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Circular Dichroism of the d–d and Charge-Transfer Bands of Bis(N-alkyl-(s)-1,2-propanediamine)Copper(II) Complexes

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In previous papers [1, 2] we reported that [$PdCl_2$-(N^1-Me_2-(s)-pn)] and [$PdCl_2$(N^2-Me_2-(s)-pn)] show quite different CD spectra from that of [$PdCl_2$((s)-pn)] in the d–d region, while the CD of [Pd(N^1-Me_2-(s)-pn)$_2$]$^{2+}$ and [Pd(N^2-Me_2-(s)-pn)$_2$]$^{2+}$ are closely similar to that of [Pd((s)-pn)$_2$]$^{2+}$ (for the abbreviations of the ligands, see Table I). These facts suggest that dissymmetric perturbations arising from the diamine chelate rings with δ-conformation can be changeable by environmental variations. The above suggestion has been substantiated by the recent crystal structure determinations of [Pd(N^1-Me_2-(s)-pn)Cl_2] and [Pd(N^2-Me_2-(s)-pn)Cl_2] [3].

TABLE I. Legend of Ligands.

Abbreviation	
(s)-pn	$H_2NCH(CH_3)CH_2NH_2$
N^1-Me-(s)-pn	$(CH_3)HNCH(CH_3)CH_2NH_2$
N^2-Me-(s)-pn	$H_2NCH(CH_3)CH_2NH(CH_3)$
N^1-Me_2-(s)-pn	$H_2NCH(CH_3)CH_2N(CH_3)_2$
N^1-Et_2-(s)-pn	$H_2NCH(CH_3)CH_2N(C_2H_5)_2$
N^2-Me_2-(s)-pn	$(CH_3)_2NCH(CH_3)CH_2NH_2$
N^1-Pr_2-(s)-pn	$H_2NCH(CH_3)CH_2N(C_3H_7)_2$
N^1-Bu_2–(s)-pn	$H_2NCH(CH_3)CH_2N(C_4H_9)_2$

In the bis(diamine)copper(II) complexes of [Cu(AA′)$_2$]$^{2+}$ type, it is well known that some kinds of solvent can coordinate to a copper(II) atom at the apical positions, and the strength of the coordination bonds between copper atom and solvent is dependent on the donor number of the solvents. Thus, it is expected that the CD spectra of [Cu(AA′)$_2$]$^{2+}$ complexes would depend highly upon the solvents used, because the interaction between solvent molecules at the apical positions and the alkyl groups on the nitrogen atoms may cause a variable structural change of the chelate rings without altering the ring conformation.

Although many CD studies on the d–d bands have been reported, there have been only a few CD studies on the charge-transfer bands. For [Cu(AA′)$_2$]$^{2+}$ complexes, the charge-transfer bands are observed in the range 30 ~ 40 × 10^3 cm^{-1}, which have been assigned to the ligand $\sigma \rightarrow d_\sigma^*$ electronic transitions [4]. In this work, we have measured the solvent effect of the CD spectra in the d–d and charge-transfer band regions of the [Cu(AA′)$_2$]$^{2+}$ complexes, and attempted to investigate the relationship between the CD behaviour in the charge-transfer band region and the structure of the diamine chelate ring. The optically active diamines used in this study are summarized in Table I.

Experimental

Preparations

The diamines, N^1-Me-(s)-pn and N^2-Me-(s)-pn were prepared according to the method described in the literature [5]. Other ligands were already synthesized [2]. All the copper(II) complexes were prepared by a method similar to the preparation of [Cu((R)-pn)$_2$] $(ClO_4)_2$ [6]. The analytical data of the new compounds are given in Table II.

Measurements

The absorption and CD spectra were obtained as previously described [2].

TABLE II. Analytical Data of the New Complexes.

Complex	C (%)	H (%)	N (%)
	Found (calcd.)	Found (calcd.)	Found (calcd.)
[Cu(N^1-Me_2-(s)-pn)$_2$]$(ClO_4)_2$	25.66 (25.74)	6.03 (6.45)	11.94 (12.00)
[Cu(N^2-Me_2-(s)-pn)$_2$]$(ClO_4)_2$	25.40 (25.74)	5.99 (6.45)	11.92 (12.00)
[Cu(N^1-Et_2-(s)-pn)$_2$]$(ClO_4)_2$	31.64 (32.15)	6.91 (6.88)	10.62 (10.70)
[Cu(N^1-Pr_2-(s)-pn)$_2$]$(ClO_4)_2$	37.30 (37.30)	7.63 (7.66)	9.67 (9.68)
[Cu(N^1-Bu_2-(s)-pn)$_2$]$(ClO_4)_2$	41.36 (41.61)	8.19 (8.25)	8.94 (8.82)

TABLE III. CD Spectral Data of the $[Cu(AA')_2](ClO_4)_2$ Complexes.

Complex	d–d Bands					CT Bands $\Delta\epsilon$ ($\bar{\nu}/10^3$ cm^{-1})
	CH_3NO_2	CH_3COCH_3	CH_3OH	H_2O	DMSO	
	$\Delta\epsilon$ ($\bar{\nu}/10^3$ cm^{-1})					
$[Cu(N^1\text{-Me-(s)-pn})_2]^{2+}$				−0.07 (16.7) +0.05 (18.7)		−3.7 (41.2)
$[Cu(N^2\text{-Me-(s)-pn})_2]^{2+}$				−0.14 (16.7) +0.07 (18.0)		−4.7 (41.6)
$[Cu(N^1\text{-Me}_2\text{-(s)-pn})_2]^{2+}$	+0.04 (16.0) −0.27 (19.9)	−0.14 (20.2)		+0.07 (15.0) −0.29 (19.2)	−0.13 (15.5) −0.09 (19.7)	−1.2 (*ca.* 33)[a] −3.3 (40.6)
$[Cu(N^2\text{-Me}_2\text{-(s)-pn})_2]^{2+}$	+0.08 (16.8) −0.43 (19.9)	+0.05 (16.1) −0.39 (19.9)		+0.02 (15.0) −0.16 (19.4)	+0.06 (15.3) −0.28 (19.2)	−1.0 (*ca.* 34)[a] −2.5 (40.3)
$[Cu(N^1\text{-Et}_2\text{-(s)-pn})_2]^{2+}$	+0.12 (15.5) −0.70 (18.5)	−0.35 (18.2)		−0.05 (14.0) −0.06 (18.5)	−0.25 (14.4) +0.19 (17.8)	−0.8 (*ca.* 33)[a] −1.4 (38.0)
$[Cu(N^1\text{-Pr}_2\text{-(s)-pn2}$	+0.15 (15.5) −0.52 (18.3)	+0.08 (15.9) −0.40 (18.3)	+0.07 (15.9) +0.06 (17.9) −0.08 (20.8)		−0.22 (14.4) +0.14 (17.5) −0.06 (21.2)	−1.6 (33.9)[b] *ca.* −1.0 (*ca.* 41)[c]
$[Cu(N^1\text{-Pr}_2\text{-(s)-pn})_2]^{2+}$	+0.14 (15.5) −0.44 (18.5)	+0.07 (15.3) −0.34 (18.4)	+0.07 (16.0) +0.08 (17.7) −0.10 (20.7)		−0.21 (14.6) +0.14 (17.5) −0.05 (21.2)	−1.7 (33.8)[b] *ca.* −1.0 (*ca.* 41)[c]

[a] In H_2O. [b] In CH_3OH. [c] Accurate values could not be obtained.

Results and Discussion

The absorption spectra of $[Cu(AA')_2]^{2+}$ complexes were measured in various solvents (CH_3NO_2, CH_3COCH_3, CH_3OH, H_2O and DMSO). It was observed that the larger the donor number of the solvent, the smaller the corresponding $\bar{\nu}_{max}$ value of the d–d band (the peak position of the absorption maximum), the order being $CH_3NO_2 > CH_3COCH_3 > CH_3OH \gtrsim H_2O > DMSO$. These facts can be elucidated in terms of the coordination ability of the solvents [7].

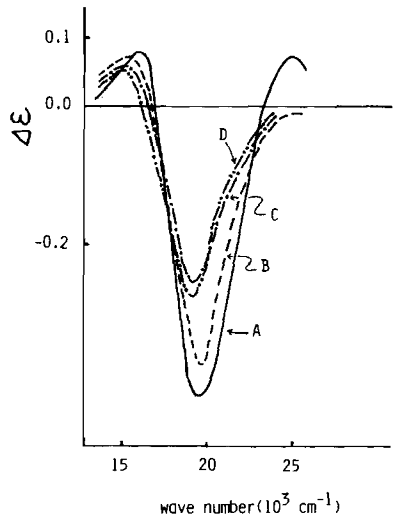

Fig. 1. CD spectra of $[Cu(N^2\text{-Me}_2\text{-(s)-pn})_2](ClO_4)_2$. A) in CH_3NO_2 (——); B) in CH_3COCH_3 (– – – – – –); C) in H_2O (——·——); D) in DMSO (——··——).

The CD spectral data of $[Cu(AA')_2]^{2+}$ are summarized in Table III. It has become apparent that the CD spectra (d–d band region) of $[Cu((R)\text{-pn})_2]^{2+}$, $[Cu(N^1\text{-Me-(s)-pn})_2]^{2+}$ and $[Cu(N^2\text{-Me-(s)-pn})_2]^{2+}$ suffer relatively small solvent effect, whereas marked solvent effect is observed for the other $[Cu(AA')_2]^{2+}$ complexes (*cf.* Figs. 1 and 2). These facts indicate that the solvent effect in the CD spectra of $[Cu(AA')_2]^{2+}$ complexes are to some extent dependent on the bulkiness of the alkyl groups on the nitrogen atoms; the steric interaction between the solvent molecules and the alkyl groups on the nitrogen atoms increases with increasing bulkiness of the alkyl group. The CD spectra of $[Cu(AA')_2]^{2+}$ in CH_3NO_2 are similar to those of the corresponding palladium(II) complexes [2], indicating that the $[Cu(AA')_2]^{2+}$ complexes are essentially of the square planar structure in CH_3NO_2 because of poor coordinating ability of the solvent. As the coordinating ability of the solvent becomes stronger, however, the changes of the CD spectra increase progressively. These facts can be explained by the assumption that progressive inrease of the coordinating ability of the solvent causes progressive changes of dissymmetric perturbations which are due to dissymmetric displacements of

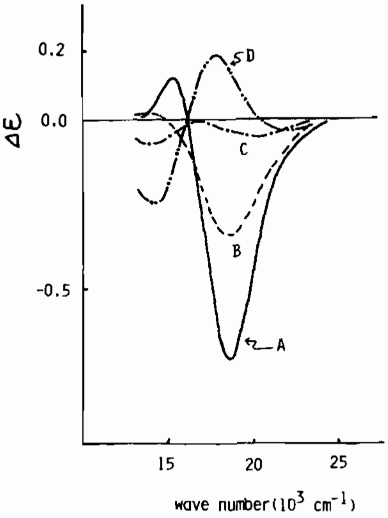

Fig. 2. CD spectra of [Cu(N^1-Et_2-(s)-pn)$_2$](ClO_4)$_2$. A) in CH_3NO_2 (———); B) in CH_3COCH_3 (– – – – –); C) in H_2O (—— . ——); D) in DMSO (—— .. ——).

the nitrogen atoms, and dissymmetric arrangements of the ring carbon atoms and the alkyl groups on the nitrogen atoms.

The ultraviolet absorption and CD spectra of all the complexes were measured in H_2O and CH_3OH. For [Cu(N^1-Me-(s)-pn)$_2$]$^{2+}$ and [Cu(N^2-Me-(s)-pn)$_2$]$^{2+}$, a single absorption band is observed at *ca.* 40 X 10^3 cm^{-1}, and two absorption bands are observed at *ca.* 33 and 40 X 10^3 cm^{-1} for other [Cu(AA')$_2$]$^{2+}$ complexes. It is noteworthy that although [Cu(N^1-Me-(s)-pn)$_2$]$^{2+}$ and [Cu(N^2-Me-(s)-pn)$_2$]$^{2+}$ show quite different CD spectra from those of other [Cu(AA')$_2$]$^{2+}$ complexes in the d–d band region, all the complexes show CD bands of minus signs in the charge-transfer band region (*cf.* Table III). Since the diamines should take δ-conformation in these complexes [2, 3, 8], it can be concluded that the signs of CD bands in the charge-transfer band region are dependent only on the conformation of the diamine chelate ring in the complexes studied here.

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