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CONFORMATIONAL ANALYSIS OF CHELATE RING SYSTEMS BY NMR

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CONTENTS

LIGAND ABBREVIATIONS

bipy	2,2′-bipyridine
2,3-bn	2,3-butanediamine
1,3-bn	1,3-butanediamine
2-bu^t-tn	2-tert-butyl-1,3-propanediamine
2-Cl-tn	2-chloro-1,3-propanediamine

dien	diethylenetriamine
dmbn	3,3-dimethyl-1,2-butanediamine
dmen	*N*,*N*′-dimethyl-1,2-ethanediamine
dmpn	*N*,*N*-dimethyl-1,2-propanediamine
dmtn	1,3-bis(methylamino)propane
dpen	1,2-diphenyl-1,2-ethanediamine
en	1,2-ethanediamine
2-Et-tn	2-ethyl-1,3-propanediamine
2-Me-dmtn	1,3-bis(methylamino)-2-methylpropane
men	*N*-methyl-1,2-ethanediamine
2,2-Me_2-tn	2,2-dimethyl-1,3-propanediamine
mpn	N^1-methyl-(*S*)-1,2-propanediamine
mptn	2-methyl-2,4-pentanediamine
mtn	*N*-methyl-1,3-propanediamine
2-OH-tn	2-hydroxy-1,3-propanediamine
pen	1-phenyl-1,2-ethanediamine
pn	1,2-propanediamine
ptn	2,4-pentanediamine
tmen	*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine
tmpn	*N*,*N*,*N*′,*N*′-tetramethyl-1,2-propanediamine
tn	1,3-propanediamine

A. INTRODUCTION

The early applications of NMR to the conformational analysis of tris(1,2-ethanediamine) complexes [1], paramagnetic nickel(II) complexes [2], and chelates in general [3] have been reviewed previously. However, since those reviews were published, a considerable number of papers have appeared in the field dealing with a larger variety of ligand types, with the use of nuclei other than ^1H; for example ^{13}C, with conformational interconversion, and with inversion of chiral donor atoms. In this review the data from these papers are presented with a consistent interpretation throughout. The treatment and interpretation of the data often differ from those in the literature. In some cases the published stereochemical conclusions are ill-founded; for others, the differences between the results quoted in this review and the published data arise simply from differences in the choice of parameters. Some $^3J_{HH}$ values in the literature have been obtained directly from the spectra by a 'first order' analysis. In most of these cases the compounds were restudied and the coupling constants obtained by a complete computer analysis.

Most of the quantitative analyses for diamagnetic complexes have been

based on the application of vicinal coupling constants of the type, $^3J_{HH}$, $^3J_{HF}$, $^3J_{PtH}$ and $^3J_{PtC}$, to the Karplus relationship, the most useful form of which for conformational analysis is that given in eqns. (1) and (2) [4], where Φ is the dihedral angle XCCY (Fig. 1). The constants, A_1 and A_2 are known to vary from system to system depending, for example, on the electronegativity of substituents [5,6], but the ratio $A_2/A_1(\alpha)$, which is the ratio of the coupling constants for $\Phi = 180°$ and $\Phi = 0°$, is thought to be less sensitive to these factors [7] although it does depend on the two interacting nuclei.

$$^3J_{XY} = A_1 \cos^2\Phi \quad 0° < \Phi < 90° \tag{1}$$

$$^3J_{XY} = A_2 \cos^2\Phi \quad 90° < \Phi < 180° \tag{2}$$

Equation (3) is a more exact relationship between the vicinal coupling constant and the dihedral angle with $A \sim 4$ Hz, $B \sim -0.5$ Hz, and $C \sim 4.5$ Hz for X=Y=H [8], but a new set of constants A, B and C are required for each closely related family of compounds and this makes it difficult to apply. The fact that B is generally negative means that $^3J_{XY}$ for $\Phi = 180°$ is larger than for $\Phi = 0°$, and that α is greater than 1. For $^3J_{HH}$, Karplus' valence-bond calculations gave $A = 4.22$, $B = -0.5$, $C = 4.5$ [8] which yields $\alpha_{HH} = 1.12$. Gopinathan and Narasimhan [9] have compared results from three different MO treatments. The values of α_{HH} calculated from their results are as follows: extended Hückel theory [10], 1.62; finite perturbation method using CNDO/2 wavefunctions, 1.31; finite perturbation method using INDO wavefunctions, 1.44.

$$^3J_{XY} = A + B \cos\Phi + C \cos^2\Phi \tag{3}$$

A number of different values of α_{HH} have been used for conformational analysis of chelate ring systems. Sudmeier and Blackmer [7] estimated that $^3J_{trans}$: $^3J_{gauche}$ is equal to 3.5, i.e. $\alpha_{HH} = 0.875$, from the observed vicinal coupling constants of protons in *trans*-2,5-dimethylpiperazine and its two protonated forms, in alkali metal and Ca^{2+} salts of propylenediaminetetraacetate and in the mono-protonated form of propylenediaminetetraacetate. It was assumed that the '*trans*' protons were exclusively at 180° and the

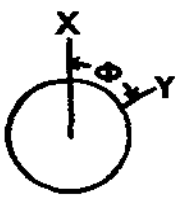


Fig. 1. Dihedral angle, XCCY, for five-membered chelate rings.

'*gauche*' at 60° [7]. These assumptions are probably invalid because of strain in the molecules, and because of the presence of a number of conformations with different dihedral angles for the protons. Cullen et al. [11] have used $\alpha_{HH} = 1.11$ taken from work by Slessor and Tracey [12]. Hawkins and Peachey [13] estimated α_{HH} to be 1.208 from an analysis of the $^3J_{HH}$ values for $[Co(CN)_4(dmbn)]^-$ (where dmbn is 3,3-dimethyl-1,2-butanediamine) in which the tert-butyl group occupies an equatorial position. In this review dealing with similar chelate ring systems, α_{HH} has been given the value 1.2.

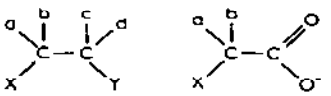
Various equations have also been derived for the relationship between $^3J_{HF}$ and Φ by theoretical calculations [9,14] and from observed coupling constants [6,15]. The values of α_{HF} vary between 1.4 and 2.2. Cullen et al. [11] chose to use a value of 1.5 for the conformational analysis of some chelate ring systems. In this review, a value of 1.6 has been determined for α_{HF} (see p. 28). Although other vicinal coupling constants have been used for the study of chelate ring conformations, for example $^3J_{PtH}$, and $^3J_{PtC}$, values of α are not currently known.

Proton chemical shift data have also been used for the quantitative conformational analysis of diamagnetic chelate ring systems [1]. However, long-range anisotropic diamagnetic shielding of the protons by substituents introduces a major error into these calculations [13]. On the other hand, for paramagnetic systems, where these diamagnetic shielding terms are not of great significance, the chemical-shift method is appropriate [2]. For ^{13}C and other nuclei for example, ^{59}Co, where orbital paramagnetic effects have a strong influence on the chemical shift, it is possible to determine conformational preferences from δ values for diamagnetic systems. A number of examples of the use of chemical shift data is given in this review.

This review has been restricted to include only bidentate chelates. However, the methods of analysis described can be applied to multidentates.

B. FIVE-MEMBERED CHELATE RINGS

The ligands have either structures I or II. The molecular structures will be



I II

given by X, Y, and where necessary, by a, b, c and d.

There are basically three types of conformations for five-membered chelate rings. The most common one is the puckered ring which exists in two enantiomeric forms, λ and δ (Fig. 2). The interconversion between these two structures is rapid, and proceeds via an envelope conformation [16]. Carbo-

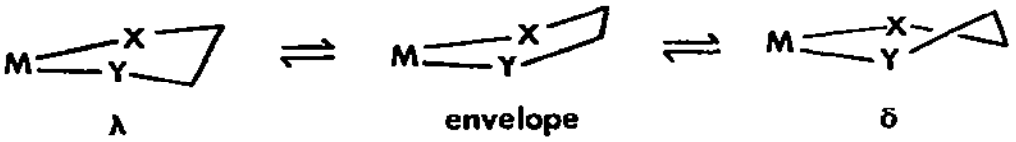


Fig. 2. Puckered and envelope conformations of five-membered chelate rings.

xylato ligands adopt a planar conformation, as in oxalate chelates, an unsymmetric envelope that can also exist in two enantiomeric chiral forms (λ and δ), or a flattened puckered conformation, e.g. α-aminocarboxylates [17]. For the puckered and envelope conformations substituents can be either axial or equatorial (Fig. 3). Conformations that have axial or equatorial substituents are designated by a subscript a or e, respectively, e.g. λ_e.

(i) Coupling-constant method ($^3J_{HH}$)

For a ligand with no substituents on the ring carbons that adopts the δ and λ puckered conformations, rapid conformational interconversion results in the observed vicinal couplings of the four protons being weighted averages of the individual couplings for the two chiralities of the conformation.

$$J_{ad} = n_\lambda (J_{ad})_\lambda + n_\delta (J_{ad})_\delta \quad (4)$$

$$J_{ac} = n_\lambda (J_{ac})_\lambda + n_\delta (J_{ac})_\delta \quad (5)$$

$$J_{bd} = n_\lambda (J_{bd})_\lambda + n_\delta (J_{bd})_\delta \quad (6)$$

$$J_{bc} = n_\lambda (J_{bc})_\lambda + n_\delta (J_{bc})_\delta \quad (7)$$

Using the Karplus relationships, eqns. (1) and (2), with the dihedral angles from Fig. 4, and eqn. (8)

$$n_\lambda + n_\delta = 1 \quad (8)$$

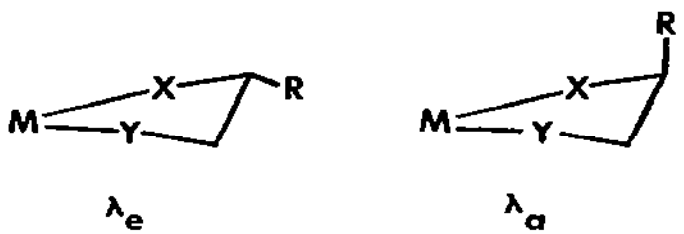


Fig. 3. Substituent orientation for puckered five-membered chelate rings.

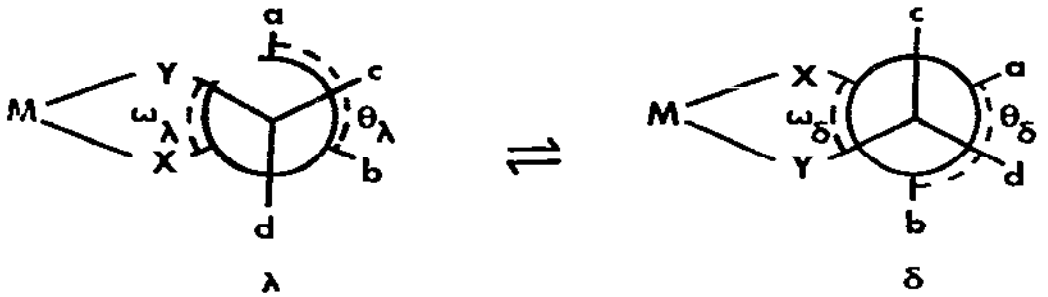


Fig. 4. Conformational interconversion for five-membered chelate rings.

the three vicinal couplings can be expressed as

$$J_{ad} = n_\lambda\left[A_2\cos^2(\theta_\lambda + \omega_\lambda) - A_1\cos^2(\theta_\delta - \omega_\delta)\right] + A_1\cos^2(\theta_\delta - \omega_\delta) \quad (9)$$

$$J_{ac} = J_{bd} = n_\lambda\left(A_1\cos^2\omega_\lambda - A_1\cos^2\omega_\delta\right) + A_1\cos^2\omega_\delta \quad (10)$$

$$J_{bc} = n_\lambda\left[A_1\cos^2(\theta_\lambda - \omega_\lambda) - A_2\cos^2(\theta_\delta + \omega_\delta)\right] + A_2\cos^2(\theta_\delta + \omega_\delta) \quad (11)$$

If it is assumed that $\theta_\lambda = \theta_\delta = 120^\circ$, and that, for these systems where there is no substituent on the ring carbons, $\omega_\lambda = \omega_\delta = \omega$, and putting $A_2/A_1 = \alpha$, $J_{ad}/J_{ac} = X$, and $J_{bc}/J_{ac} = Y$, eqns. (9)–(11) yield the following expressions for n_λ

$$n_\lambda = \left[X\cos^2\omega - \cos^2(120 - \omega)\right]/\left[\alpha\cos^2(120 + \omega) - \cos^2(120 - \omega)\right] \quad (12)$$

$$n_\lambda = \left[Y\cos^2\omega - \alpha\cos^2(120 + \omega)\right]/\left[\cos^2(120 - \omega) - \alpha\cos^2(120 + \omega)\right] \quad (13)$$

As X and Y can be determined experimentally, and the value of α is available, it is possible to solve eqns. (12) and (13) for n_λ and ω. This is only possible for systems where the rapid $\lambda \rightleftharpoons \delta$ interconversion does not make the four protons magnetically equivalent or where the λ and δ conformations are not equally populated.

If b is replaced by a substituent, ω_λ and ω_δ may not be identical and the more general equation, eqn. (14) is required.

$$n_\lambda = \left[X\cos^2\omega_\delta - \cos^2(120 - \omega_\delta)\right]/\left[\alpha\cos^2(120 + \omega_\lambda) - \cos^2(120 - \omega_\delta) - X\left(\cos^2\omega_\lambda - \cos^2\omega_\delta\right)\right] \quad (14)$$

Values of ω_δ and ω_λ are required before n_λ can be determined. Alternatively, if n_λ is known to be 1.0, ω_λ can be determined from

$$\left[\cos^2(120 + \omega_\lambda)\right]/\cos^2\omega_\lambda = X/\alpha \quad (15)$$

(ii) Chemical-shift method

Because the conformations interconvert rapidly, the observed chemical shifts of c and d are weighted averages of their values in the frozen λ and δ conformations. If it is assumed that when c and d are axial or equatorial they have chemical shifts typical of the axial (δ_a) or equatorial (δ_e) orientations, the observed chemical shifts can be expressed by eqns. (16) and (17).

$$\delta_c = n_\lambda \delta_e + (1 - n_\lambda)\,\delta_a \tag{16}$$

$$\delta_d = n_\lambda \delta_a + (1 - n_\lambda)\,\delta_e \tag{17}$$

The observed chemical shift differences $\Delta\delta^{obs}$ between c and d is given by

$$\Delta\delta^{obs} = 2n_\lambda(\delta_e - \delta_a) - (\delta_e - \delta_a) \tag{18}$$

Putting $(\delta_e - \delta_a) = \Delta\delta^{int}$ and rearranging, n_λ can be expressed as

$$n_\lambda = 0.5\left[1 + \Delta\delta^{obs}/\Delta\delta^{int}\right] \tag{19}$$

If, for a diamagnetic complex, $\Delta\delta^{int}$ is known by measuring the spectrum at sufficiently low temperature to obtain the frozen conformation, it would be possible, for some systems, to determine n_λ using eqn. (19). Long range anisotropic shieldings prevent the use of substituents such as tert-butyl groups to freeze the conformation because $\Delta\delta^{obs}$ for such systems depends on the substituent, and cannot be used as $\Delta\delta^{int}$ for other substituents that do not enforce $n_\lambda = 1$. However, for paramagnetic systems where isotropic shifts are very large compared to the shifts due to long-range anisotropic diamagnetic shieldings, it is possible to use a tert-butyl group to freeze a conformation so that $\Delta\delta^{int}$ can be determined and applied to other related systems [18].

(a) Diamines

Five-membered diamine chelate rings exist in the λ, δ puckered conformations that interconvert rapidly. The barriers for unsubstituted chelates with M–N bond lengths of 200 and 230 pm have been estimated by strain-energy minimization calculations to be 20 and 30 kJ mol^{-1}, respectively [16]. The barrier has been determined by NMR methods for complexes of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (p. 21) [19–21].

1,2-Ethanediamine, X = Y = NH_2. Due to rapid λ ⇌ δ interconversion [16] and the fact that $n_\lambda = n_\delta$, the four CH protons become magnetically equivalent in complexes of the type $[MX_4(en)]^{n+}$ and *trans*-$[MX_2(en)_2]^{n+}$. This equivalence is reflected in the Curie behaviour of the resonances for $[Ni(OH_2)_4(en)]^{2+}$ [18,22]. However, for *cis*-$[MX_2(en)_2]^{n+}$ and $[M(en)_3]^{n+}$

where $\Lambda \rightleftharpoons \Delta$ inversion is not rapid on the NMR time-scale, rapid conformational interconversion will not make the four CH protons equivalent even if the mole fractions of δ and λ conformations are the same [23]. If for, say, the Δ distribution of chelate rings (Fig. 5) the λ conformation predominates, as is predicted to happen from energy-minimization calculations [16,24], the spectrum is weighted towards the λ conformation and an AA'BB' spectrum would be expected. This has been observed for $[Ru(en)_3]^{2+}$ [25], $[Rh(en)_3]^{3+}$ [7], and $[Co(en)_3]^{3+}$ [26], and the vicinal coupling constants have been derived. From eqns. (12) and(13) it is possible to calculate the mole fractions of the δ and λ conformations and the NCCN (ω) dihedral angles [13]. The results are given in Table 1. Estimates of the free energy differences between the four Δ configurations, $\lambda\lambda\lambda$, $\lambda\lambda\delta$, $\lambda\delta\delta$ and $\delta\delta\delta$ are also included. These were obtained from eqns. (20), (21) and (22) where ΔG_1°, ΔG_2° and ΔG_3° are the free energies of the Δ-$\lambda\lambda\delta$, Δ-$\lambda\delta\delta$ and Δ-$\delta\delta\delta$ configurations relative to the Δ-$\lambda\lambda\lambda$ configuration, and where it is assumed that the free energy change for each $\lambda \rightarrow \delta$ interconversion is constant (ΔG°) except for the statistical entropy term.

$$\Delta G_1^\circ = \Delta G^\circ - RT \ln 3 \tag{20}$$

$$\Delta G_2^\circ = 2\Delta G^\circ - RT \ln 3 \tag{21}$$

$$\Delta G_3^\circ = 3\Delta G^\circ \tag{22}$$

Although the J values and the other parameters have been determined at different temperatures the errors are too large to allow the determination of enthalpy and entropy differences. It has been predicted that, as M–N increases, n_λ will decrease and ω will increase [16]. The results in Table 1 are consistent with this because the M–N bond lengths are about 200 [27], 205 [28,29], and 215 pm [30] for Co(III), Rh(III) and Ru(II), respectively. The results also are consistent with the proposal that the PO_4^{3-} ion stabilizes the Δ-$\lambda\lambda\lambda$ configuration [31,32]. The relative free energies for the various configurations of Δ-$[Co(en)_3]^{3-}$ ($\lambda\lambda\lambda$, 0; $\lambda\lambda\delta$, −0.6; $\lambda\delta\delta$, 1.4; $\delta\delta\delta$, 6.1 kJ mol^{-1}) are in excellent agreement with the results of Sargeson and co-workers

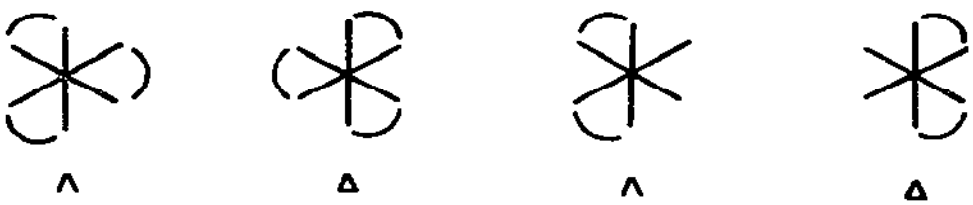


Fig. 5. Configurations of tris and *cis*-bis bidentate chelate rings.

TABLE 1

Coupling constants and conformational parameters for tris(1,2-ethanediamine) complexes [13]

T (K)	$[PO_4^{3-}]$ (mol l^{-1})	J_{ad} (Hz)	J_{ac} (Hz)	J_{bc} (Hz)	ω (deg)	n_λ	ΔG_1 (kJ mol^{-1})	ΔG_2	ΔG_3
$[Rh(en)_3]^{3+}$ [a]									
290	0.0	9.5 [b]	3.9 [b]	6.2 [b]	54.3±2.4	0.64±0.06	−1.3	0.1	4.2
366	0.0	9.4 [c]	4.4 [c]	5.3 [c]	51.2±0.8	0.67±0.03	−1.2	1.0	6.5
290	0.1	9.4 [b]	4.1 [b]	5.3 [b]	52.4±2.2	0.68±0.06	−0.8	1.0	4.9
366	0.1	9.8 [c]	4.2 [c]	5.2 [c]	52.4±1.1	0.70±0.03	−0.8	1.8	7.7
366	0.3	10.4 [c]	4.3 [c]	4.7 [c]	52.1±1.1	0.74±0.03	−0.2	3.0	9.5
$[Co(en)_3]^{3+}$ [d]									
290	0.0	9.2 [e]	5.2 [e]	4.4 [e]	46.8±2.4	0.70±0.07	−0.6	1.4	6.1
333	0.0	9.4 [f]	4.7 [f]	4.8 [f]	49.4±1.4	0.70±0.04	−0.7	1.7	7.1
366	0.0	9.9 [c]	4.3 [c]	4.5 [c]	51.3±1.1	0.73±0.03	−0.3	2.7	9.1
290	0.1	10.1 [f]	3.8 [f]	4.9 [f]	54.0±2.0	0.73±0.05	−0.3	2.2	7.2
290	0.3	11.1 [b]	3.2 [b]	4.1 [b]	57.0±3.3	0.83±0.08	1.2	5.0	11.5
333	0.3	11.0 [f]	4.1 [f]	4.2 [f]	53.0±1.8	0.79±0.05	0.6	4.3	11.0
$[Ru(en)_3]^{2+}$ [g]									
303 [h]	0.0	9.5	3.8	5.5	53.9	0.66	−1.1	0.6	5.0

[a] J values from ref. 7. [b] ±0.2. [c] ±0.1. [d] J values from ref. 26. [e] ±0.3. [f] ±0.15. [g] J values from ref. 25. [h] Approximate probe temperature for Varian HA-100.

[33] ($\lambda\lambda\lambda$, 0; $\lambda\lambda\delta$, −0.4; $\lambda\delta\delta$, 1.7; $\delta\delta\delta$, 6.7 kJ mol^{-1}) which were obtained by an indirect method [33–35] based on the concentrations of the various isomers of $[Co\{(R)\text{-pn}\}_i\{(S)\text{pn}\}_{3-i}]^{3+}$, which had been prepared under equilibrium conditions and separated chromatographically. The values of ω calculated for $[Co(en)_3]^{3+}$ are in the range of the values found recently in crystals by X-ray analysis: (+)-$[Co(en)_3]Cl_3 \cdot H_2O$, 54.5°, 55.6°, 55.6° [36]; (+)-$[Co(en)_3](NO_3)_3$, 51.9°, 51.6°, 45.7° [37]; (±)-$[Co(en)_3](SCN)_3$, 49.2°, 50.4°, 52.4° [38]; (±)$[Co(en)_3]Cl_3 \cdot 2.8\ H_2O$, 50.6° [39]; (±)-$[Co(en)_3]_2(HPO_4)_3 \cdot 9\ H_2O$, 52.4° [40]. The values of ω calculated for $[Rh(en)_3]^{3+}$ also approximate the values that have been determined by X-ray structure analysis: (±)-$[Rh(en)_3]Cl_3 \cdot 3\ H_2O$, 55.8° [28]; (+)-$[Cr(en)_3]$(+)-$[Rh(en)_3]Cl_6 \cdot 6\ H_2O$, 54.5° [29]. Strain-energy minimization calculations have predicted $\omega = 55°$ for Co(III) (M–N = 200 pm) [16,24] and $\omega = 56.5°$ for Rh(III) (M–N = 205 pm) [16].

The ^{1}H NMR spectrum of $[Ni(en)_3]^{2+}$ has been measured in various solvents, in the presence of a number of anions, and over a temperature range [18,41–45]. Due to the preference for the λ conformation when the distribution of chelate rings is Δ, separate resonances are observed for the protons that are weighted in favour of axial and equatorial positions. Because of a shift in the $\lambda \rightleftharpoons \delta$ equilibrium with temperature, these resonances do not obey the Curie Law. The n_λ value can be determined from eqn. (19). A value of 159.6 for $\Delta\delta^{int}$ at 300 K was determined from the Ni(II) complex of 3,3-dimethyl-1,2-butanediamine in which the tert-butyl group stereospecifically adopts the equatorial orientation [18]. The n_λ values for $[Ni(en)_3]^{2+}$ were in the range 0.60–0.80 at about 300 K depending on anion, concentration and solvent [18]. For example, $[Ni(en)_3]Cl_2$ in water at a concentration of 0.4 M and at 301.5 K where appropriate has the following parameters: n_λ 0.62, ΔH 1.3 kJ mol^{-1}, ΔS 0.3 JK^{-1} mol^{-1}, ΔG 1.2 kJ mol^{-1}, ΔG_1 −1.5 kJ mol^{-1}, ΔG_2 −0.3 kJ mol^{-1}, ΔG_3 + 3.6 kJ mol^{-1} [18]. In dimethyl sulfoxide, the values are n_λ 0.79, ΔH 4.2 kJ mol^{-1}, ΔS 3.0 JK^{-1} mol^{-1}, ΔG 3.3 kJ mol^{-1}, ΔG_1 + 0.6 kJ mol^{-1}, ΔG_2 + 3.9 kJ mol^{-1}, ΔG_3 + 9.9 kJ mol^{-1} [18]. Chloride and nitrate were found to increase the Δ-λ conformation through ion-association [18]. Similarly, strong donor solvents such as dimethyl sulfoxide increase $\Delta\delta^{obs}$ and hence n_λ [18]. In fact the n_λ values follow the donor number [46] of the solvent: for the tetraphenylborate salt, MeCN, D.N. 14.1, n_λ 0.60; Me_2CO, D.N. 17.0, n_λ 0.66; thf, D.N. 20.0, n_λ 0.66; $HCONMe_2$, D.N. 24.7, n_λ 0.72; Me_2SO, D.N. 29.8, n_λ 0.78 [18]. These changes in n_λ with solvent have been rationalized in terms of the stronger hydrogen-bonding between the NH_2 protons and the solvents in the Δ-λ conformation than in the Δ-δ conformation [18].

Above 340 K the rate at which the two resonances deviate from the Curie Law increases until the two lines coalesce at approximately 373 K. This is

due to the rapid $\Delta \rightleftharpoons \Lambda$ configurational inversion of the complex [42]. Approximate rates for the inversion have been calculated for aqueous solutions with and without 1.6 M NaCl [18,24] and for a Me_2SO solution by using eqn. (23) [47]

$$k_i = (\pi/\sqrt{2})(\Delta\nu_{ax,eq}^2 - \Delta\nu_T^2)^{1/2} \quad (23)$$

where $\Delta\nu_{ax,eq}$ is the frequency separation in the absence of inversion and $\Delta\nu_T$ is the observed frequency separation at temperature T, both expressed in Hz. From these rates, the enthalpies and entropies of activation have been calculated from a plot of $-R \ln(k_i h/kT)$ against T^{-1} according to the Eyring equation

$$-R \ln(k_i h/kT) = \Delta H^{\neq} T^{-1} - \Delta S^{\neq} \quad (24)$$

The data obtained are as follows: in water, $\Delta G^{\neq}$ (374 K), 65.7 kJ mol^{-1} [42]; in 1.6 M NaCl, $\Delta H^{\neq}$ 48.1 ± 6.2 kJ mol^{-1}, $\Delta S^{\neq}$ −41.2 ± 17.3 JK^{-1} mol^{-1}, $\Delta G^{\neq}$ (374 K) 63.5 kJ mol^{-1}; in Me_2SO, $\Delta H^{\neq}$ 50.3 ± 6.0 kJ mol^{-1}, $\Delta S^{\neq}$ −41.3 + 15.9 JK^{-1} mol^{-1}, $\Delta G^{\neq}$ (374 K) 65.7 kJ mol^{-1} [18]. The agreement between the results from aqueous and Me_2SO solutions is excellent and indicates that the same mechanism is occurring in both solvents, and that the solvent does not play a dominant role in the formation of the activated complex, consistent with the non-bond-rupture twist mechanism which is also supported by the large negative entropy of activation [48,49].

(R)-3,3-Dimethyl-1,2-butanediamine, $X = Y = NH_2$, $b = C(CH_3)_3$. Strain-energy minimization calculations have shown that, in octahedral complexes with M–N bond lengths of about 200 pm, 3,3-dimethyl-1,2-butanediamine forms chelate rings with the tert-butyl group exclusively in the equatorial orientation: the axial conformer is more than 12 kJ mol^{-1} higher in energy [50]. The high degree of stereoselectivity was confirmed by the strict observance of Curie behaviour by the three C–^{1}H resonances in the mono Ni(II) complex [18]. Two of these resonances in the ^{1}H NMR spectrum of $[Ni(OH_2)_4(dmbn)]^{2+}$ are for the CH–CH_2 fragment corresponding to the equatorial [1H, δ^{iso} (300 K) 171.4] and axial [2 H, δ^{iso} (300 K) 11.8] protons. For the tris Ni(II) complex $[Ni(dmbn)_3]^{2+}$, the equatorial protons are observed to resonate at δ^{iso} (301.5 K) 169.2 (cf. δ^{iso} (301.5 K) 170.9 for $[Ni(OH_2)_4(dmbn)]^{2+}$) but the resonance for the axial protons is hidden under the $C(CH_3)_3$ peak [18]. Because of the similarity in the positions of the equatorial resonances for the mono and tris complexes, it has been assumed that $(\delta_e - \delta_a)$ is the same for the two complexes [18]. Further, since the chelate rings have $n_e = 1$, $(\delta_e - \delta_a)$ has been equated to $\Delta\delta^{int}$ for the Ni(II) complexes with primary diamines. At 300 K the value is $\Delta\delta^{int}$ 159.6 [18].

Zamaraev et al. [41] have proposed that a Karplus-type equation (eqn. 25)

could be applied to the proton contact shifts of diamine chelate rings to estimate the degree of ring pucker

$$A_i = B_0 + B_2 \cos^2 \Phi_i \tag{25}$$

where A_i is the hyperfine coupling constant, B_0 and B_2 are constants, and Φ is the dihedral angle between the NiNC and NCH planes. Experimental evidence for radicals with rigid geometries has led to the conclusion that B_0 is much less than B_2 [51]. This allows the approximation

$$A_i \simeq B_2 \cos^2 \Phi_i \tag{26}$$

and the formulation of the equation

$$\delta_a^{iso}/\delta_e^{iso} = \cos^2(120 - \Phi)/\cos^2(120 + \Phi) \tag{27}$$

where Φ is defined in Fig. 6. From the above values of the isotropic shifts, Φ is calculated to be 44° [18] which is in good agreement with the value of 42° found in the solid state for $[Ni(en)_3](MeCO_2)_2 \cdot 2\,H_2O$ [52].

The vicinal coupling constants $^3J_{HH}$ (Table 2) for $[Co(CN)_4(dmbn)]^-$ have been used to determine α, the ratio of the Karplus coefficients A_2 and A_1 (eqns. 1 and 2) [13]. The (*R*) configuration of the ligand has the tert-butyl group equatorial in the λ conformation of the chelate ring, and, because this conformation is exclusively populated for octahedral complexes, i.e. $n_c = n_\lambda = 1$, α can be calculated from eqn. (15). A value of 55° was chosen for ω_λ based on results of strain-energy minimization calculations [50]. The resultant value of α, 1.2, lies within the range calculated by Karplus and others (see p. 3), and is very similar to a value previously determined for similar organic compounds [53].

For $[Mo(CO)_4(dmbn)]$ where Mo–N is about 230 pm based on the values found by X-ray analysis for $[Mo(CO)_3(dien)]$ [54], the non-bonded interactions between the tert-butyl group in an axial orientation and other atoms in the molecule (especially the apical ligands) are considerably reduced over those experienced in $[Co(CN)_4(dmbn)]^-$ where M–N is about 200 pm and the interacting groups are closer together. For the longer M–N bond length,

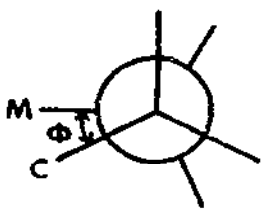


Fig. 6. Dihedral angle, MXCC, for five-membered chelate rings.

TABLE 2

Coupling constants and conformational parameters for complexes of C-substituted diamines with (R) absolute configuration. Coupling constants are in Hz, and ω in deg.

Complex	J_{ad}	J_{ac}	J_{cd}	ω_λ	ω_δ	n_λ
$[Co(CN)_4(dmbn)]^-$	13.08 [a]	3.59 [a]	−11.76 [a]	55		1.0
$[Mo(CO)_4(dmbn)]$ [g]	12.02 [a]	2.99 [a]	−11.96 [a]	57		1.0
$[Pt(NH_3)_2(dmbn)]^{2+}$	12.55 [b]	3.46 [b]	−11.57 [b]	56	56	0.94±0.07
$[Pt(bipy)(dmbn)]^{2+}$	11.53 [b]	2.94 [b]	−9.81 [b]	56	56	1.03±0.02
$[Co(CN)_4(pn)]^-$	12.29 [a]	4.05 [a]	−12.18 [a]	51	48.5	1.03±0.07
$[Co(NH_3)_4(pn)]^{3+}$	12.0 [a]	4.5 [a]	−12.0 [a]	51	48.5	0.90±0.10
$[Pt(NH_3)_2(pn)]^{2+}$	9.91 [a]	4.44 [a]	−12.24 [a]	52.5	52.5	0.66±0.05
$[Pt(bipy)(pn)]^{2+}$	9.0 [d]	4.5 [d]	−12.0 [d]	52.5	52.5	0.58
$[Pt(pn)_2]^{2+}$	9.97 [a]	4.46 [a]	−12.4 [a]	52.5	52.5	0.66±0.05
$[Pd(pn)_2]^{2+}$	9.9 [c]	4.2 [c]	−12.5 [c]	52.5	52.5	0.70±0.05
$[Mo(CO)_4(pn)]$	10.0 [a]	3.8 [a]	−11.2 [a]	57	54.5	0.63±0.10
$[Pt(bipy)(N^2,N^2\text{-dmpn})]^{2+}$	7.0 [d]	7.0 [d]		52.5	52.5	0.22
$[Pt(bipy)(N^1,N^1\text{-dmpn})]^{2+}$	12.0 [d]	4.0 [d]	−12.0 [d]	52.5	52.5	0.93
$[Cr(CO)_4(tmpn)]$ [f]	12.50 [a]	2.76 [a]	−13.26 [a]	59.1		1.0
$[Cr(CO)_4(tmpn)]$ [g]	12.62 [a]	2.76 [a]	−13.22 [a]	59.1		1.0
$[Mo(CO)_4(tmpn)]$ [f]	12.32 [a]	2.47 [a]	−13.38 [a]	60.5		1.0
$[Mo(CO)_4(tmpn)]$ [g]	12.37 [a]	2.53 [a]	−13.39 [a]	60.2		1.0
$[Co(CN)_4(pen)]^-$	12.96 [e]	4.07 [e]	−12.61 [e]	51	48.5	1.07±0.05
$[Co(NH_3)_4(pen)]^{3+}$	13.26 [e]	4.34 [e]	−12.57 [e]	51	48.5	1.03±0.11
$[Pt(pen)_2]^{2+}$	11.71 [e]	4.27 [e]	−12.22 [e]	52.5	52.5	0.84±0.07
$[Mo(CO)_4(pen)]$	12.59 [e]	3.99 [e]	−12.03 [e]	57	54.5	0.77±0.01

[a] J values from ref. 13. [b] J values from ref. 55. [c] J values from ref. 56. [d] J values from ref. 57. [e] J values from ref. 58. [f] In pyridine. [g] In acetone.

ω_λ should be larger [16]. A value of 60.4° was determined for $[Mo(CO)_4(tmpn)]$ which has $n_e = 1.0$. Strain-energy calculations suggest ω_δ is 2.5° less than ω_λ. If these angles are used for $[Mo(CO)_4(dmbn)]$ in eqn. (14) with $X = 12.22/2.99$ or 4.02, n_e is 0.8 [13]. If, however, the ω value appropriate for dmbn differs from that for the tmpn system because the tmpn has different intra-ligand interactions, and it is assumed that n_e is in fact 1. then ω can be calculated from eqn. (15) to be 57°. An X-ray structure of a simple bidentate diamine molybdenum(0) complex would facilitate an evaluation of these two alternatives.

The ^1H NMR spectra of the square-planar complexes, $[Pt(NH_3)_2(dmbn)]^{2+}$ and $[Pt(bipy)(dmbn)]^{2+}$, have been analysed [55], and the coupling constants are given in Table 2. If ω is given the value 52.5° determined from $[Pt(bipy)(men)]^{2+}$, n_e is calculated to be 1.16 ± 0.07, and 1.27 ± 0.02. respectively. A value of 56° is required for ω to reduce n_e to 1.0. This suggests that the puckering of the chelate ring for dmbn complexes is greater than for other diamines, possibly due to the need to minimize unfavourable repulsions between the bulky tert-butyl group and other atoms in the chelate. For the cobalt complexes it was also found necessary to use a larger value of ω for the dmbn complexes.

The conclusion that n_e is approximately 1.0 for the square-planar Pt(II) complexes is supported by the $^3J_{PtH}$ coupling constants. One proton has a very large value for $^3J_{PtH}$, 82.1 Hz, consistent with an equatorial orientation with a dihedral angle approaching 180° (probably in the range 160–170°) [55]. The other two ring protons are axial in the λ_e conformation and the $PtNCH_a$ dihedral angle is close to 90°, thus making $^3J_{PtH_a}$ very small. For the 1,2-ethanediamine complexes of Pt(II), $[Pt(NH_3)_2(en)]^{2+}$, $[Pt(en)_2]^{2+}$, $[Pt(bipy)(en)]^{2+}$, $[Pt(dpen)(en)]^{2+}$, in which the $^3J_{PtH}$ values for the ring protons would be the average for the axial and equatorial protons the values obtained for $^3J_{PtH}$ are 41.5 [59], 41 [59], 40 [57], and 38.8 [60], respectively. If $^3J_{PtH_a}$ is close to 0, $^3J_{PtH_e}$ would be approximately 80 Hz [57], the value obtained for the dmbn complexes.

(R)-1,2-Propanediamine, $X = Y = NH_2$, $b = CH_3$. For the paramagnetic mono Ni(II) complex, $[Ni(OH_2)_4(pn)]^{2+}$ the ^1H NMR spectrum at 329.2 K has three peaks at δ^{iso} 18.0, 21.0, and 148.3 with an intensity ratio of 3:2:1 [18]. These have been assigned to the methyl group, the C–H protons that are largely axial (Fig. 4, a and d), and the C–H proton that is largely equatorial (Fig. 4c). The methyl group prefers the equatorial orientation. The observed separation of the resonances for the $CH–CH_2$ fragment, 127.3 ppm, is less than that observed for the dmbn complex because the axial conformation, δ, is populated. The mole fraction of the λ conformation at 300 K in aqueous solution calculated from eqn. (19) is 0.95. The resonances

for the 'equatorial' and 'axial' protons showed negative and positive deviations from Curie Law, respectively, consistent with an increased population of the δ conformation at higher temperature. Analysis of the temperature dependence of $\Delta\delta^{obs}$ gave ΔH 8.1 ± 0.3 kJ mol^{-1} and ΔS + 2.0 ± 0.7 JK^{-1} mol^{-1}, with ΔG (300 K) 7.5 ± 0.5 kJ mol^{-1} [18].

For the diamagnetic (*R*)-1,2-propanediamine complexes, the mole fraction of λ_e conformation can be determined from eqn. (14). Values for ω_λ and ω_δ are required for this calculation. For the cobalt(III) octahedral complexes, ω_λ was taken to be 51°. This value was based on the value of 51.1° determined by X-ray analysis for $[Co(NH_3)_4(pn)](S_2O_6)_{1.5}$ [61], on the average value fo 51.7° for the Co(en) chelate ring from the X-ray analysis of tris complexes, (see above) and from the values of 50.2° and 50.4° determined from the analysis of the coupling constants for $[Co(NH_3)_4(men)]^{3+}$ and $[Co(CN)_4(men)]^-$ [61]. Conformational-energy minimization calculations show that the δ_a chelate ring is slightly flattened due to the unfavourable non-bonded interactions of the axial methyl group in an octahedral complex and that the value of ω is about 2.5° less than for the equatorial conformation [3]. For the square-planar Pt(II) and Pd(II) diamine complexes where M–N is about 204 pm the average value of ω determined by X-ray analysis is about 52° (Table 3). Analysis of the coupling constants of $[Pt(bipy)(men)]^{2+}$ yields a value of 52.5° for ω [61]. Energy-minimization calculations for the square-planar complexes conclude that the ω values for the axial and equatorial conformations are the same. In the absence of a crystal structure of a simple molybdenum(0) diamine complex or other evidence, ω_λ was assumed to be 57°, the value found for $[Mo(CO)_4(dmbn)]$ with $n_e = 1.0$ and ω_δ was given a value 2.5° less. Using the above values of ω_λ and ω_δ for the (*R*)-pn complexes of Co(III), Pt(II), Pd(II), and Mo(0), n_λ has been calculated from eqn. (14) and presented in Table 2.

For the octahedral Co(III) complexes, the λ_e conformation is almost exclusively populated as had been found for the paramagnetic Ni(II) complex, but in the square-planar complexes and in the octahedral complexes with long M–N bonds, n_λ is only of the order of 0.6–0.7. The conclusion that in the latter complexes the axial conformation is significantly populated is supported by the values of $^3J_{PtH}$, $^3J_{PtC}$, and $\delta(^{13}CH_3)$. For the Pt(dmbn) complexes where n_e is 1.0, $^3J_{PtH_e}$ is found to be about 82 Hz [55]. For $[Pt(NH_3)_2(pn)]^{2+}$, the ring proton which is predominantly equatorial has a $^3J_{PtH}$ value of 64 Hz and the axial proton about 10 Hz [60], consistent with approximately 20% population of the axial conformer.

The $^3J_{PtC}$ values for the methyl group in the (*meso*-2,3-butanediamine)platinum(II) complexes, $[Pt(NH_3)_2(meso\text{-}2,3\text{-}bn)]^{2+}$ and $[Pt(bipy)(meso\text{-}2,3\text{-}bn)]^{2+}$, which are found to be 27.3 [69] and 26 Hz [57], respectively, are the average values for the axial and equatorial methyls. The

TABLE 3

Structural parameters for square-planar Pt(II) and Pd(II) complexes of diamines with bond lengths in pm and angles in deg

Complex	M–N [a]	NMN	ω	Φ [a]	$MNCCH_3$	Ref.
$[Pd(en)_2]Cl_2$	203.7	83.6	54.2	41.0		62
$[Pt(en)_2]tart$	204.2	83.6	52.1	38.8		63
	204.4	82.2	53.3	41.5		
$[Pt\{(R)\text{-pn}\}_2]Cl_2 \cdot 2\,H_2O$	205.5	82.9	52		171(eq)	64
	204.5	82.9	50		87(ax)	
	204.5	80.9	49		167(eq)	
	204.5	83.6	52		93(ax)	
[$PdCl_2$(*meso*-2.3-bn)]	202.9	83.6	53.3	41.1	162.0(eq) 78.5(ax)	65
$[Pt\{(R)\text{-pn}\}(dmen)][Sb_2\text{-}tart_2] \cdot 2\,H_2O$	206.0	81.9	50.3	37.2	173.2	66
	205.5	84.2	53.8	41.5		
$[Pt(NH_3)_2(mpn)][Sb_2tart_2] \cdot H_2O$	204	84.1	51.4	39.2	169.5	67
$[Pt(mpn)Cl_2]$	202.1	83.1	51.4	39.6	159.8	68
Average	204.3	83.1	51.9	40.0	167.1(eq) 86.2(ax)	

[a] Average value for each chelate ring.

related complexes with the racemic isomer of 2,3-butanediamine have $^3J_{PtC}$ values of 49.8 [69] and 51 Hz [57], respectively. In these complexes the chelate ring is largely in the di-equatorial conformation. For $[Pt(bipy)(pn)]^{2+}$ and $[Pt(NH_3)_2(pn)]^{2+}$ the $^3J_{PtC}$ values are 38 Hz [57,67], approximately midway between the values for the *meso*- and racemic-2,3-butanediamine complexes, again consistent with a mole fraction of the order of 0.25 for the axial conformation. The ^{13}C chemical shifts for the CH_3 group for the 1,2-propanediamine complexes are also approximately midway between the values for the *meso*- and racemic-2,3-butanediamine complexes. For the $[Pt(bipy)(diamine)]^{2+}$ complexes, the δ values are 17.05, 14.40 and 18.44, respectively [57], and for $[Pt(NH_3)_2(diamine)]^{2+}$, 16.8 [67], 13.8 and 18.0 [69], respectively. The circular dichroism spectra of (1,2-propanediamine)platinum(II) complexes are consistent with the axial conformation being present with a mole fraction of about 0.25 [70]. Finally, one chelate ring in $[Pt\{(R)\text{-pn}\}_2]Cl_2 \cdot 2\,H_2O$ has been shown by X-ray analysis to have an axial methyl [64].

(R)-1-Phenyl-1,2-ethanediamine, $X = Y = NH_2$, $b = C_6H_5$. Strain-energy minimization calculations of phenylcyclohexane and related compounds have shown that the most favoured conformation has the phenyl group in an

equatorial-parallel orientation (Fig. 7) and this is 15.3 kJ mol^{-1} more stable than the axial-perpendicular structure, the more favoured of the two axial conformations [71]. The terms 'parallel' and 'perpendicular' relate to the aromatic plane with respect to the C–H bond for the proton geminal to the phenyl.

From Dreiding models of the 1-phenyl-1,2-ethanediamine chelate ring, it can be seen that in the equatorial-parallel orientation the phenyl group's non-bonded interactions with the rest of the molecule are significantly less than in the equatorial-perpendicular orientation and the two axial structures. The axial-parallel conformation is destabilized by an interaction between one *ortho*-hydrogen of the phenyl and the metal ion, whereas the axial-perpendicular conformation is destabilized by the interactions of one *ortho*-hydrogen and its adjacent $N-H_{eq}$ and the other *ortho*-hydrogen with its adjacent $C-H_{eq}$. The adoption of an unsymmetric conformation with C1 closer to the NMN plane than C2 would markedly relieve the interaction for the axial-parallel structure but not the axial-perpendicular structure, and from Dreiding models it would appear that this unsymmetric chelate conformation would make the axial-parallel conformation more stable than axial-perpendicular conformation for square-planar structures. However, in octahedral complexes the axial-parallel structure is markedly destabilized by an interaction between an *ortho*-hydrogen of the phenyl and an apical ligand, even when the chelate ring adopts the above unsymmetric structure.

Results of conformational analyses by ^1H NMR of complexes of (*R*)-1-phenyl-1,2-ethanediamine are summarized in Table 2. For the square-planar Pt(II) complex, $[Pt(pen)_2]^{2+}$, the equatorial conformation predominates but there is still a significant population ($n_a = 0.16$) of the axial conformer. This

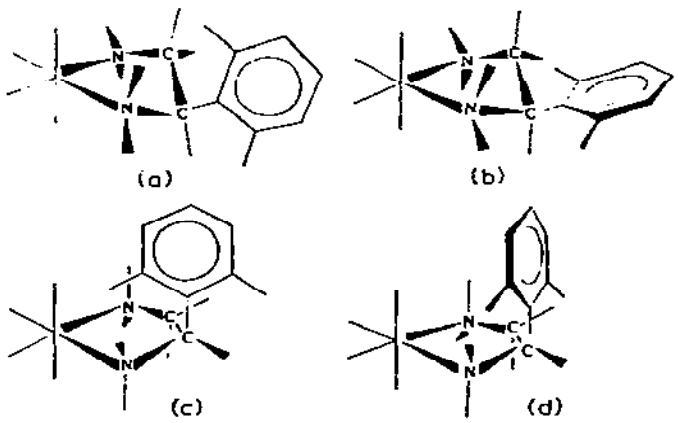


Fig. 7. Conformations of (*R*)-1-phenyl-1,2-ethanediamine: (a) equatorial-parallel; (b) equatorial-perpendicular; (c) axial-parallel; (d) axial-perpendicular [58] (reproduced with permission from Aust. J. Chem.).

is also true for the octahedral Mo(0) complex in which the long metal–ligand bonds reduce the repulsions between the axial phenyl and the apical ligand. For the octahedral Co(III) complexes the equatorial conformation is exclusively populated.

N-Methyl-1,2-ethanediamine $X = NHCH_3$, $Y = NH_2$. When the coordinated secondary amine group has the (*S*) configuration, the λ conformation has the methyl group equatorial. The ^1H NMR spectrum of $[Ni(OH_2)_4(men)]^{2+}$ in water has four peaks, which at 300 K are positioned at δ^{iso} 59.2 (2H), 125.4, 133.9 and 140.6, and which have been assigned to the two axial protons, the equatorial proton adjacent to the primary amine group, the methyl resonance, and the equatorial proton adjacent to the secondary amine [18]. The conformer populations were calculated by eqn. (19) to be n_e 0.71, n_a 0.29 [18]. A variable temperature study of the chemical shifts gave ΔH 2.1 ± 0.1 kJ mol^{-1} and ΔS −0.3 ± 0.3 JK^{-1} mol^{-1} [18]. Above 340 K in dimethyl sulfoxide, peaks for the axial and equatorial C–H resonances for $[Ni(Me_2SO)_4(men)]^{2+}$ converge at a greater rate than expected from conformational equilibrium until at 380 K the protons are completely averaged. Above this temperature, averaged peaks are observed for the two sets of protons. The averaging of the peaks is due to the inversion of the coordinated secondary nitrogen, and an approximate value for the rate of inversion has been calculated to be 6.4×10^3 s^{-1} from eqn. (23) [18].

For the above calculations of the conformer populations, the $\Delta\delta^{obs}$ value was taken from the δ values for the CH_2NH_2 protons and used in conjunction with $\Delta\delta^{int}$ from the dmbn system. Using these results and $\Delta\delta^{obs}$ for the CH_2NHCH_3 protons it was possible to calculate $\Delta\delta^{int}$ for the secondary amine group. This yielded $\Delta\delta^{int}$ 196.2 at 300 K for aqueous solutions [18]. In methanol and dimethyl sulfoxide the values were 207.4 and 212.2, respectively [18].

For diamagnetic complexes, $^3J_{HH}$ values for the CH_2CH_2 grouping can be utilized in conjunction with eqns. (12) and (13) to give values for ω and the mole fractions of the equatorial and axial conformations. Strain-energy minimization calculations show that for both square-planar and octahedral complexes of this ligand, the ω_e and ω_a values are the same [50].

Coupling constants and calculated values of n_λ and ω are given in Table 4 for $[Co(NH_3)_4(men)]^{3+}$, $[Co(CN)_4(men)]^-$, and $[Pt(bipy)(men)]^{2+}$. The population of the equatorial conformation for the men chelate is very dependent on the other ligands present, especially in the same plane as the men chelate. From Dreiding models it can be seen that for the (2,2′-bipyridine)platinum(II) complex the protons in the 6 and 6′ positions of the aromatic ligand interact severely with the equatorially-oriented $N–CH_3$ group. From the $^3J_{HH}$ values, one conformer was found to be exclusively

TABLE 4

Coupling constants and conformational parameters for complexes of *N*-methyl-1,2-ethanediamine with (*S*) absolute configuration. Coupling constants are in Hz and ω in deg [61]

Complex	J_{ad}	J_{ac}	J_{ab}	J_{cd}	J_{bd}	J_{bc}	n_λ	ω
$[Co(NH_3)_4(L)]^{3+}$	12.17	4.64	−13.10	−13.22	4.61	2.35	0.92±0.06	50.2±1.4
$[Co(CN)_4(L)]^-$	10.45	4.69	−13.26	−13.08	4.53	3.98	0.78±0.10	50.4±2.0
$[Pt(bipy)(L)]^{2+}$	1.15	4.34	−14.46	−13.09	4.04	13.88	0.0±0.08	52.5±1.2

populated. Because of the above unfavourable interaction of the equatorial N–CH_3, it has been concluded that the preferred conformer has the N–CH_3 group axial [61]. For the corresponding diammine complex where this interaction is absent it has been estimated from a circular dichroism study that n_e is 0.58 [67].

N,N'-Dimethyl-1,2-ethanediamine, X = Y = NHCH₃. Chelates of *N,N'*-dimethyl-1,2-ethanediamine have both nitrogens asymmetric which gives rise to a racemic and a *meso* form as shown in Fig. 8. In the racemic form, the two methyl groups are either both axial or both equatorial, whereas in the *meso* form both conformations have one equatorial and one axial methyl group.

In water at 301.5 K, the paramagnetic $[Ni(OH_2)_4(dmen)]^{2+}$ has five peaks in its ^1H NMR spectrum at δ 40.0, 86.7, 129.1, 133.8, and 156.3 with the broad peak at δ 86.7 consisting of two poorly resolved peaks. These have been assigned to the axial methylene protons for the racemic ligand, the four methylene protons of the *meso* ligand, the *meso* ligand's methyl protons, the racemic ligand's methyl protons, and the equatorial methylene protons for the racemic ligand, respectively [18,22]. At 301.5 K the ratio of the total areas of the methylene peaks for the racemic and *meso* isomers was 1.3:1. From eqn. (19), n_λ was calculated to be 0.80 and from a temperature dependence study of the chemical shifts, ΔH was calculated to be 2.2 ± 0.1 kJ mol^{-1} and $\Delta S - 3.9 \pm 0.2$ JK^{-1} mol^{-1} [18]. Values were also obtained for methanol and dimethyl sulfoxide solutions of the complex [18].

In dimethyl sulfoxide above 360 K the methyl resonances, and also the methylene resonances were averaged due to inversion of the coordinated nitrogens. The rate of inversion was calculated from eqn. (23) at the coalescence temperature of 370 K to be 9.0×10^3 s^{-1} [18].

Based on n_λ for the racemic isomer and the racemic: *meso* isomer ratio, the relative populations have been calculated for the conformations with two

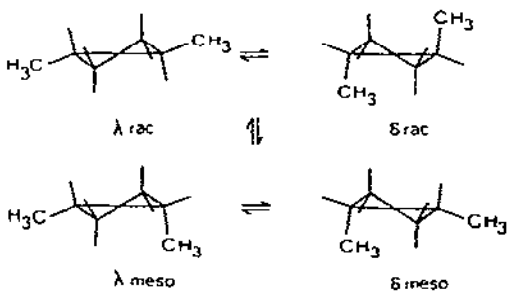


Fig. 8. Chelate rings for *N,N'*-dimethyl-1,2-ethanediamine [18] (reproduced with permission from Acta Chem. Scand.).

equatorial methyls, one equatorial and one axial methyl, and two axial methyls. The ratios at 300 K were calculated to be 1:0.96:0.25 in water, 1:0.56:0.22 in methanol, and 1:0.72:0.22 in dimethyl sulfoxide [18]. Taking into account the probability entropy term favouring the *meso* equatorial-axial configuration relative to the di-equatorial configuration, these results show that the energy difference between an axial and an equatorial *N*-methyl group for dmen does not differ markedly from the corresponding energy for the men complex.

The racemic: *meso* ratios for a number of diamagnetic complexes of dmen have been estimated from the ^{1}H NMR spectra by determining the relative band areas for specific resonances for the two isomers: $[Pt(NH_3)_2L]^{2+}$ 1.0:1 [72]; $[Pd(NH_3)_2L]^{2+}$, 1.0:1 [73]; $[Mo(CO)_4L]$, 1.5:1 [74]. Other values are in the literature [72,73] but it is not certain which of the two isomers predominates. For $[M(bipy)(dmen)]^{2+}$ one isomer clearly predominates with a ratio of 2:1 for Pt(II) [72] and 4:1 for Pd(II) [73]. Based on the severe interaction between an equatorial N–CH_3 group and the 6 and 6′ protons of the 2,2′-bipyridine, which was discussed above for the men complex, the diaxial racemic isomer is likely to predominate for these complexes.

N,N,N′,N′-Tetramethyl-1,2-ethanediamine, X = Y = N(CH$_3$)$_2$. The δ and λ conformations of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine chelate rings are equally populated. However, they are of particular conformational interest because their barrier to ring inversion is sufficiently high to allow the inversion to be frozen out at low temperature. Slow exchange ^{1}H NMR spectra have been reported for the tetrahedral complexes $[Co(NO)_2(tmen)]^+$ and $[ZnCl_2(tmen)]$ [20], for the eight-coordinate complex $[Pr([^2H_9]fod)_3(tmen)]$ [21], and for the octahedral complexes $[Cr(CO)_4(tmen)]$, $[Mo(CO)_4(tmen)]$ and $[W(CO)_4(tmen)]$ [19,75]. Approximate values of the barriers for conformational interconversion were estimated by the coalescence temperature method [76] to be 37 kJ mol^{-1} (183 K) for the tetrahedral complexes [20], and 42 kJ mol^{-1} (235 K) for the praseodymium complex [21]. A band-shape analysis has been reported for the low temperature 67.89 MHz ^{13}C spectra for the three octahedral complexes. The activation parameters for the $\delta \rightleftharpoons \lambda$ inversion are as follows: $\Delta H^{\neq}$, Cr 39.4 ± 1.2, Mo 41.5 ± 1.9, W 38.0 ± 0.8 kJ mol^{-1}; $\Delta S^{\neq}$, Cr, 5.7 ± 6.2, Mo 8.9 ± 9.1, W −4.4 ± 3.8 JK^{-1} mol^{-1}; and $\Delta G^{\neq}$ (300 K), Cr 37.7 ± 3.1, Mo 38.8 ± 3.7, W 39.3 ± 1.9 kJ mol^{-1} [19].

N^1-methyl-(S)-1,2-propanediamine, X = NH$_2$, Y = NHCH$_3$, a = CH$_3$. There are two diastereoisomers of chelated N^1-methyl-(*S*)-1,2-propanediamine with the coordinated secondary amine possessing the (*R*) or (*S*) configuration (Fig. 9). Bosnich and Sullivan [77] used the relative intensities of the N–CH_3

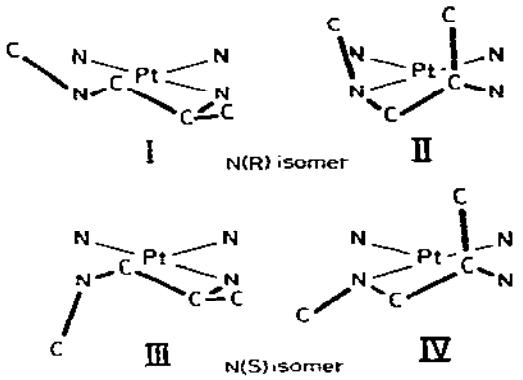


Fig. 9. The four possible conformers of $[Pt(NH_3)_2(mpn)]^{2+}$ [67] (reproduced with permission from Bull. Chem. Soc. Jpn.).

^1H NMR resonances for the two isomers in a number of Pt(II) complexes to determine the relative populations of the isomers. For the diammine, ethylenediamine and acetylacetonato complexes the ratios were approximately equal to 1. However, for the 1,10-phenanthroline complex only one $N-CH_3$ and also one $C-CH_3$ resonance were observed, consistent with one isomer having a mole fraction in excess of 0.9. The authors concluded that since the equatorial $N-CH_3$ group interacts unfavourably with the 2 and 9 protons of the 1,10-phenanthroline, the predominant isomer is most likely to have the (*S*) configuration for the nitrogen (isomer (III) Fig. 9) [77]. The alternative isomer with an axial $N-CH_3$ group has the $C-CH_3$ axial. This structure is destabilized by the 1,3-diaxial interactions of the methyl groups.

The relative populations of the δ and λ conformations for each diastereoisomer have been studied for the diammine complex [67]. Nakayama et al. [67] measured the $^3J_{PtC}$ values for the $C-CH_3$ group: (*R*)-N configuration 43 Hz and (*S*)-N configuration 35 Hz. Using the values of Erickson et al. [57] of 50 Hz for an equatorial CH_3 and 0 Hz for an axial CH_3, values of 0.86 and 0.70, respectively, were calculated for n_e for the two isomers [67].

N^1,N^1-Dimethyl-(R)-1,2-propanediamine, $X = NH_2$, $Y = N(CH_3)_2$, $b = CH_3$. Erickson et al. [57] noted that the $^3J_{PtC}$ value for the $C-^{13}CH_3$ group in $[Pt(bipy)(N^1,N^1\text{-}(R)\text{-dmpn})]^{2+}$, 43 Hz, was larger than for the analogous (*R*)-pn complex suggesting a larger n_λ value. The $^3J_{HH}$ values determined by these authors for the CH_2CH group of the diamine give n_λ 0.93 (Table 2). In the δ conformation there is an unfavourable 1,3-diaxial interaction between one $N-CH_3$ and the $C-CH_3$ group.

N^2,N^2-Dimethyl-(R)-1,2-propanediamine, $X = N(CH_3)_2$, $Y = NH_2$, $b = CH_3$. The *gauche* relationship between the equatorial C–CH_3 group and the two N–CH_3 groups in the λ conformation of chelated N^2,N^2-dimethyl-(*R*)-1,2-propanediamine would destabilize this conformation with respect to the δ conformation. In square-planar complexes such as [Pt(bipy)(N^2,N^2-(*R*)-dmpn)]$^{2+}$, the NMR data are consistent with the δ_a conformation being the dominant conformation. The $^3J_{HH}$ values for the CH_2CH group of the diamine give n_λ 0.22 (Table 2). The coupling between ^{195}Pt and C–$^{13}CH_3$ is small (20 Hz [57]). As the $PtNCCH_3$ dihedral angle is approximately 90° in the axial conformation (Table 3), the $^3J_{PtC}$ value is expected to be small if this conformation is more populated than the equatorial conformation.

N,N,N',N'-Tetramethyl-(R)-1,2-propanediamine, $X = Y = N(CH_3)_2$, $b = CH_3$. When the ^{1}H NMR spectra of [Mo(CO)$_4${(*R*)-tmpn}] and [Cr(CO)$_4${(*R*)-tmpn}] were measured in acetone down to 173 K, no changes were observed that would have been attributed to the freezing out of the conformational interconversion [13], whereas the related *N,N,N'N'*-tetramethyl-1,2-ethanediamine complexes exhibited spectra of the frozen conformations at temperatures of about 188 K [19]. This probably results from the fact that one conformation is not sufficiently populated to give rise to line broadening. The δ conformation is destabilized by 1,3-diaxial interactions between the C–CH_3 and one N–CH_3 group, and by interactions between the axial C–CH_3 group and an apical carbonyl ligand. If it is assumed that n_λ is 1.0, the observed $^3J_{HH}$ values for the $CHCH_2$ group give the following values for ω_λ: Cr(0) in pyridine and acetone, 59.1°; Mo(0) in pyridine, 60.5°; Mo(0) in acetone, 60.2° (Table 2).

(b) Amino alcohols

Amino alcohol chelate rings can exist in λ and δ conformations. The main difference between these chelates and the diamines is that the M–O bond is about 10 pm shorter than the M–N bond [78]. An axial substituent on the carbon adjacent to the oxygen would interact more strongly with apical ligands in an octahedral complex than if the substitution was at the carbon adjacent to the nitrogen. This is borne out by the results of the conformational analyses of a series of Co(III) complexes by the $^3J_{HH}$ method [79]. A value of 53° was determined for ω_λ from eqn. (15) using the observed coupling constants for [Co(NH$_3$)$_4${(*R*)-Bu^{t}CH(OH)CH_2NH_2}]$^{3+}$ and assuming n_λ is 1.0. Using this value for ω_λ, values of 1.0 were also obtained for other ligands with the (*R*)-configuration with substitution at the carbon adjacent to the oxygen. Methyl or ethyl substitution at the carbon adjacent to the nitrogen, on the other hand, did not enforce the equatorial conformation. The data are collected in Table 5.

TABLE 5

Coupling constants (Hz) and values of n_λ for tetraamminecobalt(III) complexes of amino alcohols with the (*R*) absolute configuration [79]

Amino alcohol	J_{ad}	J_{ac}	J_{cd}	n_λ
$MeCH(NH_2)CH_2OH$	12.01	5.73	−11.14	0.63±0.02
$EtCH(NH_2)CH_2OH$	11.47	5.38	−10.78	0.64±0.02
$MeCH(OH)CH_2NH_2$	12.01	3.59	−13.36	1.00±0.08
$PhCH(OH)CH_2NH_2$	12.46	3.68	−13.39	1.00±0.08
$PhCH(O)CH_2NH_2$	11.95	3.53	−11.94	1.00±0.08
$Bu^tCH(OH)CH_2NH_2$	12.74	3.91	−13.05	1.00

For the complex $[Ni(OH_2)_4(NH_2CH_2CH_2OCH_3)]^{2+}$ the axial and equatorial orientations of the OCH_3 group are equally populated as the NCH_2 protons give a sharp single line with approximately the same contact shift as the unsubstituted ligand [80]. The OCH_2 protons are not degenerate due to the asymmetry at the oxygen. From the separation of the OCH_2 resonances it was concluded that the rate of inversion at the oxygen for this complex is slow ($< 300\ s^{-1}$). For the unsubstituted ligand the inversion at the oxygen was found to be considerably faster ($> 6400\ s^{-1}$) due to an intermolecular proton exchange reaction involving hydrogen-bonded water molecules [80].

(c) Amino acids

Strain-energy minimization calculations of chelate rings formed by α-amino acids have shown that, in contrast to the $X-CH_2CH_2-Y$ systems, there are not simply two conformations of opposite chirality with well defined minima separated by a significant barrier to conformational interconversion, but instead a range of chiral envelope (Fig. 10) and planar structures which occupy a shallow energy minimum in the conformational energy surface [17]. Because of this, it is only possible to discuss conformational preferences in terms of ranges of conformations. Reviews of some paramagnetic [2] and diamagnetic [3] systems have been published previously. Since then, Erickson and his coworkers have published a series of papers on some Pt(II) complexes with N- and C-substituted amino acids in which coupling constant data are analysed in terms of conformational preferences [81–83]. Their analyses were based on a comparison of the observed $^3J_{HH}$ (NHCH), $^3J_{PtH}$, $^4J_{PtH}$, and $^3J_{PtC}$ values with those calculated for the different conformational types. The lack of a CH_2CH_2 grouping in the chelate rings prevents the application of the $^3J_{HH}$ method of analysis which was used for the diamine and amino alcohol systems.

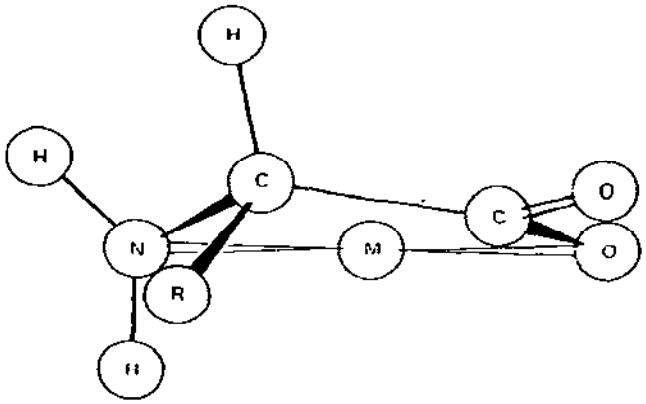


Fig. 10. Chiral envelope conformation of α-amino acid chelate rings [3] (reproduced with permission from Wiley-Interscience).

Some of the conclusions reached are as follows. In $[PtCl_2(sar)]^-$ the $N-CH_3$ group has a slight preference for the axial orientation. In contrast, the $C-CH_3$ in $[PtCl_2(ala)]^-$ prefers the equatorial orientation. These preferences are again found in the *cis-N*-methylalaninato complex $[PtCl_2(cis\text{-}mala)]^-$, but in the *trans-N*-methylalaninato complex both methyls prefer the axial orientation. The *gauche* orientation of the $N-CH_3$ and $C-CH_3$ groups has unfavourable steric interactions, which are absent in the di-axial structure, leading to an 8:1 ratio for the *trans*:*cis* isomers.

(d) Diarsenes

1-Trimethylsilyl-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $b = Si(CH_3)_3$. The large trimethylsilyl group has been assumed by Cullen et al. to adopt the equatorial orientation in tetracarbonyl complexes of the group VIB metals Cr, Mo and W with the ligand, 1-trimethylsilyl-1,2-bis(dimethylarseno)ethane [11,84,85]. The 1,3-diaxial interactions between the trimethylsilyl and the $As-CH_3$ groups are obviously severe from an inspection of Dreiding models and, in addition, the axial orientation of the trimethylsilyl group is destabilized by interactions with the apical CO ligand.

If it is assumed that n_c is equal to 1.0, ω_c can be calculated from eqn. (15). The coupling constant data and the ω values are in Table 6. The coupling constants do not vary significantly over the temperature range 307–363 K and are insensitive to solvent. The values of ω calculated for the Cr, Mo and W complexes are 51.8 ± 0.8, 54.5 ± 0.5, and 54.3 ± 0.1 respectively. X-ray analysis of some Cr(0) and Mo(0) tetracarbonyl complexes of fluorine substituted 1,2-bis(dimethylarseno) ethanes found values of ω of about 50°, with Cr–As = 243 pm and Mo–As = 258 pm [86]. The individual values of ω

TABLE 6

Coupling constants (Hz) and conformational parameters for complexes of substituted 1,2-bis(dimethylarseno)ethanes

Complex	Solvent	J_{ad}	J_{ae}	J_{ed}	ω(deg)	n_e
(a) n_e is assumed to be 1.0						
(i) 1-trimethylsilyl						
$[Cr(CO)_4L]$ [a]	$C_6H_5NO_2$	15.9	5.2	−12.7	51.5	
	C_6H_6	15.9	5.1	−12.7	52.0	
	$CHCl_3$	16.1	5.2	−12.8	51.9	
	CH_2Cl_2	15.9	5.3	−12.8	51.1	
	$(CD_3)_2CO$	16.1	5.0	−12.8	52.6	
$[Mo(CO)_4L]$ [b]	C_6H_6	15.7	4.5	−13.0	54.2	
	$CHCl_3$	15.9	4.5	−13.0	54.4	
	$(CD_3)_2CO$	16.0	4.4	−12.9	55.0	
$[W(CO)_4L]$ [b]	C_6H_6	15.9	4.5	−13.0	54.4	
	$CHCl_3$	16.0	4.6	−12.9	54.2	
	$(CD_3)_2CO$	16.0	4.5	−13.1	54.5	
(ii) 1-trichlorosilyl						
$[Cr(CO)_4L]$ [a]	C_6H_6	15.5	4.8	−12.5	52.6	
	$CHCl_3$	15.4	5.3	−12.8	50.5	
	CH_2Cl_2	15.5	5.2	−12.9	51.1	
(b) Using average ω values from (a) [c]						
(i) 1-cyano						
$[Cr(CO)_4L]$ [a]	$CHCl_3$	11.4	5.8	−12.4		0.59
	CH_2Cl_2	11.1	6.0	−13.1		0.54
	$(CD_3)_2CO$	10.2	6.1	−12.9		0.48
	$C_6H_5NO_2$ [d]	10.2	6.1	−13.0		0.48
$[Mo(CO)_4L]$ [b]	$CHCl_3$	10.1	5.4	−13.0		0.45
	$(CD_3)_2CO$	10.1	5.4	−13.3		0.45
$[W(CO)_4L]$ [b]	$CHCl_3$	11.8	5.4	−13.6		0.56
	$(CD_3)_2CO$	9.8	5.7	−13.2		0.41
(ii) 1-chloro						
$[Cr(CO)_4L]$ [a]	C_6H_6	7.5	5.2	−13.2		0.39
	$CHCl_3$	7.2	4.8	−13.4		0.39
	CH_2Cl_2	7.2	4.9	−13.6		0.42
	$(CD_3)_2CO$	6.5	4.8	−13.6		0.36
	$C_6H_5NO_2$	6.7	5.0	−13.5		0.36

[a] Coupling constants from ref. 84. [b] Coupling constants from ref. 11. [c] Average ω values: Cr, 51.8°; Mo, 54.5°; and W, 54.3°. [d] J values varied by <0.2 Hz between 307 and 373 K.

were not quoted, but based on calculations for analogous diamine systems [16], Cullen et al. estimated that, as a result of the difference in the M–As bond lengths, ω for the Mo complex should be about 2° larger than for the Cr complex, in excellent agreement with the above result [11]. Also, although

the W–As bond length is not known, it is expected to be similar to that of Mo–As [11], because the atomic radii of molybdenum and tungsten are almost identical [87]. Hence the ω values would be expected to be similar, as is indeed found.

1-Trichlorosilyl-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $b = SiCl_3$. Tetracarbonyl(1-trichlorosilyl-1,2-bis(dimethylarseno)ethane)chromium(0) has $^3J_{HH}$ values similar to the analogous trimethylsilyl derivative [84]. If it is assumed that the bulky trichlorosilyl group enforces the equatorial conformation, the dihedral angle, ω can be calculated from eqn. (15). The results for a number of solvents are in Table 6. The value of 51.4 ± 1.2 for ω is not significantly different to that calculated for the analogous trimethylsilyl derivative (51.8 ± 0.8).

1-Cyano-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $b = CN$. The cyano group is far less bulky than the trimethylsilyl and trichlorosilyl groups and from an inspection of Dreiding models of the tetracarbonyl metal complexes of 1-cyano-1,2-bis(dimethylarseno)ethane it would appear that there would not be a large energy difference between the conformations with equatorial and axial orientations of the cyano group. The observed $^3J_{HH}$ values (Table 6) support this. The mole fraction of the equatorial conformation, n_e, can be calculated from eqn. (14) if it is assumed that $\omega_e = \omega_\lambda$ and that the value of ω calculated for the analogous trimethylsilyl derivatives is applicable. The results for the Cr(0), Mo(0) and W(0) complexes in a number of solvents, which are given in Table 6, show that $n_e = 0.5 \pm 0.1$. The coupling constants were found to vary significantly with temperature [85] which would be expected if there is little preference for either conformer.

1-Chloro-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $b = Cl$. If the $^3J_{HH}$ values for the tetracarbonylchromium(0) complex of 1-chloro-1,2-bis(dimethylarseno)ethane are analysed in the same manner as for the analogous cyano derivative, the values of n_e that are obtained are about 0.4 showing a slight preference for the axial orientation for the chloro group. An axial chlorine has also been found to be preferred in 5-chloro-1,3-dioxane [88], and in diammine(2-chloro-1,3-propanediamine)platinum(II) [89].

1-Fluoro-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $b = F$. The fact that, for the tetracarbonylchromium(0) and -molybdenum(0) complexes of 1-fluoro-1,2-bis(dimethylarseno)ethane, the values for J_{ad} and J_{ae} are similar whereas J_{eF} is about 3 times the size of J_{dF} (Table 6) led Cullen et al. to conclude that the fluorine substituent strongly prefers the axial orientation [11,84,85,90]. Here, the mole fraction of the equatorial conformation was

calculated from the $^3J_{HH}$ values using eqn. (14) and the above assumptions regarding ω (Table 6). For the Cr(0) and Mo(0) complexes, n_c was calculated for a number of solvents to be 0.25 ± 0.2 and 0.32 ± 0.2, respectively, supporting the proposition of Cullen et al. that the axial orientation is preferred. Cullen et al. also analysed the J_{HF} values using $\alpha = 1.5$ [11], based on molecular orbital calculations of Govil [14]. If this value of α is used in conjunction with eqn. (14), n_c is calculated to be 0.21 and 0.25 for the Cr(0) and Mo(0) complexes, respectively, in reasonable agreement with the values calculated from $^3J_{HH}$. Values of α from about 1.4 to 2.0 have been estimated by other molecular orbital calculations and by experimental methods [6,9,14,15]. For the present systems the agreement between the n_c values calculated from $^3J_{HH}$ and those from $^3J_{HF}$ is optimized with a value of α_{HF} of about 1.6 (Table 7). This value will be used in subsequent calculations in this paper. The axial orientation is more preferred by a fluoro substituent than a chloro group in these chelates as has been found in the 5-halo-1,3-dioxane system [88].

1,1-Difluoro-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $a = b = F$. In the tetracarbonylchromium(0), -molybdenum(0) and -tungsten(0) complexes of 1,1-difluoro-1,2-bis(dimethylarseno)ethane, rapid conformational interconversion between the equienergetic conformers completely averages the $^3J_{HF}$ values and conformational information. The sums of the $^3J_{HF}$ values for the three complexes are 72, 73 and 72 Hz, respectively [11]. The analogous tricarbonylhalomanganese(I) complex has an average value for Σ^3J_{HF} of 72.0 Hz [91]. From Fig. 11, it can be appreciated that the two conformations in this complex need not be of equal energy, and that complete averaging of the

TABLE 7

Coupling constants (Hz)[a] and conformational parameters for complexes of 1-fluoro-1,2-bis(dimethylarseno)ethane

Complex	Solvent	J_{ad}	J_{ae}	n_e	J_{eF}	J_{dF}	n_e[b]	n_e[c]
$[Cr(CO)_4L]$	C_6H_6	3.6	3.4	0.25	48.7	15.7	0.22	0.27
	$CHCl_3$	3.6	3.4	0.25	48.3	15.5	0.21	0.26
	CH_2Cl_2	3.6	3.4	0.25	48.8	15.8	0.22	0.27
	$(CD_3)_2CO$	3.5	3.2	0.27	50.8	16.2	0.21	0.26
	$C_6H_5NO_2$	3.4	3.3	0.24	49.6	15.9	0.21	0.26
$[Mo(CO)_4L]$	$CHCl_3$	4.5	2.9	0.34	48.2	14.0	0.25	0.30
	$(CD_3)_2CO$	4.1	2.9	0.30	49.2	14.2	0.24	0.30

[a] From ref. 84. [b] Using $\alpha = 1.5$. [c] Using $\alpha = 1.6$.

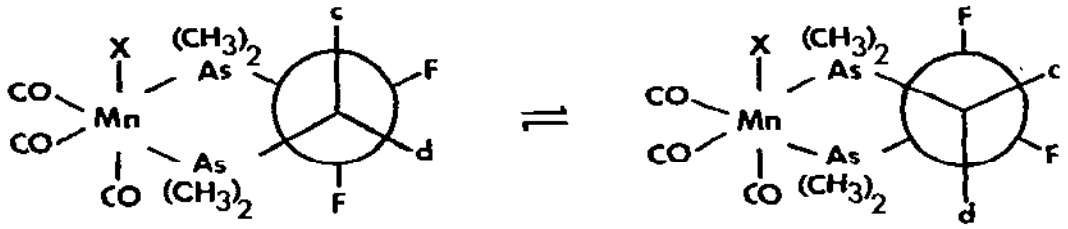


Fig. 11. Conformations of $[Mn(CO)_3X\{(CH_3)_2AsCF_2CH_2As(CH_3)_2\}]$.

$^3J_{HF}$ values is not expected. Expressions for the average coupling constants assuming that $\theta = 120°$ and the ω values for the two conformers are the same, are given in eqns. (28)–(30).

$$J_{cb} = n_1\{A_2\cos^2(120+\omega) - A_1\cos^2(120-\omega)\} + A_1\cos^2(120-\omega) \quad (28)$$

$$J_{ad} = n_1\{A_1\cos^2(120-\omega) - A_2\cos^2(120+\omega)\} + A_2\cos^2(120+\omega) \quad (29)$$

$$J_{ac} = A_1\cos^2\omega = J_{bd} \quad (30)$$

The two constants J_{ac} and J_{bd} should be equal irrespective of the conformer population. This equality should still exist if ω_I is not equal to ω_{II}. According to the data in the literature the two constants are markedly different [91]. For example, for the chloro complex in chloroform $J_{ac} = 6.7$ Hz and $J_{bd} = 12.7$ Hz. This observed inequality could result from one or more of the θ values being significantly different from 120°.

1,2-Difluoro-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $b = c = F$. Without coupling constant data for a frozen conformation it is not possible to determine quantitative conformational information for the complexes of 1,2-difluoro-1,2-bis(dimethylarseno)ethane. An attempt is described in the literature based on $^3J_{HH}$ and the premise that, since the value of $^3J_{HH}$ decreases with increasing temperature, becoming invariant above 342 K, the two conformers, diaxial and diequatorial, are equally populated at that temperature and beyond [85]. This premise is false. In addition it was claimed that, when the two fluorines are axial, $^3J_{HH}$ is given by $A_1\cos^2\omega$ [85], whereas $^3J_{HH}$ is in fact given by $A_1\cos^2(120-\omega)$.

The size of the averaged $^3J_{HH}$ [11,85,91], and the observation that $^3J_{HH}$ decreased on heating [85] suggest that the conformation with the two fluorines equatorial is preferred to an unknown but not marked degree.

1,1,2-Trifluoro-1,2-bis(dimethylarseno)ethane, $X = Y = As(CH_3)_2$, $a = b = c = F$. The two conformations of the chelate ring formed by 1,1,2-trifluoro-1,2-

bis(dimethylarseno)ethane have either two equatorial and one axial, (eea) or 1 equatorial and two axial (eaa) fluorines. In principle the conformer populations can be determined from the $^3J_{HF}$ values using eqn. (14). However, a definite conclusion cannot be reached because of difficulties in the unambiguous assignment of the geminal fluorines [11]. Results for the two alternative assignments are given in Table 8. For the tricarbonyl(halo)-manganese(I) complex, two isomers are possible for each configuration of the ligand due to the two different apical groups. However, only one isomer was detected in the NMR spectrum [91].

One assignment for a and b gives $n_{eea} = 0.0$. If this is the correct assignment the conformer with one equatorial and two axial fluorines is exclusively populated. The other assignment is consistent with both conformers being populated with a preference for the conformer with two equatorial and one axial fluorine. The n_{eea} values are solvent and temperature dependent, becoming larger with increasing dielectric constant and with decreasing temperature. For $[MnCl(CO)_3L]$ n_{eea} approaches 1.0 below 261 K.

The $^3J_{FF}$ values could also in theory be used to study conformer populations. However, the dihedral angle dependence of $^3J_{FF}$ has not been extensively researched. There is a report that it has a $\cos^2(3\Phi/2)$ dependence with maxima at 0° and 120°, and minima at 60° and 180° [92].

TABLE 8

Coupling constants (Hz) and conformational parameters for complexes of 1,1,2-trifluoro-1,2-bis(dimethylarseno)ethane at 307 K

Complex	Solvent	J_{ad}	J_{bd}	n_{eea} [a]
$[Cr(CO)_4L]$ [b]	C_6H_6	15.1	5.5	0.64
	$CHCl_3$	14.8	5.3	0.65
	CH_2Cl_2	15.0	5.3	0.66
	$(CD_3)_2CO$	17.3	5.6	0.73
	$C_6H_5NO_2$	16.0	5.4	0.73
$[Mo(CO)_4L]$ [c]	$CHCl_3$	16.1	4.7	0.72
	$(CD_3)_2CO$	19.1	5.3	0.76
$[MnCl(CO)_3L]$ [d]	$CHCl_3$	26.4	7.2	0.88
	$CHCl_3$ [e]	27.0	6.7	0.98
$[MnBr(CO)_3L]$ [f]	$CHCl_3$	26.2	7.3	0.86
	$(CD_3)_2CO$	24.8	7.9	0.74
$[MnI(CO)_3L]$ [f]	$CHCl_3$	25.2	7.5	0.80

[a] Reverse assignment of a and b yield $n_{eea} = 0.0$. [b] Coupling constants from ref. 84. [c] Coupling constants from ref. 11. [d] Coupling constants from ref. 85. [e] At 261 K. [f] Coupling constants from ref. 91.

(e) Thio ethers

1,2-Bis(alkylthio)ethane, X = Y = alkyl-S. The inversion of configuration at sulfur has been studied by ^{1}H NMR spectroscopy for unidentate [93–96] and chelate ligands [97–101]. The barrier to inversion has been found to be more than 10 kJ mol^{-1} less for sulfur than the barrier for the analogous selenium compound [94,95]. Below the coalescence temperature associated with the inversion, signals for *meso* and chiral isomers of 1,2-bis(alkylthio)ethane chelates have been observed, [97,99–101] and from these, the relative populations of these isomers can be determined. The results for the benzyl derivative coordinated to tetracarbonylchromium(0), -molybdenum(0), and -tungsten(0) are in Table 9 [97]. A band shape analysis of the spectra for these complexes has also given the barriers for inversion which are included in Table 9.

Signals from four diastereoisomers of {1,2-bis(trifluoromethylthio)-propane}dichloroplatinum(II) have been observed with the intensity ratio 1 : 1 : 2 : 8. There are asymmetric centres at S1, C2 and S2 and these give rise to a total of eight diastereoisomers which yield only four sets of signals with slow inversion at sulfur because of rapid $\lambda \rightleftharpoons \delta$ interconversion. The four sets of signals come from the following four equilibria: δ-S1(a)C2(e)S2(e) $\rightleftharpoons$ λ-S1(e)C2(a)S2(a), a *meso* isomer with the configuration S1(*S*)C2(*S*)S2(*R*); δ-S1(e)C2(e)S2(a) $\rightleftharpoons$ λ-S1(a)C2(a)S2(e), a *meso* isomer with the configuration S1(*R*)C2(*S*)S2(*S*); δ-S1(e)C2(e)S2(e) $\rightleftharpoons$ λ-S1(a)C2(a)S2(a), a chiral isomer

TABLE 9

Conformational energy differences (kJ mol^{-1}) between the *meso* and chiral isomers of the thio and seleno ether complexes and the free energies of activation (kJ mol^{-1}) for the chiral → *meso* isomerisation at 300 K

Complex	Solvent	ΔG	$\Delta G^{\neq}$
(i) $L = C_6H_5CH_2SCH_2CH_2SCH_2C_6H_5$ [a]			
$[Cr(CO)_4L]$	$CDCl_3$	2.61 ± 0.13	51.9 ± 3.1
$[Mo(CO)_4L]$	$CDCl_3$	2.88 ± 0.14	45.8 ± 3.8
$[W(CO)_4L]$	$CDCl_3$	2.35 ± 0.13	52.9 ± 2.0
(ii) $L = (CH_3)_2CHSeCH_2CH_2SeCH(CH_3)_2$ [b]			
$[PdCl_2L]$	$C_6H_5NO_2$	0.81 ± 0.10	79.5 ± 1.7
$[PdBr_2L]$	$C_6H_5NO_2$	0.59 ± 0.08	82.0 ± 2.5
$[Cr(CO)_4L]$	$CDCl_3$	1.22 ± 0.10	63.9 ± 0.4
$[Mo(CO)_4L]$	$CDCl_3$	1.11 ± 0.10	60.2 ± 0.8
$[W(CO)_4L]$	$CDCl_3$	1.44 ± 0.10	66.5 ± 0.4

[a] From ref. 97. [b] From ref. 106.

with the configuration S1(*R*)C2(*S*)S2(*R*); and δ-S1(e)C2(a)S2(e) ⇌ λ-S1(a)C2(e)S2(a), a chiral isomer with the configuration S1(*R*)C2(*R*)S2(*R*). Each of these also has an enantiomeric configuration which, of course, cannot be distinguished from it by NMR. Two of the diastereoisomers show $^{19}F-^{19}F$ coupling, and these isomers are thought to be the two *meso* isomers with the trifluoromethyl groups *syn* to one another [98]. One of these has the largest population in solution. It was assumed that this isomer was the one that crystallized from solution [98], and which was found by X-ray analysis to have the S1(*S*)C2(*S*)S2(*R*) configuration with the δ-S1(a)C2(e)S2(e) conformation [98,102]. The chelate ring's dihedral angles in the crystal were as follows: S1C1C2S2 = 47°, PtS1C1C2 = 37°, C1C2S2Pt = 33° [102].

The structure of bis{1,2-bis(methylthio)ethane}copper(II) tetrafluoroborate [103], bis{1,2-bis(ethylthio)ethane}copper(I) tetrafluoroborate [103], {1,2-bis(ethylthio)ethane}tetracarbonylchromium(0) [104], and bis{1,2-bis(carboxymethylthio)ethane}copper(I) [105], have also been determined by X-ray analysis. In the first and last of these, the substituents are in axial, equatorial positions (*meso*) whereas for the other two complexes the substituents are both axial.

(f) Seleno ethers

1,2-Bis(isopropylseleno)ethane, X = Y = $(CH_3)_2CHSe$. At ambient temperatures inversion at selenium in its chiral compounds is slow on the NMR time scale [106,107]. 1,2-Bis(alkylseleno)ethane complexes, therefore, exist as *meso* and chiral isomers. The δ and λ conformations of the *meso* isomer are equienergetic, but the gem methylene protons in theory never become equivalent on rapid conformational interconversion. For some complexes, the gem protons are degenerate, for example, in 1,2-bis(isopropylseleno)-ethanedichloropalladium(II) and its dibromo- analog [106], but in the tetracarbonylchromium(0), molybdenum(0), and tungsten(0) complexes of this ligand, the gem protons have a chemical shift difference of 17.3 ± 0.9 Hz [106].

One conformer of the chiral isomer has the two alkyl groups equatorial: for the (*R*,*R*) isomer the δ conformation. The other conformer has the two alkyl groups axial. An energy difference will exist between these two conformations. The populations of the two conformations and the dihedral angle ω can be determined from eqns. (12) and (13). In 1,2-bis(isopropylseleno)-ethanedichloropalladium(II), the spectrum of the CH_2CH_2 portion of the chiral chelate was analysed to give $J_{ad} = 11.7$, $J_{bc} = 7.6$, $J_{ac} = J_{bd} = 4.7$ Hz [106]. These values yield n_{ee} 0.65, $\Delta G_{320} = 1.65$ kJ mol^{-1}, and $\omega = 54.7°$. In the crystalline state the *meso* isomer has ω 51.4° [108]. The mole fraction of *meso* isomer was determined from the relative intensities of the *meso* and

chiral resonances to be 0.42 at 310 K. Hence the mole fractions of the three isomers are $n_{ee} = 0.4$, $n_{aa} = 0.2$ and $n_{ae} = 0.4$. The *meso* and the diequatorial chiral isomer are approximately equally populated in solution, with the diaxial chiral isomer present in half their concentrations. The stability of the *meso* relative to the diequatorial isomer is enhanced by the probability factor inherent in such isomers of about 1.7 kJ mol^{-1}, and if this is removed, it is seen that the steric interactions favour the diequatorial isomer. The *meso* isomer crystallizes from solution, and its structure has been determined by X-ray analysis [108]. Activation parameters for the inversion of the selenium donors were determined by band-shape analysis at elevated temperatures [106]. The data are accumulated in Table 9.

C. SIX-MEMBERED CHELATE RINGS

There are three basic types of conformation of six-membered chelate rings: chair (Ch), skew-boat (SB) and boat (Fig. 12). The boat is usually not significantly populated because of its unfavourable torsional arrangement and, in some complexes, severe non-bonded interactions involving substituents on C2 [109]. The SB conformation is chiral and exists in δ and λ

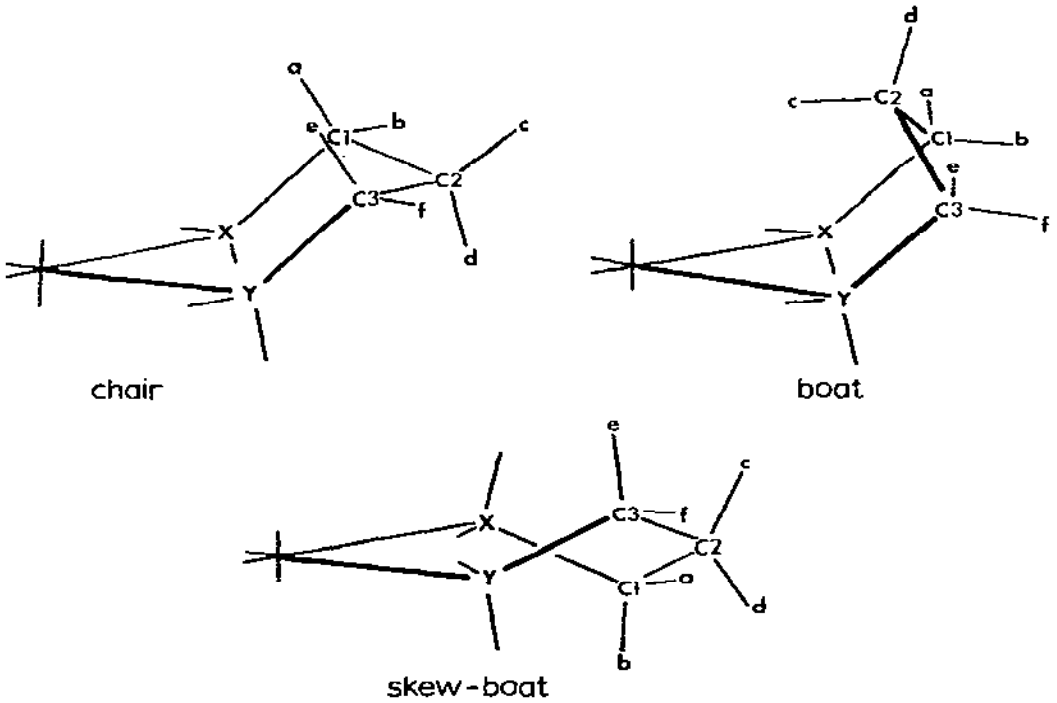


Fig. 12. Conformations of six-membered chelate rings.

Fig. 13. Dihedral angles, XC1C2C3 and C1C2C3Y, for six-membered chelate rings.

forms. It is very flexible and has the facility to adopt a range of unsymmetric conformations [109]. There are two achiral chair conformations, which in some systems are identical.

Chair to chair interconversion for diamine chelates generally has a lower barrier than for cyclohexane [109]. The minimum energy pathway for complexes with metal–donor atom bond lengths of the order of 200 pm has as its transition state a conformation where one $^{\alpha}C$ is out of the coordination plane and the other $^{\alpha}C$ and $^{\beta}C$ are in the plane [109]. This pathway has the SB conformation as an intermediate. Two alternative pathways which pass through a symmetrical boat conformation, have transition-state structures with the XCCCY fragment coplanar, or with the CXMYC fragment coplanar [19,50]. For metal–donor atom bond lengths of the order of 230 pm and longer, the pathway via the structure with the CXMYC fragment coplanar would appear to be most preferred of the three and to be of a relatively low energy [19].

The geometric parameters that are important for the conformational analysis include the dihedral angles XC1C2C3 (ω) (Fig. 13), and MXC1C2 (Φ). Two other parameters, D_1, the acute angle between the planes MXY and XC1C3Y, and D_2, the acute angle between the planes XC1C3Y and C1C2C3, have been used as indices of the degree of puckering of the chair conformations [110,111].

(i) Coupling-constant method ($^3J_{HH}$)

The application of the Karplus equation to $^3J_{HH}$ for six-membered chelates is based on the dihedral arrangement in Fig. 13. The dihedral angles ω_1 and ω_2 are equal in some systems but in others they are not.

(a) Diamines

Meso-2,4-pentanediamine, $X = Y = NH_2$, $b = f = CH_3$. Energy-minimization calculations predicted that chelate rings formed by *meso*-ptn are exclusively

in the Ch_{ee} conformation [112,113]. The X-ray structure of (+)-[Co(*meso*-ptn)$_3$][Co(CN)$_6$] · 5 H$_2$O has this structure with ω_e 65 ± 4° [114]. Assuming Ch_{ee} is exclusively populated in solution, ω_e was calculated from J_{ad} and J_{ae} using eqn. (31) for the complexes in Table 10.

$$X = J_{ad}/J_{ae} = \alpha \cos^2(120 + \omega_e)/\cos^2\omega_e \qquad (31)$$

For five octahedral complexes, and for square-planar [Pt(NH$_3$)$_2$(*meso*-ptn)]$^{2+}$ ω_e was calculated to be 61 ± 3°. Lower values were obtained for [Pt(NH$_3$)$_2$Cl$_2$(*meso*-ptn)]$^{2+}$ and for [Pt(bipy)(*meso*-ptn)]$^{2+}$. For the first of these the accuracy in the coupling constants was not high and this could account for the lower value. The second complex contains the rigid 2,2′-bipyridine. Its C6-H and C6′-H protons interact with the N–H$_e$ protons on *meso*-ptn and the structural changes that follow could account for the lower value of ω_e (56.9°). These unfavourable interactions could also yield a concentration of the SB_{ea} conformation.

TABLE 10

Coupling constant and conformational data for complexes of *meso*-ptn and 2-bu^t-tn

Complex	J_{ad}	J_{ae}	ω_e [a]
L = meso-*2,4-pentanediamine*			
[Co(NH$_3$)$_4$L]$^{3+}$ [b]	11.72	1.91	63.8
[Co(CN)$_4$L]$^-$ [b]	11.49	2.06	62.4
[Pt(NH$_3$)$_2$Cl$_2$L]$^{2+}$ [c]	10.5	2.5	57.6
[Pt(NH$_3$)$_2$Br$_2$L]$^{2+}$ [c]	11.0	2.0	62.1
[Pt(NH$_3$)$_2$(OH)$_2$L]$^{2+}$ [c]	11.0	2.5	58.4
[Pt(NH$_3$)$_2$(OH$_2$)$_2$L]$^{4+}$ [c]	11.0	2.3	59.8
[Pt(NH$_3$)$_2$L]$^{2+}$ [b]	11.5	2.1	62.1
[Pt(bipy)L]$^{2+}$ [b,d]	10.6 [d]	2.0	54.4
	10.87 [b]	2.72	56.9
[PdL$_2$]$^{2+}$ [e]	11.0	2.5	58.4
[PtL$_2$]$^{2+}$ [e]	11.0	2.3	59.8
L = *2-tert-butyl-1,3-propanediamine*			
[Pt(bipy)L]$^{2+}$ [f]	10.9	3.5	52.0
[Pd(bipy)L]$^{2+}$ [f]	11.0	3.13	54.4
[PtL$_2$]$^{2+}$ [f]	11.25	2.9	56.2
[PdL$_2$]$^{2+}$ [f]	11.2	2.9	56.1

[a] Calculated from eqn. (31) assuming 100% Ch. [b] Coupling constants from ref. 74. [c] Coupling constants from ref. 115. [d] Coupling constants from ref. 116. [e] Coupling constants from ref. 59. [f] Coupling constants from ref. 135.

Racemic-2,4-pentanediamine, $X = Y = NH_2$, $b = e = CH_3$. The two chair conformations of the chelate ring formed by the chiral isomer of 2,4-pentanediamine have one equatorial and one axial methyl group, i.e. Ch_{ea}. For the (*R*,*R*) isomer, the δ-SB conformation has two axial methyls, whereas the λ-SB has two equatorial methyls. The X-ray determined structures of Δ-$[Co\{(R,R)\text{-ptn}\}_3]Cl_3 \cdot 2H_2O$ [118], Λ-$[Co\{R,R)\text{-ptn}\}_3]Cl_3 \cdot H_2O$ [119], *cis*-$[Co(NH_3)_2\{(R,R)\text{-ptn}\}_2]Cl_3 \cdot H_2O$ [120], and $[Co(NH_3)_4\{(\pm)\text{ptn}\}]_2(S_2O_6)_3 \cdot 4H_2O$ [121] have the chelate ring in the SB_{ee} conformation, consistent with the predictions of conformational-energy minimization calculations [112,113,117,121]. In contrast in the square-planar cor[illegible]. $[Pt\{(S,S)\text{-ptn}\}_2]Cl_2 \cdot H_2O$, the rings are in the Ch_{ea} conformation [122].

The ^1H NMR spectra of all the (±)-ptn complexes have the common feature of two triplets for the ring protons when the CH_3 protons are decoupled from them. The difference lies in the size of the coupling constants: $[Co(NH_3)_4L]^{3+}$, 7.6 [121]; $[Co(CN)_4L]^-$, 7.0 [121]; Δ-$[Co\{(R.R)\text{-L}\}_3]^{3+}$, 8.7 [121]; Λ-$[Co\{(R,R)\text{-L}\}_3]^{3+}$, 8.4 [121]; $[Mo(CO)_4L]$, 6.3 [121]; $[Pt(NH_3)_2Cl_2L]^{2+}$, 7.0 [115]; $[Pt(NH_3)_2(OH)_2L]^{2+}$, 7.5 [115]; $[Pt(NH_3)_2(OH_2)_2L]^{4+}$, 7.5 [115]; $[Pt(NH_3)_2L]^{2+}$, 5.5 [59]; $[Pt(OH_2)_2L]^{2+}$, 5.3 [59]; $[Pt(bipy)L]^{2+}$, 5.9 Hz [121]. This A_2B_2 pattern is consistent with rapid interconversion between two chair conformations. For the skew-boat conformation, the SB_{ee} structure must be greatly preferred over the SB_{aa}, and the spectrum should have an AA′BB′ pattern. Under certain circumstances, this pattern can approximate an A_2B_2 pattern of two 1:2:1 triplets which is observed for the (±)-ptn chelates. It has been shown that, for the octahedral complex $[Co(NH_3)_4L]^{3+}$, the ^1H NMR spectrum is consistent with the skew-boat conformation [121]. A value of 33° for ω, found from the X-ray determined structure was used to calculated the coupling constants J_{ad} (8.78 Hz) and J_{ac} (6.46 Hz) from the Karplus relationships given in eqns. (32) and (33) [121].

$$J_{ad} = J_{cf} = A_2 \cos^2(120 + \omega) \tag{32}$$

$$J_{ac} = J_{df} = A_1 \cos^2\omega \tag{33}$$

The observed coupling constant is the average of J_{ad} and J_{ac}. The ^1H NMR spectrum was shown to be inconsistent with an exclusive chair conformation [121]. It should be noted that the cobalt(III) complex of (*R*.*R*)-pentanediaminetetraacetate, in which the ligand is sexadentate and the diamine chelate ring fixed in a skew-boat structure, has a t[illegible] signal for the β-CH_2 group, with *J* about 8 Hz [123].

The ^1H NMR spectra of the other octahedral complexes of (±)-ptn can also be shown to be consistent with a skew-boat conformation with an average dihedral angle of 33°. The following values for the coupling con-

stants J_{ad} and J_{ac}, have been calculated from eqns. (32) and (33): $[Co(CN)_4L]^-$, 8.09 and 5.97 Hz; Δ-$[Co\{(R,R)\text{-}L\}_3]^{3+}$, 10.00 and 7.38 Hz; Λ-$[Co\{(R,R)\text{-}L\}_3]^{3+}$, 9.66 and 7.14 Hz; $[Mo(CO)_4L]$, 8.65 and 5.35 Hz; $[Pt(NH_3)_2Cl_2L]^{2+}$, 8.05 and 5.95 Hz; $[Pt(NH_3)_2(OH)_2L]^{2+}$, 7.63 and 6.37 Hz; $[Pt(NH_3)_2(OH_2)_2L]^{4+}$, 7.63 and 6.37 Hz.

If it is assumed that the conformation exists totally as SB_{ee} with $\omega(SB_{ee}) = 33°$, and that the A_2 and A_1 values from the corresponding *meso*-ptn complex apply, the calculated values for J_{obs} are: $[Co(NH_3)_4L]^{3+}$, 8.1 Hz; $[Co(CN)_4L]^-$, 7.9 Hz; $[Pt(NH_3)_2L]^{2+}$, 7.9 Hz; $[Pt(bipy)L]^{2+}$, 7.5 Hz. The results for the Co(III) complexes are in reasonable agreement with the observed coupling constants, with the smaller values of J_{obs} possibly being due to the presence of a small amount of the Ch_{ea} conformation. The square-planar Pt(II) complexes obviously do not exist exclusively in the skew-boat conformation. If it is assumed that the chair conformations, and not the skew-boat conformation, are populated, J_{obs} results from the average of J_{ad} and J_{ac} that are, in turn, each averaged over the two equienergetic chair conformations

$$J_{ad} = 0.5\{A_2\cos^2(120 + \omega_a) + A_1\cos^2(120 - \omega_a')\} \quad (34)$$

$$J_{ac} = 0.5(A_1\cos^2\omega_a + A_1\cos^2\omega_a') \quad (35)$$

$$J_{obs} = 0.5(J_{ad} + J_{ac}) \quad (36)$$

where $\omega_a = \omega_1$ and $\omega_a' = \omega_2$ (Fig. 13). Eqn. (34) applies where $\omega_a' \geqslant 30°$; otherwise eqn. (37) applies.

$$J_{ad} = 0.5\{A_2\cos^2(120 + \omega_a) + A_2\cos^2(120 - \omega_a')\} \quad (37)$$

Again, if A_2 and A_1 are calculated from the data for the analogous *meso*-ptn complexes, it is possible, in theory, to derive values of ω_a' and ω_a necessary to account for J_{obs}. For $[Pt(NH_3)_2L]^{2+}$, if the chairs are symmetric, J_{obs} can be accounted for if $\omega_a = \omega_a' = 33°$, i.e. a very flattened chair conformation. On the other hand, a number of unsymmetric structures with ω_a' about 24° and ω_a about 60° are consistent with the data [74]. For the bipy complex, $\omega_a' = 10°$ and $\omega_a = 60°$ is a solution [74]. These results are surprising, considering the relatively undistorted chair conformation found for $[Pt\{(S,S)\text{-ptn}\}_2]Cl_2 \cdot H_2O$ [122]. However, if it is assumed that the chair conformation is undistorted with $\omega_a = \omega_a' = 60°$, then J_{ad} and J_{ac} are calculated to be 6.96 and 2.40 Hz, giving J_{obs} as 4.68 Hz for $[Pt(NH_3)_2L]^{2+}$, and 6.59 and 2.28 Hz, giving J_{obs} as 4.44 Hz for $[Pt(bipy)L]^{2+}$. The higher values found for J_{obs} for the square-planar Pt(II) complexes can be accounted for by the existence of both the chair and SB_{ee} conformations, and the mole fractions of each conformation can be calculated from eqns. (38)–(40) [74].

J_{obs} is the average of J_{ad} and J_{ae} and $n(\mathrm{Ch})$ is the mole fraction of the two interconverting, equienergetic chair conformations.

$$J_{ad} = n(\mathrm{Ch})\, J_{ad}(\mathrm{Ch}) + n(\mathrm{SB_{ee}})\, J_{ad}(\mathrm{SB_{ee}}) \tag{38}$$

$$J_{ae} = n(\mathrm{Ch})\, J_{ae}(\mathrm{Ch}) + n(\mathrm{SB_{ee}})\, J_{ae}(\mathrm{SB_{ee}}) \tag{39}$$

$$n(\mathrm{Ch}) + n(\mathrm{SB_{ee}}) = 1 \tag{40}$$

For $[Pt(NH_3)_2L]^{2+}$ and $[Pt(bipy)L]^{2+}$ $n(\mathrm{Ch})$ is calculated to be 0.75 and 0.54 respectively assuming the angles $\omega_{SB} = 33°$ and $\omega_a = \omega_a' = 60°$. The free energy difference between the skew-boat and chair conformations at 300 K is 2.7 kJ mol^{-1} for $[Pt(NH_3)_2L]^{2+}$ and 0.4 kJ mol^{-1} for $[Pt(bipy)L]^{2+}$. This marked increase in the population of the chair conformations in the square-planar complexes compared with that for the Co(III) complexes where the skew-boat conformation was preferred, results from the reduced unfavourable non-bonded interactions of the chair's axial methyl group in these Pt(II) complexes. As was suggested for the *meso*-ptn complexes of Pt(II), it is possible that the larger population of the skew-boat conformation for the bipy complex than the diammine complex could be due to unfavourable interactions between the bipy C6–H and C6′–H protons with the $N–H_e$ protons in the chair conformation. That the skew-boat conformation exists at all for these square-planar complexes in solution is probably due to the presence of solvent molecules oriented in the fifth and sixth coordination positions which would lead to a preference for the substituent to be equatorial [124].

1,3-Butanediamine, $X = Y = NH_2$, $f = CH_3$. Since the X-ray structure of $[Pt\{(S,S)\text{-ptn}\}_2]Cl_2 \cdot H_2O$ shows that the chair conformation with one methyl axial is not significantly distorted in square-planar complexes [122], it is probably correct to assume that for square-planar complexes of 1,3-bn, the predominant conformations are Ch_e and Ch_a. This assumption can be tested using $^3J_{HH}$, as can the alternative assumption that the predominant equilibrium is between Ch_e and SB_e.

Coupling constant data are available for $[Pt(bipy)(1,3\text{-bn})]^{2+}$: $J_{ee} = 3.3$, $J_{de} = 9.2$, $J_{ad} = 9.4$, $J_{ae} = 3.3$, $J_{be} = 6.3$, and $J_{bd} = 3.5$ [116]. These values were obtained by first-order approximation. If it is assumed that Ch_e is solely populated, J_{ad}/J_{ae} (eqn. 31), J_{de}/J_{ee} (eqn. 41) and J_{be}/J_{bd} (eqn. 42) yield values of 49.7, 50.0 and 66.7 for ω_e. The lack of consistency between these values shows that another conformation must be considered.

$$J_{de}/J_{ee} = \alpha \cos^2(120 + \omega_e)/\cos^2\omega_e \tag{41}$$

$$J_{be}/J_{bd} = \cos^2(120 - \omega_e)/\cos^2\omega_e \tag{42}$$

If it is assumed that the other conformation is SB_e, the mole fraction of Ch_e, $n(Ch_e)$, can be calculated from eqns. (43)–(45), where $X = J_{dc}/J_{ce}$, $Y = J_{ad}/J_{ae}$ and $Z = J_{bc}/J_{bd}$. For $\omega_{SB} < 30°$, the coefficient α must be used in conjunction with $\cos^2(120 - \omega_{SB})$ in eqn. (44).

$$n(Ch_e) = \alpha \cos^2(120 + \omega_{SB}) - X \cos^2\omega_{SB}/X\left[\cos^2\omega_e - \cos^2\omega_{SB}\right] - \alpha\left[\cos^2(120 + \omega_e) - \cos^2(120 + \omega_{SB})\right] \quad (43)$$

$$n(Ch_e) = \cos^2(120 - \omega_{SB}) - Y \cos^2\omega_{SB}/Y\left[\cos^2\omega_e - \cos^2\omega_{SB}\right] - \alpha \cos^2(120 + \omega_e) + \cos^2(120 - \omega_{SB}) \quad (44)$$

$$n(Ch_e) = \alpha \cos^2(120 + \omega_{SB}) - Z \cos^2\omega_{SB}/Z\left[\cos^2\omega_e - \cos^2\omega_{SB}\right] - \cos^2(120 - \omega_e) + \alpha \cos^2(120 + \omega_{SB}) \quad (45)$$

A value of 56.9° has been taken for ω_e for $[Pt(bipy)(1,3\text{-bn})]^{2+}$ as this is the value found for the analogous *meso*-ptn complex. A reliable value for ω_{SB} is not known. X-Ray structural studies have found values in the order of 30–35° [111,118,121]. The three equations yield markedly different values for $n(Ch_e)$ for ω_{SB} values between 25 and 40° and therefore it can be concluded that the $Ch_e \rightleftharpoons SB_e$ equilibrium does not predominate. If it is assumed that the predominant equilibrium is between Ch_e and Ch_a, $n(Ch_e)$ can be calculated from eqns. (46)–(48).

$$n(Ch_e) = X \cos^2\omega_a - \cos^2(120 - \omega_a)/\alpha \cos^2(120 + \omega_e) - \cos^2(120 - \omega_a) - X\left(\cos^2\omega_e - \cos^2\omega_a\right) \quad (46)$$

$$n(Ch_e) = Y \cos^2\omega_a' - \cos^2(120 - \omega_a')/\alpha \cos^2(120 + \omega_e) - \cos^2(120 - \omega_a') - Y\left(\cos^2\omega_e - \cos^2\omega_a'\right) \quad (47)$$

$$n(Ch_e) = Z \cos^2\omega_a' - \alpha \cos^2(120 + \omega_a')/\cos^2(120 - \omega_e) - \alpha \cos^2(120 + \omega_a') - Z\left(\cos^2\omega_e - \cos^2\omega_a'\right) \quad (48)$$

where ω_a is the dihedral angle C1C2C3Y, and ω_a' is XC1C2C3. If the values $\omega_a = 60°$ and $\omega_a' = 10°$ that were calculated for Ch_a for $[Pt(bipy)\{(\pm)\text{-ptn}\}]^{2+}$ are used for $[Pt(bipy)(1,3\text{-bn})]^{2+}$ with ω_e 56.9°, $n(Ch_e)$ calculated from eqn. (48) differs markedly from the values calculated from eqn. (46) and eqn. (47). However, if it is assumed that $\omega_e = \omega_a = \omega_a' = 56.9$, $n(Ch_e)$ is calculated to be 0.65 ± 0.01 from these three equations. The agreement shows that the equilibrium $Ch_e \rightleftharpoons Ch_a$ can explain the observed coupling constants. It would appear that in $[Pt(bipy)(1,3\text{-bn})]^{2+}$ the chair conformation with the axial methyl is not distorted by the presence of the axial methyl as was indeed found for $[Pt\{(S,S)\text{-ptn}\}_2]Cl_2 \cdot H_2O$ [122]. The free energy

difference between Ch_a and Ch_e at the probe temperature of about 300 K is 1.5 kJ mol^{-1}.

For the octahedral complex, $[Co(NH_3)_4(1,3\text{-bn})]^{3+}$, the following coupling constants were obtained: J_{ee}, 2.11; J_{de}, 11.71; J_{ad}, 12.94; J_{ae}, 2.17; J_{be}, 3.02; and J_{bd}, 3.27 Hz [74]. If it assumed that Ch_e is solely populated, values of ω_e can be calculated from eqns. (31), (41) and (42). The values obtained (63.4°, 62.3° and 59.3°) support the assumption that the Ch_e conformation is exclusively populated. Reliable values for the coupling constants are not available for other 1,3-bn complexes.

2-Methyl-2,4-pentanediamine, $X = Y = NH_2$, $b = e = f = CH_3$. Conformational-energy minimization calculations show that only two conformations are populated for the mptn chelate ring, a flattened chair and an unsymmetric boat, both with two equatorial and one axial methyl groups [61]. These conformations have been found by X-ray analysis for the complexes, $[Co(NH_3)_4(mptn)][ZnCl_4]Cl$ and $[Pt(bipy)(mptn)](NO_3)_2 \cdot 0.5\ H_2O$, respectively [61]. If one conformation is exclusively populated, the torsional angle XC1C2C3 (ω_e) can be determined from eqn. (31) and the vicinal proton–proton coupling constants, J_{ad} and J_{ae}. The observed values for J_{ad} and J_{ae} and the calculated ω_e values are as follows: $[Co(NH_3)_4(mptn)]^{3+}$, 11.46, 1.33 Hz, 68.3°; $[Co(CN)_4(mptn)]^-$, 11.30, 1.28 Hz, 68.6°; $[Pt(bipy)(mptn)]^{2+}$, 11.41, 1.97 Hz, 62.9° [74]. These values of ω_e are to be compared with the values 64.7° and 74.6° determined by crystal structure analysis for the chair and boat conformations of the above complexes, and with the following values calculated by the energy minimization technique: $[Co(NH_3)_4(mptn)]^{3+}$, chair 68.1°, boat 79.6°; $[Pt(bipy)(mptn)]^{2+}$ chair, 57.3°, boat 76.8° [61].

If it is assumed that both conformations are present in solution, the mole fractions of the chair, and hence the boat conformation, can be calculated from eqn. (43) where for this system ω_{SB} is the torsional angle for the boat conformation, and the values of ω adopted for the chair and boat conformation are those determined by the conformational-energy minimization calculations. The calculated n_{Ch} values are 0.97, 0.94 and 0.63 for the complexes $[Co(NH_3)_4(mptn)]^{3+}$, $[Co(CN)_4(mptn)]^-$, and $[Pt(bipy)(mptn)]^{2+}$ [74].

2-Tert-butyl-1,3-propanediamine, $X = Y = NH_2$, $c = bu^t$. The tert-butyl group is usually assumed to adopt an equatorial orientation exclusively. In the six-membered diamine chelates, an axial tert-butyl group at C2 does not interact unfavourably with the metal or any apical ligand. The major destabilizing influence is a non-bonded interaction with the $N–H_a$ protons, which can be minimized by reducing D_2.

If it is assumed that the tert-butyl group enforces the Ch_e conformation

exclusively, the dihedral angle ω_c can be calculated using eqn. (49). Data are in Table 10. The values of ω_c are about 5° less than those for the analogous *meso*-ptn complexes. This could be due to a ring distortion resulting from some interaction of the equatorial tert-butyl group or it could be due to the axial conformation being populated. If it is assumed that $\omega_c = \omega_a$ and that the values of ω_c for the *meso*-ptn complexes are appropriate, $n(\mathrm{Ch_c})$ can be calculated: for $[Pt(bipy)(2\text{-bu}^t\text{-tn})]^{2+}$ it is 0.74, and for $[Pt(2\text{-bu}^t\text{-tn})_2]^{2+}$ 0.76.

$$J_{ad}/J_{bd} = \alpha \cos^2(120 + \omega_c)/\cos^2\omega_c \tag{49}$$

2-Hydroxy-1,3-propanediamine, $X = Y = NH_2$, $c = OH$. The spectra of $[Pt(NH_3)_2(2\text{-OH-tn})]^{2+}$, $[Pt(2\text{-OH-tn})_2]^{2+}$, and $[Pt(NH_3)_2Cl_2(2\text{-OH-tn})]^{2+}$ have been analysed by Appleton and Hall [125]. For $[Pt(NH_3)_2(2\text{-OH-tn})]^{2+}$, $J_{ad} = 5.2$ and $J_{bd} = 0.8$ Hz which is consistent with the OH group being axial with $\omega_a = 74°$ calculated from eqn. (50).

$$J_{ad}/J_{bd} = \cos^2(120 - \omega_a)/\cos^2\omega_a \tag{50}$$

The other two complexes have similar coupling constants. In hydroxycyclohexane, the OH group prefers the equatorial orientation [126], but in some heterocyclic systems the axial structure is stabilized by H-bonding interactions [127]. For the above complex, Appleton and Hall proposed that the axial conformation is stabilized by H-bonding to the $N\text{–}H_a$ protons [125]. This interaction is optimized if D_2 and concomitantly ω_a are increased.

2-Chloro-1,3-propanediamine, $X = Y = NH_2$, $c = Cl$. A chlorine atom substituted at C2 also appears to stabilize $\mathrm{Ch_a}$. The vicinal coupling constants for $[Pt(NH_3)_2(2\text{-Cl-tn})]^{2+}$ are $J_{ad} = 5.0$ and $J_{bd} = 2.6$ Hz [125]. If the chelate ring has $n_a = 1$, ω_a is equal to 65° (eqn. 50). The axial orientation is stabilized by $N\text{–}H_a \cdots Cl$ interactions.

1,3-Bis(methylamino)propane, $X = Y = NHCH_3$. When this ligand is coordinated, there are three diastereomers possible: (*R,S*), (*R,R*) and (*S,S*). Appleton and Hall have shown from the ^1H NMR spectrum of $[Pt(NH_3)_2(dmtn)]^{2+}$, that the ratio of concentrations of the *meso* and chiral forms is 28:1 [128], whereas for $[Pt(bipy)(dmtn)]^{2+}$ only one isomer was detected and that was concluded to be the *meso* isomer [116].

The 270 MHz spectrum of $[Pt(NH_3)_2(dmtn)]^{2+}$ was analyzed for the *meso* isomer to give $J_{ad} = J_{de} = 13.2$, and $J_{ae} = J_{bc} = J_{bd} = J_{ce} = J_{cf} = J_{af} = 2.6$ Hz [128]. When the ratio J_{ad}/J_{ac} is substituted into eqn. (31), the dihedral angle ω is calculated to be 60.8°. From the equality $J_{ac} = J_{bc} = J_{bd}$, it can be concluded that ω equals 60° in agreement with the result from J_{ad}/J_{ac}.

Therefore, as far as the XC1C2C3Y fragment is concerned, there is little distortion from the ideal torsional geometry. The above result is consistent with one chair conformation predominating, probably Ch_{ee} with both $N-CH_3$ groups equatorial.

For $[Pt(bipy)(dmtn)]^{2+}$ the corresponding coupling constants to the above are 12 and 3 Hz, respectively [116]. From J_{ad}/J_{ae} and eqn. (31), ω can be calculated to be 56.7°, similar to that found for $[Pt(bipy)(meso\text{-}ptn)]^{2+}$. However, the equality $J_{ae} = J_{be} = J_{bd}$ suggests 60°. The precision of the coupling constant data is perhaps the reason for this discrepancy. The coupling constants are again consistent however, with one conformation predominating. In the Ch_{ee} structure the $(N-CH_3)_e$ groups would interact unfavourably with C6–H and C6′–H of the bipyridine ring and cause some distortion of the chelate ring. On the other hand, in Ch_{aa} the 1,3-diaxial interactions of the $(N-CH_3)$ groups would destabilize the conformation. This interaction could be decreased by reducing D_1. It is not clear from the $^3J_{HH}$ data whether Ch_{ee} or Ch_{aa} predominates. However, from the results for $[Pt(bipy)(2\text{-}Me\text{-}dmtn)]^{2+}$ it appears that Ch_{aa} would be preferred.

1,3-Bis(methylamino)-2-methylpropane, $X = Y = NHCH_3$, $c = CH_3$. Although a number of configurations are possible for this chelate with *meso* and chiral isomers for the two donor groups and axial/equatorial orientations of the $C-CH_3$ group, the ^1H NMR spectrum of $[Pt(bipy)(2\text{-}Me\text{-}dmtn)]^{2+}$ is consistent with one isomer being dominant with $J_{ad} = J_{de} = 12.5$ Hz and $J_{bd} = J_{df} = 2$ Hz [116]. These constants are consistent with $C-CH_3$ being equatorial in a chair conformation with $\omega_c = 64°$ (eqn. 49). There are three possible configurations with $C-CH_3$ equatorial: one with one axial and one equatorial $N-CH_3$, another with two equatorial $N-CH_3$ groups, and a third with two axial $N-CH_3$ groups. Under the conditions of the experiment, interconversions between these three structures were not possible. Since only one $N-CH_3$ resonance is observed even at 270 MHz, the stable isomer is unlikely to have the axial-equatorial configuration. The coupling constants between a and NH, and b and NH were determined: $J_{aNH} = 4$Hz and $J_{bNH} = 0$ Hz [116]. These are consistent with the diaxial configuration for the $N-CH_3$ groups with D_1 reduced to remove the 1,3-diaxial interactions, because in this structure the dihedral angles aC1NH and bC1NH are of the order of 40–50° and 70–80°, respectively [116]. In contrast, if the two $N-CH_3$ groups were both equatorial the dihedral angles would be about 180° and 60°, respectively and the associated coupling constants would both be larger than were observed. It would appear therefore that the interaction between the $(N-CH_3)_e$ groups and C6–H and C6′–H of bipy destabilizes that conformation relative to the diaxial structure.

(b) Diarsenes

1,3-Bis(dimethylarseno)propane, $X = Y = As(CH_3)_2$. The Cl-d_2 compound was used by Cullen et al. to study the conformations formed by 1,3-bis(dimethylarseno)propane and its 2-tert-butyl derivative [129]. For $[M(CO)_4L]$ complexes where M is Cr(0), Mo(0) and W(0), the ^1H NMR spectra had a symmetric AA'BB' pattern with deuterium decoupling which is consistent with a fast $Ch \rightleftharpoons Ch$ equilibrium. Cullen used the '*R* method' of Lambert [130] and Buys [131,132] to calculate ω from eqn. (51).

$$R = J_{trans}/J_{cis} = 3 - 2\cos^2\omega/4\cos^2\omega \quad (51)$$

The values of ω for the three complexes were in the range 66–68°. Here, the dihedral angle is calculated by

$$J_{ad}/J_{bd} = \left[\alpha\cos^2(120+\omega) + \cos^2(120-\omega)\right]/2\cos^2\omega \quad (52)$$

Using the data in Table 11, ω was found to be between 65 and 66° for the three complexes.

TABLE 11

Coupling constant ($^3J_{HH}$ in Hz) and conformational data for complexes of arsenic chelates

Complex	J_{ad}	J_{bc}	J_{bd}	J_{ac}	ω
L = 1,3-bis(dimethylarseno)propane					
$[Cr(CO)_4L]$ [a]	9.7		2.2		65.3
$[Mo(CO)_4L]$ [a]	9.7		2.1		65.9
$[W(CO)_4L]$ [a]	9.7		2.1		65.9
$[MnCl(CO)_3L]$ [b]	13.4	6.4	2.2	2.2	65.6
$[MnBr(CO)_3L]$ [b]	13.4	6.0	2.0	2.6	64.9 [c]
$[MnI(CO)_3L]$ [b]	13.6	5.9	1.9	2.8	64.7 [c]
L = 1,3-bis(dimethylarseno)-2-tert-butylpropane					
$[Cr(CO)_4L]$ [a]	11.7		1.3		68.8
$[Mo(CO)_4L]$ [a]	11.3		0.8		73.5
$[W(CO)_4L]$ [a]	11.5		0.5		77.4
$[Ni(CO)_2L]$ [c]	11.7		0.9		72.7
[Ni(PFP)L [c,d]	12.3		1.2		70.2
$[Mn(CO)_3ClL]$ [b] (isomer A)	12.6 [f]		0.7 [f]		75.5
$[Mn(CO)_3BrL]$ [b] (isomer A)	11.0 [f]		2.2 [f]		60.6
$[Mn(CO)_3IL]$ [b] (isomer A)	11.2 [f]		2.1 [f]		61.7
$[Mn(CO)_3BrL]$ [b] (isomer B)	11.6 [f]		2.1 [f]		62.1

[a] *J* values from ref. 129. [b] *J* values from ref. 133. [c] *J* values from ref. 135. [d] PFP is $^-OC(CF_3)_2C(CF_3)_2O^-$. [e] Calculated from average of J_{bd} and J_{ac}. [f] Errors larger than for other complexes because spectra are deceptively simple.

For $[MnX(CO)_3L]$ where X is Cl, Br and I, ABCD patterns were obtained for the deuterium decoupled spectra [133]. This was interpreted by Cullen et al. as evidence of the chelate ring being 'locked', not undergoing the Ch ⇌ Ch equilibrium. The two chair conformations need not necessarily be of the same energy for these complexes because of the different interactions between the apical ligands, X and CO, and the atoms in the chelate ring (Fig. 14). Since an X-ray analysis of $[MnCl(CO)_3L]$ had shown structure (A) in Fig. 14 to be present in the crystalline state [134], Cullen et al. [135] concluded that this structure predominates in solution. The degrees of preference and the dihedral angle, ω, can be determined from eqns. (53) and (54) where n_1 is the mole fraction of one of the conformations, if it is assumed that ω has the same value in the two chair conformations.

$$J_{ad}/J_{bd} = n_1\{\alpha \cos^2(120+\omega) - \cos^2(120-\omega)\} + \cos^2(120-\omega)/\cos^2\omega \tag{53}$$

$$J_{bc}/J_{ac} = n_1\{\cos^2(120-\omega) - \alpha \cos^2(120+\omega)\} + \alpha \cos^2(120+\omega)/\cos^2\omega \tag{54}$$

For the chloro derivative, n_1 and ω were calculated to be 0.82 and 65.6°, respectively. The X-ray analysis found $\omega = 70$–$71°$ with $D_1 = 31°$ [134]. For the bromo and iodo complexes, J_{ac} and J_{bd} were found to have different values. This result is inconsistent with a Ch ⇌ Ch equilibrium or a Ch ⇌ SB equilibrium, and possibly results from an incorrect analysis of the spectra. If the averages of the two constants are taken (i.e. for Br, 2.3 and for I, 2.35), similar n_1 values to that obtained for the chloro compound are calculated with lower values of ω: 64.9° for the bromo, and 64.7° for the iodo compound.

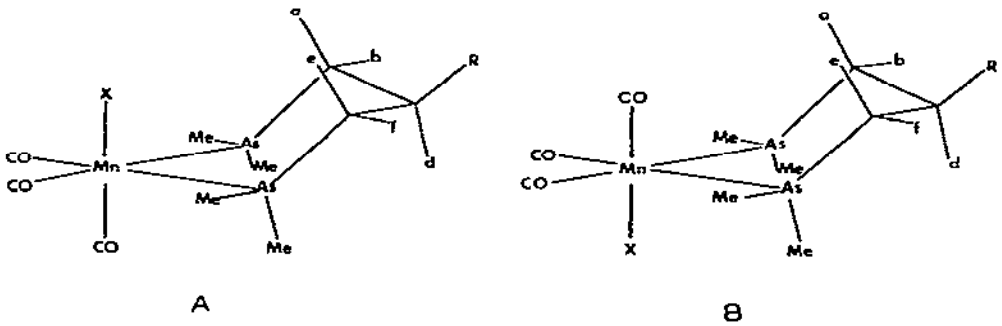


Fig. 14. Chair conformations of $[Mn(CO)_3XL]$. L is either 1,3-bis(dimethylarseno)propane (R = H) or 1,3-bis(dimethylarseno)-2-tert-butylpropane, ($R = C(CH_3)_3$).

1,3-Bis(dimethylarseno)-2-tert-butylpropane, $X = Y = As(CH_3)_2$, $c = C(CH_3)_3$. Vicinal coupling constants for complexes of the 2-tert-butyl derivative of 1,3-bis(dimethylarseno)propane are given in Table 11. All are consistent with one chair predominating. In fact, from an examination of Dreiding models it is clear that the 1,3-diaxial interactions between the two axial methyls and the tert-butyl group are so great that Ch_a would not be populated. The AsCCC dihedral angle, ω_c, has been calculated from eqn. (49). The data are in Table 11.

For 1,3-bis(dimethylarseno)propane the Cr(0), and W(0) complexes were found to have similar values of ω in the range 65 to 66°. For the tert-butyl derivative, however, there is a significant increase in ω compared to the unsubstituted ligand. This probably results from the need to reduce repulsive interactions between the tert-butyl group and C1–H_e and C3–H_e. The increased puckering of the ring would be facilitated by an increase in M–As, and hence the values of ω are in the order W > Mo > Cr. The nickel complexes [Ni(CO)$_2$L] and [Ni(PFP)L] where PFP is $^-OC(CF_3)_2C(CF_3)_2O^-$ also show relatively large values of ω.

In [MnX(CO)$_3$L], there are four possible chair structures, two of which have an axial tert-butyl group and are therefore not significantly populated. The remaining two, isomers A and B, are shown in Fig. 14. Cullen et al. assigned the structures as shown because isomer A is more thermally stable than isomer B [133]. The spectra for both isomers A and B are ABX, but are deceptively simple "and therefore have a large probability for error in the values" of J_{ad} and J_{bd}. Whether this is the reason for the large difference in the ω values, is not known.

(c) Seleno ethers

1,3-Bis(methylseleno)-2,2-dimethylpropane, $X = Y = SeCH_3$, $c = d = CH_3$. The *meso* isomer of the ligand forms two chair chelate rings, one with the two $SeCH_3$ groups equatorial (Ch_{ee}) and the other with the two $SeCH_3$ groups axial (Ch_{aa}). In both, the gem methyls at C2 occupy equatorial and axial positions. From Dreiding models it is apparent that the two 1,3-diaxial interactions between the $SeCH_3$ and CCH_3 groups in Ch_{aa} renders the conformation energetically unfavourable. In Ch_{ee}, the axial C–CH_3 group would also destabilize the conformation to some degree due to repulsive interactions with other atoms in the chelate. In both skew-boat conformations, one $SeCH_3$ group would be axial and one equatorial. The repulsions experienced by the axial group would increase further the energy of this structure compared to Ch_{ee}.

Both chair conformations for the chiral isomer have one equatorial and one axial $SeCH_3$ and the 1,3-diaxial interaction of the latter group with

$(C-CH_3)_a$ would markedly destabilize both chair conformations.In one skew-boat conformation (SB_{ee}) the two $SeCH_3$ groups would be equatorial, in the other axial, (SB_{aa}). Further, in both SB_{ee} and SB_{aa} neither $C-CH_3$ would be axial.

The ^1H NMR spectra of $[M(CO)_4L]$ where M is Cr(0), Mo(0) and W(0) have been recorded at low temperature, and the changes in the spectra with temperature are consistent with the freezing out of two exchanging conformations at below about 240 K [136]. The activation parameters for the exchange reaction were calculated by band-shape analysis and the data are collected in Table 12.

Both species have an AB pattern for $^aCH_2$. The different $SeCH_3$ signals are not resolved, but the most populated species has a single peak for the $C-CH_3$ groups whereas the other species has two peaks. It was claimed that the exchange was between the two unequally populated *meso*-chair conformations and not between two configurations of the donor groups mainly because the $\Delta S^{\neq}$ values were inconsistent with Se inversion. However, it is unlikely that Ch_{aa} would be populated significantly. From the inspection of Dreiding models, it would appear that the two most favoured conformations are Ch_{ee} and SB_{ee}. The spectra are indeed consistent with Ch_{ee} (*meso*) $\rightleftharpoons SB_{ee}$ (chiral). For Ch_{ee}, two $C-CH_3$ signals would be expected for the axial and equatorial groups, whereas for SB_{ee} only one signal would be obtained and both conformations would have AB patterns for the methylenes as was in fact found. This equilibrium involves both conformational interconversion

TABLE 12

Complexes of 1,3-bis(methylseleno)-2,2-dimethylpropane in $CDCl_3$ [a]

Complex	T(K)	n(Ch) [b]	n(SB) [b]	$-\Delta G^0_{Ch \rightleftharpoons SB}$
(i) Conformational energy data (ΔG in kJ mol^{-1})				
$[Cr(CO)_4L]$	240	0.46	0.54	0.3
$[Mo(CO)_4L]$	210	0.31	0.69	1.4
$[W(CO)_4L]$	250	0.40	0.60	0.8

(ii) Activation parameters at 300 K ($\Delta G^{\neq}$ and $\Delta H^{\neq}$ in kJ mol^{-1}, $\Delta S^{\neq}$ in J K^{-1} mol^{-1})	$\Delta G^{\neq}$ [c]	$\Delta H^{\neq}$ [c]	$\Delta S^{\neq}$ [c]
$[Cr(CO)_4L]$	61.6±0.5	50.2±4.2	−39.0±12.0
$[Mo(CO)_4L]$	55.9±0.5	49.3±2.9	−22.0±14.0
$[W(CO)_4L]$	62.6±0.5	66.5±3.5	−13.0±14.0

[a] Data from ref. 136. [b] ±0.02. [c] Ch_{ee} (*meso*) → SB_{ee} (chiral).

and Se inversion, and therefore the $\Delta S^{\neq}$ values are not inconsistent with this. The relative populations of the conformations and the free energy differences are included in Table 12.

(ii) ^{195}Pt coupling constants

Appleton and Hall first applied $^3J_{PtH}$ and $^4J_{PtH}$ to the conformational analysis of six-membered diamine chelates [59,115]. Table 13 contains a summary of the available data for $^3J_{PtH}$ and also for $^2J_{PtC}$ and $^3J_{PtC}$.

Square-planar Pt^{2+} complexes of 2-substituted diamines that exist predominantly in one chair conformation such as $[Pt(NH_3)_2(2\text{-Cl-tn})]^{2+}$ have $^3J_{PtH_a}$ and $^3J_{PtH_e}$ values of the order of 20 and 65 Hz, respectively, consistent with the *gauche* and *trans* relationship for these nuclei. From the investigation of $^3J_{HH}$, the chloro and hydroxo derivatives are known to have the substituent axial, and $^{\alpha}CH_a$ is proton b which has the smaller value for $^3J_{PtH}$, whereas for the tert-butyl derivative, the substituent is mainly equatorial and therefore $^{\alpha}CH_a$ is proton a.

TABLE 13

^{195}Pt coupling constants with ^1H and ^{13}C (Hz)

Complex	$^3J_{Pta}$	$^3J_{Ptb}$	$^2J_{Pt^{\alpha}C}$	$^3J_{Pt^{\beta}C}$	$^3J_{PtCH_3}$
$[Pt(NH_3)_2(tn)]^{2+}$		43 [a]			
$[Pt(tn)_2]^{2+}$		43 [a]			
$[Pt(bipy)(tn)]^{2+}$		42 [b]	25	40.0 [b]	
$[Pt(bipy)(1,3\text{-bn})]^{2+}$			23, 23	35	32 [b]
$[Pt(NH_3)_2(meso\text{-ptn})]^{2+}$	15 [c]		22.5	15.6	46.9 [d]
$[Pt(bipy)(meso\text{-ptn})]^{2+}$			20.5	33.7	38.1 [d]
$[Pt(NH_3)_2\{(R,R)\text{-ptn}\}]^{2+}$			25	21	31 [e]
$[Pt\{(R,R)\text{-ptn}\}_2]^{2+}$		38.5 [c]			
$[Pt(bipy)\{(R,R)\text{-ptn}\}]^{2+}$		31 [b]	22.0	20.5	35.2 [d]
$[Pt(bipy)(mptn)]^{2+}$			20.5 [f], 17.6 [g]	26.4	23.4 [f], 22.0 [f], 41.8 [g,d]
$[Pt(2\text{-bu}^t\text{-tn})_2]^{2+}$	22	62 [h]			
$[Pt(bipy)(2\text{-bu}^t\text{-tn})]^{2+}$	30.5	54.5 [h]			
$[Pt(NH_3)_2(2\text{-OH-tn})]^{2+}$	66.4	22.1 [i]			
$[Pt(2\text{-OH-tn})_2]^{2+}$	63.3	22.3 [i]			
$[Pt(NH_3)_2(2\text{-Cl-tn})]^{2+}$	65.2	18.2 [i]			
$[Pt(NH_3)_2Cl_2(2\text{-OH-tn})]^{2+}$	46.2	9.6 [i]			

[a] Ref. 59. [b] Ref. 116. [c] Ref. 115. [d] Ref. 74. [e] Ref. 122. [f] C2. [g] C4. [h] Ref. 135. [i] Ref. 125.

If it is assumed that $\alpha = 1.2$ applies and that the 2-chloro and 2-hydroxy compounds are exclusively in the Ch_a conformation, the dihedral angle Φ = PtNC1C2, can be calculated from

$$^3J_{PtH_e}/^3J_{PtH_a} = \alpha \cos^2(120 + \Phi)/\cos^2(120 - \Phi) \quad (55)$$

From the data in Table 13, Φ is calculated to be 65.3° for $[Pt(NH_3)_2$(2-Cl-tn)$]^{2+}$, 68.8° for $[Pt(NH_3)_2$(2-OH-tn)$]^{2+}$, 70° for $[Pt$(2-OH-tn)$_2]^{2+}$, and 60° for $[Pt(NH_3)_2Cl_2$(2-OH-tn)$]^{2+}$. The $^3J_{HH}$ coupling constants for the 2-bu^t-tn complexes were consistent with $n(CH_e) = 0.74$ and 0.76 for [Pt(bipy)(2-bu^t-tn)$]^{2+}$ and $[Pt$(2-bu^t-tn)$_2]^{2+}$, respectively. Using these values and eqn. (56) where $X = {}^3J_{PtH_e}/{}^3J_{PtH_a}$, Φ is calculated to be 64° and 42°, respectively.

$$n(CH_e) = \left[X\alpha \cos^2(120 + \Phi) - \cos^2(120 - \Phi)\right]/(1 + X) \times \{\alpha \cos^2(120 + \Phi) - \cos^2(120 - \Phi)\} \quad (56)$$

The value for $[Pt$(2-bu^t-tn)$_2]^{2+}$ seems low by comparison to the other values of Φ and could result from $n(CH_e)$ being in fact higher than 0.76. If $n(CH_e)$ is 1, Φ would be 70°.

For $[Pt($*meso*-ptn$)_2]^{2+}$, in which the $^\alpha$C protons would be axial, $^3J_{PtH}$ was found to be 15 Hz [115], consistent with the *gauche* angular relationship. The average value of $^3J_{PtH_a}$ and $^3J_{PtH_e}$ for the Pt^{2+} complexes of 2-substituted ligands in Table 13 is 42.6, in agreement with the values of $^3J_{PtH}$ found for the tn complexes (43 Hz), in which the rapid chair $\rightleftharpoons$ chair equilibration would average the coupling constants. Appleton and Hall used an average value of 40 Hz, found from the value of $^3J_{PtH}$ of 41 Hz for $[Pt(NH_3)_2$(en)$]^{2+}$ [115] but for this complex, the different value of Φ compared with that for the six-membered ring complexes would probably yield different values of $^3J_{PtH_e}$ and $^3J_{PtH_a}$.

If $^3J_{PtH_a}$ is taken to be 15 Hz as found for the *meso*-ptn complex, $^3J_{PtH_e}$ is calculated to be 71 Hz, using the value of 43 Hz for the averaged coupling constants. For $[Pt\{(R,R)$-ptn$\}_2]^{2+}$ if it is assumed that both SB_{ee} and $Ch_{ea} \rightleftharpoons Ch_{ae}$ conformations exist in the same ratio as calculated for $[Pt(NH_3)_2\{(\pm)$-ptn$\}]^{2+}$ using $^3J_{HH}$ (n(Ch) = 0.75), then the expected value of $^3J_{PtH}$ is calculated to be 36 Hz, in reasonable agreement with the observed value of 38.5 Hz. A similar calculation for [Pt(bipy)$\{(\pm)$-ptn$\}]^{2+}$ yields a value of $^3J_{PtH}$ of 30 Hz which agrees well with the value of 31 Hz found for this complex.

The $^4J_{PtH}$ value for an α-substituted methyl is maximized when CH_3 is equatorial because, in this orientation, the optimum angular relationship occurs [115]. The following values were obtained: $[Pt(NH_3)_2$(1,3-bn)$]^{2+}$, 3.5; $[Pt(NH_3)_2(OH_2)_2$(1,3-bn)$]^{4+}$, 6.5; $[Pt(NH_3)_2Cl_2$(1,3-bn)$]^{2+}$, 5.2;

$[Pt(NH_3)_2(meso\text{-ptn})]^{2+}$, 6.5; $[Pt(NH_3)_2(OH_2)_2(meso\text{-ptn})]^{4+}$, 6.5; $[Pt(NH_3)_2Cl_2(meso\text{-ptn})]^{2+}$, 5.0; $[Pt(NH_3)_2\{(R,R)\text{-ptn}\}]^{2+}$, < 2; $[Pt(NH_3)_2(OH_2)_2\{(R,R)\text{-ptn}\}]^{4+}$, 3.8; and $[Pt(NH_3)_2Cl_2\{(R,R)\text{-ptn}\}]^{2+}$, 2.5 Hz [115]. Comparison of $^4J_{PtH}$ for $\alpha_{C\text{-}CH}$ for the analogous *meso*-ptn and 1,3-bn complexes shows that in the square-planar complex $[Pt(NH_3)_2(1,3\text{-bn})]^{2+}$ $n(Ch_e)$ is less than 1 as was found from the $^3J_{HH}$ method, but in the octahedral complexes $n(Ch_e)$ is in fact 1, again as was found from $^3J_{HH}$. For the (±)-ptn complexes, $^4J_{PtH}$ values are much smaller than those for the analogous *meso*-ptn complexes consistent with a large population of the chair conformations.

Coupling constants between ^{195}Pt and $^{\beta}C$, $^3J_{Pt^{\beta}C}$, and between ^{195}Pt and $^{\alpha}C\text{-}CH_3$, $^3J_{PtCH_3}$, are dependent on the dihedral angle PtN1C1C2 (Φ). Erickson et al. state that for six-membered diamine Pt(II) complexes, $^3J_{Pt^{\beta}C}$ is consistently observed to be 30 to 40 Hz [137], in line with values of Φ in the range 50 to 60° which would be expected from X-ray data. However, values outside this range have been observed, with values around 20 Hz reported for (*R*,*R*)-ptn complexes. The value for $[Pt(NH_3)_4(meso\text{-ptn})]^{2+}$ appears surprisingly low, but based on the observations of Erickson et al. for the complex [Pt(bipy)(*cis*-1,3-cyclohexanediamine)]$^{2+}$ [137], a value of 15.6 Hz for $^3J_{Pt^{\beta}C}$ would be obtained for a Φ value of 66°, assuming a dual coupling path to $^{\beta}C$. The average value of Φ for $[Pt\{(S,S)\text{-ptn}\}_2]Cl_2 \cdot H_2O$ where the conformation found for the ptn chelate ring is a relatively undistorted chair [122], as is expected for *meso*-ptn chelate rings, is 64.4°. With a small variation in Φ in the range 50–70° producing a large variation in the coupling constant due to the $\cos^2$ relationship, it is not surprising that complexes expected to have conformational similarities show considerable variation in $^3J_{Pt^{\beta}C}$. The difference in the $^3J_{Pt^{\beta}C}$ values and therefore in the MXCC dihedral angle for the diammine and bipy complexes of *meso*-ptn could be due to distortions in the ring which are necessary to overcome the unfavourable interactions between the bipy C6–H and C6′–H protons and $N\text{–}H_e$ protons of the ptn ring. Therefore, $^3J_{Pt^{\beta}C}$ is not considered as a useful probe in the conformational analysis of these systems.

The coupling constant $^3J_{PtCH_3}$ provides more useful information, as the axial and equatorial orientations of the methyl group have $PtNCCH_3$ dihedral angles of ca. 90° and ca. 180°, respectively, leading to large differences in $^3J_{PtCH_{3a}}$ and $^3J_{PtCH_{3e}}$.

If it is assumed that $^3J_{PtCH_{3a}}$ is 0 and $^3J_{PtCh_{3e}}$ is 47 Hz, based on the value found for $[Pt(NH_3)_2(meso\text{-ptn})]^{2+}$, then the value expected for the (*R*,*R*)-ptn complexes, assuming only the $CH_{ea} \rightleftharpoons CH_{ae}$ interconversion is occurring, is around 23 Hz. The values of 31 Hz and 35.2 Hz found for $[Pt(NH_3)_2\{(R,R)\text{-ptn}\}]^{2+}$ and [Pt(bipy){(*R*,*R*)-ptn}]$^{2+}$ are not consistent with symmetric chair conformations, but are consistent with values of n(Ch)

for the two complexes of 0.67 and 0.50 respectively, in reasonable agreement with the values of 0.75 and 0.54 found using the $^3J_{HH}$ method.

The value of $n(Ch_e)$ of 0.68 calculated for $[Pt(bipy)(1,3\text{-bn})]^{2+}$ using the above values of 0 and 47 Hz and $^3J_{PtCH_{3_a}}$ and $^3J_{PtCH_{3_e}}$ is also in good agreement with the value calculated by the $^3J_{HH}$ method (0.65).

The low value found for $[Pt(bipy)(meso\text{-ptn})]^{2+}$ (38.1 Hz) could be due to structural changes necessary to overcome unfavourable non-bonding interactions of the bipy C6–H and C6′–H protons and the N–H_e protons of the ptn chelate ring, which could yield a concentration of the SB_{ea} conformation.

The values of $^3J_{Pt^{195}CH_3}$ for $[Pt(bipy)(mptn)]^{2+}$ (C4, 41.8 Hz; C2, 23.4 and 22.0 Hz [74]) are consistent with the conclusion from the $^3J_{HH}$ method that the chair and unsymmetric boat conformations have mole fractions of 0.63 and 0.37, respectively. The C4 methyl is in an equatorial orientation *trans* to the metal in both conformations, whereas the C2 methyls exchange between axial and equatorial orientations with MNCC torsional angles of 90 and 160° on conformational interconversion.

(iii) ^{13}C Chemical shifts

Dalling and Grant have analysed the ^{13}C chemical shifts of methyl substituted cyclohexanes in terms of the effects of equatorial and axial methyl groups on, for example, $\delta^{\alpha}C$, $\delta^{\beta}C$, and $\delta^{\gamma}C$. This has allowed the prediction of whether a methyl group is largely axial or equatorial [138,139]. A similar analysis is possible for diamine metal chelates. Chemical shift data for six-membered diamine chelates are given in Table 14. The shift parameters are derived as follows:

For M(*meso*-ptn)

$$\delta^{\alpha}C = \delta^{\alpha}C(tn) + \alpha_e + \gamma_e \tag{57}$$

$$\delta^{\beta}C = \delta^{\beta}C(tn) + {}^2\beta_e \tag{58}$$

For octahedral complexes of 1,3-bn

$$\delta C1 = \delta^{\alpha}C(tn) + \gamma_e \tag{59}$$

$$\delta C3 = \delta^{\alpha}C(tn) + \alpha_e \tag{60}$$

$$\delta C2 = \delta^{\beta}C(tn) + \beta_e \tag{61}$$

The values of $\gamma_e + \alpha_e$ and β_e calculated from the above equations for the tetraammine complexes of *meso*-ptn(9.0 and 7.4) and 1,3-bn (8.8 and 7.2) are in good agreement, but the same agreement was not found for the Pt(bipy) square-planar complexes (8.0 and 7.4, cf. 13.8 and 7.0) because $n(Ch_e)$ is not equal to 1 for $[Pt(bipy)(1,3\text{-bn})]^{2+}$.

TABLE 14

^{13}C Chemical shift data [f] for six-membered diamine chelates

Complex	$^{\alpha}C$	$^{\beta}C$	CH_3
$[Co(NH_3)_4(tn)]^{3+}$ [a]	38.8	25.6	
$[Co(CN)_4(tn)]^{-}$ [a]	41.2	26.5	
$[Pt(bipy)(tn)]^{2+}$ [a]	42.2	28.1	
$[Co(tn)_3]^{3+}$ [a]	38.5	25.2	
$[Co(NH_3)_4(1,3\text{-bn})]^{3+}$ [a]	46.9, 39.5	32.8	23.1
$[Pt(bipy)(1,3\text{-bn})]^{2+}$ [b]	49.8, 41.6	35.1	22.4
$[Co(NH_3)_4(meso\text{-ptn})]^{3+}$ [a]	47.8	40.3	23.1
$[Co(CN)_4(meso\text{-ptn})]^{-}$ [a]	49.7	41.4	24.6
$[Pt(bipy)(meso\text{-ptn})]^{2+}$ [a]	50.2	42.8	22.6
cis-$[Co(NH_3)_2(meso\text{-ptn})_2]^{3+}$ [a]	48.2, 48.1, 47.9, 47.6	40.0	23.6
cis(C_1)-$[Co(CO_3)(meso\text{-ptn})_2]^{+}$ [c]	48.5, 48.2, 47.7	42.2, 41.2	23.7
cis(C_2)-*syn*-$[Co(CO_3)(meso\text{-ptn})_2]^{+}$ [c]	48.2, 47.3	41.5	23.6, 23.1
cis(C_2)-*anti*-$[Co(CO_3)(meso\text{-ptn})_2]^{+}$ [c]	48.1, 47.8	42.1	23.5
cis(C_1)-$[Co(C_2O_4)(meso\text{-ptn})_2]^{+}$ [c]	48.2, 47.9, 47.5, 47.4	40.9	23.2
cis(C_2)-$[Co(C_2O_4)(meso\text{-ptn})_2]^{+}$ [c]	48.6, 47.5	41.4	23.5, 23.1
$[Co(NH_3)_4\{(R,R)\text{-ptn}\}]^{3+}$ [a]	44.1	37.8	23.6
$[Co(CN)_4\{(R,R)\text{-ptn}\}]^{-}$ [a]	45.1	38.8	24.1
$[Pt(NH_3)_2\{(R,R)\text{-ptn}\}]^{2+}$ [d]	46.6	40.6	21.9
$[Pt\{(R,R)\text{-ptn}\}_2]^{2+}$ [d]	46.8	40.7	21.8
$[Pt(bipy)\{(R,R)\text{-ptn}\}]^{2+}$ [a]	46.9	40.3	21.7
trans-$[Co(NH_3)_2\{(R,R)\text{-ptn}\}_2]^{3+}$ [c]	44.1	37.8	23.9
Λ-*cis*-$[Co(NH_3)_2\{(R,R)\text{-ptn}\}_2]^{3+}$ [e]	45.1, 44.3	37.8	24.1, 23.9
Δ-*cis*-$[Co(NH_3)_2\{(R,R)\text{-ptn}\}_2]^{3+}$ [e]	44.6, 44.1	37.6	24.0, 23.8
Λ-$[Co\{(R,R)\text{-ptn}\}_3]^{3+}$ [a]	45.0	37.9	24.1
Δ-$[Co\{(R,R)\text{-ptn}\}_3]^{3+}$ [a]	44.6	37.9	24.1
$[Co(NH_3)_4(mptn)]^{3+}$ [a]	51.3, 43.2	45.2	32.8, 23.2, 26.7
$[Co(CN)_4(mptn)]^{-}$ [a]	51.2, 44.4	46.2	33.5, 26.2, 24.8
$[Pt(NH_3)_2(mptn)]^{2+}$ [a]	52.7, 46.5	45.0	28.9, 26.3, 22.8
$[Pt(bipy)(mptn)]^{2+}$ [a]	54.8, 47.0	47.8	30.6, 27.6, 22.4

[a] Ref. 74. [b] Ref. 116. [c] Ref. 140. [d] Ref. 122. [e] Ref. 142. [f] Using dioxane (67.4 ppm) as ref.

Distortions in some systems, coupled with the problem that one particular conformation is not preferred make a similar analysis impractical for other compounds, for example in $[Pt(bipy)(mptn)]^{2+}$.

(iv) Isotropic proton chemical shifts

Nickel(II) complexes of 1,3-diamines have been studied by Sarneski and Reilley [143] and the spectra of the complexes are summarized in Fig. 15. The β protons are shielded relative to the chemical shifts of these protons in analogous diamagnetic complexes. In $[Ni(OH_2)_4(tn)]^{2+}$ where there is rapid chair $\rightleftharpoons$ chair interconversion that renders the two β protons equivalent, one β resonance is observed. One resonance is also observed for the (±)-ptn

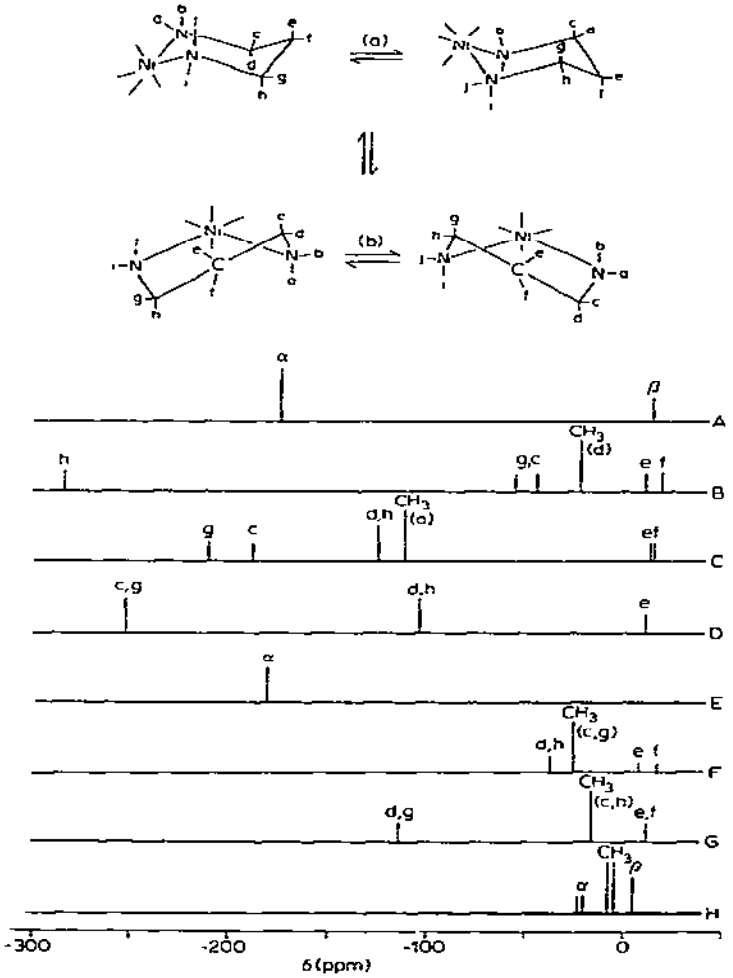


Fig. 15. Schematic representation of NMR spectra of nickel(II) complexes of 1,3-diamine ligands in D_2O: (A) $Ni(tn)^{2+}$; (B) $Ni(1,3\text{-bn})^{2+}$; (C) $Ni(mtn)^{2+}$; (D) $Ni(2\text{-Et-tn})^{2+}$; (E) $Ni(2,2\text{-Me}_2\text{-tn})^{2+}$; (F) $Ni(meso\text{-ptn})^{2+}$; (G) $Ni\{(\pm)\text{-ptn}\}^{2+}$; (H) $Ni\{(\pm)\text{-ptn}\}_2^{2+}$. Chair$\rightleftharpoons$ chair (a) and skew-boat$\rightleftharpoons$skew-boat (b) equilibria are shown [143]. (Reproduced with permission from Inorg. Chem., copyright 1974 American Chemical Society.)

complex where chair ⇌ chair ⇌ skew-boat interconversion is present. However, in the 1,3-bn, *N*-methyl-1,3-propanediamine and *meso*-ptn complexes, two β proton resonances are observed consistent with the predominance of one chair conformation. The isotropic shift for the β protons of (±)-ptn is approximately equal to the average of the shifts for the two β protons of *meso*-ptn. The two resonances for the mtn complex are close together showing that the preference for one chair conformation is slight, whereas the separation for 1,3-bn is similar to that for *meso*-ptn showing that one chair predominates in the 1,3-bn complex. For the complex with 2-ethyl-1,3-diaminopropane (2-Et-tn) the single β resonance was observed close to the less shielded resonance for *meso*-ptn. One chair predominates but not to the exclusion of the other chair.

The α-H and α-CH_3 resonances were shifted to less shielded positions relative to the analogous diamagnetic resonances. The isotropic shifts for α-H protons are dependent on the dihedral angle NiN1C1C2 (Φ) (Fig. 6). An equatorial proton has an approximate *trans* relationship with the metal and hence has a large isotropic shift. An axial proton has a *gauche* relationship with the metal and has a much smaller chemical shift. The ratio of the isotropic shifts for the axial and equatorial protons in a fixed conformation provides a means of calculating Φ using eqn. (27).

The α proton in $[Ni(OH_2)_4(meso\text{-ptn})]^{2+}$ has an isotropic shift of 36.8 ppm which obeys Curie Law. This is consistent with the chelate adopting the Ch_{ee} structure exclusively. The α proton in $[Ni(OH_2)_4\{(\pm)\text{-ptn}\}]^{2+}$ has an isotropic shift of 114 ppm but this resonance does not obey Curie Law because a plot of δT against T has a non-zero slope showing that the chelate is not exclusively in one conformation or solely in the interconverting chair conformations. The skew-boat conformation must be populated.

Before it is possible to calculate the mole fraction of skew-boat conformation, the isotropic shift of an equatorial proton in a chair must be known. Sarneski and Reilley [143] determined this from the spectrum of the nickel(II) complex of *cis, cis*-1,3,5-triaminocyclohexane which is a terdentate chelate locked in a conformation with the α-proton equatorial. It possesses an isotropic shift of 324 ppm [144]. However, this multidentate chelate has a rigid structure and it is unlikely that the geometry of its six-membered chelate rings is the same as that for simple bidentate chelates. Nevertheless, it provides an approximate value for the equatorial α-proton. Here, the equatorial isotropic shift was determined from the average of the axial and equatorial shifts which was assumed to be the value for $[Ni(OH_2)_4(tn)]^{2+}$. 175 ppm. The averages for the other compounds approximated this value. If 36.8 ppm is taken as the value for an axial α-proton, then the equatorial proton would have an isotropic shift of 313.2 ppm which is very similar to the value used by Sarneski andReilley [143]. From the ratio of the two shifts,

the dihedral angle, Φ, is calculated to be about 50° (cf. $[Ni(OH_2)_2(tn)_2](NO_3)_2$, $\Phi = 53.3°$ [145], $[Ni(OH_2)_2(tn)_2](ClO_4)_2$, $\Phi = 59.9°$ [146].

The position of the α-proton resonance for $[Ni(OH_2)_4\{(\pm)\text{-ptn}\}]^{2+}$, 114 ppm, does not correspond to the averaged value for the axial and equatorial α-protons, 175 ppm. If the sole equilibrium was between the two Ch_{ae} conformations, agreement would have been expected if the presence of an axial methyl did not significantly change the Φ value. As noted above, the fact that the α-proton resonance did not obey Curie Law shows that there is an equilibrium between the chair and skew-boat conformations. The skew-boat conformation that would be present would be SB_{ee}, in which the α-proton is in an axial orientation. In order to calculate the mole fraction of SB_{ee} that is present it is necessary to know the intrinsic value of the isotropic shift for the axial α-proton in this conformation. Sarneski and Reilley assumed a value of 15000 ± 3000 ppm K for δT for this proton based on the proposition that the dihedral angle NiN1C1a would be similar for the chair and skew-boat conformations and hence the isotropic shift for the axial α-proton, a, in the skew-boat would be similar to that in the chair [143]. This proposition is not supported by evidence from X-ray structural data nor from conformational-energy minimization data. From the X-ray studies, Φ is of the order of 46–65° for the chair and 61–71° for the skew-boat. Conformational analysis of $[Co(NH_3)_4\{(R,R)\text{-ptn}\}]^{3+}$ gave an average Φ value of 53° for the minimum-energy chair and a value of 72.5° for the skew-boat [121]. If these two values were taken as being applicable to the nickel(II) system, the ratio of isotropic shifts of the axial α-proton in the skew-boat and chair conformations would be 3.0, and hence the isotropic shift for the axial α-proton in the skew-boat conformation would be about 110 ppm, very similar to the value found for $[Ni(OH_2)_4\{(R,R)\text{-ptn}\}]^{2+}$. We would conclude, therefore, that the mole fraction of the skew-boat conformation is very high, probably in excess of 0.9. Sarneski and Reilley, on the other hand, calculated that the skew-boat has a mole fraction of only 0.46 [143].

For $[Ni(OH_2)_4(1,3\text{-bn})]^{2+}$, three conformations are likely to be present, Ch_e, SB_e and Ch_a. Using the data derived from the (R,R)-ptn complex, Sarneski and Reilley calculated mole fractions of 0.88, 0.08, and 0.04 for the above three conformations from the isotropic shifts of the α-protons, and a value of 0.83 for $\{n(Ch_e) - n(Ch_a)\}$ from the isotropic shifts of the β-protons [143]. However, as pointed out above, there is some doubt concerning the value used for the intrinsic isotropic shift of the axial α-proton in a skew-boat conformation.

From the spectrum of $[Ni(OH_2)_4(mtn)]^{2+}$ it is apparent that one conformer predominates, but the preference for that conformation is much less

than the preference for the preferred conformation in $[Ni(OH_2)_4(1,3\text{-bn})]^{2+}$. It is not clear whether the preferred conformation has the *N*-methyl group axial or equatorial.

The spectrum for $[Ni(OH_2)_4(2\text{-Et-tn})]^{2+}$ is particularly interesting because the various resonances approximate Curie Law behaviour, suggesting either one conformer is exclusively present, or two conformers of equal energy are present, or isotropic shifts for the two types of conformation are very similar. The fact that two resonances are observed separated by 149 ppm shows that one conformer predominates so that the α-protons have unequal axial and equatorial character. The isotropic shifts (107 and 256 ppm) are inconsistent with one chair being exclusively populated: they are consistent with a mole fraction ratio, $n(Ch_e)/n(Ch_a) = 0.77/0.23$, but the Curie Law behaviour would require that the conformer distribution does not arise from enthalpy factors which would appear to be untenable [143]. However, the isotropic shifts are consistent with the exclusive population of a conformer with $\Phi = 70°$. The skew-boat conformation has a Φ value of this order of magnitude but, for this ligand, there are two equienergetic skew-boat conformations and an averaged resonance could be expected for the α protons. Our interpretation of the results for this ligand is that the Ch_e conformation predominates and that Φ is about 70°. In support of this the β-proton resonates at a similar position to the axial β-proton in $[Ni(OH_2)_4(meso\text{-ptn})]^{2+}$ [143].

The temperature dependence of δT for the α-proton resonance of $[Ni(tn)_3]^{2+}$ was analysed in terms of the racemization of the complex and the free energy of activation for this reaction was calculated to be 58.6 kJ mol^{-1} at 345 K [141].

(v) ^{59}Co chemical shifts

Cobalt-59 has a chemical shift range of 13,000 ppm [147]. The shift is particularly sensitive to factors controlling its orbital paramagnetism [148]. Cobalt(III) has a $^1A_{1g}$ ground state in its octahedral complexes. This gains a magnetic moment through the mixing in of the $^1T_{1g}$ excited state, and the magnitude of the moment the ground state acquires is related to the energy difference between the $^1A_{1g}$ and $^1T_{1g}$ energy levels and hence to the energy of the first spin-allowed absorption band. It is also necessary to consider the nephelauxetic effect [147].

The sensitivity of $\delta^{59}Co$ to electronic effects makes it a good nucleus for conformational analysis. The spectra of a series of tetraamminecobalt(III) complexes of six-membered diamine chelates and of three tris(diamine)-cobalt(III) have been measured [74]. The chemical shifts relative to $[Co(NH_3)_6]^{3+}$ are as follows: for $[Co(NH_3)_4L]^{3+}$ with tn 28.2; 1,3-bn, 21.2;

meso-ptn, +18.2; (*R*,*R*)-ptn, −39.5; mptn, 100.3 ppm; for $[CoL_3]^{3+}$ with tn, 157.1; (*R*,*R*)-ptn (Δ configuration), −34.8, and (*R*,*R*)-ptn (Λ configuration), +85.5 ppm. For each series there is a range of chemical shift in excess of 100 ppm. The mono complexes with tn, 1,3-bn and *meso*-ptn in which the chair conformation is expected to predominate have $\delta^{59}Co = 22.3 \pm 5.3$ ppm. The mptn complex which has an axial methyl has $\delta^{59}Co = 100.3$ ppm. The (*R*,*R*)-ptn complex which has the SB_{ee} conformations has $\delta^{59}Co = -39.5$ ppm, 139.8 ppm away from the resonance for the mptn complex with a chair conformation possessing an axial methyl. For the tris complexes, X-ray structural studies have shown that in the crystalline state, Δ and Λ-$[Co\{(R,R)\text{-ptn}\}_3]^{3+}$ have skew-boat conformations with the methyl groups equatorial [118,119]. Conformational-energy minimization calculations predict the skew-boat conformations would be almost exclusively populated for both configurations [113]. In contrast, $[Co(tn)_3]^{3+}$ has chair conformations in the solid state [149,150] and is predicted by conformational-energy minimization calculations [109,113] to have the chair conformation predominating with ΔG about 3.5 kJ mol^{-1}. The ^{59}Co resonance for the tris complexes of (*R*,*R*)-ptn are more shielded than the $[Co(tn)_3]^{3+}$ resonance with the Δ configuration showing the major difference. The results for the mono and tris complexes support the conclusions from the $^3J_{HH}$ values that the cobalt(III) complexes of (*R*,*R*)-ptn have the skew-boat conformation predominating in solution.

D. CONCLUSIONS

Coupling constant and chemical shift data from NMR spectra of chelate complexes can provide structural information about the chelate ring, the populations of conformations, and the barrier to conformation or configuration interconversion. The most powerful technique is based on the application of $^3J_{HH}$ values to the Karplus equation. Analysis of the coupling within a CH_2–CH_2 unit can provide the torsional angles within the unit, and the populations of the conformations. For systems with $CH(R)CH_2$ one of these pieces of information is required before the second can be determined. There are three sources for the torsional angle data, X-ray structures, conformational-energy minimization calculations, and coupling constant analyses for related CH_2–CH_2 fragments or for related $CH(R)CH_2$ fragments in chelates where the conformational populations are known.

Other coupling constants, for example $^3J_{HF}$, $^3J_{PtH}$ and $^3J_{PtC}$, also have been successfully applied to this problem, and have the same limitations. Isotropic chemical shifts within nickel(II) complexes have been used for conformational analysis.

The methods applied in this review to bidentate chelates can be applied to

multidentate chelates. It is recommended that researchers in this area determine coupling constants by second order analysis, and make use of good quality molecular models when considering the conformational possibilities.

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