Inorganica Chimica Acta, *162* (1989) 65–70

Conformation-control in Planar Metal Complexes (Cu^{2+}, Pd^{2+}, Pt^{2+}) of Ethylenediamine Derivatives with a Chiral N-substituent and Interpretation of CD Spectra Based on Regional Rule

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(Received January 16, 1989)

Abstract

Planar metal complexes (Cu^{2+}, Pd^{2+}, Pt^{2+}) of N-substituted ethylenediamine, *N*-{(*R*)-α-methylbenzyl}ethylenediamine (*R*-mben), *N*-{(*S*)-α-methylbenzyl}ethylenediamine (*S*-mben) and *N*-(L-menthyl)ethylenediamine (mten), have been prepared and their stereochemistry (configuration around the nitrogen and ethylene conformation) is examined in view of the vicinal effect of the chiral N-substituent. Each complex shows significant circular dichroism (CD) at the ligand field band. The CD spectra of the present complexes and related copper(II) complexes with N-substituted (*R*)-1,2-propanediamines are reasonably interpreted in terms of the regional rule (hexadecadal rule).

Introduction

Metal complexes of ethylenediamine (en) derivatives with a substituent on the ethylene backbone, such as 1,2-propanediamine, are known to prefer the equatorial conformer with respect to the orientation of the substituent [1–3]. In this way the conformation of the en chelate can be controlled as either δ or λ if a chiral diamine (*R* or *S*) is coordinated to a metal ion. For example, the preferred conformation for (*R*)-1,2-propanediamine (*R*-pn) complexes is known to be λ [1–3].

Some N-substituted (*R*)- or (*S*)-1,2-propanediamine derivatives are also known [4–7]. As far as we know, however, diamines with an asymmetric center at the N-substituent have not been used as ligands. When a chiral substituent is introduced into the nitrogen of en, the configuration about the nitrogen and thence the conformation of the en chelate of its complexes are expected to be controlled by the 'vicinal effect' of the chiral group. As an extension of our previous studies on stereochemical control of metal complexes by means of intramolecular noncovalent interactions [8], we have examined the stereochemistry of planar copper(II), palladium(II) and platinum(II) complexes of N-substituted en derivatives with a chiral group, *N*-(L-menthyl)ethylenediamine (mten), *N*-{(*R*)-α-methylbenzyl}ethylenediamine (*R*-mben), and *N*-{(*S*)-α-methylbenzyl}ethylenediamine (*S*-mben) (see Fig. 1). Related copper(II) complexes of *R*-pn derivatives possessing an achiral group at the nitrogen were reported to show complicated CD spectra [7], but any reasonable interpretation has not been made so far. Thus, this study was undertaken to rationalize the CD spectra of planar metal (Cu^{2+}, Pd^{2+}, Pt^{2+}) complexes of those N-substituted diamines on the basis of a regional rule.

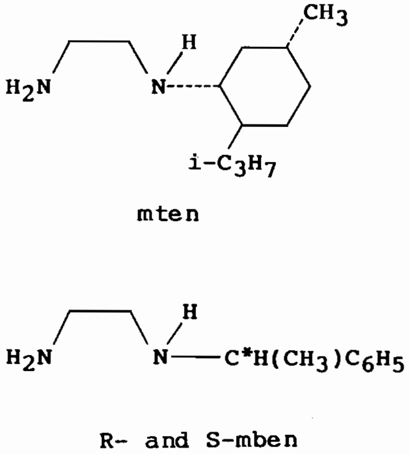

Fig. 1. Chemical structure of ligands.

Experimental

Materials

L-Menthylamine was obtained by the literature method [9]. (*R*)- and (*S*)-α-Methylbenzylamine were

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purchased from Aldrich Chemical Co. *N*-(*p*-Tolylsulfonyl)aziridine was prepared by the literature method [10].

Preparations

R-mben, *S*-mben and mten were prepared by similar procedures. The synthesis of mten is described as a representative of them. To a hot solution of L-menthylamine (3.0 g) in acetonitrile (60 cm^3) a solution of *N*-(*p*-tolylsulfonyl)aziridine (3.8 g) in acetonitrile was added dropwise, and the mixture was refluxed for 5 h. On concentrating the reaction mixture to a small portion, crude *N*-(L-menthyl)-*N'*-(*p*-tolylsulfonyl)ethylenediamine was obtained as a yellow viscous substance. This was dissolved into a mixture of acetic acid (100 cm^3) and hydrobromic acid (100 cm^3), and the solution was refluxed for 10 h. Then the volume of the solution was concentrated to *c.* 10 cm^3 and made alkaline by adding an aqueous KOH solution. *N*-(L-Menthyl)ethylenediamine was extracted with ether and purified by vacuum distillation (95 ℃/13mmHg) as colorless liquid.

The ligands were identified in their metal complexes as shown below.

[Cu(mten)$_2$](ClO$_4$)$_2$

A methanolic solution of mten (100 mg) was dropwise added to a stirred solution of copper(II) perchlorate hexahydrate (185 mg) in methanol. The resulting violet crystals were collected by filter suction, washed with a small amount of methanol, and dried *in vacuo*. *Anal.* Found: C, 43.51; H, 7.80; N, 8.47. Calc. for $C_{24}H_{52}Cl_2CuN_4O_8$: C, 43.73; H, 7.95; N, 8.50%.

[Cu(R-mben)$_2$](ClO$_4$)$_2$ and [Cu(S-mben)$_2$](ClO$_4$)$_2$

These complexes were obtained as violet prisms in a way similar to that of [Cu(mten)$_2$](ClO$_4$)$_2$. *Anal.* Found (*R*-form): C, 39.71; H, 5.27; N, 9.60; (*S*-form): 40.30; H, 5.42; N, 9.59. Calc. for $C_{20}H_{32}Cl_2CuN_4O_8\cdot 0.5H_2O$: C, 40.04; H, 5.54; N, 9.34%.

[Pd(mten)$_2$](PF$_6$)$_2$

Palladium(II) chloride (30 mg) and potassium chloride (20 mg) were stirred in water. To the resulted yellow solution was added dropwise an ethanolic solution of mten under stirring to give a clear solution. Adddition of an aqueous solution of NH_4PF_6 (slight excess) to the reaction mixture resulted in the precipitation of pale yellow microcrystals. They were collected, washed with methanol, and dried over P_2O_5 in a vacuum desiccator. *Anal.* Found: C, 35.76; H, 6.69; N, 6.67. Calc. for $C_{24}H_{52}N_4P_2F_{12}Pd$: C, 36.35; H, 6.61; N, 7.06%.

[Pt(mten)Cl$_2$]

An ethanolic solution of mten (large excess) was added to an aqueous solution of potassium tetrachloroplatinate(II) (0.4 g) with stirring and the mixture was heated for 2 h. The resulted precipitate was separated by filter suction and crystallized from acetonitrile as yellow prisms. *Anal.* Found: C, 31.08; H, 5.61; N, 6.06. Calc. for $C_{12}H_{26}N_2Cl_2Pt$: C, 31.04; H, 5.64; N, 6.03%.

Measurements

Elemental analyses of C, H, and N were obtained at the Elemental Analysis Service Center, Kyushu University. Electronic spectra were recorded on a Shimadzu UV-210 Spectrometer in acetonitrile. Circular dichroism (CD) spectra were recorded on a Jasco J-600 Spectropolarimeter in acetonitrile or pyridine at room temperature.

Results and Discussion

Copper(II) complexes of diamines generally adopt a planar configuration and the symmetry around the metal is often approximated by D_{4h}. Under this symmetry the order of d orbitals is established as: $e_g < b_{2g} < a_{1g} < b_{1g}$ [11–13]. Hence, three d–d transitions ($a_{1g} \rightarrow b_{1g}$, $b_{2g} \rightarrow b_{1g}$, and $e_g \rightarrow b_{1g}$ from lower energy) occur in the visible region, though the transitions often appear as a superposed band in electronic spectra because of similar transition energies of the d–d components. The split d–d components can be recognized by circular dichroism (CD) spectra if chiral diamines such as (*R*)- or (*S*)-pn are utilized as ligand [5].

The copper(II) and palladium(II) complexes obtained in this study are presumed to take *trans* structure with respect to the N-substituent, as demonstrated for bis(*N*-ethylenediamine)copper(II) and related complexes [14]. Based on Dreiding model considerations the *cis* structure is indeed unlikely for the mten complexes and very difficult for the mben complexes because of steric hinderance between the N-substituents in the *cis* structure.

The electronic and CD spectra of [Cu(*R*-mben)$_2$](ClO$_4$)$_2$ and [Cu(*S*-mben)$_2$](ClO$_4$)$_2$ are given in Fig. 2. Electronic spectra of the complexes in acetonitrile are exactly the same and show a superposed d–d band at 17 600 cm^{-1}. As naturally expected their CD spectra are enantiomeric to each other and show significant CD at the d–d band. Evidently an asymmetry around the nitrogen donor atom is induced by the vicinal effect of the chiral α-methylbenzyl group attached to the nitrogen and thence the en conformation is fixed to either δ or λ. The CD induced at the d–d band is apparently comprised of three components in acetonitrile. When measured in pyridine, on the other hand, four CD bands are clearly seen.

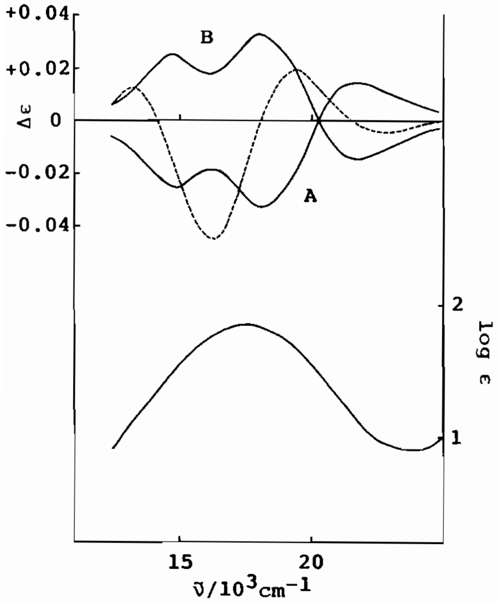

Fig. 2. Absorption and CD spectra of (A) [Cu(R-mben)$_2$]-(ClO$_4$)$_2$ and (B) [Cu(S-mben)$_2$](ClO$_4$)$_2$ in acetonitrile. The dotted line indicates the CD spectrum of [Cu(R-mben)$_2$]$^{2+}$ in pyridine.

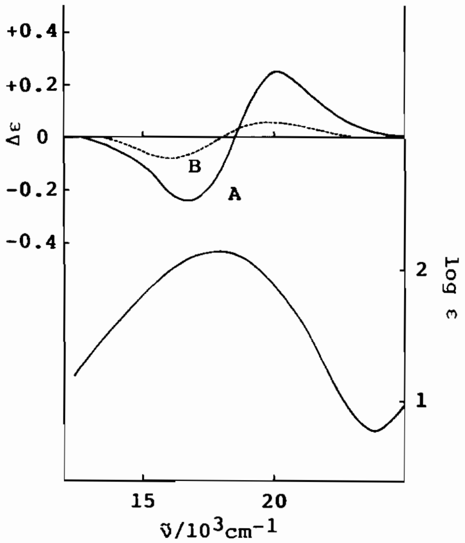

Fig. 3. Absorption and CD spectra of (A) [Cu(mten)$_2$]-(ClO$_4$)$_2$ and (B) [Cu(menthylamine)$_4$]$^{2+}$ in acetonitrile.

Resolution of four CD bands in this solvent probably results from the red shift of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition by the axial coordination of a pyridine molecule [11]. Evidently d_{xz} and d_{yz} orbitals are not degenerate in this complex irrespective of coordination and non-coordination at the axial site, and the approximation of D_{4h} symmetry is no more valid for this complex.

The absorption and CD spectra of [Cu(mten)$_2$]-(ClO$_4$)$_2$, [Pd(mten)$_2$](ClO$_4$)$_2$ and [Pt(mten)Cl$_2$] in acetonitrile are given in Figs. 3, 4 and 5, respectively.

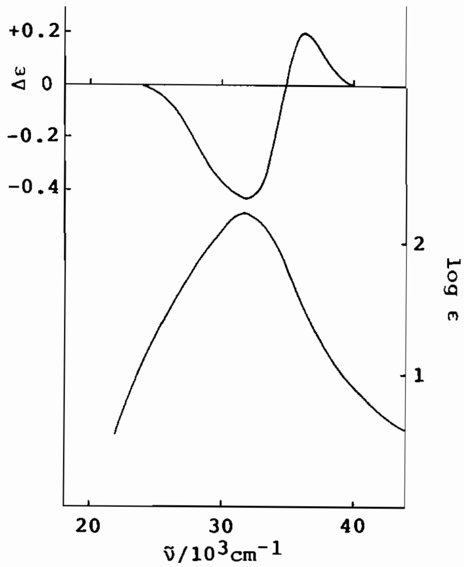

Fig. 4. Absorption and CD spectra of [Pd(mten)$_2$](ClO$_4$)$_2$ in acetonitrile.

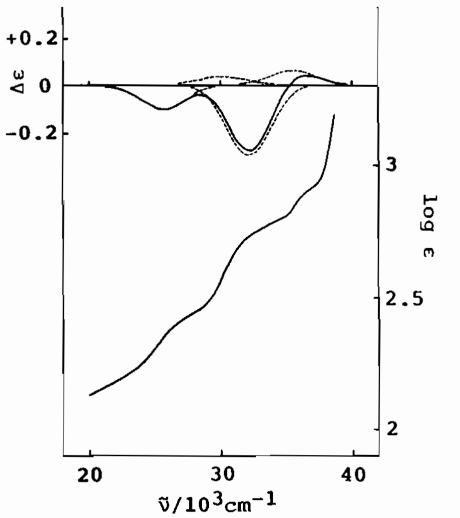

Fig. 5. Absorption and CD spectra of [Pt(mten)Cl$_2$] in acetonitrile. The dotted curves indicate the computer analysis of the spectrum based on Gaussian curve.

Again, all the complexes show significant CD at the ligand field band, indicating that the configuration around the nitrogen and thence the en conformation are controlled by the vicinal effect of the L-menthyl group attached to the nitrogen. The trace B in Fig. 3 is the CD spectrum of the copper(II) complex of L-menthylamine, prepared in acetonitrile by mixing copper(II) perchlorate and excess L-menthylamine. Marked resemblance between the traces A and B suggests that the L-menthyl group exerts a dominant effect on the optical activity at the d–d band.

For [Cu(mten)$_2$]$^{2+}$ and [Pd(mten)$_2$]$^{2+}$ two CD bands are found at the corresponding d–d band. For

[Pt(mten)Cl$_2$] of more lowered symmetry three CD bands are resolved, but the computer analysis of the CD spectrum on the basis of Gaussian curve has revealed that there are four CD components as indicated by dotted curves in Fig. 5. The result adds a support to the splitting of d_{xz} and d_{yz} orbitals. Probably the splitting of d_{xz} and d_{yz} orbitals is also the case for [Cu(mten)$_2$]$^{2+}$ and [Pd(mten)$_2$]$^{2+}$, though CD spectral analysis for these complexes are difficult.

It should be emphasized that the CD spectra of [Cu(mben)$_2$]$^{2+}$ (*R* or *S* ligand) and [Cu(mten)$_2$]$^{2+}$ apparently differ from each other. Further, previous CD spectral investigations on copper(II) complexes with N-substituted *R*-pn derivatives have shown that the CD spectral feature depends upon the nature of the N-substituent [7]. It is generally noticed that the CD sign at the highest d–d band region is inversed on N-substitution of [Cu(*R*-pn)$_2$]$^{2+}$.

It is unlikely that the order of d orbitals in [Cu(diamine)$_2$]$^{2+}$ is drastically altered when alkyl groups are substituted at the nitrogen of en or pn. We believe that the order of d orbitals for those symmetry-lowered complexes is essentially similar to that under D_{4h} ($e_g < b_{2g} < a_{1g} < b_{1g}$) except for the splitting of e_g (d_{xz} and d_{yz}) orbitals. Single crystal X-ray analysis for bis(*N*-ethylenediamine)copper(II) and related complexes [14] has revealed that the complex adopts *trans* configuration and the Cu–N distance along the unsubstituted nitrogens (we tentatively denote *x* axis) is significantly short compared with the Cu–N distance along the substituted nitrogens (*y* axis). The elongation of the Cu–N distance on the substitution at the nitrogen may be attributed to the steric effect of the N-substituent (F-strain) and this is probably the main reason for the splitting of d_{xz} and d_{yz} orbitals. The orbital order in such *trans* complexes, therefore, must be $d_{yz} < d_{xz}$.

Thus, the complexity in CD spectra of planar complexes of N-substituted diamines arises from the facts that (i) all the d orbitals are split so that all the possible d–d transitions occur in close energies and (ii) the N-substituent may cause a Cotton effect on each d–d transition. Taking into consideration these points we have rationalized qualitatively the CD spectra of those complexes in terms of a regional rule, which was applied for some chiral cobalt(III) and other metal complexes of six-coordination to correlate optical activity at d–d transitions with the substituent's orientation [15]. Octant sign rule was first applied for six-coordinate cobalt(III) complexes of various types [15], but later it was shown that the hexadecadal rule (tetragonal rule) is more suitable for *trans*-dichlorodiaminecobalt(III) complexes of *R*-pn or N-substituted en [16, 17]. Thus, the latter rule was adopted for the present purpose.

According to the hexadecadal rule, as depicted in Fig. 6, the sign of a Cotton effect induced by a substituent is defined by the sector (shaded and unshaded) to which the perturbing substituent is placed. The sign of the Cotton effect for a particular d–d transition may be determined theoretically [18] based on the Rosenfeld equation [19] or empirically from the relations observed between the optical activity at d–d transitions and the location of perturbing substituents in the coordinate frame of the metal complex [16]. The latter course is adopted here. By convention the chelate ring spans the region between the +*x* and +*y* axes. In the case of [Cu(*R*-pn)$_2$]$^{2+}$ (λ conformation) of approximated D_{4h} symmetry the ethylene chain as perturbing substituent is always placed in the shaded sector (Fig. 7A). Therefore, a substituent oriented in a shaded sector gives a positive Cotton effect to the $a_{1g} \rightarrow b_{1g}$ and $e_g \rightarrow b_{1g}$ components whereas a negative Cotton effect to the $b_{2g} \rightarrow b_{1g}$ component (or vice versa). This assignment is consistent with that for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition (corresponding to the $b_{2g} \rightarrow b_{1g}$ transition) of *trans*-[CoN$_4$L$_2$] [16]. It should be emphasized that even if d_{xz} and d_{yz} orbitals are split the $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions are not resolved in CD spectra because of the same plus sign in the Cotton effect.

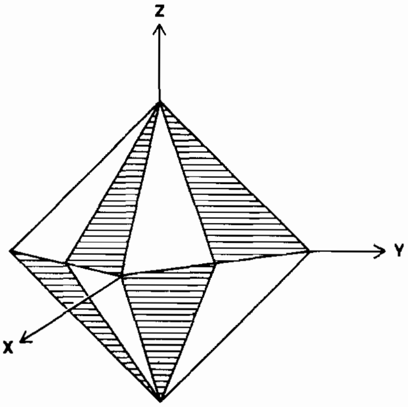

Fig. 6. Hexadecadal rule relating the position of substitution to optical activity.

The Effect of N-substitution on the Cotton Effect

Since it is generally accepted that the N-substituent prefers equatorial orientation, the N-substituent and the chain group of a diamine ligand give rise to dissymmetric potentials of opposite sign to the optical rotation at each d–d transition (see Fig. 7B). Thus, for *trans* copper(II) complexes of N-substituted en or pn derivatives the dissymmetric fields along the *x* and *y* axes differ from each other. That is, the dissymmetric field along the unsubstituted nitrogens (*x* axis) remains essentially unchanged but the field along the substituted nitrogens (*y* axis) contains a contribution from the added N-substituent. When the contribution from the N-substituent is larger than that from the chain group (this is indeed

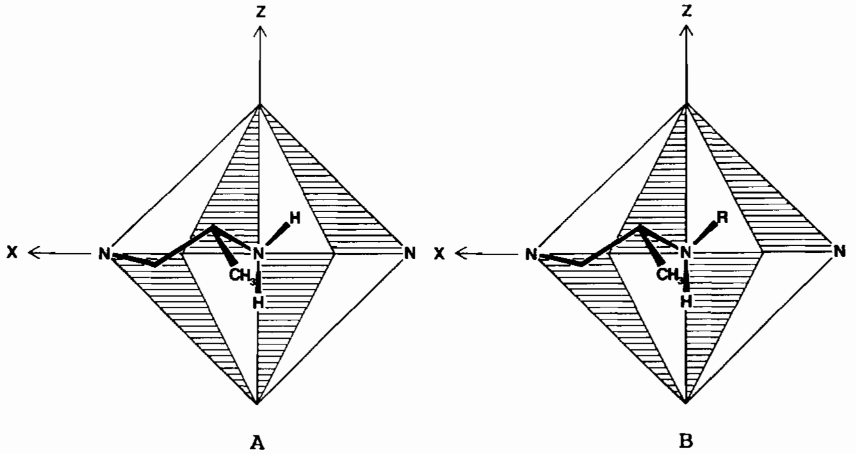

Fig. 7. The projection of diamine on xz plane for (A) R-pn and (B) N-substituted R-pn (λ conformation).

the case for the present complexes as demonstrated by the similar CD spectra of $[Cu(mten)_2]^{2+}$ and $[Cu(menthylamine)_4]^{2+}$, see Fig. 3) the sign of the Cotton effect along the y axis should be inversed. Naturally, the effect of N-substitution is mainly reflected in the CD sign of the $d_{yz} \rightarrow d_{x^2-y^2}$ transition. The CD signs of the $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are also affected by N-substitution but the effect must be much less sensitive, because the CD due to these transitions should be caused by the sum of the dissymmetric fields along the x and y axes.

Based on the above discussion the CD signs of the $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xz} \rightarrow d_{x^2-y^2}$ transitions, which are the first and second d–d components from the higher energy, can be used to diagnose the conformation (δ or λ) for planar copper(II) complexes of N-substituted en and pn derivatives. Thus, the (– and +) CD pattern from higher energy corresponds to δ conformation whereas the (+ and –) pattern to λ conformation. Therefore, the conformation is decided as δ for $[Cu(mten)_2]^{2+}$ and $[Cu(R\text{-}mten)_2]^{2+}$ and λ for $[Cu(S\text{-}mten)_2]^{2+}$.

Since the identity of the electronic absorption and circular dichroism spectra of planar d^9 and d^8 metal complexes is well known [11], the above discussions for planar copper(II) complexes are also valid for palladium(II) and platinum(II) complexes. The CD spectral pattern (+ and – from higher energy) found for $[Pd(mten)_2]^{2+}$ and $[Pt(mten)Cl_2]$ indicates δ conformation of the en chain.

CD Spectral Features for Metal Complexes of N,N′-disubstituted or N,N,N′,N′-tetrasubstituted pn Derivatives

With these ligands (L) only 1:1 type complexes like $[MLX_2]$ have been obtained because of inter-ligand steric repulsion in the 1:2 type. In this case the dissymetric fields along the x and y axes are essentially similar and both the $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions are subject to the dissymmetric effect of the equatorially-oriented N-substituent (note: in the complex with tetra-substituted pn of the substituents is axially-oriented but this substituent exerts practically no effect upon optical activity). Thus, for planar 1:1 complexes of di- and tetra-substituted R-pn derivatives the Cotton effect at the highest energy d–d transition ($d_{xz,\,yz} \rightarrow d_{x^2-y^2}$) is expected to appear as 'inversed' (– sign). The inversion of the CD sign on tetramethyl-substitution of R-pn is indeed found for palladium(II) complexes [20]. In previous papers, however, the inversion of the CD sign was attributed to a change of dissymmetric displacement of the donor nitrogens from the square plane.

In conclusion it is found that the conformation of planar complexes of en derivatives with a chiral N-substituent is fixed to either δ or λ because of the vicinal effect of the substituent. The conformation can be diagnosed by the CD induced at the d–d bands in terms of the hexadecadal rule and the principle can be applicable to planar complexes of chiral (R or S) pn and its N- and N,N′-substituted derivatives.

Acknowledgement

The authors thank the Ministry of Education of Japan for a Grant-in Aid for Scientific Research (No. 42430011).

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