Coordination Chemistry Reviews, 92 (1988) 1–28
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

NONCOVALENT INTERLIGAND INTERACTIONS IN METAL COMPLEXES

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(Received 16 April 1987)

CONTENTS

A. INTRODUCTION

Noncovalent hydrophobic interactions are known to occur in biomolecules and contribute to the formation of structural conformations required for the specificity of biological processes [1]. In the field of coordination chemistry, electrostatic and hydrogen bonding interactions play an important role in defining the distinct conformation of metal complexes. Little attention, however, has been given to bonding interactions between hydrophobic groups in complexes, though interligand steric repulsion within a complex molecule has often been used to cause distortion of the configuration around the metal ion. This is probably because the interests of coordination chemists have been directed towards the inner coordination sphere of the central metal, i.e. the coordination geometry, the character of the metal–ligand bond and the electronic structure of the metal ion.

Bonding energies between hydrophobic groups are generally weak (about 1 kcal mol^{-1}) even in water [1,2] and are weaker in polar organic solvents.

0010-8545/88/$9.80

For metal complexes with normal molecular weights, the interaction energies must be a few kilocalories at best. However, it can readily be shown that such weak interactions can have a significant effect on metal complexes. As an example, consider an equilibrium between two isomeric species A and B: $A \rightleftharpoons B$ ($K = [A]/[B]$). From the well-known relationship, $\Delta G^\circ = -RT \ln K$, between the free energy difference ΔG° and the equilibrium constant K, the value of K is calculated to be 5.4 if ΔG° is 1 kcal mol^{-1} and 29 if ΔG° is 2 kcal mol^{-1}. This means that one of the isomeric species exists predominantly in solution if the free energy difference exceeds 1 kcal mol^{-1}. At present, there is an increasing number of papers that claim the importance of noncovalent interactions in coordination chemistry.

In this article, the noncovalent interligand interactions which make significant contributions to the stereochemistry, stability and other features of metal complexes are discussed. The aim of the discussion is not to review this subject comprehensively but to illustrate the scope of the phenomenon and provide a useful foundation for future research in this little-studied area. The interactions of interest are intramolecular, but some intermolecular interactions which closely relate to essential problems in coordination chemistry are also included.

B. STEREOSELECTIVITIES

It is well known that a metal ion interacts with a dissymmetric environment through three major mechanisms: (1) the vicinal effect (chirality induced at the metal by the simple presence of an asymmetric atom on the ligand), (2) the conformational effect (chirality arising when the asymmetric atom is in a chelate ring), and (3) the configurational effect (chirality due to an asymmetric disposition of chelate rings about the metal [3]. In general, optical activity arising from the vicinal effect is at least one order of magnitude smaller than that from the conformational effect [4] and two orders of magnitude smaller than that from the configurational effect [5]. Thence the stereoselectivities of metal complexes can be inspected by the optical activity induced at the ligand-field bands, if ligands with a chiral residue are available.

The importance of intramolecular interligand interactions in stereoselectivities was first pointed out in our laboratories for the cobalt(III) complexes with Schiff's bases derived from *l*-menthyl 3-(*o*-hydroxybenzoyl)propionate (mop) and a racemic amino acid, $[Co(mop{=}aa)_2]^-$ (aa = gly, ala, val, leu) (Fig. 1) [6]. The chiral residue (*l*-menthyl) is far apart from the chelate ring, and hence the optical activity induced by its vicinal effect should be very small ($\Delta\epsilon \approx 10^{-2}$ dm^3 cm^{-1} mol^{-1}). However, the circular dichroism (CD) found in the visible region (520 nm) for these complexes is quite large. This

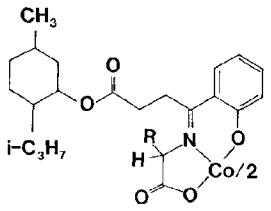

Fig. 1. Chemical structure of $[Co(mop{=}aa)_2]^-$.

fact and the observation of optical activity for $[Co(mop{=}gly)_2]^-$ clearly demonstrate that the chirality of the complexes is configurational in origin. The complexes are presumed to adopt the *mer* configuration, as demonstrated for potassium bis[*N*-(3-methylsalicylidene)threoninato]cobaltate(III) [7]. Thus an enantiomer of *mer*-$[Co(mop{=}aa)_2]^-$ is stereoselectively formed, though the absolute configuration of the preferred enantiomer (diastereoisomer to be exact) is unknown.

The complexes have been prepared in different solvents in the hope of clarifying the origin of the stereoselectivity (Table 1) [8]. It was found that the CD intensity decreased in the following order of the solvents: ethanol > methanol > dimethyl sulfoxide (DMSO) > *N*,*N*-dimethylformamide (DMF) > acetonitrile (AN). This solvent trend can reasonably be explained only in terms of an aromatic solvent-induced shift (ASIS) [9]. Thus, when determining the difference between the chemical shifts in carbon tetrachloride and in benzene, $\Delta\delta = \delta(CCl_4) - \delta(C_6H_6)$, for the molecules used as solvents, a good correlation was found between $\Delta\delta$ and the induced CD intensity $\Delta\epsilon$, as exemplified by $[Co(mop{=}val)_2]^-$ in Fig. 2. The results imply that in the solvents of low $\Delta\delta$ (equal to ASIS) (ethanol and methanol) the *l*-menthyl group in the side-chain can interact with the aromatic nucleus of the ligand, and this interaction (defined as CH/π interaction by Nishio [10]) brings about an asymmetry of the configuration of the complexes. However, in the

TABLE 1

CD intensities induced near 520 nm for $[Co(mop{=}aa)_2]^-$

Complex	Solvent				
	EtOH	MeOH	DMSO	DMF	AN
$[Co(mop{=}gly)_2]^-$	0.07	–	–	–	
$[Co(mop{=}ala)_2]^-$	0.40	0.24	0.14	0.12	0
$[Co(mop{=}val)_2]^-$	0.21	0.20	0.06	0.05	0
$[Co(mop{=}leu)_2]^-$	0.24	0.18	0.09	0.07	0

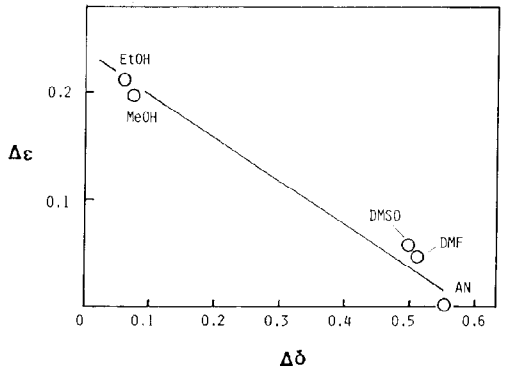

Fig. 2. Correlation between the induced CD intensity ($\Delta\epsilon$) and $\Delta\delta$ of solvents used for the preparation of $[Co(mop{=}val)_2]^-$.

solvents of high $\Delta\delta$ (DMSO, DMF and AN) the interaction between the solvent molecules and the aromatic ring is strong enough to suppress the interligand CH/π interaction.

By the use of these complexes a partial asymmetric transformation of racemic amino acids has been achieved [3].

The stereoselectivity of the complexes $[Co(cop{=}aa)_2]^-$ containing a cholesteryl residue instead of *l*-menthyl is much lower and CD is induced only in ethanol or methanol [8].

More prominent stereoselectivities are expected to occur for $[M(ab)_3]$-type complexes if three noncovalent interligand interactions operate cooperatively within the molecule. Such a ligand is 1-*l*-menthyloxy-3-benzoylacetone (H(*l*-moba)) (Fig. 3(a)), a 1,3-diketone with a chiral *l*-menthyl group and a phenyl group in the molecule [11]. For its 1 : 3-type complexes, two geometrical isomers (*fac* and *mer*) are expected and each isomer is diastereoisomeric with respect to the central atom and the chirality of the menthyl group. In the complex molecule, interligand interactions are possible between the *l*-menthyl group of one ligand and the aryl group of the neighboring ligand, and such interactions are expected to cause a stereoselectivity to afford predominantly one of the diastereoisomers (*fac*-Δ or *fac*-Λ).

The cobalt(III) complex $[Co(l\text{-moba})_3]$ isolated was suggested to prefer the *fac* configuration on the basis of ^{1}H NMR spectra [11]. This was worth noting since the cobalt(III) complexes with unsymmetrical 1,3-diketones were generally obtained as a mixture of *fac* and *mer* isomers with the predominance of the latter [12]. This complex exhibited unexpectedly large optical activity at the first *d–d* band (Fig. 4) [11], suggesting stereoselective

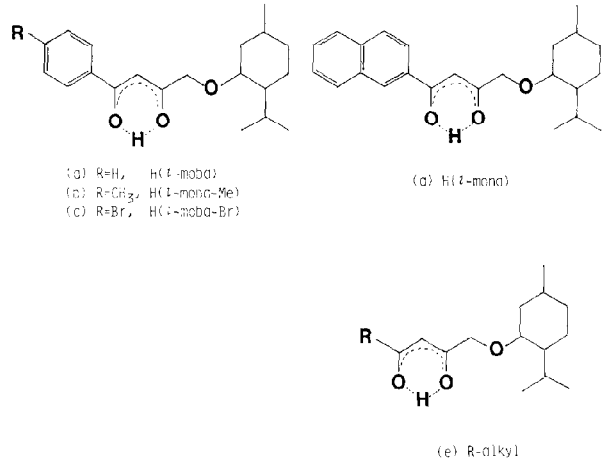

Fig. 3. Chemical structures of some 1,3-diketones with a chiral menthyl group.

formation of one of the diastereoisomers. The CD of [Co(*l*-moba)$_3$] was essentially the same in magnitude though opposite in sign as that of Λ-[Co(acac)$_3$] [13], indicating the preferred configuration of [Co(*l*-moba)$_3$] to be Δ.

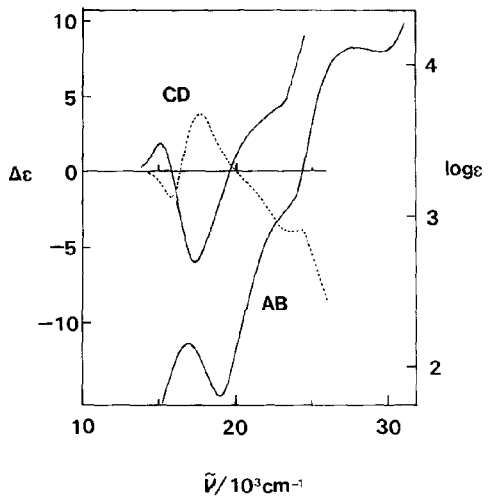

Fig. 4. Absorption (AB) and CD spectra of [Co(*l*-moba)$_3$] (———) and CD spectrum of Λ-[Co(acac)$_3$] (— — —).

The chromium(III) complex [Cr(*l*-moba)$_3$] [11] also exhibited a large CD at 15 500 and 18 500 cm^{-1} (d–d transition components of $^4T_{1g} \leftarrow {}^4A_{2g}(O_h)$ under lowered D_3 symmetry [14]). Comparison with Δ-[Cr(acac)$_3$] [15] indicated the preferred configuration of [Cr(*l*-moba)$_3$] also to be Δ. The CD intensity of this complex was about one third of that of Δ-[Cr(acac)$_3$], suggesting a partial resolution in this case.

Similar stereoselectivity was found for [Mn(*l*-moba)$_3$] [11]. This is particularly worth noting since manganese(III) complexes are in general labile and are believed to be hardly resolved because of facile racemization [16].

Further investigation of stereoselectivities of cobalt(III) and chromium(III) complexes using 1-*l*-menthyloxy-3-(*p*-methylbenzoyl)acetone (H(*l*-moba-Me) (Fig. 3(b)) [17,18], 1-*l*-menthyloxy-3-(*p*-bromobenzoyl)acetone (H(*l*-moba-Br)) (Fig. 3(c)) [17,18] and 1-*l*-menthyloxy-3-(2-naphthoyl)acetone (H(*l*-mona)) (Fig. 3(d)) [19] revealed the preferred configuration of the complexes to be always *fac*-Δ. In the complexes of 1-*l*-menthyloxy-3-acylacetones [20,21] (see Fig. 3(e)), however, the stereoselectivities observed were generally low and their preferred configurations were dependent upon the nature of the alkyl group. This suggests that interactions between alkyl (or alicyclic) groups are very weak in organic solvents and less effective than CH/π interactions in giving rise to stereoselective complexes.

From the above studies using H(*l*-moba) and its homologs, it was suggested that the noncovalent interaction controlling the stereoselectivity of the complexes could be depicted as the form of a right-handed three-bladed propeller about the metal ion (Fig. 5(a)). However, such discussions based on inert complexes are not exactly valid because we cannot rule out the possibility of isolating one form among the diastereoisomers or the operation of some kinetic mechanism in their stereoselectivity. In order to

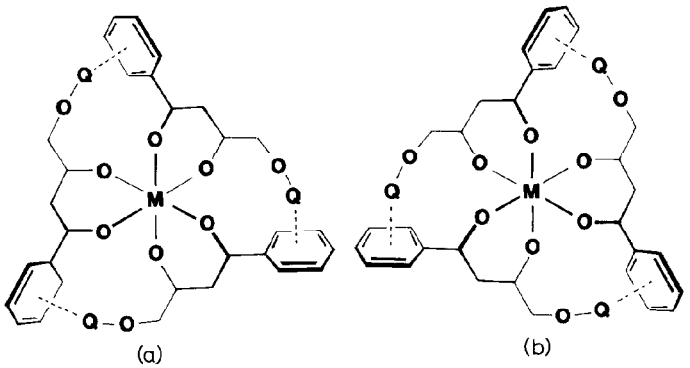

Fig. 5. Schematic representation of interligand CH/π interaction supposed for [M(*l*-moba)$_3$] (Q = *l*-menthyl).

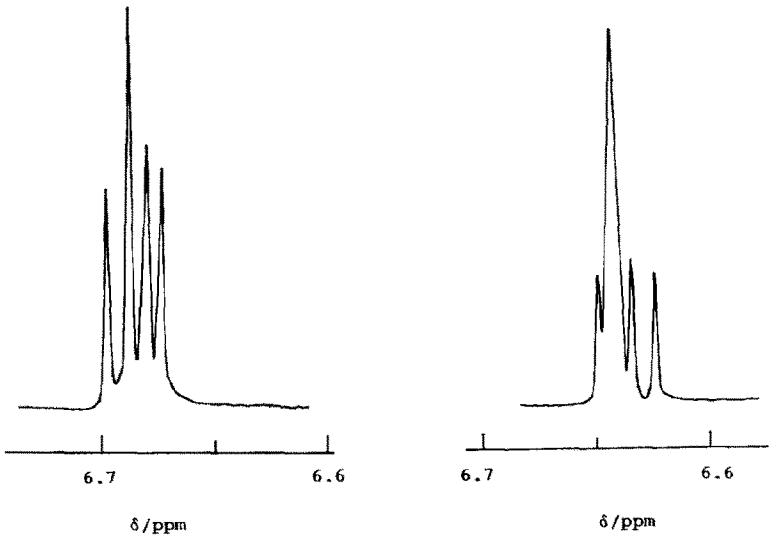

Fig. 6. 400 MHz ^{1}H NMR spectra of [Al(*l*-moba)$_3$] (left) and [Ga(*l*-moba)$_3$] (right).

demonstrate definitely the operation of noncovalent interligand interaction, the use of labile metal ions was recommended. Hence the stereoselectivities of the complexes of IIIA and IIIB elements (scandium, yttrium, lanthanum; aluminum, gallium, indium) were examined using H(*l*-moba) and H(*l*-moba-Me) [22]. The aluminum and gallium complexes showed a relatively slow isomerization in solution and their *fac* and *mer* isomers were detectable by methine proton NMR signals as shown in Fig. 6. One intense signal is attributed to the *fac* isomer and three weak signals to the *mer* isomer. The *fac*-to-*mer* ratios determined from the methine proton intensities (0.8 for [Al(*l*-moba)$_3$], 1.7 for [Al(*l*-moba-Me)$_3$], 1.5 for [Ga(*l*-moba)$_3$] and 2.5 for [Ga(*l*-moba-Me)$_3$]), exceed the statistical value (*fac*: *mer* = 1/3), demonstrating significant stereoselectivity in the complexes. For the other complexes, fast equilibrium is achieved between the isomers [23].

All the complexes showed two CD bands at the ligand π–π^* transition band near 330 nm and their CD pattern was the same (positive (+) to negative (−) change with decreasing wavelength). This implies that an equilibrium is achieved among the diastereoisomers in solution and the preferred configuration is the same for all the complexes. By comparison with the CD spectra of *l*-[Si(acac)$_3$]$^+$ [24] and *l*-[Ge(acac)$_3$]$^+$ [25], the preferred configuration was assigned to *fac*-Λ. This differs from the previous assignment in the cobalt and chromium complexes [11,17–19]. In the course of our CD spectral investigations, it was noticed that the CD spectra

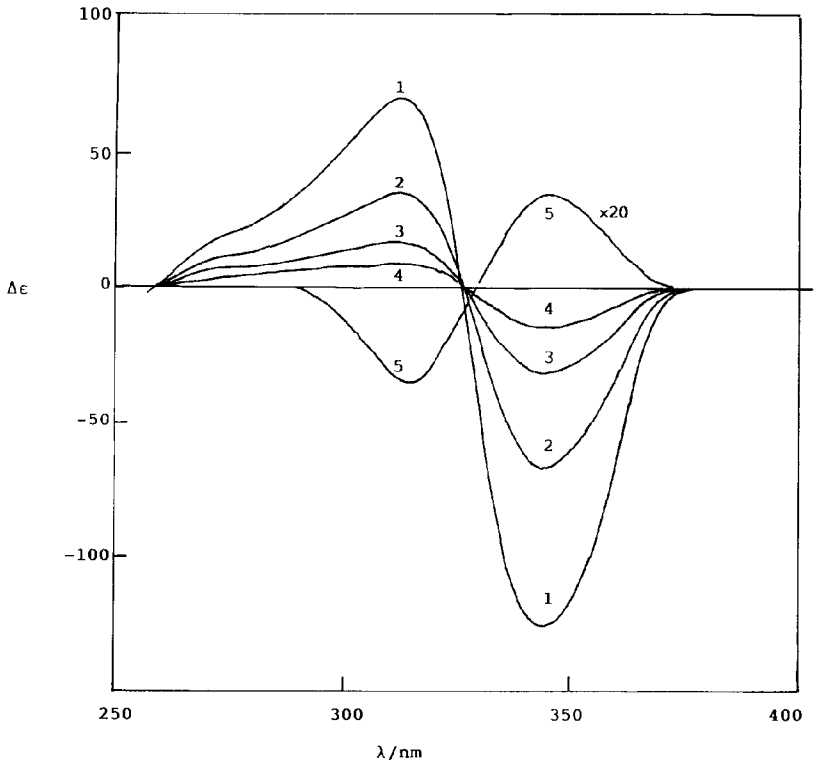

Fig. 7. CD spectral change with time of [Al(*l*-moba-Me)$_3$]: curve 1, soon after dissolution; curve 2, after 15 min; curve 3, after 25 min; curve 4, after 35 min; curve 5, after 105 min.

of the aluminum complexes changed with time as shown in Fig. 7. The spectrum obtained soon after dissolution has the (− and +) pattern which is exactly that of the Δ configuration, but the spectrum changed to that of the Λ configuration within 2 h. Evidently the aluminum complexes were obtained as *fac*-Δ, presumably because this configuration was preferred in crystal packing, but the isomer was equilibrated in solution to afford predominantly *fac*-Λ. This was probably the situation for the cobalt(III) and chromium(III) complexes, and our previous results for those complexes must be partly retracted in view of the above observation. However, noncovalent interactions undoubtedly occur and a schematic representation is the form of a left-handed three-bladed propeller as given in Fig. 5(b).

As seen in Table 2 the CD induced at the ligand π–π^* band increases on going from the scandium to the lanthanum complex or from the aluminum to the indium complex in each ligand system. Indeed, there is good correla-

TABLE 2

Absorption and CD spectral data for IIIA and IIIB element complexes [a]

	l-moba				*l*-moba-Me			
	AB	CD			AB	CD		
	λ_{max}/nm (ϵ)	$\Delta\epsilon$ (λ/nm)			λ_{max}/nm (ϵ)	$\Delta\epsilon$ (λ/nm)		
Sc	334 (44900)	−2.4	(321)	+3.0 (351)	335 (45200)	−4.2 (322)		+5.3 (353)
Y	334 (43400)	−6.4	(318)	+7.2 (349)	335 (43500)	−8.3 (326)		+9.5 (353)
La	336 (41600)	−7.6	(320)	+8.6 (355)	336 (41900)	−11.1 (322)		+11.1 (356)
Al	326 (71800)	−0.38	(316)	+0.45 (346)	326 (70900)	−1.7 (317)		+1.7 (347)
Ga	324 (63900)	−1.2	(316)	+1.7 (343)	325 (64500)	−3.0 (318)		+3.5 (348)
In	322 (47800)	−4.2	(314)	+5.5 (343)	323 (47600)	−5.8 (318)		+6.7 (347)

[a] Determined in CH_2Cl_2.

tion between $\log(\Delta\epsilon/\epsilon)$ and the ionic radius of the central atom (Fig. 8), where $\Delta\epsilon$ is the average of the absolute values of two CD bands and ϵ is the extinction coefficient of the π–π^* transition (per molecule). The result suggests that the optimum contact between the *l*-menthyl and the aryl groups is attained when the central atom is sufficiently large. This fact adds strong support to the noncovalent intramolecular interaction depicted in Fig. 5(b).

Similar studies on stereoselectivities of tris(1,3-diketonato)M(III) complexes have been made using (+)-hydroxymethylenecamphor (+hmc) [26–28] and (+)-3-acetylcamphor (+atc) [28–30]. On the basis of the resolution of the diastereoisomers for $[Co(+atc)_3]$ [29,30] and $[Cr(+atc)_3]$ [29], the isomer predominantly formed is *mer*-Λ for both cases. Their stereoselectivities, however, are relatively low and the proportion of the *mer*-Λ is only 45%–48% for $[Co(+atc)_3]$ and 38% for $[Cr(+atc)_3]$. Low stereoselectivities for those complexes may be attributed to the fact that there is little interligand contact within each molecule [31].

Recently, stereoselectivities associated with lanthanoid complexes have been investigated with chiral 1,3-diketones derived from D-camphor [32,33]. It is shown that generally the complexes exhibit no optical activity at the *f*–*f* transition bands [32] probably because of the absence of intramolecular interligand interactions within a molecule owing to the larger ionic radius of the lanthanoid ions. However, it has been found that these complexes exhibit intense optical activity when dissolved in donating solvents [33]. It is presumed that the ligation with solvent molecules causes crowding of the camphorato ligands, and the complex then adopts the configuration minimized energetically by the interligand interactions.

Lanthanoid complexes of chiral 1,3-diketones with sufficiently long side-residues to permit interligand interactions are expected to cause stereoselec-

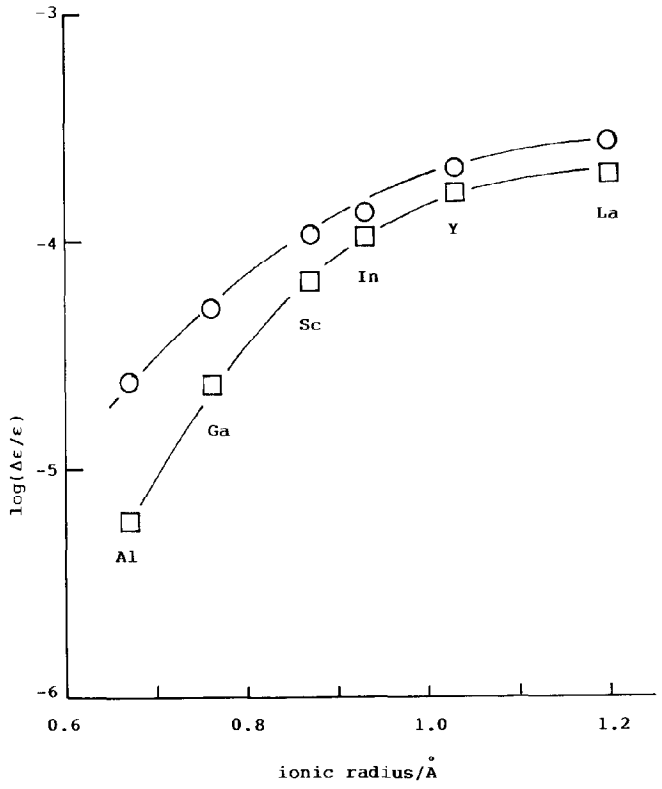

Fig. 8. Correlation between $\log(\Delta\epsilon/\epsilon)$ and ionic radius (Shannon–Prewitt) for [M(*l*-moba)$_3$] (○) and [M(*l*-moba-Me)$_3$] (□).

tivity even in nondonating solvents. Indeed, tris(D,D-dicampholylmethanato)europium(III) [33] exhibits fairly strong circular-polarized luminescence (CPL) in $CHCl_3$ or CCl_4. Lanthanoid complexes with H(*l*-moba) [34] also showed optical activity at *f–f* transition bands. The CD intensities of the complexes are significantly large when compared with those of the lanthanoid complexes of L-amino acids or optically active Schiff's bases [35,36], demonstrating the chirality to be configurational. These complexes are essentially monomeric at the concentrations used for CD measurements (10^{-2}–10^{-3} M). Hence it is reasonable to suppose that the *fac*-Λ form is predominantly formed for the complexes by analogy to the case of the IIIA and IIIB element homologs. [Ln(*l*-moba-Me)$_3$] shows a higher stereoselectivity than [Ln(*l*-moba)$_3$] [37]. This trend is the same as that found for the nontransitional element homologs [22].

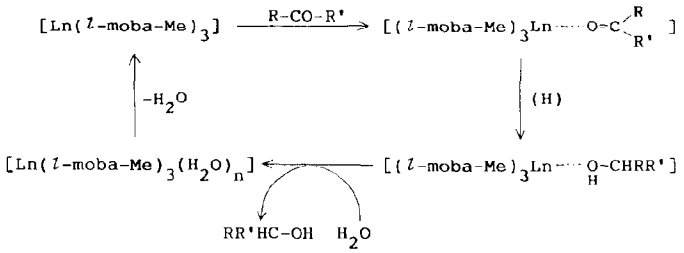

Fig. 9. Asymmetric reduction scheme of ketones to alcohols.

The sterically controlled *fac*-Λ-[Ln(*l*-moba-Me)$_3$] complexes have been applied to the asymmetric reduction of ketones to optically active alcohols [38]. The general reaction scheme is shown in Fig. 9. For example, (*R*)-1-phenylethanol was obtained in 89.4% enantiomer excess when acetophenone was reduced with $NaBH_4$ in the presence of [Gd(*l*-moba-Me)$_3$]. The function of the lanthanoid complexes is not catalytic, but the complexes can be recovered (90%) and utilized for further study.

For planar [Cu(*l*-moba)$_2$] and *trans*-octahedral [Ni(*l*-moba)$_2$(H_2O)$_2$] [39], such an interligand interaction as supposed for [M(*l*-moba)$_3$] is unlikely to occur because of the planar arrangement of the diketonate molecules. However, the CD intensities induced at the ligand-field bands are unexpectedly large when compared with those of the complexes with simple amino acids. The optical activities found presumably contain contributions from some origins other than the vicinal effect. It was found that the CD of [Ni(*l*-moba)$_2$(H_2O)$_2$] decreased in intensity and finally disappeared on adding an amine, an alcohol, DMF or DMSO. One plausible explanation is that a noncovalent interaction occurs between the *l*-menthyl group and the chelate π-system within a ligand molecule (Fig. 10) but this interaction is hindered by bulky bases coordinated at the apical sites. Single-crystal X-ray analysis for [Cu(*l*-moba)$_2$] [40] gave no direct evidence for the intraligand *l*-menthyl/chelate-π interaction but indicated the *l*-menthyl group to be in close proximity to the phenyl ring of the neighboring complex molecule.

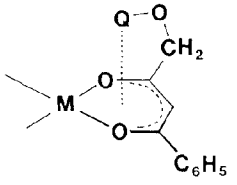

Fig. 10. Supposed menthyl/chelate-π interaction (Q = *l*-menthyl).

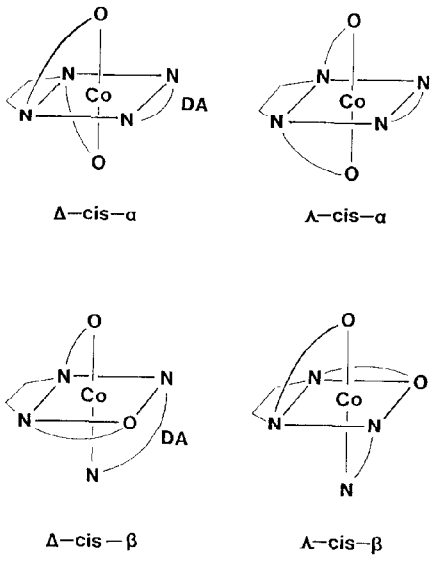

Fig. 11. Isomeric structures of [Co(*l*-mobaen)(DA)]$^+$.

Tetrahedral [Be(*l*-moba)$_2$] and [Be(*l*-moba-Me)$_2$] [22] showed intense CD at the intraligand π–π^* transition (negative to positive change with decreasing wavelength), indicating predominant formation of one of the diastereoisomers, $\Delta(l)$ or $\Lambda(l)$. The intraligand *l*-menthyl/chelate-π interaction was assumed as the origin of the stereoselectivity of this complex. However, their stereoselectivity should be discussed with care because beryllium complexes are generally inert.

Similar intramolecular noncovalent interactions occur in the complexes [M(*l*-mobaen)] (M = Cu, Ni, Co) of the quadridentate Schiff's base (H_2(*l*-mobaen)) obtained by the 2:1 condensation of H(*l*-moba) and ethylenediamine [41]. The complexes are essentially planar but show significant CD in the visible region, demonstrating that the configuration is more or less distorted towards a tetrahedron. A negative CD near 18×10^3 cm^{-1} [42,43] for the copper(II) and nickel(II) complexes indicates dextral distortion of their configurations.

Mixed chelates [Co(*l*-mobaen)(DA)]PF_6 (DA = en, tn, bip, phen) [41] were obtained by air oxidation of [Co(*l*-mobaen)] in the presence of a diamine. These complexes may adopt either the *cis*-α or *cis*-β configuration, and for these configurations the complexes are diastereoisomeric with respect to the central metal and the menthyl residue (Fig. 11). NMR spectra have revealed that the complexes where D is en or tn are of the hitherto

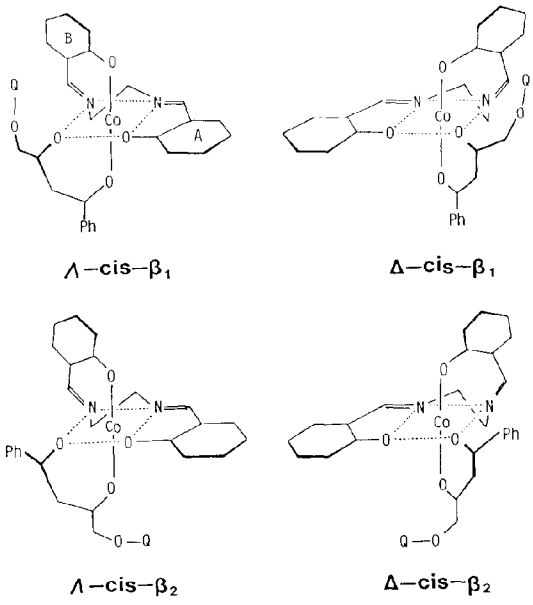

Fig. 12. Possible isomeric structures of [Co(SB)(*l*-moba)] (Q = *l*-menthyl).

unknown *cis*-α configuration, whereas the complexes where D is bip or phen are of the *cis*-β configuration. All the complexes show strong optical activity in the visible region. The preferred configuration for the bip and phen complexes is determined as Δ in the light of CD spectral results for *cis*-β cobalt(III) mixed chelates whose absolute configuration has been confirmed [44]. The preferred configuration for the en and tn complexes cannot be determined unambiguously because of the lack of CD spectral data for *cis*-α complexes, but the configuration is considered as Λ where the intraligand *l*-menthyl/chelate-π interaction dominates to maintain the same distortion of *l*-mobaen as of Δ-[Co(*l*-mobaen)]. The stereoselectivity in the bip and phen complexes (Δ-*cis*-β), however, may be associated with an interligand interaction between the *l*-menthyl group of *l*-mobaen and the π system of the diamine.

Similar stereoselectivity has been observed in mixed chelates [Co(SB)(*l*-moba)] (SB = *N*,*N*′-disalicylideneethylenediamine and homologs) [45]. For these complexes four isomers are considered with respect to the coordination attitude of *l*-moba^{2-} and the asymmetry about the central metal (Fig. 12). On the basis of ^{1}H NMR spectra, two geometrical isomers, *cis*-β_1 and *cis*-β_2, were in equilibrium with excess formation of the former ([*cis*-β_1]/[*cis*-β_2] = 3–6). Further, the absolute configuration preferred for the

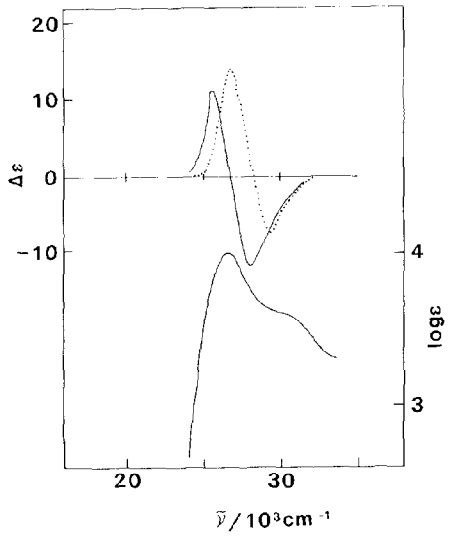

Fig. 13. Electronic and CD spectra of [Zn(sal-ment)$_2$].

cis-β_1 form was shown to be Λ by comparison with the CD spectra of mixed chelates with (1*S*,2*S*)-1,2-cyclohexanediamine instead of en. The stereoselectivities observed were attributed to the interligand interaction between the *l*-menthyl group of *l*-moba$^-$ and a benzene ring of the Schiff's base.

The stereoselectivities of [Co(SB)(L-aa)] (L-aa = L-amino acidate ion) have been extensively studied by Fujii and coworkers [46,47]. Stereoselectivities of the complexes are principally determined by interligand steric repulsions [46], but in the case of β_2-[Co(tfacen)(L-aa)] (H_2tfacen: Schiff's base derived from trifluoroacetylacetone and ethylenediamine), interligand noncovalent interactions are suggested to occur between the trifluoromethyl group and the residue of L-aa [47].

The stereoselectivities of tetrahedral or pseudotetrahedral bis(*N*-*l*-menthylsalicylaldiminato)M(II) [M(sal-ment)$_2$] and bis(*N*-*l*-menthyl-3-methylsalicylaldiminato)M(II) [M(Mesal-ment)$_2$] (M = Co, Cu, Ni, Zn) have been studied [48]. [Zn(sal-ment)$_2$] showed positive and negative CD (from lower frequency) at the π–π^* transition involving the π-orbital function of the azomethine group (Fig. 13). The CD pattern and intensity are essentially similar to those of [Zn(sal-(*R*)-pn)] [43], which is known to show a slight distortion towards a tetrahedron (sinistral chirole) owing to a conformational requirement of the (*R*)-1,2-propane bridge. This fact suggests that a high stereoselectivity occurs in this complex to produce predominantly the Λ form.

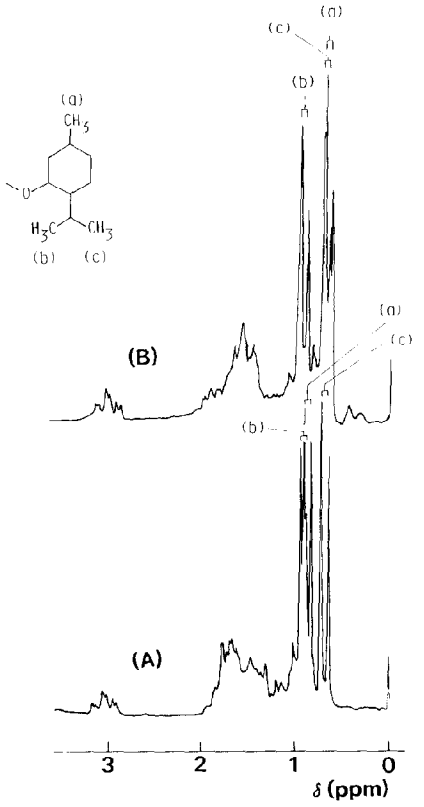

Fig. 14. ^{1}H NMR spectra of H(sal-ment) (A) and [Zn(sal-ment)$_2$] (B).

The ^{1}H NMR spectra of H(sal-ment) and [Zn(sal-ment)$_2$] were compared to gain insight into the origin of this stereoselectivity (Fig. 14). Methyl signals for the free ligand are seen at 0.930, 0.883 and 0.704 ppm, while the methyl signals for [Zn(sal-ment)$_2$] are seen at 0.937, 0.708 and 0.675 ppm. Inspection of both spectra reveals that only the 0.883 ppm signal (attributable to the methyl (a) [49]) shifts significantly upfield on complexation. It is suggested that the methyl (a) of the *l*-menthyl residue interacts with the π system of the neighboring ligand (chelate-π or aromatic-π, or both) and this interaction leads to the stereoselective formation of the isomer of the complex.

Similar stereoselectivity occurs in [Cu(Mesal-ment)$_2$], which bears a marked CD spectral similarity to [Cu(sal-(*R*)-pn)] (with sinistral chirole) in the visible to near-UV region.

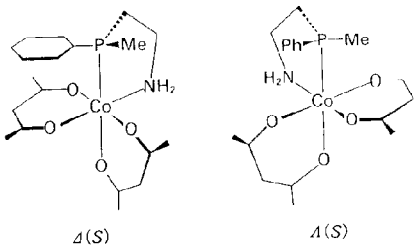

Fig. 15. Diastereoisomeric isomers of $[Co(acac)_2(aebpp)]^+$.

Pseudotetrahedral $[Ni(sal\text{-}ment)_2]$ and tetrahedral $[Co(sal\text{-}ment)_2]$ and $[Co(Mesal\text{-}ment)_2]$ also showed significant CD at their *d–d* bands, demonstrating a high stereoselectivity in these complexes. It is natural to assume the Λ configuration for the complexes.

Novel stereoselectivity associated with the interaction between an aromatic ring and the acac chelate ring has been suggested for the bis(acetylacetonato)cobalt(III) complexes with aminoalkylphosphine chelates [50]. The complexes are diastereoisomeric with respect to the central metal and the asymmetric phosphorus if different groups are on the phosphorus atom. For $[Co(acac)_2(aebpp)]^+$ with (*S*)-aminoethylbutylphenylphosphine (aebpp), for example, the Δ-*S*/Λ-*S* ratio was found to be 2.7. An analogous stereoselectivity was recognized for $[Co(acac)(en)(aempp)]^{2+}$ (aempp = aminoethylmethylphenylphosphine) (Δ-*S*/Λ-*S* = 1.6), while no stereoselectivity occurred in $[Co(en)_2(aempp)]^{3+}$. For the diastereoisomers of $[Co(aac)_2(aebpp)]^+$ and $[Co(acac)(en)(aempp)]^{2+}$ a distinct structural difference is seen in the orientation of the phenyl substituent. For the Δ-*S* isomer the phenyl is located above the acac chelate rings with an interplane distance suitable for stacking, while such a phenyl/chelate parallel arrangement is impossible in the Λ-*S* isomer (Fig. 15).

C. STABILITY ENHANCEMENTS IN TERNARY COMPLEXES

(i) Nucleotide complexes

Sigel and coworkers have studied ternary complexes such as M^{2+}(nucleotide)(phen) as models of enzyme/metal ion/substrate interactions in biological systems and found that the stacking occurring between the purine or pyrimidine ring of a nucleotide and the aromatic part of bipy or phen significantly enhances the stabilities of the ternary complexes [51–58].

Consider the M^{2+}/ATP^{4-}/phen system [56] as an example. The stability constants of the ternary systems are defined by eqns. (1)–(3):

$$M^{2+} + ATP^{4-} + \text{phen} \rightleftharpoons M(ATP)(\text{phen})^{2-}$$

$$\beta^{M}_{M(ATP)(\text{phen})} = [M(ATP)(\text{phen})]/[M][ATP][\text{phen}] \quad (1)$$

$$M(ATP)^{2-} + \text{phen} \rightleftharpoons M(ATP)(\text{phen})^{2-}$$

$$K^{M(ATP)}_{M(ATP)(\text{phen})} = [M(ATP)(\text{phen})]/[M(ATP)][\text{phen}] \quad (2)$$

$$M(\text{phen})^{2+} + ATP^{4-} \rightleftharpoons M(ATP)(\text{phen})^{2-}$$

$$K^{M(\text{phen})}_{M(\text{phen})(ATP)} = [M(ATP)(\text{phen})]/[M(\text{phen})][ATP] \quad (3)$$

The overall stability constant $\beta^{M}_{M(ATP)(\text{phen})}$ is connected with $K^{M(ATP)}_{M(ATP)(\text{phen})}$ and $K^{M(\text{phen})}_{M(\text{phen})(ATP)}$ by eqn. (4) and eqn. (5) respectively:

$$\log K^{M(ATP)}_{M(ATP)(\text{phen})} = \log \beta^{M}_{M(ATP)(\text{phen})} - \log K^{M}_{M(ATP)} \quad (4)$$

$$\log K^{M(\text{phen})}_{M(\text{phen})(ATP)} = \log \beta^{M}_{M(ATP)(\text{phen})} - \log K^{M}_{M(\text{phen})} \quad (5)$$

Then one obtains the relationship

$$\Delta \log K_M = \log K^{M(ATP)}_{M(ATP)(\text{phen})} - \log K^{M}_{M(\text{phen})}$$

$$= \log K^{M(\text{phen})}_{M(\text{phen})(ATP)} - \log K^{M}_{M(ATP)} \quad (6)$$

$\Delta \log K_M$ corresponds to the equilibrium constant of the equation

$$M(ATP)^{2-} + M(\text{phen})^{2+} \rightleftharpoons M(ATP)(\text{phen})^{2-} + M^{2+}$$

When taking into account only statistical effects, $\Delta \log K_M$ should be -0.4 for octahedral complexes and -0.6 for tetrahedral complexes [59].

TABLE 3

$\Delta \log K_M$ values for ternary complexes $[M(ATP)\text{phen}]^{2+}$

M^{2+}	$\log K^{M}_{M(ATP)}$	$\log K^{M}_{M(\text{phen})(ATP)}$	$\Delta \log K_M$
Ca^{2+}	3.88	4.52	+0.64
Mg^{2+}	4.24	4.65	+0.41
Mn^{2+}	4.91	5.03	+0.12
Zn^{2+}	5.10	5.32	+0.22
Cu^{2+}	6.03	6.08	+0.05

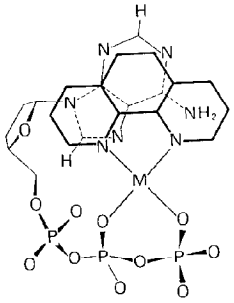

Fig. 16. Intramolecular stacking supposed for $[M(phen)(ATP)]^{2-}$.

$\Delta \log K_M$ values for $M(ATP)(phen)^{2-}$ determined by potentiometric titration are given in Table 3 [56]. Notably all the $\Delta \log K_M$ values found for $M(ATP)(phen)^{2-}$ are much larger than the statistical value of -0.4. This implies that ATP^{4-} preferentially combines with $M(ATP)^{2-}$ rather than M^{2+}. A new absorption in the near-UV region for the ternary complexes is taken as good indication of a charge-transfer-type stacking interaction between the purine and phenanthroline ring. The supposed stacking interaction is schematically shown in Fig. 16.

NMR spectral evidence for the interligand stacking is given in Fig. 17 with the Zn^{2+}/UTP^{4-}/bipy system [57] as an example. In comparing the spectra of UTP^{4-} and the UTP^{4-}/bipy system, no substantial shift of the

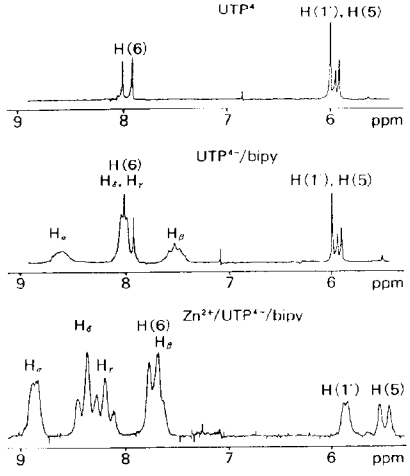

Fig. 17. ^1H NMR spectra of UTP^{4-}, UTP^{4-}/bipy and Zn^{2+}/UTP^{4-}/bipy systems.

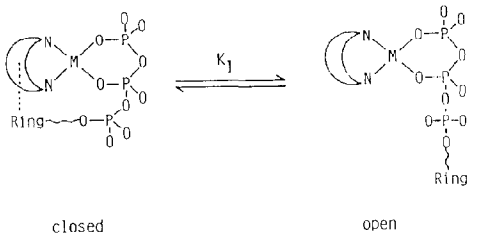

Fig. 18. Equilibrium between the closed and open isomers.

UTP^{4-} protons is observed. When zinc(II) ion is added to the UTP^{4-}/bipy system, the spectrum dramatically changes owing to the occurrence of the uridine/bipy stacking. The interaction between uridine and bipy is intramolecular in the Zn^{2+}/UTP^{4-}/bipy system while intermolecular in the UTP^{4-}/bipy system.

The ternary complexes have been found to exist as the closed (stacked) and open isomers which are in equilibrium in solution (Fig. 18) [58]. Intramolecular isomerization constants K_I (= [closed]/[open]) have been estimated by ^1H NMR shift measurements. It is generally found that K_I decreases with the change of the base as phen, bipy and trp^-. This suggests that the size of the π system is important for effective interligand stacking.

The formation constants of the ternary system, $Cu^{2+}/ATP^{4-}/A$ (A = bipy, phen and others), have been determined in dioxane–water solutions [60], and it was found that the intramolecular stacking interaction between the tertiary amine and the purine moiety decreases in the following order of solvents: water > 25% dioxane > 50% dioxane (Table 4).

The ternary complexes involving an amino acidate group instead of the tertiary amines have also been investigated by potentiometric titrations and the ^1H NMR technique [61,62]. The results suggested intramolecular hydrophobic interactions between the purine moiety and the alkyl residues of

TABLE 4

Δ log K values of the ternary complexes [CuA(ATP)] in aqueous, 25vol.%dioxane–75vol.% water and 50vol.%dioxane–50vol.%water media

Complex [a]	Aqueous medium	25vol.%dioxane –75vol.%H_2O	50vol.%dioxane –50vol.%H_2O
$[CuA^1(ATP)]$	+0.58	−0.15	−0.24
$[CuA^2(ATP)]$	+0.05	−0.10	−0.29
$[CuA^3(ATP)]$	–	+0.57	+0.25
$[CuA^4(ATP)]$	–	−1.10	−1.23

[a] A^1 = bip; A^2 = phen; A^3 = 2-(2′-pyridyl)benzimidazole; A^4 = 2-(2′-pyridyl)imidazoline.

amino acidates, except for the case with the alaninate group. The increase in stability for these complexes is rather small compared with the ternary complexes with the tryptophanate group, in agreement with the general recognition that the ring/alkyl interaction is weaker than the ring/ring stacking.

Thermodynamic investigations have been carried out for the ternary systems with ATP^{4-} and the tryptophanate or alaninate group [63]. The larger positive ΔH and less positive ΔS accompanying formation of $[M(ATP)(trp)]^{3-}$ compared with $[M(ATP)(ala)]^{3-}$ were attributed to the presence of the interligand stacking in the former complex.

Recently, the structures of ternary complexes with nucleotides or their analogs have been determined by X-ray analyses [64–69]. The results have provided direct evidence for intramolecular stacking between purine and bipy or phen in some ternary complexes [64–66], though intramolecular interactions that might occur in solutions are often overwhelmed by the intermolecular interactions in crystals.

(ii) Amino acidate complexes

About 20 years earlier it was found that some ternary complexes of amino acids (ML^1L^2) are more stable than their parent complexes (ML^1_2 and ML^2_2) [70–75]. For complexes composed of an acidic amino acid (asp, glu etc.) and a basic amino acid (arg, lys etc.), an electrostatic interaction operating between the acidic and basic residues stabilizes the ternary complexes relative to their parent complexes [76–80]. However, such a stabilization has also been recognized for complexes with a combination of amino acids where no electrostatic interaction occurs [61,81,82]. For those complexes it is noted that one (or both) of the amino acidate ligands contains an aromatic residue. Fisher and Sigel [61] have shown that interligand hydrophobic interactions (π/π stacking of rings or CH/π interaction between a ring and an alkyl group) contribute to the stabilization of the ternary complexes. For these amino acidate complexes the closed and open isomers are also in equilibrium. In general, K_1 is larger when both amino acidates contain an aromatic residue. For example, the closed-isomer percentage is 90% for Cu(D-his)(L-trp), while it is only 15% for Cu(D-his)(L-val) and nearly 0% for Cu(D-his)(L-leu) [61].

As expected, the interligand interaction is naturally dependent upon the chiralities of the amino acidate groups, and thence stereoselectivities of the complexes appear. For example, Cu(L-his)(L-trp) is more stable than Cu(L-his)(D-trp), while Cu(D-his)(L-phe) is more stable than Cu(L-his)(L-phe) [61].

Similar interligand interactions contributing to stability enhancement have also been recognized for ternary complexes composed of an amino

acidate and bipy or phen [61,83,84]. Yamauchi and Odani [83] have evaluated the interligand stacking effect upon the stabilization of Cu(DA)(AA) on the basis of the following equation:

$$Cu(DA)(Ala) + Cu(en)(AA) \overset{K}{\rightleftharpoons} Cu(DA)(AA) + Cu(en)(Ala)$$

$$\log K = \log \beta_{Cu(DA)(AA)} + \log \beta_{Cu(en)(Ala)} - \log \beta_{Cu(DA)(Ala)} - \log \beta_{Cu(en)(AA)}$$

In this case the interligand interaction is possible only for Cu(DA)(AA), and log K means the stability of the complex relative to Cu(en)(Ala). The stability order determined is phen > 2-aminoethylpyridine > histamine for Da and Htrp > try > tyr for AA, and Cu(phen)(Htry) showed the largest stabilization (log $K = 2.22$). The interligand stacking interaction in solution is supported by ^{1}H NMR spectral investigations for Pd(II) homologs [84]. X-ray structural analyses for [Cu(phen)(L-tyr)]$ClO_4 \cdot 3H_2O$ and [Cu(hista)(L-tyr)]ClO_4 have revealed the intramolecular interligand stacking in these complexes [85].

The stereoselectivities in the formation of metal(II) complexes of dipeptides have been studies in aqueous solution, and it is found that the stabilities of copper(II) complexes of optically "pure" deprotonated dipeptides with side-residues (DD or LL diastereoisomers) are more stable than those of their "mixed" counterparts (DL or LD diastereoisomers) [86–89]. It is believed that the positive stabilization found for the optically "pure" complex is the result of the hydrophobic interaction between the two residues, which are on the same side with respect to the coordination plane and close to each other in the DD (or LL) complex but are on opposite sides of the basal plane in the DL (or LD) complex. This was supported by a thermodynamic investigation on a series of copper(II) complexes of diastereoisomeric couples of dipeptides [90]: the enthalpy changes accompanying the formation of the complexes with DD (or LL) diastereoisomers are significantly less positive than those associated with the corresponding DL (or LD) species.

(iii) Other ternary complexes

Stability enhancements by interligand stacking have been reported for the ternary complexes of a sulfate or a carboxylate containing a hydrophobic residue and bipy or phen [91,92]. In the Cu^{2+}/phen/phCA$^-$ system (phCA$^-$ = benzoate, 2-phenylacetate, 3-phenylpropionate, 4-phenylbutylate, 5-phenylvalerate) [91], the intramolecular stacking between the phenyl ring of phCA$^-$ and phen is maximal when phCA$^-$ is 3-phenylpropionate.

D. OTHER CONTRIBUTIONS

(i) Pfeiffer effect

Miyoshi et al. studied the Pfeiffer effect for solutions of $[M(phen)_3]^{2+}$ ($M = Co^{II}$, Ni^{II}, Zn^{II}) involving *d*-cinchonine hydrochloride, *l*-strychnine or *d*-α-bromocamphor-π-sulfonate as an environmental compound, and suggested the importance of a hydrophobic interaction based on the effect of a salt or an alcohol added to the solutions [93,94]. However, electrostatic interaction plays a role in the Pfeiffer effect in the $[Cr(ox)_3]^{3-}$/*d*-cinchonineH^+ system [95]. The enriched enantiomer is of the Δ form for $[M(phen)_3]^{2+}$ whereas it is of the Λ form for $[Cr(ox)_3]^{3-}$. Thus molecular recognition of hydrophobic origin differs from that of electrostatic origin, reflecting the fact that alkaloids can have multiple recognition sites.

Pfeiffer effects for $[Co(phen)_3]^{2+}$ and $[Cr(ox)_3]^{3-}$ were compared using *d*-cinchonine · HCl and related alkaloids as environmental compounds (Fig. 19) [96]. The direction of the equilibrium shift for $[Co(phen)_3]^{2+}$ is determined by the configuration around the C-9 atom to which the quinolyl group is attached. It is presumed that $[Co(phen)_3]^{2+}$ associates with the cinchonium ion through hydrophobic stacking with the quinolyl ring. However, $[Cr(ox)_3]^{3-}$ is subject to the asymmetry around the C-8 atom, probably through the electrostatic interaction with the positive charge on the N(1) atom to which the asymmetric C-8 is directly bound.

If the hydrophobic and electrostatic interactions operate cooperatively in the Pfeiffer effect with alkaloids, the equilibrium shift between the enantiomers should be considerably enlarged. This has been realized in the $[Cr(ox)_2(phen)]^-$/*d*-chinidineH^+ system [96] where both hydrophobic stacking between phen and the quinoline ring of the alkaloid and electrostatic bonding between ox^{2-} and NH^+ of the alkaloid are possible in the Δ isomer (Fig. 20), leading to high enrichment of this enantiomer. More detailed examinations on the Pfeiffer effect of $[Cr(ox)_2(phen)]^-$ and $[Cr(ox)_2(bipy)]^-$

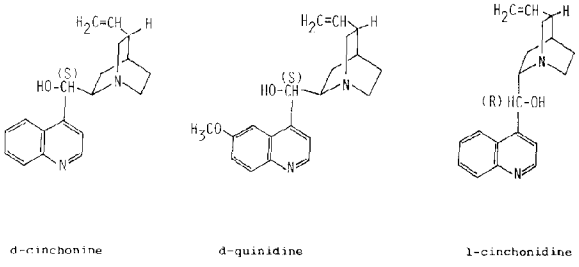

Fig. 19. Stereochemistries of some alkaloids.

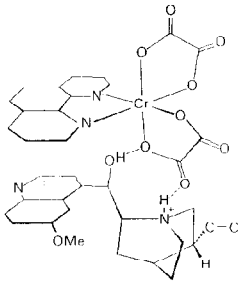

Fig. 20. Intermolecular interactions supposed for $[Co(ox)_2(phen)]^-$/*d*-chinidineH^+.

were recently carried out with the monochloride alkaloid salts, their N(1)-methyl and 9-acetoxy derivatives in water, and the discriminating interactions of the alkaloids were applied to the resolution of $[Cr(ox)_2(phen)]^-$ [97].

(ii) Resolution by chirality recognition

The salting effect of Δ-$[Ni(phen)_3]^{2+}$ on the solubility of racemic $[M(acac)_3]$ ($M = Co^{III}$, Cr^{III}) was investigated [98], and it was found that the Δ form of the enantiomers was extracted more than the Λ form, enriching in the aqueous phase. The salting-in effect is explained in terms of the attractive force between $[Ni(phen)_3]^{2+}$ and $[M(acac)_3]$ through hydrophobic interactions, where two complexes can come close to each other along their C_3-fold axis only in the Δ-Δ pair. The percentage resolution of $[M(acac)_3]$ was low but could be improved up to 20% by applying the salting-in effect of the $[Ni(phen)_3]^{2+}$ ion to chromatography with SP-Sephadex [99].

In contrast with the above situation, the Λ isomer of $[Fe(phen)_3]^{2+}$ was preferentially adsorbed on a clay (montmorillonite) modified by Δ-$[Ni(phen)_3]^{2+}$ [100]. This selectivity is presumed to arise from the tendency of Δ-$[Ni(phen)_3]^{2+}$ to pair with the Λ form of $[Fe(phen)_3]^{2+}$ on the silicate sheet of the clay through side-by-side molecular stacking. Using this clay, the cobalt(III) chelates of the type $[Co(acac)_2(aa)]$ (aa = amino acidate ions) have been partially resolved into configurational isomers, and the effect of the side-chain residue of the amino acid on molecular recognition has been discussed [101].

(iii) Coordination kinetics

The rates of complex formation of $[NiX]^{2+}$ (X = phen, 5-Mephen, 3,4,7,8-Me_4phen, bipy, terpy) with NH_3, benzylamine and aromatic bases have been determined by stopped-flow techniques [102]. In the case of aromatic

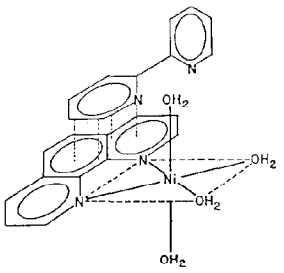

Fig. 21. A possible stacking interaction between bipy and $[Ni(phen)(H_2O)_4]^{2+}$.

bases the rate constants for these reactions were much greater than those with $[Ni(H_2O)_6]^{2+}$. The large rate enhancements on complex formation have been attributed to the stacking interaction between the coordinated ligand and the incoming ligand. The supposed stacking interaction can assist the substitution rate only if the incoming ligand is sufficiently flexible to permit one donor group to be oriented in a position suitable to replace a water molecule while the rest of the molecule is in a stacked arrangement. Thus bipy addition to $[Ni(phen)(H_2O)_4]^{2+}$ is 24 times faster than ammonia addition, whereas phen addition is only twice as fast: the more flexible bipy can interact as shown in Fig. 21, whereas phen cannot. The formation rate constants generally increase when the size of the π system in the bound ligand becomes larger. Further, it was found that the rate enhancements were greatly reduced in 65vol.% MeOH–35 vol.%H_2O.

(iv) Effects on electronic properties at metal center

It is known that some planar complexes form molecular complexes with organic electron donors or acceptors by so-called Mulliken's charge-transfer (CT) interactions [103–105]. Such CT complexes have been characterized by strong absorption in the visible to near-IR region.

Recently, we have examined Cu(II)–Ni(II) complexes of "strati-bis" Schiff's bases, H_4(*R*-sata) and H_4(*R*-sacta) (Fig. 22) [106]. The complexes are regarded as "mononuclear" with the $[NiN_2O_2]$ residue, since the nickel(II) ion is diamagnetic. The ESR parameters $A_{\parallel}$ and $g_{\parallel}$ due to the copper were found to differ considerably from those of the relevant mononuclear copper(II) complexes. Reduced $A_{\parallel}$ values imply electron delocalization from the $[CuN_2O_2]$ part to the $[NiN_2O_2]$ part to stabilize the copper(I) state in the stacked configuration. Indeed, the reduction of copper(II) to copper(I) in the CuNi complexes occurs at a higher potential than in the relevant Cu complexes, and the reduced $Cu^{I}Ni^{II}$ species were found to be considerably

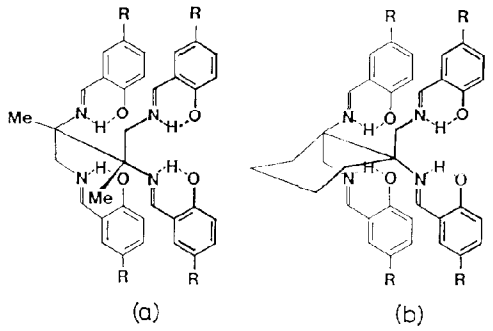

Fig. 22. Chemical structures of (a) H_4(*R*-sata) and (b) H_4(*R*-sacta).

stable to oxidation by molecular oxygen. On the basis of the shifts in redox potential (0.4–0.5 V), the stabilization energy of the copper in the CuNi complexes is estimated at about 8–12 kcal mol^{-1}. Similar positive shifts in redox potential were observed for the Cu_2^{II} [107], Fe_2^{II} [108], Fe_2^{III} [108], Mn_2^{II} homologs [109].

The above results strongly suggest the possibility that interligand hydrophobic interactions can affect the electronic properties of the central metal ion.

E. CONCLUDING REMARKS

From the above discussion it is evident that noncovalent interligand interactions play significant roles in various ways in metal complexes, especially in the shift of equilibria among complex species. It should be emphasized that the interactions often occur even in organic solvents and give rise to pronounced effects on metal complexes. Further detailed investigation of noncovalent interligand interactions by the use of simple metal complexes may serve to gain a comprehensive understanding of the more subtle chemical and physical characteristics of complexes and their reactivities. Such investigations may also serve to provide an insight into the complicated phenomena of metal-containing biological systems and the design of new complexes of functional significance.

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