Coordination Chemistry Reviews, 29 (1979) 87—127

ISOMERISM IN COMPLEXES OF BIDENTATE LIGANDS WITH ENANTIOTOPIC DONOR ATOMS

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(Received 30 January 1979)

CONTENTS

ABBREVIATIONS

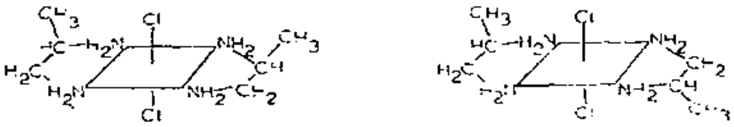
acac	2,4-pentanedionate(1-)
bn	2,3-butanediamine
bipy	bipyridyl
chn	1,2-cyclohexanediamine
cpn	1,2-cyclopentanediamine
dach	1,4-diazacycloheptane
das	2,3-diaminosuccinate(2-)
dptn	1,3-diphenyl-1,3-propanediamine
dtch	1,4-dithiacycloheptane
dtd	5,8-dithiadodecane
dth	2,5-dithiahexane

dto	3,6-dithiaoctane
EDDA	ethylenediaminediacetate
en	1,2-ethanediamine
Et_2Me_2en	3,4-dimethyl-3,4-hexanediamine
Ettn	2-ethyl-1,3-propanediamine
gly	glycinate
ibn	1-methyl-1,2-propanediamine
Metn	2-methyl-1,3-propanediamine
N,N'-Et_2en	*N,N'*-diethyl-1,2-ethanediamine
N,N'-Me_2dmtn	*N,N'*-dimethyl-2,2-dimethyl-1,3-propanediamine
N,N'-Me_2en	*N,N'*-dimethyl-1,2-ethanediamine
N,N'-Me_2tn	*N,N'*-dimethyl-1,3-propanediamine
ox	oxalate(2-)
pte	1,2-bis(phenylthio)ethane
pn	1,2-propanediamine
ptn	2,4-pentanediamine
stien	1,2-diphenyl-1,2-ethanediamine
TACN	1,4,7-triazacyclononane
tn	1,3-propanediamine
tnBr	2-bromo-1,3-propanediamine
tnCl	2-chloro-1,3-propanediamine
tnOH	1,3-diamino-2-propanol
tnSCN	2-thiocyano-1,3-propanediamine

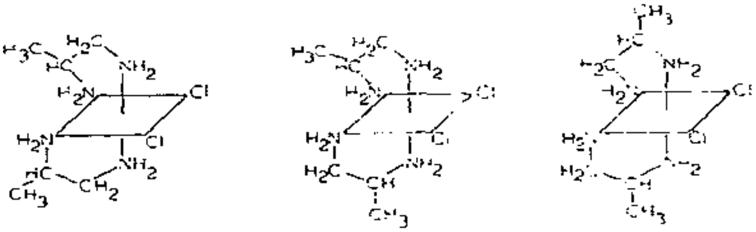
A. INTRODUCTION

It has long been recognized that metal ion complexes containing unsymmetrical "AB" [1] bidentate ligands, such as amino acids and unsymmetrical diamines, may exhibit geometrical isomerism dependent upon the end-for-end orientations of the AB ligands. Thus, in 1907, it was pointed out by Werner and Fröhlich [2] that the presence of the unsymmetrical ligand 1,2-propanediamine leads to two possible isomers in *trans*-$[Co(pn)_2Cl_2]^+$ and to three isomers in the *cis* complex (excluding isomerism resulting from chiral centers) (Fig. 1).

Although Werner eventually separated geometrical isomers resulting from the presence of 1,2-propanediamine in a complex (*cis*-$[Co(en)(pn)(NO_2)_2]^+$) [3], other workers had by that time reported [4] the separation of two isomers of tris(glycinato)cobalt(III) which were correctly ascribed as being due to the unsymmetrical nature of the ligand. It is now known that the red, nearly insoluble β form of $[Co(gly)_3]$ is the facial isomer while the violet, soluble α form is the meridional isomer [5] (Fig. 2). Meridional isomers have also been termed "meridonal" [6], "meridianal" [7] and "meridial" [8]. The designations "*cis*" and "*trans*" [5], "bis-*cis*" and "*trans-cis*" [5], "1, 2, 3" and "1, 2, 4" [4], "*cis-cis*" and "*cis-trans*" [9], "facial" and "peripheral" [10], and "1, 2, 3" and "1, 2, 6" [11] are other terms which have been used to



trans

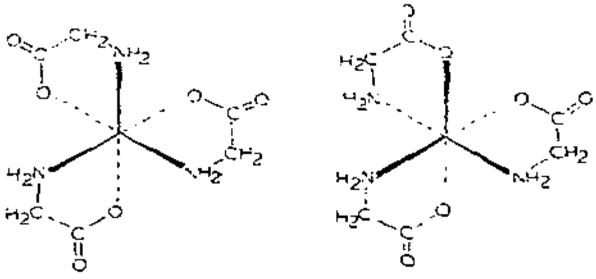


cis

Fig. 1. Geometrical isomerism in $[Co(pn)_2Cl_2]^+$.

distinguish the geometrical isomers of tris AB complexes or of the related Ma_3b_3 compounds.

The isomerism discussed above is dependent upon the distinguishability of the donor atoms (ligators) of the AB bidentate. The chemical dissimilarity may be due to elemental differences in the ligators themselves, as in monothioacetylacetonate (I) [7], environmental differences, as in 1,2-propanediamine (II), or both, as found in α-aminoacidate ligands (III). In rare cases, isomerism owing to the presence of bidentate ligands with diastereotopic [12] ligators has been reported. One example is provided by the isomers observed in the NMR spectra of complexes of unsymmetrically disubstituted dithiocarbamates (IV), where slow rotation ahout the C—N bond causes the

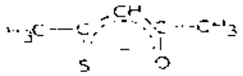


FACIAL

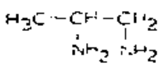
MERIDIONAL

Fig. 2. Geometrical isomers of $[Co(gly)_3]$.

two ligators to be non-equivalent [13].

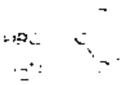


I

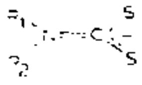


$H_3C-CH(NH_2)-CH_2(NH_2)$

II



III



IV

Bidentate ligands lacking any element of symmetry relating the donor atoms (i.e., "unsymmetrical" AB ligands [1]) will always contain distinguishable ligators. The requirement that there be no symmetry element relating the donor atoms is, however, overly restrictive. It is only necessary that there be no performable symmetry operation (a proper rotation) relating the donor atoms. Thus, bidentate ligands containing ligators which are related only by non-performable operations (improper rotations) have distinguishable extremities and, though not widely recognized, such ligands can give isomeric complexes corresponding one-to-one with those obtainable with AB bidentates [14,15]. In this article, we survey the literature of complexes containing bidentate ligands with donor atoms which are related only by non-performable symmetry operations with particular emphasis on the isomers which can arise owing to the presence of such ligands. The ligands discussed are divided, somewhat artificially, into two types — meso and prochiral.

B. STEREOTOPIC RELATIONSHIPS AND SYMMETRY LABELS

The reader should refer to the papers of Mislow and Raban [12] and Hirschmann and Hanson [16] for a complete discussion of stereotopic relationships.

Groups (or atoms) within a molecule which are distinguishable by any physical method are said to be heterotopic. The sole requirement for groups to be heterotopic is that they not be related by any element of gyrosymmetry [16], i.e., by any operations involving rotations of the molecule as a whole and readily occurring bond torsions. If the donor atoms of a free bidentate ligand are heterotopic, isomerism will always be possible for the complexes formed upon attachment of that ligand to coordination sites which, when all other ligands present are included, are themselves heterotopic. This leads to the well-known isomerisms possible for complexes of AB ("unsymmetrical") bidentates.

Heterotopic donor atoms may be constitutionally heterotopic, as is usually the case for AB bidentates, or they may be stereoheterotopic, where steric differences alone account for the distinguishability. In the latter case, the ligators may be enantiotopic, if they are related by an improper rotation axis in any energetically unique [16] conformer, or diastereotopic. Diastereotopic and constitutionally heterotopic donor atoms of a ligand are distinguishable under all circumstances, and typical AB bidentates contain ligators belonging to one or the other of these two classes. On the other hand, enantiotopic donor atoms are differentiable only in a chiral environment.

In our discussion of metal chelate stereochemistry, it will prove useful to be able to designate the symmetries of the species obtained by appropriate brief labels. Unfortunately, point group designations cannot be rigorously applied to non-rigid molecules [17], which are common in chelate systems. The application of point groups to describe a system by characterizing all important conformers treated as rigid entities (see, e.g., ref. 18) leads to needless complexity here. The "dynamic symmetry" [19] of a fluxional molecule can be described by the group which is the direct product of the group of symmetry operations for the rigid skeleton and the group of permutation operations corresponding to conformation interconversions [20,21]. However, the naming of this effective symmetry group either leads to labels with which most chemists are unfamiliar [22,23] or, when given the label corresponding to the isomorphous point group (as suggested by some [24,25]), can in some cases yield a point group having no obvious relation to the geometry of the molecule.

We will employ the point group of the conformer of "highest symmetry" [22], if such a conformer can be unambiguously determined, to designate the "effective symmetry" of the chelates described. Stereotopic relationships which hold for the fluxional molecule can then be determined from the point group symmetry of this conformer, which must be energetically unique [16]. The highest symmetry conformer can be loosely described as having a "conformationally averaged" or "time-averaged" geometry. This is, of course, the "apparent geometry" of a non-rigid molecule when determined by any method (isomer counting, NMR, etc.) whose intrinsic time scale is longer than that required for the molecule to adopt all energetically feasible conformations for fractions of time corresponding to those required for a Boltzmann distribution. In this article, complete rotational averaging is assumed for all freely rotating chelate ring substituents, and monodentate ligands are treated as point ligands.

In some cases (for example, where secondary amines are donors), new centers of stereoisomerism may arise upon coordination. In the determination of stereotopic relationships, the free ligand must be constrained to maintain any centers of stereoisomerism created upon coordination.

C. COMPLEXES OF MESO BIDENTATE LIGANDS

(i) Meso ligands

Meso bidentate ligands contain constitutionally equivalent ligators in oppositely chiral environments. Such a ligand may be designated "*RS*" (as opposed

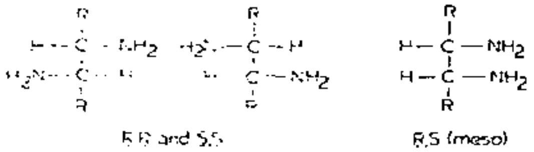
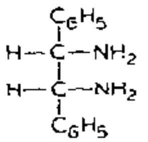


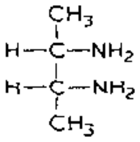
Fig. 3. Stereoisomers of symmetrically disubstituted 1,2-ethanediamines.

to "AA" and "AB" used, respectively, to designate symmetrical and unsymmetrical bidentate ligands) to indicate that the ligand halves are distinguishable by their chiralities, which most commonly may be assigned as "*R*" and "*S*" [26].

Perhaps the most investigated meso bidentates have been the symmetrically disubstituted 1,2-ethanediamines. Here we examine the steric properties of this group of molecules specifically; however, our observations hold for a number of related systems. Typical meso disubstituted 1,2-ethanediamines are *ms*-1,2-diphenyl-1,2-ethanediamine (V) and *ms*-2,3-butanediamine (VI).



V



VI

The symmetrically disubstituted 1,2-ethanediamines contain two chiral centers and exist as three diastereomers (Fig. 3). The *R*,*R* and *S*,*S* enantiomers possess twofold rotation axes for all conformations differing by rotation about the central carbon—carbon bond (treating the R and NH_2 groups as point substituents) and, therefore, contain homotopic amino ligators. The amino groups of the *R*,*S* (meso) diastereomer may be related by improper rotations depending upon the molecular conformation (Fig. 4). In the antiperiplanar (ap) rotamer [27], the NH_2 groups are related by an inversion center; while in the high energy eclipsed synperiplanar (sp) form, they are related by a mirror plane. Since in these two energetically unique rotamers the amino

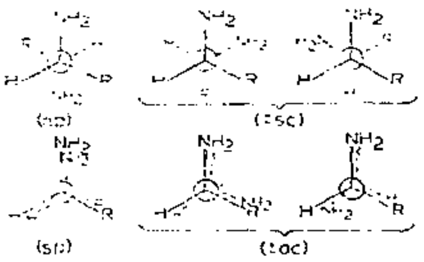


Fig. 4. Staggered and eclipsed conformers of meso 1,2-disubstituted 1,2-ethanediamines.

Fig. 5. Chair conformers of *cis*-1,2-cyclohexanediamine.

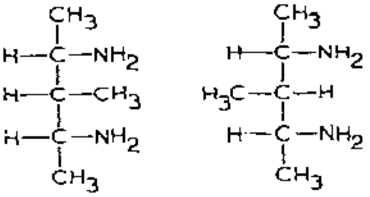
groups are related only by improper axes, these groups are enantiotopic [16]. It is of interest that when free rotation is possible, there is likely to be a sizeable fraction of these meso molecules in asymmetric conformations (±sc) [28]. Even in cyclic meso molecules where there may be some rigidity, there will usually be a number of conformers possible. In *cis*-1,2-cyclohexanediamine, the two conformers expected to be of lowest energy (the enantiomeric chair forms) have no non-trivial symmetry (Fig. 5). Only certain higher energy conformers containing eclipsed amino groups have symmetry-related nitrogen atoms.

In any situation where conformational interconversion is slow or where there is an unequal distribution of enantiomeric (energetically non-unique) [16] conformers, nominally enantiotopic groups within a meso molecule may become diastereotopic. This undoubtedly contributes to the NMR differentiation of nominally enantiotopic groups in chiral solvents or in the presence of chiral solutes or shift reagents [29]. Similarly, the stabilization of one conformation over the others by coordination can cause groups which are enantiotopic in a free meso bidentate to become diastereotopic.

One can, of course, design rigid meso systems. *R*,*S*-2,4-adamantanediol, VII, is one such potential ligand with strict C_s symmetry (ignoring the hydroxyl protons) [30].

VII

We finally call attention to *ms*-3-methyl-2,4-pentanediamine (VIII) which can exist as a pseudochiral pair [31]. As in other meso molecules, the ligators are located in oppositely chiral portions of the molecule and are chemically equivalent in an achiral environment.



VIII

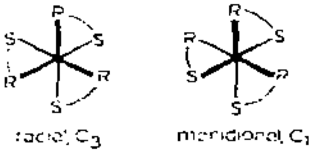


Fig. 6. Facial and meridional isomers of tris meso octahedral complexes.

(ii) Octahedral tris chelates

Octahedral complexes containing three identical *R*,*S* (meso) bidentate ligands can exist as two diastereomers (ignoring Δ,Λ isomerism [32]). These are illustrated in Fig. 6 where the designations "facial" and "meridional" denote the similarities to the corresponding isomers in tris complexes of AB bidentates.

(a) cis-1,2-Cyclopentanediamine and cis-1,2-cyclohexanediamine complexes. Though the possibility for facial and meridional isomers in tris meso systems was first pointed out for tris(*ms*-2,3-butanediamine) complexes (by Woldbye and Borch in 1967 [14]), such isomers were first isolated for tris(*cis*-1,2-cyclopentanediamine)cobalt(III) [33]. The two isomers (Fig. 7), which are separable by cation exchange chromatography, have identical absorption spectra with some differences in their CD spectra. Despite the difference in effective symmetries, ^{1}H NMR spectroscopy fails to distinguish between the two isomers. It is likely that the second, more intensely colored chromatographic fraction isolated [33] is the meridional form since statistical factors favor formation of this isomer [34]. The complex $[Ni(cis\text{-}cpn)_3]^{2+}$ has also been prepared, though the presence of isomers has not been demonstrated [33].

More recently, the facial and meridional isomers of the tris(*cis*-1,2-cyclohexanediamine) complexes of cobalt(III) and chromium(III) have been separated and characterized [35]. The absorption and CD spectra of the two isomers are similar for both systems. Those differences which do exist indicate more strain and distortion in the meridional isomers as expected. As is found

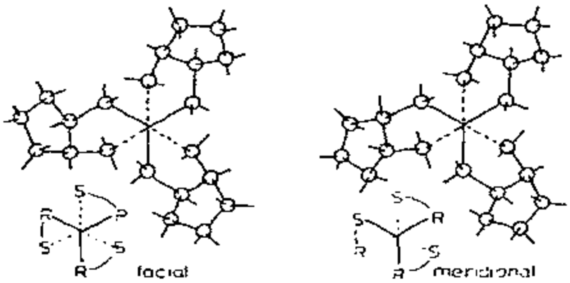


Fig. 7. Facial and meridional isomers of $[Co(cis\text{-}cpn)_3]^{3+}$.

for $[Co(cis\text{-}cpn)_3]^{3+}$, the facial and meridional forms of $[Co(cis\text{-}chn)_3]^{3+}$ cannot be unambiguously identified by ^1H NMR spectroscopy; however, the proton-decoupled ^{13}C NMR spectra clearly distinguish between the facial isomer, with three equivalent chelate rings, and the meridional form, with no symmetry. The meridional/facial ratio for equilibrated $[Co(cis\text{-}chn)_3]^{3+}$ in aqueous solution at 90°C is 1.43 [35] which, after accounting for the statistical entropy contribution of $R \ln 3$ [34], indicates that the enthalpy of the meridional form is 2.3 kJ mol^{-1} higher than that of the facial form.

The preparations of $[Ni(cis\text{-}chn)_3]X_2 \cdot n\ H_2O$ salts ($X = Cl^-, Br^-, NO_3^-, ClO_4^-$) have been reported [36] but the possible isomerism was not discussed.

(b) ms-2,3-Butanediamine complexes.

Studies have been reported on tris chelates of *ms*-2,3-butanediamine with a variety of metal ions [14,37—42]. When chelated in a gauche conformation, this meso ligand must have one methyl group axial and the other equatorial [43]. Such a conformation has been found in an X-ray structure determination on $[PdCl_2(ms\text{-}bn)]$ [44].

That the optically active isomers of 1,2-symmetrically disubstituted 1,2-ethanediamines, such as (±)-2,3-butanediamine, can adopt chelate ring conformations with both methyl groups in the lower energy equatorial position (Fig. 8) is believed to account for the higher stabilities observed for complexes of the active isomers compared with those of the meso isomers [38,45]. Kinetics involving loss of substituted 1,2-ethanediamine ligands from complexes also indicate a lower stability for complexes containing meso ligands [46,47]. Owing to the very bulky phenyl substituents of 1,2-diphenyl-1,2-ethanediamine, it has proven difficult to synthesize tris meso complexes,

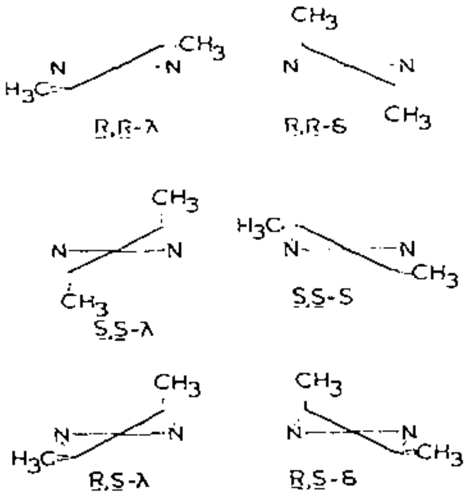


Fig. 8. Conformers of 2,3-butanediamine chelate rings.

although the tris active complexes form readily [45,48] (however $[Ni(ms\text{-}stien)_3]^{2+}$ has been prepared [49]). The stability differences observed between complexes of meso and active 1,2-symmetrically disubstituted 1,2-ethanediamines are also found in equilibrium [50—53] and kinetic [54] studies on complexes containing polydentate ligands incorporating these 1,2-ethanediamines.

A calorimetric study on complexes of *ms*- and *l*-2,3-butanediamine [55] indicates an average value of ~8 kJ mol^{-1} for the strain energy per axial CH_3 group in chelate rings containing meso ligands. This value is considerably higher than the value of about 4 kJ mol^{-1} calculated from reported stability constant data on 1 : 1 complexes of 2,3-butanediamine [38] but is in relatively good agreement with values of 9.2 kJ mol^{-1} [56] and 8.8 kJ mol^{-1} [57] found from molecular mechanics calculations.

Proton NMR spectra of tris(*ms*-2,3-butanediamine) complexes show two methyl resonances which have been ascribed to axial and equatorial methyl groups whose interconversion is slow on the NMR time scale [14]. However, others have pointed out [15,58] that the two methyl groups are diastereotopic in the chiral tris chelates and therefore nothing can be said about the rate of conformational equilibration from the observation of methyl group non-equivalence. In fact, the observations of a single methine signal in the methyl-decoupled ^1H NMR spectrum of $[Co(NH_3)_4(ms\text{-}bn)]^{3+}$ [59], single methine and ethylene signals in the ^1H spectrum of $[Pt(en)(ms\text{-}bn)]^{2+}$ [59] and a single methyl doublet in the ^1H NMR spectrum of $[Pt(NH_3)_2(ms\text{-}bn)]^{2+}$ [60] indicate that there is rapid interconversion between the δ- and λ-gauche forms of chelated *ms*-2,3-butanediamine in aqueous solutions of these compounds at room temperature.

Bagger [61] has shown that the ^{195}Pt-^{13}C coupling constants observed in the ^{13}C NMR spectra of $[Pt(NH_3)_2(ms\text{-}bn)]^{2+}$ and $[Pt(NH_3)_2(l\text{-}bn)]^{2+}$ can be explained assuming the Karplus-type relationship $J \sim a \cos^2\phi$ where $\phi \sim 180$ deg for axial methyl groups, $\phi \sim 90$ deg for equatorial methyl groups, and $a \sim 50$ Hz. Thus, for the *ms*-2,3-butanediamine complex, where there is apparent averaging of axial and equatorial groups owing to rapid $\delta \leftrightarrow \lambda$ equilibration, the value $J = 27.3$ Hz is approximately the average of $J = 49.8$ Hz observed for the *l*-2,3-butanediamine complex, where the methyl groups are expected to be primarily equatorial, and $J \sim 0$ Hz predicted for a complex with axial methyl groups. A similar conclusion has been reached by others in ^{13}C NMR studies on $[Pt(bipy)(bn)]^{2+}$ and related complexes [62].

Facial and meridional isomerism in a tris complex of *ms*-2,3-butanediamine has been studied only for the complex $[Co(ms\text{-}bn)_3]^{3+}$, whose isomers (Fig. 9) have been separated by column chromatography [40] and partially separated by fractional recrystallization [41].

Fac- and *mer*-$[Co(ms\text{-}bn)_3]^{3+}$ can be distinguished by ^1H NMR spectroscopy [40]; however, ^{13}C NMR spectroscopy proves to be much less ambiguous in identifying these isomers [63]. The ^1H-decoupled ^{13}C NMR spectrum of *fac*-$[CO(ms\text{-}bn)_3]^{3+}$, with C_3 symmetry, shows only two methyl carbon resonances and

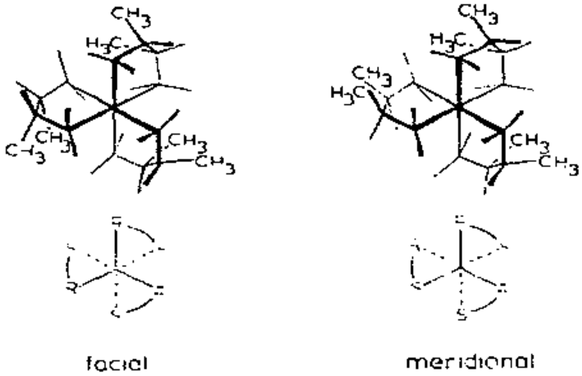


Fig. 9. Facial and meridional isomers of $[Co(ms\text{-}bn)_3]^{3+}$.

two methine carbon resonances. Here those carbon atoms which are enantiotopic in the free ligand become magnetically non-equivalent owing to the unequal energies of the *lel* and *ob* conformers [43] even when chelate ring inversion is rapid [40]. A similar non-equivalence is seen for the *ms*-2,3-butanediamine ligand in the ^{13}C NMR spectrum of $[Co(en)_2(ms\text{-}bn)]^{3+}$ [64]. All atoms which are enantiotopic in the free ligand must become diastereotopic in the chiral tris chelate. The meridional isomer of $[Co(ms\text{-}bn)_3]^{3+}$, with its C_1 symmetry, exhibits a ^{13}C NMR spectrum with additional splittings owing to the non-equivalence of all of the carbon atoms in this molecule [63].

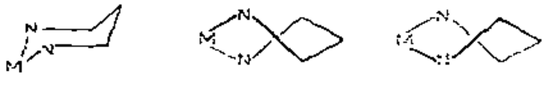
That the facial and meridional isomers of $[Co(ms\text{-}bn)_3]^{3+}$ can be identified by NMR spectroscopy contrasts with the inability of either 100 MHz ^1H NMR [65] or 22.6 MHz ^{13}C NMR spectroscopy [66] to identify the facial and meridional isomers of $[Co(l\text{-}pn)_3]^{3+}$ (though ^{59}Co-decoupled 251 MHz ^1H NMR spectroscopy may prove more useful in this case [67]). In the 1,2-propanediamine complex, however, the tendency for the single methyl group to remain equatorial forces the chelate rings into a relatively fixed conformation irrespective of their environment. On the other hand, small steric differences between the non-equivalent chelate rings of *mer*-$[Co(ms\text{-}bn)_3]^{3+}$ may induce each ring, where there must be one axial and one equatorial methyl group, to spend a different percentage of time in a given conformation. This time-averaged conformational non-equivalence can then give rise to chemical shift differences between chemically similar atoms in different chelate rings. That this explanation is correct is indicated by the fact that ^1H NMR spectroscopy does identify the facial and meridional isomers of tris(2-methyl-1,2-propanediamine)cobalt(III), where this ligand, like *ms*-2,3-butanediamine, must have one methyl group axial and one equatorial when chelated [68].

Niketić and Woldbye have calculated an energy difference of 2.9 kJ mol^{-1} between the *lel* forms of the facial and the more-strained meridional isomers of tris(*ms*-2,3-butanediamine) complexes using molecular mechanics calculations [56]. The relative isomer abundances for [Co(*ms*-bn)$_3$]$^{3+}$ predicted using this energy difference, taking into account the statistical factor [34] favoring formation of the meridional complex, agree well with isomer abundances reported for [Co(*ms*-bn)$_3$]$^{3+}$ [40]. The agreement, however, is probably largely fortuitous since there are many more conformers than just the all-*lel* forms for this system and, owing to the flexible nature of *ms*-2,3-butanediamine chelate rings, with one axial and one equatorial methyl group, there are likely to be relatively small energy differences between them. Isomer counting techniques show that there are four conformers possible for a facial isomer and eight conformers possible for a meridional isomer (with its three non-equivalent chelate rings) [69]. Using the parameters and molecular mechanics program of DeHayes and Busch [70], Them [57] has calculated free energies for all twelve conformers of one configuration (Δ or Λ) of facial and meridional [Co(*ms*-bn)$_3$]$^{3+}$. When weighted over all possible conformers, these results give a calculated meridional/facial ratio of 2.9 : 1 at 298°C for an equilibrium system. Unfortunately, the ratio of meridional and facial isomers of [Co(*ms*-bn)$_3$]$^{3+}$ appears to vary widely (from 1.4 : 1 to 3.5 : 1) depending upon the synthetic method used [40,63]. NMR spectra of a labile tris(*ms*-2,3-butanediamine) complex in solution could give the isomer distribution; however, the only such study carried out to date was on a paramagnetic complex [Ni(*ms*-bn)$_3$]$^{2+}$ where the broadness of the NMR resonances apparently obscures any indication of two isomers [71].

(c) ms-2,4-Pentanediamine complexes

Six-membered diamine chelate rings are considerably more flexible than the five-membered rings discussed earlier [72]. 1,3-Propanediamine chelate rings are known to exist in both chiral skew boat and achiral chair conformations (Fig. 10) in both the solid state [73] and solution [74]. Molecular mechanics calculations [70,75,76] indicate that the chair conformation is somewhat more stable than the skew boat in an isolated chelate ring. This result is supported by the observation that the chelate rings in most crystal structures of 1,3-propanediamine complexes have a chair conformation [77].

The symmetrically substituted propanediamine ligand 2,4-pentanediamine exists as three isomers (Fig. 11). The presence of methyl groups on 6-membered diamine chelate rings significantly changes the preferred ring conforma-



chair λ-skew boat δ-skew boat

Fig. 10. Conformations of six-membered chelate rings.

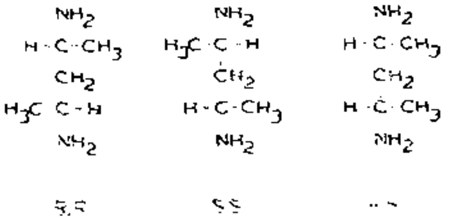


Fig. 11. Isomers of 2,4-pentanediamine.

tion in some cases. Thus, while chelated *ms*-2,4-pentanediamine can exist in a chair conformation with both methyl groups equatorial, this is impossible for the *R,R* and *S,S* ligands which may prefer, therefore, the higher energy skew boat conformation (Fig. 12) [78]. Indeed, crystal structures on *R,R*-2,4-pentanediamine chelates have shown skew boat ring conformations [79,80].

The presence of a sharp methyl doublet in the ^{1}H NMR spectrum of [Co-$(NH_3)_4$ (*ms*-ptn)]$^{3+}$ has been taken to indicate a chair conformation with equivalent equatorial methyl groups for the six-membered chelate ring [81]. These data, however, do not rule out the presence of other conformers with rapid conformational averaging to give methyl groups which are equivalent on the NMR time scale. On the other hand, temperature-dependent solution studies of contact shifts in Ni(*ms*-ptn)$^{2+}$ [82] and of coupling constants in a number of Pt(II) and Pt(IV) complexes of *ms*-2,4-pentanediamine [60,83] demonstrate unequivocally the presence of 6-membered chelate rings in predominantly chair conformations with no significant amounts of other conformers.

The synthesis of [Co(*ms*-ptn)$_3$]$^{3+}$ has been reported and the ^{1}H NMR spectrum described [84]. Since the presence of a meridional isomer (Fig. 13) was ruled out owing to steric hindrance (when the chelate rings are in a chair conformation), the broad methyl resonance observed in the ^{1}H NMR spectrum of

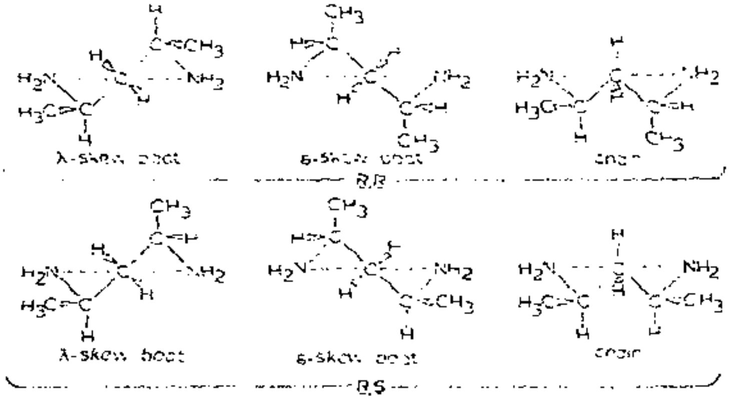
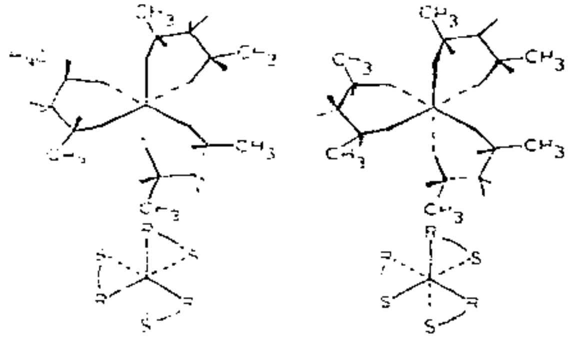


Fig. 12. Some possible conformations of 2,4-pentanediamine chelate rings.



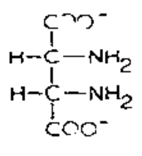
facial, C_3 meridional, C_1

Fig. 13. Facial and meridional isomers of $[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{ptn})_3]^{3+}$.

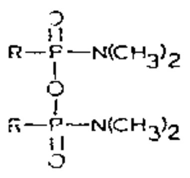
this complex was ascribed to overlapping peaks owing to the presence of two non-equivalent sets of methyl groups in a C_3 facial isomer [84]. However, both isomers have since been isolated from reaction mixtures by ion-exchange chromatography [85] and an X-ray structure determination has been carried out on the hexacyanocobaltate(III) salt of the facial isomer [86]. The two diastereomers of $[\mathrm{Co}(\mathit{ms}\text{-}\mathrm{ptn})_3]^{3+}$ are easily distinguished by both ^{1}H and ^{13}C NMR spectroscopy. There are a greater number of peaks in the NMR spectra of the lower symmetry meridional isomer [85]. Limited molecular mechanics calculations have been carried out on one diastereomer (presumably the facial form) [56].

(d) Tris complexes of other meso bidentates.

The tris chelate of cobalt(III) with *ms*-2,3-diaminosuccinate (IX) coordinated through only nitrogen atoms has been prepared [87]. Any facial and meridional isomers present could not be separated by chromatography and the ^{1}H NMR spectrum was too complex to be fruitfully analyzed. The preparations of a number of tris chelates using mixtures of meso and racemic isomers of several *P,P'*-dialkyl-*N,N,N',N'*-tetramethylpyrophosphoramides (X), presumably coordinated through oxygen, have been described [88]. Surprisingly, the proton-decoupled ^{31}P NMR spectrum of a magnesium complex showed only two peaks (corresponding to meso and racemic ligands) even though 16 non-enantiomeric isomers are possible for the complex [15]. Though $[\mathrm{Ni}(\mathit{ms}\text{-}\mathrm{stien})_3]^{2+}$ has been prepared [49], the isomerism possible has not been investigated.



IX



X

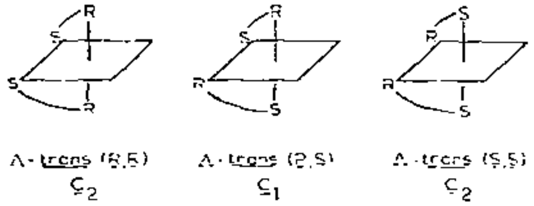


Fig. 14. Diastereomers of octahedral *cis* bis chelates containing two meso (*RS*) bidentate ligands.

Some tris chelates containing only two meso bidentates are discussed in the next section.

(iii) cis Octahedral bis chelates

Octahedral complexes containing two meso bidentate ligands coordinated *cis* with the remaining two coordination sites occupied by two like monodentate ligands or by a symmetrical bidentate can exist as three non-enantiomeric diastereomers — two having a conformationally averaged C_2 symmetry and the other a C_1 symmetry (Fig. 14). Though related isomers in $[M(AB)_2(AA)]$ complexes have been widely studied [89—91] only one system of *cis*-[M-$(RS)_2X_2]$ chelates has been thoroughly investigated — that containing the ligand *ms*-2,4-pentanediamine.

(a) ms-2,4-Pentanediamine complexes.
The complexes [Co(acac)(*ms*-ptn)$_2$]$^{2+}$ and [Co(ox)(*ms*-ptn)$_2$]$^{+}$ have been prepared and two of the three diastereomers possible (Fig. 15) have been separated for the oxalate derivative by solubility differences [92]. The ^{1}H NMR spectra were consistent with the symmetries C_1 and C_2 for the two isomers obtained. In agreement with a crystal structure determination [93], the C_2 isomer obtained was assigned as Λ-*trans*(*RR*)(enantiomeric to Δ-*trans*(*SS*)) since molecular models predict this C_2 diastereomer to be the less sterically hindered [92].

Crystal structure determinations have been carried out on two different

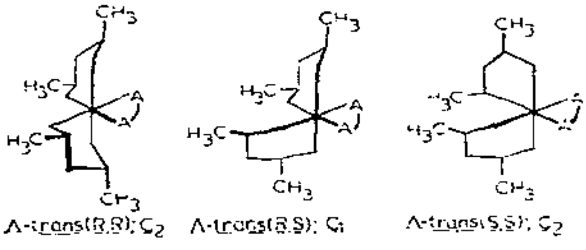
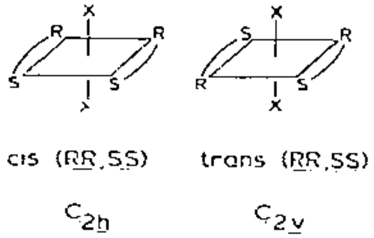
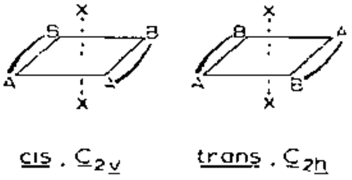


Fig. 15. Diastereomers of [Co(AA)(*ms*-ptn)$_2$]$^{n+}$.



cis (RR,SS) C_{2h} trans (RR,SS) C_{2v}



cis , C_{2v} trans , C_{2h}

Fig. 16. Isomers possible for complexes containing two meso bidentate ligands in a planar coordination.

Fig. 17. Isomers possible for complexes containing two unsymmetrical bidentate ligands in a planar coordination with the highest symmetries possible indicated.

crystals containing the less sterically hindered C_2 diastereomer — optically pure Λ-*trans*(*RR*)-[Co(ox)(*ms*-ptn)$_2$] $ClO_4 \cdot H_2O$ [93] and the corresponding racemic compound (anhydrous) [94]. Both structures have cations with 6-membered chelate rings in a chair conformation related by pseudo [93] or crystallographic [94] two-fold rotation axes.

Boucher and Bosnich [95] have prepared all the possible isomers of both the *cis*-bis and *trans*-bis (vide infra) isomers of [Co(*ms*-ptn)$_2$X$_2$] and have studied the interconversions. The more sterically hindered C_2 isomer of [Co-(CO$_3$)(*ms*-ptn)$_2$]$^+$ was prepared by a kinetic method starting with one of the isomers of *trans*-[Co(*ms*-ptn)$_2$Cl$_2$]$^+$ [95].

Molecular mechanics calculations have been carried out on the Λ-*trans*(*RR*) isomers of [Co(*ms*-ptn)$_2$(*R*,*R*-ptn)]$^{+3}$ and [Co(*ms*-ptn)$_2$(*S*,*S*-ptn)]$^{+3}$; however, the other isomers possible were not included for comparison [77].

(iv) trans Octahedral and planar bis chelates

Complexes containing two meso bidentate ligands in a planar coordination can exist as two isomers which may be designated "*cis*" and "*trans*" based on the relative orientations of chiral centers having the same chirality (Fig. 16). It is of interest that the highest symmetries possible for the well-known *cis* and *trans* isomers of planar bis(AB) systems (Fig. 17) are not the same as for the respective isomers of the bis(*RS*) complexes.

The two *trans* sites in the C_{2v} bis meso chelate are non-equivalent [95] and when occupied by two different monodentate ligands can give rise to two isomers which meet both the criteria of Nourse for pseudo-chirality [31] and the criteria of Hirschmann and Hanson for pseudo-asymmetry [96] (Fig. 18).

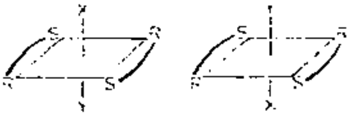


Fig. 18. Pseudochiral isomers of [M(*RS*)$_2$XY].

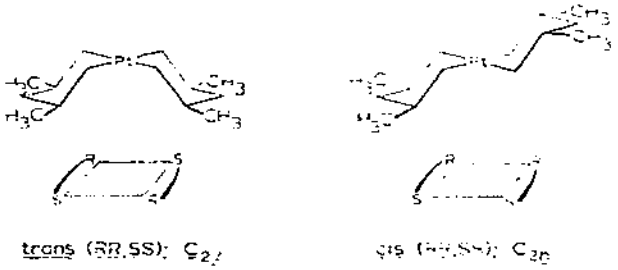


Fig. 19. Isomers of $[Pt(ms\text{-}ptn)_2]^{2+}$.

(a) ms-2,4-Pentanediamine complexes

Square-planar bis(*ms*-2,4-pentanediamine)platinum(II) and palladium(II) complexes have been prepared and a partial separation of the two possible isomers (Fig. 19) has been carried our for the platinum(II) compound [97]. Structures have been assigned based on the colors of the tetrachloroplatinate(II) salts of the isomers obtained. One of the $PtCl_4^{2-}$ salts exhibits a coloration indicative of a close cation/anion interaction while the other does not. Since a *cis*(*RR*,*SS*) isomer (designated "*trans*" in the original paper [97] to describe the relative orientations of the chair conformers) should prevent contact with $PtCl_4^{2-}$ anions both above and below the coordination plane, this structure has been assigned to the isomer whose $PtCl_4^{2-}$ salt shows no indication of cation/anion contact. The two isomers are not differentiable by 60 MHz ^{1}H NMR spectroscopy [60].

Cis(*RR*,*SS*) and *trans*(*RR*,*SS*) isomers of *trans*-$[Co(ms\text{-}ptn)_2X_2]^+$ (X = Cl^-, CH_3COO^-) have been prepared and characterized [95] (Fig. 20). It has been proposed that the *cis*(*RR*,*SS*) isomer is more stable than the *trans*(*RR*,*SS*) isomer since a similar "steplike" C_{2h} configuration is observed in crystal structures of *trans*-$[M(tn)_2X_2]^{n+}$ systems [95]. The structures of the two isomers of *trans*-$[Co(ms\text{-}ptn)_2(CH_3COO^-)_2]^+$ have been assigned using ^{1}H NMR spectroscopy to show the non-equivalence of the axial acetate groups in the C_{2v} isomer.

(b) ms-1,2-Diphenyl-1,2-ethanediamine complexes.

Since Lifschitz et al. first reported the syntheses of both yellow diamagnetic and blue paramagnetic forms of $Ni(ms\text{-}stien)_2X_2$ [48,98], these complexes

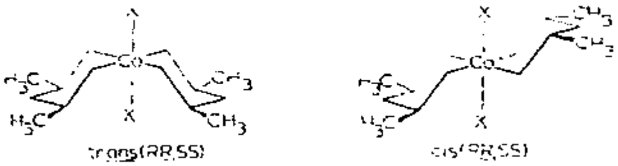
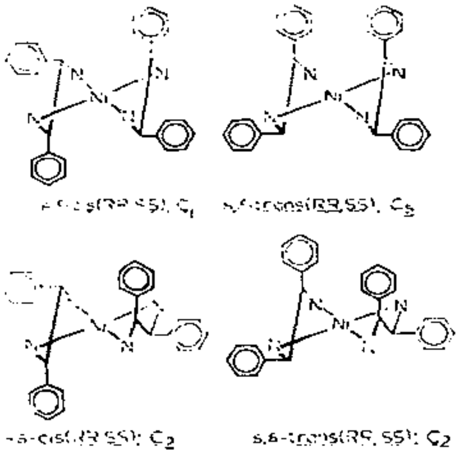


Fig. 20. Isomers of *trans*-$[Co(ms\text{-}ptn)_2X_2]^{n+}$.



δ,λ-cis(RR,SS); C_i δ,λ-trans(RR,SS); C_s

δ,δ-cis(RR,SS); C_2 δ,δ-trans(RR,SS); C_2

Fig. 21. Isomers and conformers possible for planar or tetragonal $[Ni(stien)_2]^{2+}$ and $[Ni(stien)_2X_2]^{n+}$ complexes (enantiomers are not shown).

have been extensively investigated. Crystal structures indicate that the diamagnetic forms of most or all of the bis(*ms*-1,2-diphenyl-1,2-ethanediamine) complexes are planar, four-coordinate while the paramagnetic complexes are tetragonal, six-coordinate with two axial solvent molecules or anions in addition to the planar coordination of the two bidentate ligands [99—101]. That a chelate ring containing a meso symmetrically disubstituted 1,2-ethanediamine ligand will always have one axial substituent to interfere with the axial coordination sites explains why *ms*-1,2-diphenyl-1,2-ethanediamine shows a much greater tendency than the active forms to give planar, diamagnetic complexes with nickel(II) [102].

The possibility for two isomers of planar or tetragonal $Ni(ms\text{-}stien)_2X_2$ complexes has been pointed out [48]. The isomers should exhibit symmetries lower than those expected for the conformationally averaged case (Fig. 16), the exact symmetry depending on whether the two bidentate ligands have the same conformation (δ,δ or λ,λ) or have opposite conformations (δ,λ) (Fig. 21). Crystal structures of both blue and yellow crystals isolated from bis(*ms*-1,2-diphenyl-1,2-ethanediamine)nickel(II) dichloroacetate solutions have been reported [99,101]. The blue crystals contain tetragonal cationic complexes with axial water molecules. The yellow crystals contain both tetragonal complexes with axial dichloroacetate groups and planar cationic complexes in a 2 : 1 ratio. All three of the discrete complexes whose structures have been determined lie on crystallographic centers of symmetry and, therefore, are present as the *cis*(*RR*,*SS*) isomer with a δ,λ conformation.

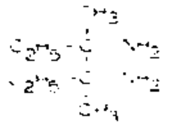
Steric constraints may explain the fact that only the *cis*(*RR*,*SS*) isomer in a δ,λ conformation is observed in the structure determinations cited [99,101]. The δ,λ conformation is believed to be sterically favored in planar bis(1,2-diaminoethane) complexes [43]. Furthermore, the *cis*(*RR*,*SS*) isomer permits the axial phenyl groups to be on opposite sides of the coordination plane where interaction between them is minimal. This is not possible for a *trans*-(*RR*,*SS*) isomer (Fig. 21). Though a number of additional bis complexes containing *ms*-1,2-diphenyl-1,2-ethanediamine [45—49] or its derivatives [103] have been reported, in all but one case there is no indication of which isomers are present. The splitting of ν(As—O) in the IR spectrum of Ni(*ms*-stien)$_2$-(ClO$_4$)$_2$ · 2(C$_6$H$_5$)$_3$AsO [49] may indicate the presence of coordinated (C$_6$H$_5$)$_3$AsO ligands in the non-equivalent axial sites of a *trans*-(*RR*,*SS*) isomer.

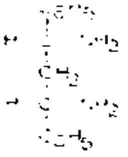
(c) Planar and tetragonal bis complexes of other meso bidentate ligands.

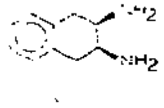
Nickel(II) and copper(II) form 1 : 2 complexes with *ms*-diaminosuccinate-(2-) (IX), and the complexes may be isolated as the sodium salts, Na$_2$[M-(das)$_2$] · XH$_2$O [104]. The copper complex is apparently coordinated only through the nitrogen atoms. No isomerism has been reported or discussed for the copper complex which could exhibit *cis*(*RR*,*SS*) and *trans*(*RR*,*SS*) isomers.

Bis chelates of platinum(II) and palladium(II) with *cis*-1,3-diaminocyclohexane have been prepared [105] and a crystal structure determination on the palladium complex [106] has shown the presence of the *cis*(*RR*,*SS*) isomer.

Other reported planar or tetragonal bis complexes containing meso bidentates where isomerism has not yet been investigated are [Cu(*ms*-bn)$_2$](ClO$_4$)$_2$ [107], [Ni(*ms*-bn)$_2$]X$_2$ (X = Cl, Br) [42], [Cu(Et$_2$Me$_2$en)$_2$]$^{2+}$ ("Et$_2$Me$_2$en" = 3,4-dimethyl-3,4-hexanediamine (XI)) [108], *trans*-[CoCl$_2$(*ms*-dptn)$_2$]Cl ("dptn" = 1,3-diphenyl-1,3-propanediamine (XII)) [109], and the 1 : 2 nickel-(II) and copper(II) complexes of *cis*-1,2-cyclohexanediamine [36] and *cis*-2,3-diaminotetralin (XIII) [110]. The interesting ligand *cis*-2,3-diamino-*trans*-decalin (XIV), containing diastereotopic donor atoms, is also discussed [110].

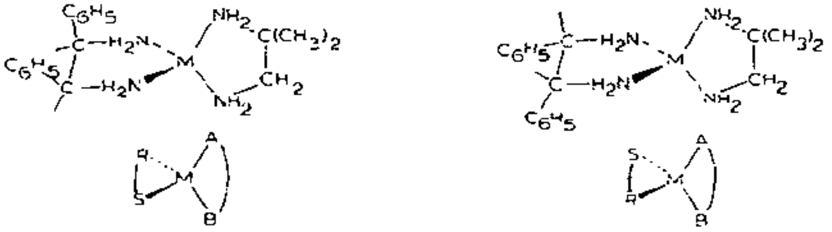




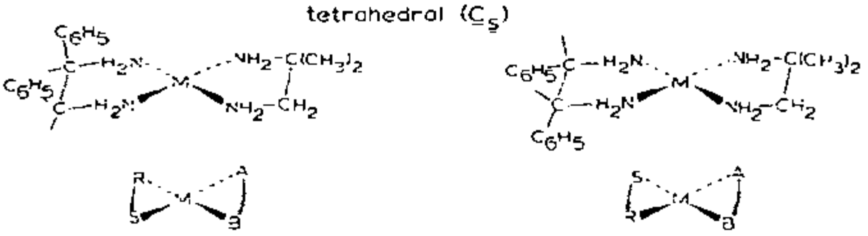


(v) Other complexes containing meso bidentates

The unique symmetry properties of meso bidentate ligands were employed in a classic, early study to determine which of two coordination geometries —



tetrahedral (C_s)

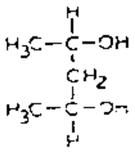


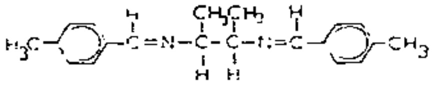
planar (C_1)

Fig. 22. Isomers possible for four-coordinate complexes containing one meso bidentate ligand (*ms*-stien) and one AB bidentate ligand (ibn).

square-planar or tetrahedral — was exhibited by platinum(II) [111] and palladium(II) [112]. As discussed in the next section, tetrahedral complexes containing two meso bidentates or two unsymmetrical (AB) bidentates are potentially resolvable into a pair of enantiomers; however, this is not true when a tetrahedral complex contains one meso ligand and one achiral AB ligand. In this case, the conformationally averaged complex will possess a mirror plane and can only exhibit geometrical isomerism. On the other hand, a planar four-coordinate complex containing one meso and one AB bidentate possesses no S_n axis, and optical isomerism is possible. This is illustrated in Fig. 22 where the meso ligand is *ms*-1,2-diphenyl-1,2-ethanediamine and the AB ligand is 2-methyl-1,2-propanediamine. The resolution of the mixed-ligand complexes [Pt(*ms*-stien)(ibn)]$^{2+}$ and [Pd(*ms*-stien)(ibn)]$^{2+}$ [111,112] provided some early evidence for a planar coordination in these compounds.

Most of the complexes containing only one meso bidentate ligand cannot exhibit isomerism of the type discussed in this review. However, we will briefly describe some of these systems here to call attention to some of the meso ligands available. A complex of *ms*-2,4-pentanediol (XV) with oxoboron has been prepared and the crystal structure reported [113]. The ligand 2,3-diazabicyclo[2.2.1]hept-2-ene (XVI) is a potential bidentate, though in the complexes studied it functions as a unidentate or bridging ligand [114—116]. *cis*-Endo-*N*,*N*′-di(4-methylbenzylidene)-*ms*-2,3-butanediamine (XVII) is an interesting derivative of *ms*-2,3-butanediamine and the crystal structure of a tetrahedral nickel(II) complex containing this ligand has been reported [117].





The crystal structure of an interesting dioxo bridged binuclear complex of osmium(VI) containing *cis*-1,2-cyclohexanediolate(2-) ligands has been reported [118]. The isomer found was centrosymmetric containing osmium atoms with opposite absolute configurations.

(vi) Ligands with chiral centers at the donor atoms

A number of ligands can develop enantiotopic donor atoms upon coordination. This can occur either because rapidly interconverting centers of stereoisomerism are stabilized (as is the case for *N*-substituted amines) or because the presence of the metal ion creates an asymmetric center either at the donor atom or elsewhere. An example of the latter situation is provided by the ligand $B_3H_8^-$ where two boron atoms which are homotopic in the free ion become chiral and enantiotopic in a complex [119]. The tetrahedral complex $Be(B_3H_8)_2$ with C_2 symmetry exists as an enantiomeric pair owing to the presence of these two enantiotopic chiral centers (Fig. 23) [120]; however, the molecule is fluxional [121]. Two enantiomers also arise in tetrahedral com-

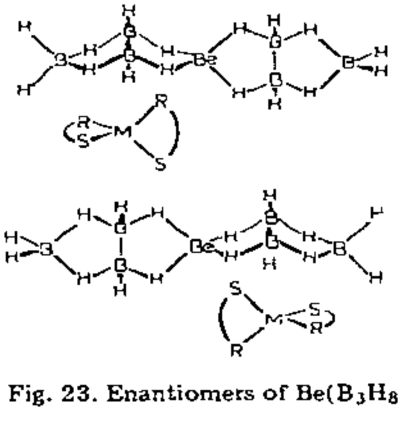


Fig. 23. Enantiomers of $Be(B_3H_8)_2$.

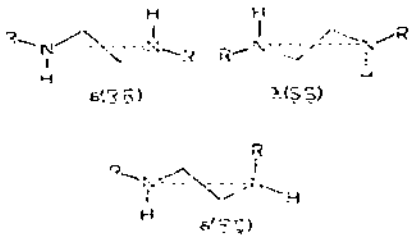


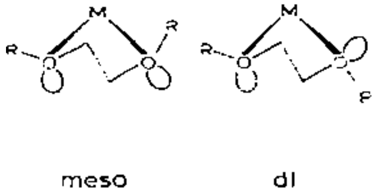
Fig. 24. Diastereomers of coordinated *N*,*N*′-dialkyl-1,2-ethanediamines.

plexes containing two AB bidentates [122,123]. Gas-phase ^{1}H NMR spectra of $(CH_3BeB_3H_8)_2$ indicate the presence of a methyl-bridged binuclear structure existing as two interconverting isomers [121]. The $B_3H_8^-$ complexes comprise the only system discussed in this section where chiral centers are formed at non-donor atoms.

When coordinated, *N*,*N*′ symmetrically substituted diamines [124,125] can exist in (*R*,*R*), (*S*,*S*) or (*R*,*S*) forms with chiral centers at the nitrogen atoms. The (*R*,*R*) and (*S*,*S*) forms of coordinated *N*,*N*′-disubstituted-1,2-ethanediamines are expected to be sterically favored since, unlike the meso form, ring conformations with both substituents equatorial are possible (Fig. 24). This may explain why only (*R*,*R*) and/or (*S*,*S*) forms of the bidentate ligand are found in several *trans*-[Co(*N*,*N*′-Me$_2$en)$_2$X$_2$]$^+$ complexes [126,127], in [Cu(*N*,*N*′-Et$_2$en)(NO$_2$)$_2$] [128] and in (+)$_{350}$-[Pt(*R*-pn)(*N*,*N*′-Me$_2$en)][Sb$_2$-(C$_4$H$_2$O$_6$)$_2$] · 2 H$_2$O [129]. On the other hand, several systems containing meso forms of *N*,*N*′-disubstituted-1,2-ethanediamines are known. Some examples follow.

Interconverting *dl* and *meso* forms of *N*,*N*′-disubstituted-1,2-ethane-diamines have been identified in aqueous solutions of several complexes by ^{1}H NMR spectroscopy. Equilibrated solutions of [Pt(*N*,*N*′-Me$_2$en)(NH$_3$)$_2$]$^{2+}$ and [Pt(*N*,*N*′-Me$_2$en)(bipy)]$^{2+}$ exhibit room-temperature *dl* : *meso* ratios of approximately 1 : 1 and 2 : 1, respectively [130]. A 1 : 1 ratio has been reported for [Pt(NH$_3$)$_2$(EDDA)], where the ethylenediaminediacetate ligand is coordinated through the nitrogen atoms [131]. Finally, the *dl* : *meso* ligand ratio in Ni(*N*,*N*′-Me$_2$en)$^{2+}$ is 1.4 : 1, a value corresponding to a free energy difference of 0.88 kJ mol^{-1} (32°C) [132].

Only (*R*,*S*) forms of the diamine ligands are believed to the present in [Co-(*N*,*N*′-Me$_2$en)$_2$(ox)]$^+$ and [Co(*N*,*N*′-Me$_2$en)$_2$(CO$_3$)]$^+$ [133]. Steric arguments and ^{1}H NMR spectra indicate that the only isomers isolated for these complexes are the Λ-*trans*(*S*,*S*) and Δ-*trans*(*R*,*R*) enantiomers (Fig. 14). Preliminary X-ray diffraction results on Ni(*N*,*N*′-Me$_2$en)$_2$(NO$_3$)$_2$ and Ni(*N*,*N*′-Me$_2$en)$_2$Br$_2$ showing that the nickel(II) ions lie at crystallographic centers of symmetry are consistent with *trans* octahedral structures containing either *dl* pairs of ligands or two meso ligands in a *cis*(*RR*,*SS*) form (Fig. 16) [134]. There is no indication of the ligand forms present in a series of related *trans*



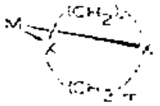


Fig. 25. Meso and *dl* forms of coordinated ethyleneglycol (R=H) and its derivatives.

Fig. 26. Chelation of cyclic diaza (X=NH) and dithia (X=S) ligands.

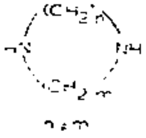
nickel(II) complexes containing *N,N'*-dimethyl- and *N,N'*-diethyl-1,2-ethanediamine ligands [135].

Since the (*R,S*) form of a coordinated *N,N'*-dialkyldiamine which forms a six-membered, chair-conformer chelate ring can have both alkyl groups equatorial, one might expect a meso diastereomer to be favored for coordinated *N,N'*-disubstituted 1,3-propanediamine. In agreement with this, ^{1}H NMR spectroscopy of aqueous solutions of $[Pt(N,N'\text{-}Me_2tn)(NH_3)_2]Cl_2$ shows that the meso/racemic ratio is 2.8 [136]. Moreover, crystal structures of tetrahedral $[Zn(N,N'\text{-}Me_2dmtn)I_2]$ and $[Cd(N,N'\text{-}Me_2dmtn)I_2]$ show that the bidentate ligands have the meso form [137].

Symmetrical diols and dialkoxy ligands, and their sulfur analogs can also exhibit meso and *dl* forms with chiral centers at the donor atoms. Though an attempt to identify these forms in a ^{1}H NMR study of nickel(II) ethyleneglycol and ethyleneglycoldimethylether complexes (Fig. 25) was not successful, apparently owing to rapid interconversion [138], an NMR study on the platinum(II) and palladium(II) 2,5-dithiahexane complexes $[Pt(dth)Cl_2]$ and $[Pd(dth)Cl_2]$ in hexadeuterodimethylsulfoxide [139] shows the presence of rapidly interconverting *RS* and *RR,SS* ligand isomers. Similarly, an NMR spectrum of $[Rh(dth)_2Cl_2]^+$ in D_2O [140] indicates the presence of the five NMR-distinguishable (non-enantiomeric) isomers possible for a "D_{4h}" complex with four chemically similar chiral centers [69]. Metal ions with a planar coordination of two bidentate 2,5-dithiahexane ligands with *RS* configurations have been found in X-ray structure investigations on $[Co(dth)_2(ClO_4)_2]$ [141], $[Cu(dth)_2(BF_4)_2]$ [142] and $[Re_2Cl_5(dth)_2]$ [143,144]. The first two structures cited exhibit the *cis*(*RR,SS*) isomeric form (Fig. 16), while the latter structure is *trans*(*RR,SS*). Crystal structure determinations have also been reported on two additional structures containing symmetrical dithiaethers coordinated in an *RS* form; however, neither $[W_2S_2Cl_8dth]$ [145] nor the 1,2-bis(phenylthio)-ethane complex $[Au_2Cl_2ptc]$ [146], both of which contain centrosymmetric binuclear species, can exhibit isomerism of the type discussed in this article.

Additional complexes whose crystal structures show the presence of symmetrical dithiaethers coordinated *RR,SS* are $[Cu(dth)Cl]_x$ [147], the 3,6-dithiaoctane complexes $[Cu(dto)_2]BF_4$ [142] and $[Cr(dto)(CO)_4]$ [148], and the 5,8-dithiadodecane complex $[Cu(dtd)Cl_2]_2$ [149]. A large number of complexes containing symmetrical dithiaethers of uncertain configuration have been reported [140,150—163].

In some cases, a ligand may have a structure such that coordination can reasonably give only the meso form. Certain cyclic diaza (XVIII) and dithia (XIX) ligands are of this type. Here, the donor atoms, which are homotopic in the limit of rapid conformational equilibration, become oppositely chiral upon coordination owing to steric constraints (Fig. 26).



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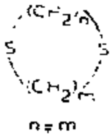

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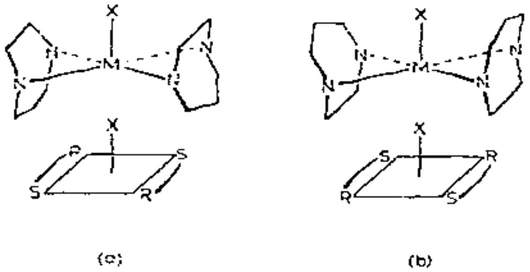
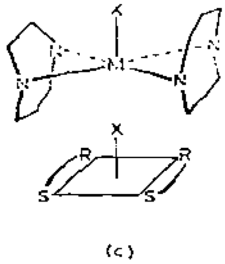
Square-pyramidal complexes of copper(II) [164—166] and cobalt(II) [167] containing two bidentate 1,4-diazacycloheptane ligands and an axial monodentate ligand have been prepared. The complexes can exist in three isomeric forms — two of C_{2v} symmetry and one of C_s symmetry (Fig. 27). A crystal structure of a salt containing the complexes $[Cu(dach)_2NO_3]^+$ and $[Cu(dach)_2H_2O]^{2+}$ shows that both of these cations have the C_{2v} structure shown

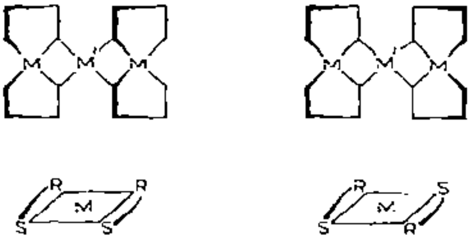


C2v, trans (RR,SS)



Cs, cis (RR,SS)

Fig. 27. Isomeric forms possible for square pyramidal $[M(dach)_2X]^{n+}$ complexes.



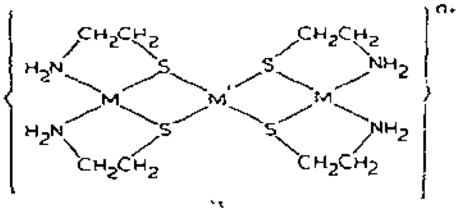
C_{2h} C_{2v}

Fig. 28. Isomers possible for $[M\{M'(NH_2CH_2CH_2S)_2\}_2]^{n+}$. Absolute configuration assignments are for M' > M in priority.

in Fig. 27a [168]. No evidence has been found for any of the square-pyramidal copper(II) or cobalt(II) 1,4-diazacycloheptane complexes existing in more than one isomeric form.

Both planar and tetragonal (i.e., *trans*-octahedral) bis chelates of nickel(II) with 1,4-dithiacycloheptane have been reported [169,170]. With either of these coordination geometries, two isomers (Fig. 16) can exist. No isomerism has been reported for these systems.

The reactions of a number of bis(β-mercaptoethylamine)metallates, $M(NH_2CH_2CH_2S)_2$, with a range of metal ions yield the trinuclear complexes $[M'\{M(NH_2CH_2CH_2S)_2\}_2]^{n+}$ (XX), where steric constraints force a meso configuration for the $M(NH_2CH_2CH_2S)_2$ "ligand" whenever the ligand coordination geometry is planar (M = Ni(II), Pd(II)) [171,172]. If the coordination geometry at the central metal ion is also planar, two isomers are possible (Fig. 28). A crystal structure has shown the idealized C_{2h} structure for the cationic complex in $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$, where metal—metal bonds may dictate the isomer formed [173].

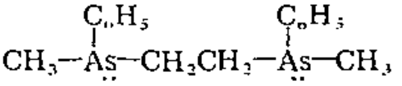


An interesting situation results when the central metal ion is tetrahedral (M = Cd(II), Cu(I), or Hg(II)) [172]. In this case there are also two isomers possible but these must be enantiomeric to one another.

A number of related trinuclear complexes containing ligands similar to β-mercaptoethylamine have also been reported [174,175].

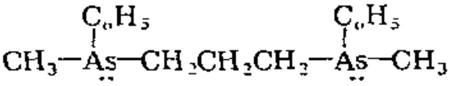
Several families of bidentate ligands possess stereochemically stable chiral centers at the donor atoms in the free ligands. Some of these are discussed here.

The meso and racemic forms of 1,2-bis(methylphenylarsino)ethane (XXI) have been separated by chromatography of the dichloropalladium(II) complexes and, when liberated from the complexes, the isomeric ligands do not interconvert [176]. A large number of complexes prepared from meso/racemic mixtures of this ligand and also of 1,3-bis(methylphenylarsino)propane (XXII) have been reported but isomerism has not been investigated [177].



$CH_3-\underset{\cdot\cdot}{\overset{\overset{C_6H_5}{|}}{As}}-CH_2CH_2-\underset{\cdot\cdot}{\overset{\overset{C_6H_5}{|}}{As}}-CH_3$

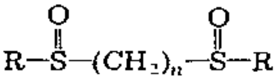
XXI



$CH_3-\underset{\cdot\cdot}{\overset{\overset{C_6H_5}{|}}{As}}-CH_2CH_2CH_2-\underset{\cdot\cdot}{\overset{\overset{C_6H_5}{|}}{As}}-CH_3$

XXII

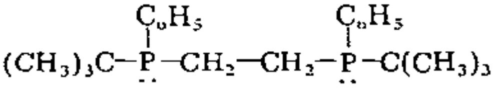
Sulfinyl groups can coordinate through either oxygen or sulfur and the sulfur atom is stereochemically rigid [178]. Meso and racemic forms of 1,2-bis-(methylsulfinyl)ethane (XXIII) and bis(methylsulfinyl)methane (XXIV) can be separated by complex formation [179]. A detailed study of complexation with divalent ions has been reported for the racemic isomer only of 1,2-bis-(methylsulfinyl)ethane [180]. Copper(II), cobalt(II) and nickel(II) tris chelates of *ms*-bis(phenylsulfinyl)methane (XXV) and *ms*-1,2-bis(phenylsulfinyl)ethane (XXVI) have been prepared but the isomerism possible has not been examined [181].



$R-\overset{\overset{O}{\|}}{S}-(CH_2)_n-\overset{\overset{O}{\|}}{S}-R$

(XXIII) $R = CH_3, n = 2$
(XXIV) $R = CH_3, n = 1$
(XXV) $R = C_6H_5, n = 1$
(XXVI) $R = C_6H_5, n = 2$

cis-Dichloride and *cis*-dihydride complexes of platinum(II) with *P,P'*-di-*tert*-butyl-*P,P'*-diphenyl-1,2-ethanediphosphine (XXVII) have been prepared [182]; however, the isomeric composition of the ligand was not known. ^1H NMR spectra indicated that the isomeric form used was pure meso or pure racemic.



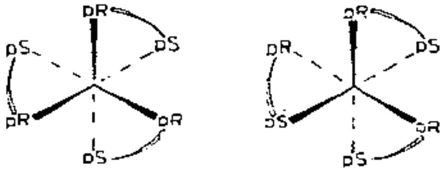
$(CH_3)_3C-\underset{\cdot\cdot}{\overset{\overset{C_6H_5}{|}}{P}}-CH_2-CH_2-\underset{\cdot\cdot}{\overset{\overset{C_6H_5}{|}}{P}}-C(CH_3)_3$

XXVII

D. COMPLEXES OF PROCHIRAL BIDENTATE LIGANDS

(i) Prochiral ligands

A molecular achiral center which becomes chiral when a unique, new group is substituted for either of two like groups attached to that center is designated a "prochiral center", and the two like groups are termed "prochiral groups" [183]. The most common prochiral assembly, and the most important type



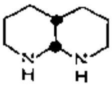
facial , $\underline{C}_3$ meridional , $\underline{C}_1$

Fig. 29. Facial and meridional isomers of tris prochiral octahedral complexes.

discussed in this article, consists of a tetrahedral atom which is attached to three types of ligands (which may include lone pairs) to give the species Xa_2bc. The substitution of a fourth unique ligand for each of the two like ligands in turn yield a pair of enantiomers. The prochiral groups are enantiotopic and distinguishable and may be uniquely labeled *pro-R* ("*pR*") and *pro-S* ("*pS*") using sequence rules [183].

In the following sections, we discuss isomerism in complexes of ligands containing enantiotopic donor atoms located in prochiral portions of the molecules. These "*pRpS*" ligands, with their distinguishable ligators, can give rise to the same types of isomers as those possible with *RS* (and AB) ligands. For example, in tris chelates of *pRpS* ligands, facial and meridional isomers (Fig. 29) are possible just as in tris meso complexes (Fig. 6). Since the effective symmetries of the complexes obtained with prochiral ligands are identical to those obtained for similar complexes with meso bidentates (but not, in all cases, with AB ligands!), much of the earlier discussion of geometry and isomerism for complexes of meso ligands holds here. For convenience, therefore, the complexes of prochiral ligands are discussed by ligand type rather than by coordination geometry.

The division of ligands with enantiotopic ligators into meso and prochiral types is instructional but admittedly somewhat artificial. For example, *trans*-decahydro-1,8-naphthyridine (XXVIII) contains prochiral nitrogen atoms which become chiral centers upon coordination [184].



XXVIII

In general, discrimination between prochiral groups [185], except as it applies to isomerism and isomer identification, will not be discussed. For an example of some recent work in this area with metal ion complexes, see ref. 186.

(ii) Substituted 1,3-propanediamines

(a) 2-Methyl-1,3-propanediamine

This ligand (XXIX) was first employed in an early investigation of the stereo-

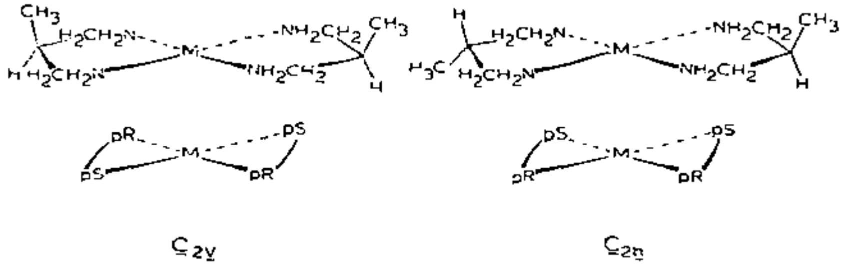
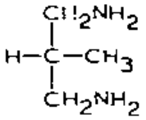


Fig. 30. Isomers of planar $[M(Metn)_2]^{n+}$ complexes.

chemistry of Ni(II) where it was recognized that a planar or tetragonal geometry of $[Ni(Metn)_2]^{2+}$ could result in two isomers (Fig. 30) [187]. That no indication of isomerism was found is not surprising in view of the lability of Ni(II) complexes. Attempted separation of the isomers expected for $[Pt(Metn)_2]^{2+}$ has also been unsuccessful [188], and ^{1}H NMR data on an aqueous solution of this complex gives no indication of more than one isomer [60].



$$\begin{array}{c} CH_2NH_2 \\ | \\ H-C-CH_3 \\ | \\ CH_2NH_2 \end{array}$$

In the same year that the Pt(*RS*)(AB) complex $[Pt(ms\text{-}stien)(ibn)]^{2+}$ was resolved to provide additional early evidence for a planar coordination geometry for platinum(II) (vide supra) [111], an attempt was made to employ the Pt(*pRpS*)(AB) complex, $[Pt(Metn)(ibn)]^{2+}$, for the same purpose [189]. Like the meso-ligand-containing system, the platinum prochiral ligand complex should also exist as a pair of enantiomers (Fig. 31), though the attempted resolution failed.

The tris complex $[Co(Metn)_3]^{3+}$ has been prepared, and the facial and meridional isomers (Fig. 32) have been separated by chromatography on a cation exchange resin [190]. The isomers are easily identified by their ^{13}C NMR spectra. The spectrum of the C_3 facial isomer exhibits the expected four peaks

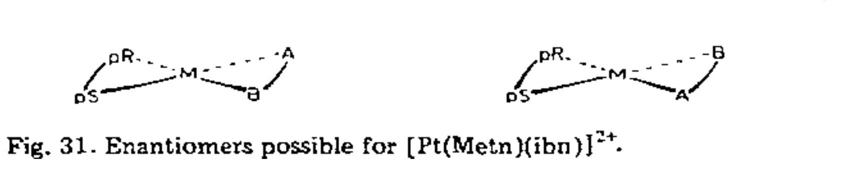


Fig. 31. Enantiomers possible for $[Pt(Metn)(ibn)]^{2+}$.

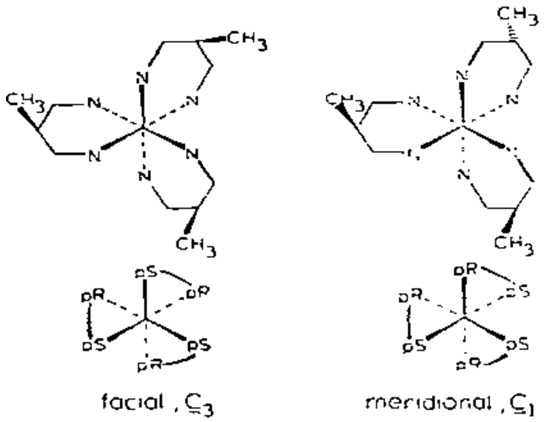


Fig. 32. Isomers of Δ-$[Co(Metn)_3]^{3+}$.

which can be assigned to methyl, methine and two diastereotopic methylene carbon atoms. The spectrum of the C_1 meridional complex exhibits additional peaks.

A crystal structure of *fac*-$[Co(Metn)_3]Cl_3$, which has been only partially refined owing to a disorder problem, shows a skew boat conformation for the six-membered ring [190]. Although such a conformation has been observed for unsubstituted 1,3-propanediamine chelate rings [191], it is unexpected here since a chair conformer can form with the methyl group equatorial. Moreover, ^1H NMR data on $Ni(Ettn)^{2+}$ show that the presence of an alkyl substituent at the 2 position increases the probability of a chair conformation [82]. It may be that packing effects cause formation of a skew boat chelate ring conformer in solid *fac*-$[Co(Metn)_3]Cl_3$.

(b) 1,3-Diamino-2-propanol

The chemistry of 1,3-diamino-2-propanol is complicated by the presence of three potential donor atoms. This ligand tends to be either bidentate, coordinating through two nitrogen atoms, or tridentate, where it often acts as a bridging ligand [193].

Planar (or tetragonal) complexes containing two 1,3-diamino-2-propanol ligands coordinated to Ni(II) [187], Pt(II) and Pd(II) [192] and Cu(II) [194—198] have been prepared. Attempts to separate the C_{2h} and C_{2v} isomers possible (similar to those in Fig. 30) have been unsuccessful for the Ni(II) [187] and Pt(II) and Pd(II) [192] complexes, though the ^1H NMR spectrum of $[Pt(tnOH)_2]^{2+}$ in solution indicates the presence of two isomers in approximately equal amounts [199]. X-ray studies on a number of copper complexes, $[Cu(tnOH)_2X_2]$ ($X = NO_3^-$ [194], Cl^- [195], SCN^- [196], $^-OOCC_6H_4COO^-$ [197] and $SeCN^-$ [198]), show the presence of octahedral complexes with four nitrogens in a plane and axial coordination of the anions. Only the idealized C_{2h} isomer (Fig. 30 with $-CH_3$ replaced by $-OH$) is pre-

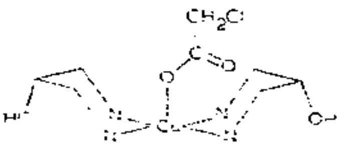


Fig. 33. Cationic complex $[Cu(tnOH)_2(CH_2ClCOO)]^+$.

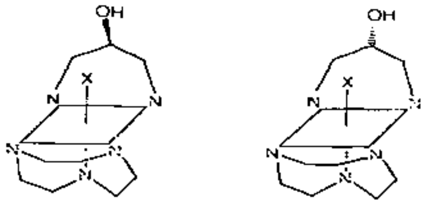


Fig. 34. Isomers of $[Co(TACN)(tnOH)X]^{2+}$ (X = Cl, Br).

sent in these structures. The actual crystallographic symmetry in all cases is lowered to C_i.

A crystal structure determination on a salt containing the square-pyramidal complex $[Cu(tnOH)_2(CH_2ClCOO)]^+$ [200], which can exist in three isomeric forms corresponding to those shown in Fig. 27, shows the isomer with the hydroxyl groups pointing away from the axial monochloroacetate ligand (Fig. 33).

Structural data have been reported for a number of additional copper structures where the 1,3-diamino-2-propanol is not coordinated [201] or is present as a bridging ligand [202—204] or where only one prochiral ligand is present and thus no isomerism is possible [205].

Tris(2,3-diamino-2-propanol)cobalt(III), with only the nitrogen atoms coordinated, has been reported though the facial/meridional isomerism possible has not been discussed [206]. Earlier attempts to prepare this complex gave only bis complexes, in some of which the ligand was tridentate [207]. Trinuclear complexes containing both Co(II) and Co(III) coordinated to 2,3-diamino-2-propanol have also been prepared [208].

The two stereoisomers possible for $[Co(TACN)(tnOH)X]^{2+}$ (Fig. 34) have been observed in the ^{13}C NMR spectrum of a solution of the chloro derivative (X = Cl) and have been separated for the bromo derivative (X = Br) [209]. The isomers have been assigned based on the relative rates of hydrolysis. Only one of the isomers has the OH group of the 1,3-diamino-2-propanol ligand in a correct placement for coordination, and that isomer should bydrolyze faster.

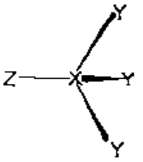
(c) 2-Chloro-, 2-bromo- and 2-thiocyano-1,3-propanediamine

The complexes $[Ni(tnBr)_2]^{2+}$ and $[Ni(tnSCN)_2]^{2+}$ have been prepared though the isomers possible were not separated [187]. The possibility for isomerism in $[Pt(tnCl)_2]^{2+}$ and $[Pd(tnCl)_2]^{2+}$ has been recognized, but the isomers possible were not separated [192] nor was isomerism indicated in the ^1H NMR spectra [199]. The tris complex $[Co(tnBr)_3]^{3+}$ has also been reported [206].

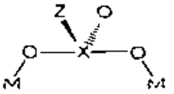
(iii) Tripod ligands

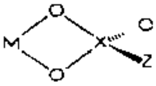
Ligands containing three equivalent donor atoms Y connected to a tetrahedral atom X (which may itself be a donor [210]) are well known (XXX).

When such a ligand acts as a bidentate through Y donors only, the ligand becomes prochiral.



Sulfite [211], selenite [212] and alkylsulfates [213] can form complexes where at least some of the ligands present are bound through oxygen atoms only — either as bridging ligands or to a single metal ion center. When this occurs, the donors become enantiotopic (XXXI and XXXII). This behavior could also be exhibited by thiosulfate; however, no complexes are known where thiosulfate is bidentate through oxygen only [214].



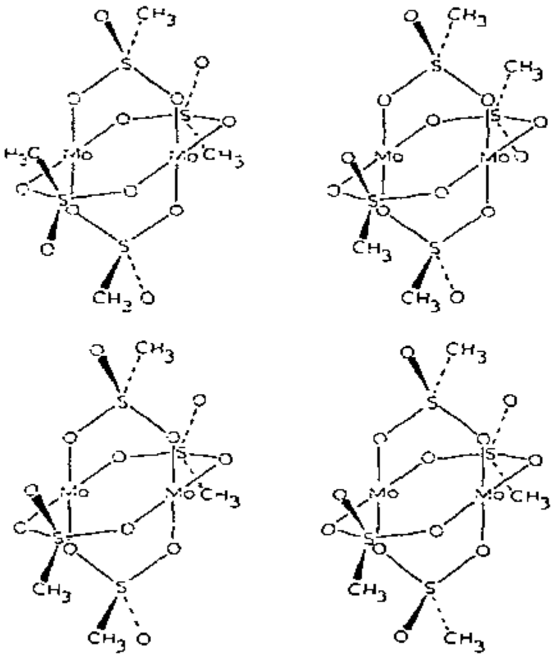


Bridging methylsulfate ligands are present in the binuclear complexes [Mo_2-$(CH_3SO_3)_4$] and *trans*-[$Mo_2(CH_3SO_3)_2X_4$]$^{2-}$ (X = halide) [213]. That the former complex can exist as four isomers (Fig. 35) may explain the complicated IR spectrum observed for this compound [213]. The halide compounds can exist in two isomeric forms. The isomerism possible for these systems has not been studied.

A special type of "tripod" ligand is any simple ligand Z—X where X contains three lone pairs of electrons. If two of these pairs coordinate by bridging and if the geometry about the donor atom is non-planar, one can consider the two coordinating pairs to be enantiotopic. Thus, binuclear complexes dibridged by alkoxides, hydroxides or their sulfur or selenium analogs may occur in two isomeric forms. Disregarding the rest of the molecule, the two possible $M_2(XZ)_2$ moieties are shown in Fig. 36.

Though a large number of structures have been determined by X-ray diffraction techniques for hydroxy-bridged binuclear complexes [215], in most cases the hydrogen positions are not well-defined. For a non-planar geometry about the bridging hydroxyl ions, as is clearly shown in at least one structure [216], the presence of crystallographic inversion centers in many of the structures studied [203, 216—225] shows that these must have the "C_{2h}" configuration for the $M_2(OH)_2$ fragment. A D_2 symmetry for one dicopper(II) complex, however, indicates a planar geometry about the bridging hydroxyl groups in this case [226].

The structures of four dialkoxide-bridged complexes have been reported [227—229]. That these binuclear structures exhibit somewhat flattened geometries about the bridging oxygen donor atoms is indicative of oxygen hy-



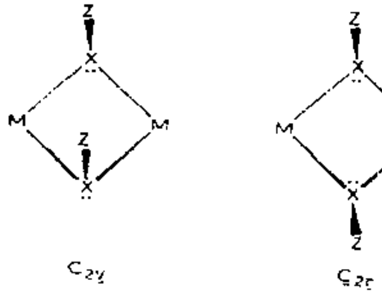


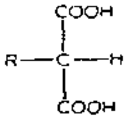
Fig. 35. Isomers possible for $[Mo_2(CH_3SO_3)_4]$.

Fig. 36. Possible $M_2(XZ)_2$ moieties and their idealized symmetries.

bridization between sp^2 and sp^3 [229]. These centrosymmetric complexes all possess the C_{2h} form of the $M_2(OR)_2$ groupings.

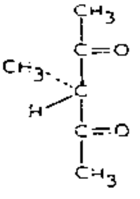
(iv) Other prochiral ligands

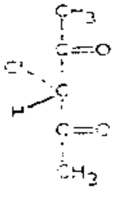
Substituted malonic (propanedioic) acid (XXXIII) [230] can act as a prochiral bidentate ligand though little work on complexes of these ligands has been reported. Salts containing 1 : 1 ratios of Cu(II) and Zn(II) with methyl-, ethyl-, n-propyl- and isopropylmalonate have been reported [231], and 1 : 1 complexes of Ni(II) with butylmalonate [232] and of Si(IV) with methylmalonate [233] have been prepared. Solution studies have been reported on bis(benzylmalonato)manganese(II), -cobalt(II) and -nickel(II) [234]. Monokis-, bis- and tris(methylmalonato)chromium(III) [235] and bis- and tris(bromomalonato)chromium(III) [236] complexes have been prepared. Isomerism owing to the presence of the prochiral ligands has not been noted for any of these systems.



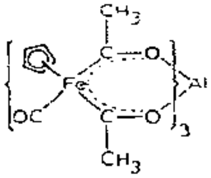
$$R-\underset{\displaystyle COOH}{\overset{\displaystyle COOH}{C}}-H$$

Complexes of acetylacetone can be prepared with the bidentate ligand in the uncharged diketo form [237], and when there are two different substituents at the 3 position, a prochiral ligand can result. Such complexes have been reported for 3-methylacetylacetone (XXXIV) [238] and (as a reaction intermediate) for 3-chloroacetylacetone (XXXV) [239] though no isomerism owing to the presence of the prochiral ligands was possible in these cases.

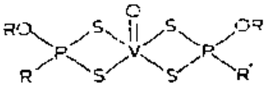




An interesting system containing a prochiral β-diketonate analog where isomerism owing to the presence of enantiotopic donor atoms in the free ligand occurs is the tris complex of Al(III) with the metallo-β-diketonate ligand η^5-$C_5H_5(OC)Fe(CH_3CO)_2^-$ (XXXVI) [240]. The iron atom lies at a center of prochirality, and the facial and meridional forms of the aluminum complex have been identified by ^{1}H NMR spectroscopy. The equilibrium mixture is nearly statistical and contains approximately 30% facial isomer.



Only one of the three isomers possible for a series of oxovanadium(IV) alkoxy-ethyl- and alkoxy-phenyldithiophosphinates (XXXVII) is indicated to be present in solutions by ESR [241]. The three isomers possible are analogous to those shown in Fig. 27.



Some other bidentate prochiral ligands which have been reported to give complexes where isomerism owing to the presence of enantiotopic donor atoms either is not possible or has not been investigated are the phosphorus ylid anion $(CH_2)_2P(C_6H_5)(CH_3)^-$ (XXXVIII) [242], the hydrogeniminodiace-

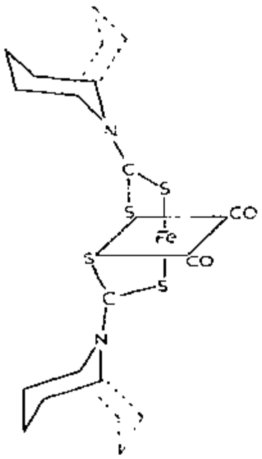
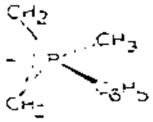
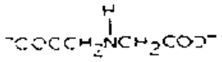


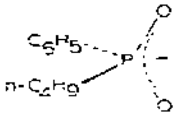
Fig. 37. Structural isomers possible for $[(C_5H_{10}NCS_2)_2Fe(CO)_2]$.

tate ion (XXXIV) [243], and the n-butylphenylphosphinate ligand (XL) [244].





$^{-}OOCCH_2\overset{H}{N}CH_2COO^{-}$



In some cases, normally homotopic ligators can become enantiotopic in the limit of slow conformational equilibration. A case where this is true has been discussed in the literature [245]. Bis(cyclopentamethylenedithiocarbamato)iron(II) dicarbonyl can exist as three isomers when the six-membered ring is locked in a chair conformation (Fig. 37). Only that isomer drawn with complete lines was found in an X-ray structure determination [245]. Though the authors [245] discuss the possibility of two non-enantiomeric isomers, three are possible — two of C_2 symmetry and one of C_1 (see Fig. 14). When conformationally rigid, the cyclopentamethylenedithiocarbamate ligand is prochiral; however, there is no prochiral center.

E. SUMMARY

When coordinated, bidentate ligands with heterotopic donor atoms can give rise to an isomerism which is not possible with bidentates containing homotopic ligators. Discussed herein are the bidentate ligands with enantiotopic donor atoms. Such ligands give isomeric complexes corresponding one-to-one in number but not necessarily in symmetry with those obtained with AB bidentates.

It is apparent that the classifications "symmetric" and "unsymmetric" for bidentate ligands are ill-defined and often misleading. Ligands with enantiotopic donor atoms contain non-trivial symmetry elements (in at least one conformation) and yet yield complexes whose stereochemistries are similar to those we associate with the presence of "unsymmetrical" AB ligands. We propose the terms "cumambic" (L. cum ambito: "with rotation") and "sinambic" (L. sine ambito: "without rotation") to designate respectively bidentate ligands with and without rotationally equivalent donor atoms. Thus cumambic ligands are those with homotopic ligators (AA bidentates) and sinambic ligands are those with heterotopic ligators (AB, *RS* and *pRpS*).

ACKNOWLEDGEMENTS

We thank the National Institutes of Health (grant number GM22435) and the Univeristy of New Mexico Research Allocations Committee for financial support of the research from our laboratory reported herein. We also thank the National Science Foundation (grant number MPS 06111) for partial funding of the FT NMR data system used to collect ^{13}C NMR data on $[Co(Metn)_3]^{3+}$ and $[Co(ms\text{-}bn)_3]^{3+}$. The contributions of Dr. Bruno Morosin of Sandia Laboratories, Albuquerque, New Mexico (USA) and Dr. Charles Campana of the University of New Mexico in carrying out the X-ray crystal structure determination on $[Co(Metn)_3]Cl_3$ are gratefully acknowledged. We also thank Mr. C.J. Hilleary for his many contributions to this article and some of the work described herein. Finally, R.E.T. would like to thank the University of New Mexico for a sabbatical leave during which time this review was completed.

NOTE ADDED IN PROOF

Since submission of this article, a number of pertinent papers have appeared. The complexes $[Co(ms\text{-}stien)_3]^{3+}$ and $[Co(NH_3)_4(ms\text{-}stien)]^{3+}$ have been synthesized [246]. A ^{13}C NMR spectrum of the unstable tris chelate indicates the presence of both the meridional and facial isomers.

Molecular mechanics calculations have been reported for all possible isomers of $[Co(ms\text{-}bn)_3]^{3+}$ [247]. The results are similar to those obtained by Them [57].

Crystal structure determinations have been reported for the free ligand *ms*-1,2-bis(phenylsulphinyl)ethane and its dichloroplatinum(II) adduct [248] and for the complex tetracarbonyl[tetrakis(methylthio)ethene-S,S″]chromium, where the sulfur donor atoms have opposite configurations [249]. Isomerism owing to the presence of a sinambic ligand is not possible for either complex.

Papers inadvertently overlooked, report the characterization of the two possible isomers of *trans*-RuL_2Cl_2 (L = *ms*-P,P′-diphenyl-P,P′-dimethyl-1,2-ethanediphosphine) [250] and a crystal structure determination on the *trans* (*RR,SS*) isomer [251]. Studies have also been reported on Os(II) [252], Fe(II) [253], and Co [253] complexes of this diphosphine ligand.

The crystal structure of a 1 : 1 complex of Pd(II) with a meso diselenoethane derivative has also been reported [254].

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