Circular Dichroism of Bis(diamine)copper(II) Complexes

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Summary The c.d. sign of *d–d* transitions in bis(diamine)-copper(II) complexes cannot be predicted by the conformational effect.

RELATIONSHIPS between c.d. behaviour and structure have been proposed for several copper(II) complexes with optically active amino-acids,[1] amino-acid amides,[2] peptides,[3] and amino-alcohols,[4] and a diamine.[5] We report here the c.d. sign in the *d–d* transition region for copper(II) complexes with various optically active diamines.

The diamines used were (*R*)-1,2-diaminopropane (A), (*R*)-*trans*-1,2-diaminocyclohexane (B), (*S*)-1,2-diamino-3-methylbutane (C), (*S*)-3-methyl-4-amino-2-azabutane (D), (*S*)-4-amino-4-methyl-2-azabutane (E), (*S*)-2-aminomethylazacyclopentane (F), (*S*)-3-aminoazacyclohexane (G), and (*S*)-3-aminoazacycloheptane (H). C.d. maxima for the copper(II) complexes are in Table 1.

TABLE 1

C.d. of the complexes. Δε *values are given with* ν_{max} (*in* $cm^{-1} \times 10^{-3}$) *in parentheses*

Complexes				
(I)	$Cu(A)_2(ClO_4)_2$	0·201(19·5)	−0·056(17·5)	0·025(15·3)
(II)	$Cu(B)_2(ClO_4)_2$	0·432(19·5)	−0·083(17·5)	0·050(15·4)
(III)	$Cu(C)_2(ClO_4)_2$	−0·309(19·5)	0·066(17·4)	−0·048(15·3)
(IV)	$Cu(D)_2(ClO_4)_2$[a]	0·050(19·6)	−0·098(16·5)	
(V)	$Cu(E)_2(ClO_4)_2$[a]	0·044(19·0)	−0·049(15·5)	
(VI)	$Cu(F)_2(NO_3)_2H_2O$[b]	?	0·410(17·5)	−0·170(15·3)
(VII)	$Cu(G)_2(ClO_4)_2$[c]	0·160(20·0)	−0·200(17·3)	
(VIII)	$Cu(H)_2(ClO_4)_2$[c]	0·395(20·5)	−0·658(17·6)	

[a] These bands were not resolved. [b] Although the existence of the band corresponding to this was shown by the absorption spectra, the sign of the c.d. peak was not determined. [c] One small positive component was found in these complexes at *ca.* 18,500 cm^{-1}.

The observed c.d in the 400—700 nm region showed two components but some showed unsymmetrical curves. The observed c.d. curves were analysed on the assumption that a c.d. curve is composed of a few Gaussian curves. In complexes (I)—(III) three components were found near 20,000, 17,500, and 15,000 cm^{-1} denoted ν_1, ν_2, and ν_3 respectively.

TABLE 2

Relationships between the observed c.d. signs (ν_1) *and empirical rules*

Complexes	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
Observed sign	+	+	−	+	+	?	+	+
Conformation of the chelate ring	λ	λ	δ	δ	δ	?	λ	λ
Rule 1[a]	+	+	−	−	−	?	+	+
Rule 2[b]	+	+	−	?	?	?	+	+

[a] Conformation of chelate ring.[6] [b] Hexadecant rule.[7]

In elongated D_{4h} symmetry, which is probable for bis(diamine)copper(II) complexes, the ground state is $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^2(d_{x^2-y^2})$, so that ν_1, ν_2, and ν_3 were tentatively assigned to $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions, respectively.

For each complex the relative signs of ν_1, ν_2, and ν_3 were constant, *i.e.*, the sign of ν_1 was the same as that of ν_3 and the sign of ν_2 was opposite to that of ν_1 or ν_3.

The c.d. sign of ν_1 ($d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$) was compared with that predicted by empirical rules (Table 2). Both rule 1 (conformational aspect) and rule 2 (hexadecant rule) gave a correct prediction for the complexes (I), (II), (III), (VII), and (VIII), but in the complexes containing *N*-methylpropylenediamine (IV) and (V), their c.d. signs were not sufficiently explained by the rules. Rule 1 gave an opposite sign to that observed, and rule 2 gave an uncertain prediction because the contribution of the *N*-methyl group was considered to be opposite to that of the chelating methylene groups. It was difficult to estimate the relative contributions of the *N*-methyl group and the chelating methylene groups, so it was not possible to decide whether the hexadecant rule applied for these complexes or not.

(*Received*, 15*th December* 1971; *Com.* 2131.)

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