whereas in case of diamine complexes (Table I) the shift towards longer wavelengths does not exceed 40 nm as one passes to solvents with stronger donor properties (from $\text{C}_6\text{H}_5\text{NO}_2$ to DMFA).

It could be assumed that in the diamine complexes studied we do not reach such a degree of steric overcrowding when the detachment of axial ligands, causing the changes in the spectra, begins (*e.g.*, absorption spectra of unsubstituted α -amino acid complexes are also almost not temperature-depen-

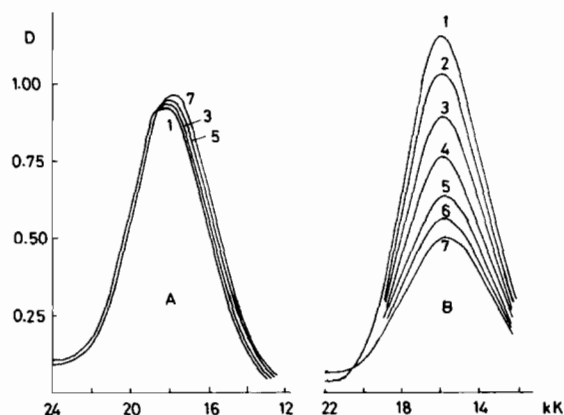


Fig. 2. Temperature dependence of electronic spectra of copper(II) complexes with (R)- N^1,N^2 -dimethyl-1,2-diaminopropane in nitrobenzene (A) and with (R)- N^1,N^2 -dibenzyl-1,2-diaminopropane in dimethylformamide (B): 1. 15°, 2. 25°, 3. 35°, 4. 45°, 5. 55°, 6. 65°, 7. 75° C.

dent). It is, however, known [3] that tri- and tetra-substituted 1,2-diamines, because of strong steric interactions, do not form mononuclear bis-chelates with the copper ion, but give binuclear bridge structures. So, at least in case of disubstituted ligands, steric interactions must already be sufficiently pronounced.

The main cause of the difference in the behavior of N -substituted 1,2-diamine and α -amino acid complexes is, in our opinion, that the former have a 2+ charge, whereas amino carboxylate complexes are neutral. The positive charge of the complex must significantly strengthen the bonding of axial donors. Measurements of the electrical conductivity of solutions (Table I) show that copper(II) complexes with diamines act as 2:1 electrolytes only in solutions with a good coordinative capacity but, practically, do not dissociate in solvents, which do not solvate ions readily ($\text{C}_6\text{H}_5\text{NO}_2$) or in media with a low dielectric constant (THF). In the solvents of the first group, solvent molecules act as the axial ligands, whereas in the solvents belonging to the second group the axial positions are, evidently, occupied by perchlorate anions. This exchange of solvent molecules for counter-ions results in the levelling-off of the effect of solvent type on absorption spectra.

The charging of diamine complexes also enables one to explain the inverse, as compared with amino acid complexes, temperature dependence of absorption spectra. With increasing temperature the dielectric constant of the medium drops and, therefore, electrostatic and ion-dipole interactions become stronger, which strengthens the metal-axial ligand bond and causes a certain shift of absorption maximum towards longer wavelengths (Fig. 2).

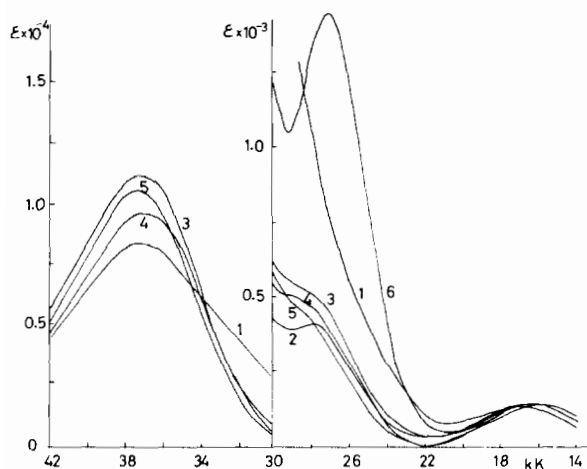


Fig. 3. Electronic spectra of the copper(II) complex with (R)-N¹,N¹,N²,N²-tetramethyl-1,2-diaminopropane in methanol (1), acetone (2), water (3), ethanol (4), acetonitrile (5) and with (R)-N¹,N²-dibenzyl-1,2-diaminopropane in methanol (6).

An interesting observation is that the complexes of N¹,N²-dibenzyl-1,2-diamines differ from all the other complexes studied. Their solutions in dimethylformamide display a sharp drop in extinction on rising the temperature (Fig. 2), and in methanol a new band at *ca.* 380 nm with $\epsilon \approx 1500 \text{ l mol}^{-1} \text{ cm}^{-1}$ is observed to appear. Absorption in this spectral region is characteristic of binuclear complexes [3, 9] of tetramethyl derivatives of 1,2-diaminopropane and diaminoethane. However, the unusual properties of N¹,N²-dibenzyl-1,2-diamine complexes can be hardly explained in terms of the binuclear structure, as follows from the data of Table I and Fig. 3.

All attempts to isolate this specific form of complexes resulted either in non-crystallizable products or initial mononuclear N¹,N²-dibenzyl-1,2-diamine complexes.

Experimental

Synthesis of Ligands

1,2-diaminoethane, N¹,N¹,N²,N²-tetramethyl-1,2-diaminoethane and (R,S)-1,2-diaminopropane were commercial products and were purified by distillation over metallic sodium.

(R)-1,2-diaminopropane was obtained from (R,S)-1,2-diaminopropane by the crystallization of its salt with d-tartaric acid according to [10]. $[\alpha]_{\text{D}}^{20} = -32.5^\circ$ ($c = 1.40$; benzene), lit. [10] $[\alpha]_{\text{D}}^{20} = -34.2^\circ$ ($c = 1$; abs. benzene).

(R)-N¹,N²-dibenzyl-1,2-diaminopropane was obtained by the hydrogenation of the bis-Schiff base, obtained from (R)-1,2-diaminopropane and

benzaldehyde. B.p. 143–147 °C at 6×10^{-3} mm Hg, $[\alpha]_{\text{D}}^{20} = -37.3^\circ$ ($c = 2.1$; ethanol). Calc. for C₁₇H₂₂N₂: C 80.2%, H 8.7%, N 11.0%; found: C 80.4%, H 8.9%, N 11.3%.

(R)-N¹-benzyl-1,2-diaminopropane was obtained by the reduction of D-alanine benzylamide with lithium-aluminum hydride in THF according to standard procedure [11]. $[\alpha]_{\text{D}}^{20} = -24.2^\circ$ ($c = 1.2$; ethanol). Calc. for C₁₀H₁₅N₂: C 73.1%, H 9.8%, N 17.0%; found: C 72.8%, H 9.9%, N 16.7%.

(R)-N¹,N²-dimethyl-1,2-diaminopropane and N¹,N²-dimethyl-1,2-diaminoethane were obtained by the reduction of the corresponding bis-formyl derivatives with lithium aluminum hydride according to [12]. It should be borne in mind that the procedure, described in [12], for obtaining bis-formyl derivative by the reaction of chloral with 1,2-diaminoethane yields, in the case of 1,2-diaminopropane, (R)-N-formyl-N'-(β-trichloroethylidene)-1,2-diaminopropane. Calc. for C₆H₉N₂Cl₃O: C 31.1%, H 3.9%, N 12.1%, Cl 46.0%; found: C 31.0%, H 3.9%, N 12.2%, Cl 46.1%; $[\alpha]_{\text{D}}^{20} = +69.3^\circ$ ($c = 0.7$; ethanol); b.p. 137–139 °C, whose reduction, as that of bis-formyl derivative, results in N¹,N²-dimethyl-1,2-diaminopropane.

(R)-N¹,N²-dimethyl-1,2-diaminopropane. Calc. for C₅H₁₄N₂: C 58.8%, H 13.7%, N 27.4%; found: C 58.3%, H 13.7%, N 27.2%; $[\alpha]_{\text{D}}^{20} = -37.8^\circ$ ($c = 1.2$; benzene); b.p. 125–127 °C.

N¹,N²-dimethyl-1,2-diaminoethane. Calc. for C₄H₁₂N₂: C 54.5%, H 13.6%, N 32.9%; found: C 53.9%, H 13.8%, N 31.2%; b.p. 125–127 °C.

(R)-N¹,N¹,N²,N²-tetramethyl-1,2-diaminopropane was obtained by the reductive formylation of (R)-1,2-diaminopropane according to [13]. $[\alpha]_{\text{D}}^{20} = +39.3^\circ$ ($c = 1.7$; benzene); b.p. 141–143 °C.

N-benzyl and N,N'-dibenzyl-1,2-diaminoethane were obtained by the hydrogenation of a mixture of Schiff bases obtained from 17 ml (0.23 M) of 1,2-diaminoethane and 28 ml (0.26 M) of benzaldehyde and separated by distillation. Yield of N-benzyl-1,2-diaminoethane is 7.4 g, b.p. 75–76 °C at 5×10^{-4} mm Hg; of N,N'-dibenzyl-1,2-diaminoethane is 13.7 g, b.p. 150–152 °C at 10^{-4} mm Hg.

Synthesis of Complexes

Most of the complexes were obtained by mixing equimolar amounts of 1,2-diamine and Cu(ClO₄)₂·6H₂O solutions in ethanol. This immediately, or after the addition of a small quantity of diethylether, resulted in sedimentation of a crystalline complex which was filtered off and purified by recrystallization. The analytical data are given in Table I.

(N¹,N²-dibenzyl-1,2-diaminoethane)₂Cu(ClO₄)₂ was obtained by shaking up an aqueous solution containing 8 g (0.021 m) of Cu(ClO₄)₄·6H₂O with the toluene solution of N¹,N²-dibenzyl-1,2-diaminoethane (10 g, 0.042 m). This results in the deposi-

tion of blue viscous oil which was extracted by adding 500 ml of hot toluene. The oil is partially dissolved in the toluene and partially crystallized. The toluene layer was separated and concentrated by evaporation. The residue was combined with the crystals and dissolved in acetone. A little toluene was then added, and the mixture was left for the night to crystallize. 19.0 g of blue crystals were obtained, which, when dried at 152 °C and 1 mm Hg, change into a lilac modification with the loss of 10.7% of initial weight. Analysis of the blue modification: calc. for $\text{CuC}_{32}\text{H}_{20}\text{N}_4\text{Cl}_2\text{O}_8 \cdot \text{C}_6\text{H}_5\text{CH}_3$: Cu 7.79%, N 6.88%; found: Cu 7.46%, N 6.6%.

$((R)\text{-N}^1, \text{N}^2\text{-dibenzyl-1,2-diaminopropane})_2\text{Cu}(\text{ClO}_4)_2$ was obtained in the same way as the analogous 1,2-diaminoethane complex but, because of its good solubility in toluene and poor crystallizability, it was impossible to obtain it in the solid state. The toluene layer containing the extracted complex was, therefore, concentrated by evaporation. The residue was then twice treated with an ethanol-benzene mixture and evaporated. The residue was dissolved in a small quantity of benzene and lyophilically dried, which makes it possible to obtain the complex in the form of a dry solid product.

Investigation of Complexes

Absorption spectra of complexes were recorded at concentrations of 1×10^{-3} – 5×10^{-3} m/l for the visible region and 10^{-5} – 10^{-4} m/l for the UV region in thermostatted 2 and 1 cm cells, respectively, on a Specord UV-Vis (Zeiss, Jena, DDR) recording spectrophotometer. Accuracy of temperature control $\pm 0.1^\circ$.

Electrical conductivity of solutions of complexes was determined with the help of OP-208 (Radelkis, Hungary) conductometer at concentration of solutions 5×10^{-5} – 10^{-2} m/l and temperature 25 °C.

Magnetic susceptibility of complexes was determined by the method of Evans [14] on a Hitachi R-20 NMR spectrometer at the temperature of 32 °C.

Infrared spectra of complexes were recorded in KBr on a UR-20 (Zeiss, Jena, DDR) spectrophotometer.

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