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The Stereochemistry of Copper(II) Complexes Containing *N*,*N*′-Di-8-quinolylethylenediamine and Its Optically Active Derivatives

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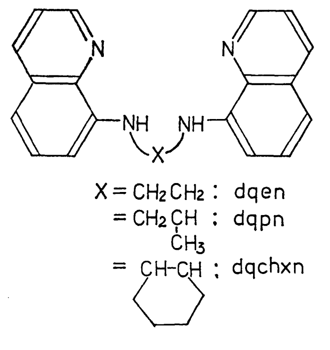
Copper(II) complexes of a series of quadridentate ligands, *N*,*N*′-di-8-quinolylethylenediamine (dqen), (*R*)-*N*,*N*′-di-8-quinolylpropylenediamine {(*R*)-dqpn}, and (*R*,*R*)-*N*,*N*′-di-8-quinolyl-1,2-cyclohexanediamine {(*R*,*R*)-dqchxn}, have been prepared. Their d-d absorption spectra, magnetic moments, and molar conductivities indicate that the complexes have a five-coordinated structure, in which one of the quinoline groups of the ligands occupies an apical position. The circular dichroism (CD) spectra of the optically active ligands and their complexes exhibit exiton couplets in the ligand's $\pi^* \leftarrow \pi$ transition region. From the signs of the couplets, the preferable configurations of the (*R*)-dqpn and (*R*,*R*)-dqchxn complexes are assigned to Δ.

A number of papers have been published on metal complexes with 8-aminoquinoline and its derivatives.[1] Nielsen and Dahl prepared copper(II) complexes of *N*,*N*′-di-8-quinolylalkanediamines (dqdiamine), but conclusive evidence for the structure of the complexes is lacking.[1d] These quadridentate ligands are interesting in their intermediate character between aliphatic and aromatic systems, and also in the variety of stereochemistry of their metal complexes. The dqdiamines are structurally similar to quadridentate Schiff base-type ligands such as *N*,*N*′-disalicylideneethylenediamine (salen). Although stereochemical studies of the complexes with such Schiff bases have been extensively done,[2] none of bqdiamine complexes are known thus far.



This paper will deal with the stereochemistry of copper(II) complexes of dqen and optically active (*R*)-dqpn and (*R*,*R*)-dqchxn. Molecular models predict that the steric interaction between 2 and 2′ protons of the dqdiamine would prevent the formation of square-planar complexes. The deviation from co-planarity of the two coordinated quinoline nuclei will bring about a dissymmetric configuration about the metal ion. The ligands derived from optically active diamines are expected to coordinate to metal ions with sterically preferred configurations because of the conformational requirements of the diamine chelate rings.

Experimental

N,N′-*Di-8-quinolylethylenediamine (dqen).* This was prepared according to the method described in the literature.[1b] Recrystallization from ethanol gave prismatic tan crystals; mp 162—163 °C.

*(*R*)*-N,N′-*Di-8-quinolylpropylenediamine {(*R*)-dqpn}.* Racemic propylenediamine (pn) was resolved by the method of Dwyer *et al.*[3] *R*-pn was obtained by the neutralization of its tartrate (3 mol, 67.27 g) with barium hydroxide. After the filtration of barium tartrate, the filtrate was used directly for the next condensation process. To the filtrate in a 2-dm^3 three-necked flask fitted with a mechanical stirrer, a condenser, and a thermometer, were added 8-hydroxyquinoline (0.6 mol, 87.10 g) and sodium disulfite (0.6 mol, 114.13 g), after which the mixture was gently refluxed for 7 days with stirring. The reaction mixture was made alkaline with a 50% aqueous sodium hydroxide solution at 60 °C, and after cooling the mixture was extracted with benzene. The extract was washed with water and dried over anhydrous potassium carbonate. After the removal of the solvent, 40.64 g of a pale brown oil was obtained. The crude oil (10 g) was purified as a hexane solution through an Al_2O_3 column. Pale yellow small plates (6.56 g) were obtained after the removal of the solvent, and recrystallized from hexane; mp 96.3—97.0 °C.

(R,R)-Di-8-quinolylcyclohexanediamine {(R,R)-dqchxn}. This was prepared according to a method similar to that for (*R*)-dqpn, using *R*,*R*-cyclohexanediamine[4] (chxn) in place of R-pn. Recrystallization from benzene gave yallow needles; mp 174—174.5 °C.

[$CuCl_2$(dqen)]. Copper(II) chloride dihydrate (0.85 g in 20 cm^3 of ethanol) and dqen (1.6 g in 100 cm^3 of ethanol) were mixed, and the resulting green solution was stored in a refrigerator overnight. The green crystals deposited were filtered off, washed with ethanol and ether, and air-dried; 1.2 g.

[$CuCl_2$(R)-dqpn]·1/2H_2O. This was prepared by a method similar to that used for [$CuCl_2$(dqen)].

[$CuCl_2$(R,R)-dqchxn]. Copper(II) chloride dihydrate (0.85 g in 100 cm^3 of ethanol) and (*R*,*R*)-dqchxn (20 cm^3 of benzene) were mixed. The resultant dark green solution was evaporated to about 50 cm^3 and stored in a refrigerator. The dark green crystals thus deposited were filtered, washed with ethanol, and ether, and air-dried; 0.65 g.

Measurements. Electronic absorption spectra were recorded on a Shimadzu Double 40-R spectrophotometer. The circular dichroism spectra were recorded on Jasco J-20 and Jasco J-20A spectropolarimeters. The magnetic measurements were carried out at room temperature (24—25 °C) by the Gouy method, using distilled water as the calibrant. The conductivities were determined on a TOA CM-6A conductometer at 25 °C.

Results and Discussion

Optically active ligands of the type, *N*,*N*′-di-8-

Table 1. Elemental analysis and some properties of ligands and complexes

Compound	Found (Calcd %) C	H	N	Magnetic moments and conductances μ_{eff} (B.M.)	(Λ_M, Ω^{-1} cm^2 mol^{-1}) H_2O	CH_3OH
dqen	76.61 (76.40)	5.94 (5.77)	18.61 (17.85)			
(*R*)-dqpn	75.54 (76.81)	5.96 (6.14)	17.32 (17.06)			
(*R*,*R*)-dqchxn	78.58 (78.23)	6.58 (6.56)	15.20 (15.20)			
[$CuCl_2$(dqen)]	52.92 (53.22)	4.32 (4.04)	12.44 (12.49)	1.99	248	101
[$CuCl_2${(*R*)-dqpn}] 1/2H_2O	53.34 (53.46)	4.74 (4.48)	11.64 (11.87)	2.00	221	92
[$CuCl_2${(*R*,*R*)-dqchxn}]	55.02 (55.34)	5.09 (5.03)	9.80 (10.25)	1.97	217	118

quinolylalkanediamine, and their complexes are described for the first time. The results of the elemental analysis and other properties of the ligands and their copper(II) complexes are presented in Table 1.

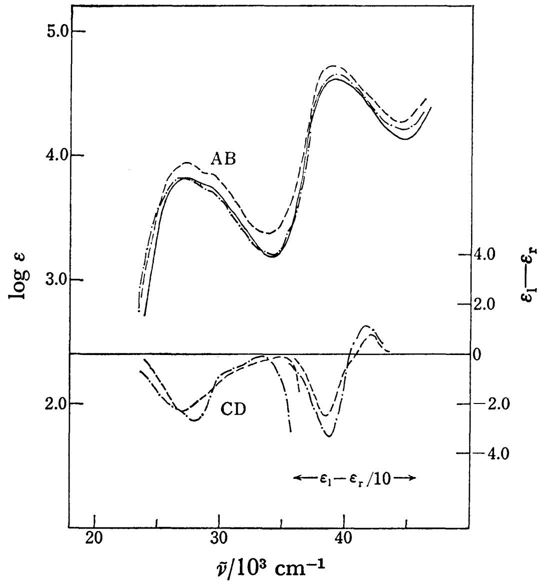


Fig. 1. Absorption(AB) and circular dichroism(CD) spectra of (——) dqen, (– – –) (*R*)-dqpn and (-·-·-) (*R*,*R*)-dqchxn in methanol.

Table 2. Absorption (AB) and circular dichroism (CD) data in 10^3 cm^{-1}, (log ε) and ($\varepsilon_l-\varepsilon_r$)

Compound	AB	CD
dqen	27.03 (3.81)	
	sh 29.41 (3.72)	
	39.06 (4.61)	
(*R*)-dqpn	27.03 (3.93)	27.40 (− 2.37)
	sh 28.99 (3.85)	
	39.37 (4.70)	38.46 (−26.10)
		42.02 (+ 7.11)
(*R*,*R*)-dqchxn	27.03 (3.80)	27.76 (− 2.76)
	sh 28.99 (3.71)	
	39.06 (4.58)	38.76 (−32.20)
		41.67 (+11.50)
[$CuCl_2$(dqen)]	sh 11.11 (1.43)	
	15.15 (1.86)	
	31.75 (3.98)	
	33.33 (4.01)	
	43.48 (4.74)	
[$CuCl_2${(*R*)-dqpn}]· 1/2H_2O	sh 11.11 (1.53)	
	15.63 (2.05)	14.71 (+ 0.81)
	31.75 (3.97)	31.75 (− 2.42)
	33.33 (4.00)	
		40.65 (− 9.44)
	43.48 (4.69)	43.48 (+38.4)
[$CuCl_2${(*R*,*R*)-dqchxn}]	sh 11.11 (1.73)	12.50 (− 0.02)
	16.13 (2.15)	15.63 (+ 0.72)
	31.75 (3.95)	32.26 (+ 4.85)
	33.56 (3.98)	
		41.32 (−16.60)
	43.48 (4.70)	43.10 (+24.92)

Ligands. The electronic absorption and CD spectra of the ligands in methanol are shown in Fig. 1. Their band locations and intensities are summarized in Table 2. The substitution of propylenediamine or cyclohexanediamine for the ethylenediamine moiety of dqen produces little change in the absorption spectra. The two main absorption bands, centered at about 27000 and 40000 cm^{-1}, are due to the $\pi^*\leftarrow n$ and $\pi^*\leftarrow\pi$ transitions of the quinoline nuclei.[5] A negative-positive CD couplet[6] (from lower to higher energy), centered at *ca.* 40000 cm^{-1}, is observed for the optically active ligands. The strong Cotton effects do not usually arise from the vicinal induction of assymmetric carbons. These CD patterns should arise from exiton splitting of the transitions of the quinoline nuclei. Similar coupled CD spectra have been reported for the optically active Schiff bases containing conjugated systems, such as (*R*)-*N*,*N*′-disalicylidenepropylenediamine and (*R*,*R*)-*N*,*N*′-disalicylidenecyclohexanediamine.[2a–2c,2g] Figure 2 shows the three possible conformations of (*R*)-dqpn (a, b, c) and the only possible conformation of (*R*,*R*)-dqchxn (d). Of the three possible conformations of (*R*)-dqpn, (a) and (b) should give rise to strong optical activity, since in (c) the two quinoline nuclei are *trans*-parallel, resulting in inactive coupling. The pattern and intensities in the CD spectrum of the (*R*)-dqpn are quite similar to those of (*R*,*R*)-dqchxn, which necessarily has the (d) conformation, regulated by the fused cyclohexane ring. This result indicate that the most stable conformation of (*R*)-dqpn is the (a) conformer in

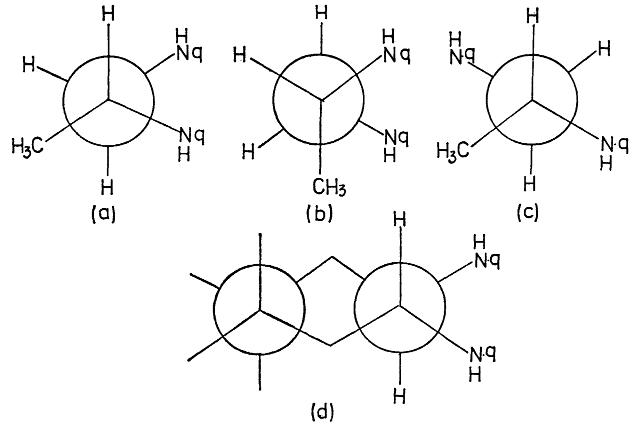


Fig. 2. Conformations of (R)-dqpn (a, b, c) and the only possible conformation of (R,R)-dqchxn (d); q denotes quinoline nuclei.

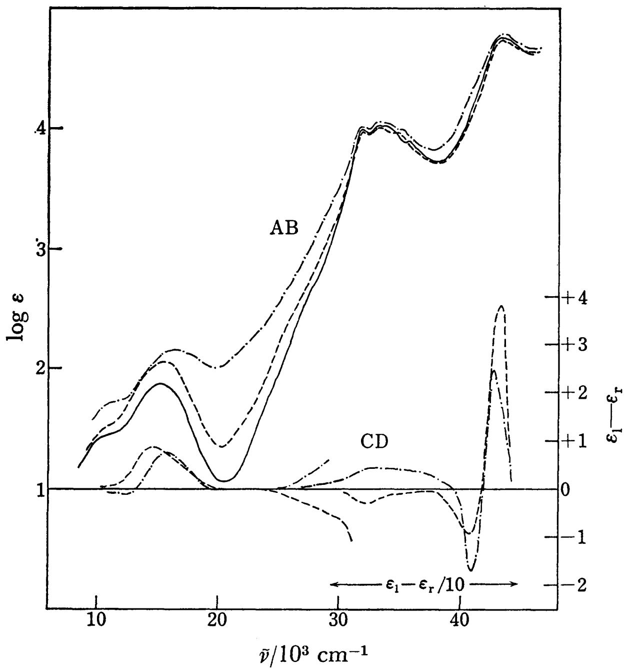


Fig. 3. Absorption (AB) and circular dichroism (CD) spectra of (——) [$CudqenCl_2$], (----) [Cu(R)-dqpn-Cl_2] and [Cu(R,R)-dqchxnCl_2] in H_2O.

methanol.

Copper(II) Complexes. Figure 3 shows the electronic absorption and CD spectra of the series of copper(II) complexes in water. The absorption bands in the 10000—20000 cm^{-1} region are due to the d–d transitions. Each complex gives a shoulder at *ca.* 11000 cm^{-1} and a main peak at *ca.* 15000 cm^{-1}. It is known that for many copper(II) complexes, a shoulder appears at about 11000 cm^{-1} as a result of ligation along the tetragonal axis.[7-9] It might be difficult for the present ligands to take square-planar arrangements in the copper(II) complexes because of the steric hindrance between 2 and 2′ quinoline protons. The weak shoulders at *ca.* 11000 cm^{-1} suggest the apical ligation of one or two quinoline group(s) of the ligands that is, a *cis* type coordination of dqdiamine to the copper(II) ion. Although the *cis* complexes have two different geometrical arrangements, *cis*α and *cis*β, the present complexes are probably *cis*β (Fig. 4), since the steric interaction between the bulky terminal chelate moiety and the substituents of the central diamine chelate ring might be greater in *cis*α than in *cis*β.[10] The magnetic moments of the three complexes (Table 1) are within the range of those reported for the five-coordinated or octahedral complexes,[1g] and higher than those of planar complexes (μ_{eff}; 1.8—1.9 B. M.).[11] The molar conductivities indicate that all the complexes are 1 : 1 electrolytes in methanol, and 1 : 2 electrolytes in an aqueous solution.[12] These results imply that the complexes have five-coordinated structure, [CuCl(dqdiamine)]Cl in the solid state, and that they dissociate into [CuCl(dqdiamine)]$^+$ and Cl^- ions in methanol. When the complexes are dissolved in water, the coordinated Cl^- ion will be replaced by the H_2O molecule to give bivalent complex cation, *i.e.*, [Cu(H_2O)(dqdiamine)]$^{2+}$.

The cyclohexanediamine bridge of (R,R)-dqchxn will exclusively take the λ-gauche[13] conformation upon coordination, because it has a *trans*-fused chelate ring. In the (R)-dqpn complex, however, a conformational inversion of the propylenediamine chelate moiety is possible wherein the C-methyl group is axial for the δ, and equatorial for the λ conformation. Since the overall CD pattern of the (R)-dqpn complex is similar to that of the (R,R)-dqchxn complex, the central chelate conformation and the absolute configuration of the (R)-dqpn complex must be the same as those of the (R,R)-dqchxn complex. Thus, the preferred conformation of the propylenediamine chelate moiety should be λ with the methyl group being equatorial.

The (R)-dqpn and (R,R)-dqchxn complexes give positive main Cotton effects in the d-d region. Unfortunately, the absolute configurations of the complexes cannot be known at present from the Cotton effects in this region. Sharp couplet CD components (negative and positive from lower to higher energy) centered at 42000 cm^{-1}, corresponding to the ligand $\pi^* \leftarrow \pi$ absorption bands, are seen for both complexes. The observation of a CD couplet with opposite-signed components corresponding to the ligand $\pi^* \leftarrow \pi$ transitions indicates that the two quinoline nuclei take a dissymmetric arrangements as has been mentioned. Since the CD pattern in the $\pi^* \leftarrow \pi$ couplet of the ligands did not change upon complexation, the dissymmetric arrangement of the free ligands must be maintained in their complexes. Figure 4 shows schematic drawings of the

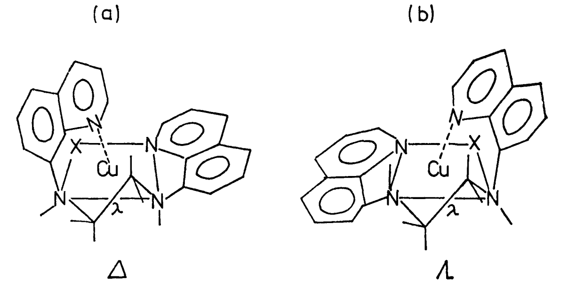


Fig. 4. Schematic structures of (a) Δ-*cis*β[CuX(λ-dqdiamine)]$^+$, (b) Λ-*cis*β[CuX(λ-dqdiamine)]$^+$ ions.

Δ-*cis*β and Λ-*cis*β forms of $[\mathrm{CuX}(\lambda\text{-dqdiamine})]^+$ ($\mathrm{X}=\mathrm{Cl}^-$). It is clear that the dissymmetric arrangement of the ligand does not change on complexation in the case of the Δ-*cis*β form. The steric interaction between alkyl protons of the central chelate bridge and the π-electron cloud of the apically ligated quinoline nuclei seems to be greater in Λ-*cis*β than in Δ-*cis*β. Therefore, the Δ-*cis*β might be more probable than the Λ-*cis*β in the present complexes. Such behavior is in agreement with the exiton coupling theory. As defined by Bosnich,[14] when the configuration is Λ, the negative component of the $\pi^*\leftarrow\pi$ couplet will lie at higher energy, while it will lie at a lower energy when the chirality is Δ, the latter corresponding to the present complexes.

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