Conformational Analyses of the Isomers of the Systems $[Co(men)_n(en)_{3-n}]^{3+}$ (men = *N*-methylethane-1,2-diamine, en = ethane-1,2-diamine; *n* = 1–3)†

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A molecular mechanics study of the configurational/conformational isomers of the system Λ-$[Co(men)(en)_2]^{3+}$ (men = *N*-methylethane-1,2-diamine, en = ethane-1,2-diamine) (16 isomers), and the geometric/configurational/conformational isomers of the systems Λ-$[Co(men)_2(en)]^{3+}$ (72 isomers) and Λ-$[Co(men)_3]^{3+}$ (88 isomers) has been undertaken using the MM2 force field. Calculated steric energies (adjusted for statistical factors) are used to predict isomer ratios in the three systems, which are compared with experimentally determined thermodynamic stabilities. Comparisons are also made between calculated geometries and X-ray molecular structures where these are available. For the Λ-$[Co(men)_2(en)]^{3+}$ system the calculations not only correctly predict the order of stability of the three possible geometric isomers, but also the most stable conformation for each of these cases. For the Λ-$[Co(men)_3]^{3+}$ system the two most stable forms observed experimentally are among the three forms of the molecule (of the 88 possible) calculated to be the most stable. Comparison of the geometric parameters for the two crystal structures and corresponding energy-minimized structures shows that the agreements are very good. The significance of statistical factors in thermodynamic comparisons of this type is discussed.

The classic paper in 1959 by Corey and Bailar,[1] which addressed ligand stereospecificity in metal complexes, inspired a large number of experimental studies measuring relative thermodynamic stabilities of stereoisomers of metal complex systems, and also a development of computational methods for assessment and prediction of their structural features.

One of the asymmetric ligands of particular interest has been (±)-propane-1,2-diamine (pn). Experimental studies of the various $[Co\{(\pm)pn\}_n(en)_{3-n}]^{3+}$ systems (*n* = 0–3, en = ethane-1,2-diamine) were made by Dwyer and Sargeson and co-workers[2–5] and these studies have been widely quoted to exemplify stereospecific effects in transition-metal co-ordination compounds. Furthermore, following the initial calculations of isomer stabilities,[1] there have been a number of conformational analyses of these systems, *viz.* by Gollogly and Hawkins,[6] Crossing and Snow,[7] Laier and Larsen,[8] Hambley and co-workers,[9,10] and most recently from our laboratories.[11]

In these complexes $[Co(pn)_n(en)_{3-n}]^{3+}$ isomerism arises from four sources: configurational isomerism of the chelate rings about the octahedral metal centre (Δ/Λ),[12] configurational isomerism about the chiral carbon centre in the pn ligand (*R*/*S*),[12] conformational isomerism within the five-membered chelate rings formed by the bidentate pn and en ligands (δ/λ),[12] and geometric isomerism due to the relative mutual dispositions of the methyl substituents in the $[Co(pn)_3]^{3+}$ and $[Co(pn)_2(en)]^{3+}$ species (*fac*/*mer*).[12]

Within a pn chelate ring the orientation of the substituent methyl group may be characterized as axial or equatorial to the mean plane of the ring (by analogy with the terminology used for substituted carbocyclic ring systems). This orientation is dependent on both the configuration *R*/*S* and the ring conformation: for pn in its complexes there is a substantial thermodynamic preference for the equatorial orientation.[1–11] Accordingly, the isomeric possibilities for metal complexes containing the pn ligand are limited since the absolute configuration about the chiral carbon centre predetermines the conformation of the ring: for example, *R*-pn gives a λ ring conformation for the methyl substituent to be equatorial.

In the related ligand men (*N*-methylethane-1,2-diamine) the methyl substituent is situated on one of the nitrogen atoms and this nitrogen donor becomes asymmetric only on co-ordination. However, as noted previously,[13–16] the axial/equatorial character of the *N*-methyl substituent in co-ordinated men is less pronounced than that of *C*-methyl substituents in pn, so that both conformations λ and δ may exist for a particular absolute configuration (*R*/*S*) about the chiral nitrogen centre. We have recently discussed the isomeric possibilities for the $[Co(men)_3]^{3+}$, $[Co(men)_2(en)]^{3+}$ and $[Co(men)(en)_2]^{3+}$ systems and have reported the synthesis of these complexes and characterization of the stable isomers produced,[16] and the structural details of several of the isolated isomers.[17,18]

Following the impressive predictive results of the thermodynamic stabilities of the $[Co(pn)_n(en)_{3-n}]^{3+}$ system using the MM2 force field,[11] we have calculated thermodynamic stabilities for the extended group of isomer possibilities for the analogous men complexes, along with the detailed structures of the most stable isomers of each system. These calculations are now reported and the results are compared with our experimental thermodynamics and structural results on these three systems.

The MM2 force field can only be used to study the relative thermodynamic stabilities of metal complexes in which there are the same number and type of atomic interactions (which excludes, for example, linkage isomers). The subtlety of the differences between a large number of closely related species in each of the present systems

† *Supplementary data available* (No. SUP 56800, 34 pp.): steric energy terms and calculated and observed geometric structure parameters and torsion angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

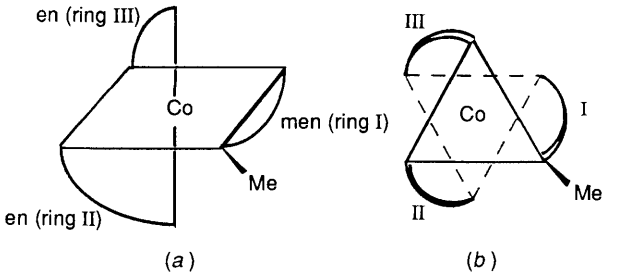

Fig. 1 Representations of the Λ-$[Co(men)(en)_2]^{3+}$ molecule, where (*b*) shows the view along the pseudo-C_3 axis

Table 1 Steric energies (kJ mol^{-1}) for the isomers of Λ-$[Co(men)(en)_2]^{3+}$; superscript * denotes the men ring

	Conformer							
Diastereoisomer	δ*δδ	δ*δλ	δ*λδ	λ*δδ	δ*λλ	λ*δλ	λ*λδ	λ*λλ
Λ-*R*	44.5	48.8	45.0	52.2	49.0	54.1	54.1	53.7
Λ-*S*	62.3	60.7	67.2	51.4	61.5	58.0	54.2	57.0

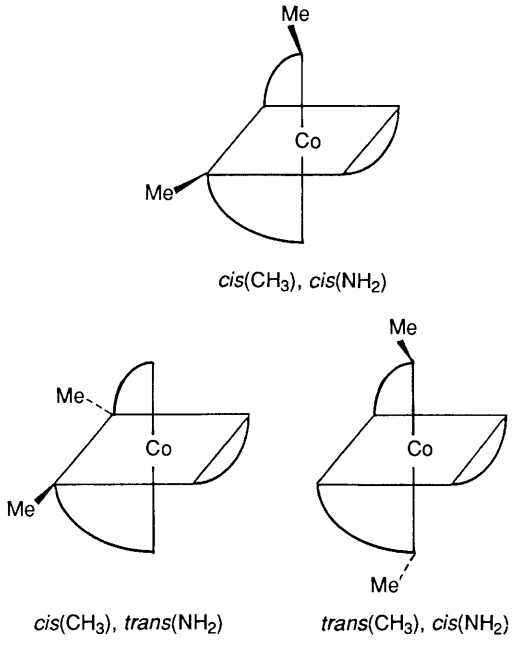

Fig. 2 Representations of the geometric isomers of the Λ-$[Co(men)_2(en)]^{3+}$ cation

provides an exceptional test of the molecular mechanics computational method.

Results and Discussion

The MM2 force field can be calibrated to reproduce both structure and heats of formation, and both of these aims have been achieved for organic molecules because of the enormous experimental data set available. The method has been applied to a substantial number of inorganic complexes:[19] however, relative to the organic systems, there is a paucity of thermodynamic data and so the force field has been calibrated only to reproduce structure. Therefore, the steric energies calculated can only be loosely related to heats of formation for co-ordination compounds. Previous studies[11] indicated that the predominant contributing interactions to the total steric energy of the $[Co(pn)_n(en)_{3-n}]^{3+}$ species were the organic components, and therefore the difference in thermodynamic energies would be expected to be closely related to the difference in steric energies. The thermodynamic and structural aspects of the calculations will be considered separately.

The isomer possibilities for $[Co(men)_3]^{3+}$, $[Co(men)_2(en)]^{3+}$ and $[Co(men)(en)_2]^{3+}$ have been elaborated previously.[16] The IUPAC nomenclature rules[12] do not allow the isomers and conformers in these complicated systems to be distinguished. This distinction requires that the stereochemical parameters (*R*/*S*, λ/δ) for the three chelate rings be specified in some definite sequence. Ring-order conventions were developed previously for the $[Co(men)_3]^{3+}$ system in particular,[16] and these conventions are extended in the present paper to the $[Co(men)_2(en)]^{3+}$ and $[Co(men)(en)_2]^{3+}$ systems to enable all possible conformers to be specified. For each complex system the discussion is limited to the Λ absolute configuration about the metal centre: there will be a corresponding enantiomeric set of stereoisomers for the Δ absolute configuration.

Thermodynamic Considerations.—$[Co(men)(en)_2]^{3+}$. Fig. 1 illustrates two representations of the Λ-$[Co(men)(en)_2]^{3+}$ molecule. The men ligand may co-ordinate to give the asymmetric *N*-methyl centre in either the *R* or *S* configuration, and as an independent factor each of the en and men rings may adopt either a δ or λ conformation.

Each molecule (Λ absolute configuration) is viewed along the pseudo-C_3 axis such that the N-*methyl group is directed towards the observer* (on the upper nitrogen of the men ring). The rings are then listed in a *clockwise order*. The parameters (δ/λ) for the unique men ring are designated with an asterisk, and are listed first. For each internal diastereoisomer Λ-*R* and Λ-*S* there are eight conformer arrangements. They are listed with their calculated steric energies in Table 1.

On the basis of these calculated energies, high stereospecificity would be expected in this complex and the Λ*R*/Δ*S* racemic pair would be preferred by a ratio >40:1 over its internal diastereoisomer (Δ*R*/Λ*S*) at 25 °C, based on the summation of the contributions of the eight conformers of each internal diastereoisomer. Since no statistical factors are present in this system, ΔH_{steric} can be equated to a 'free energy' for the species involved, so that the predicted equilibrium ratios of the most stable conformers of Λ-$[Co(men)(en)_2]^{3+}$ in equilibrium solution can then be calculated: Λ-*R*-δ*δδ, 1.00; Λ-*R*-δ*λδ, 0.82; Λ-*R*-δ*δλ, 0.18; and Λ-*R*-δ*λλ, 0.16. For the Λ configuration around the metal centre there is generally a thermodynamic preference for the δ conformation, as observed in the $[Co(en)_3]^{3+}$ and $[Co(pn)_n(en)_{3-n}]^{3+}$ systems.[11] Experimentally only one diastereoisomer was observed as explained by the calculations, but its conformational composition is at present unknown.

$[Co(men)_2(en)]^{3+}$. For $[Co(men)_2(en)]^{3+}$ there are three possible geometries arising from the *cis* and *trans* relative positions of the CH_3 and NH_2 groups in the two men ligands: the *trans*(CH_3), *cis*(NH_2), the *cis*(CH_3), *trans*(NH_2) and the *cis*(CH_3), *cis*(NH_2) forms (Fig. 2). Each geometry has three (or four) possible configuration combinations of the two asymmetric nitrogen donors of the men rings: *RR*, *SS*, *RS* (and *SR*). The *RS* and *SR* forms are identical for the two geometries with *trans* components, but for the *cis*(CH_3), *cis*(NH_2) geometry the *RS* and *SR* forms are distinct. Thus there is a total of ten stereoisomers for each configuration Λ or Δ of the complex, each of which has eight possible ring conformation combinations. Some of these conformers are equivalent by C_2 symmetry (see below) so that there is a total of 72 isomers for each configuration of this complex cation.

In designating these 72 forms, each molecule (Λ absolute configuration) is viewed along the pseudo-C_3 axis, and the rings are listed in a *clockwise order* with the parameters of the unique en ring denoted by an asterisk, and listed first. For the *trans*(CH_3), *cis*(NH_2) and *cis*(CH_3), *trans*(NH_2) geometries the orientation of the molecule along the pseudo-C_3 axis is not important since the *positions* of the two men rings will be interchanged by the two-fold symmetry of the geometry (*i.e.* ignoring *R*/*S* configurations).

For the *trans*(CH_3), *cis*(NH_2) and *cis*(CH_3), *trans*(NH_2)

Table 2 Steric energies (kJ mol^{-1}) for the isomers of Λ-[Co(men)$_2$(en)]$^{3+}$; superscript * denotes the en ring

	Conformers								
	δ*δδ	λ*δδ	δ*λδ	δ*δλ	λ*δλ	λ*λδ	δ*λλ	λ*λλ
trans(CH$_3$), *cis*(NH$_2$)								
RR	61.8[a]	67.2	← 66.4 →		← 71.8 →		74.7	74.6
RS	78.9	79.2	88.8	*64.9*	73.3	84.5	76.5	82.5
SS	105.6	94.0	← 93.8 →		← 92.2 →		80.1	87.0
cis(CH$_3$), *trans*(NH$_2$)								
RR	60.4[b]	58.5[b]	← 68.8 →		← 77.3 →		69.4	77.2
RS	76.8	80.3	*67.1*	85.4	86.6	85.0	79.5	78.9
SS	104.1	110.4	← 88.4 →		← 91.1 →		80.7	79.6
cis(CH$_3$), *cis*(NH$_2$)								
RR	75.9	74.7	72.3	89.0	91.3	76.5	81.8	84.0
RS	78.4	76.8	87.1	*67.6*	73.4	83.7	72.0	76.6
SR	74.3	82.4	75.6	87.2	90.0	78.0	97.0	96.5
SS	96.4	97.6	92.5	79.1	87.1	86.3	80.0	84.3

Energies within 7.5 kJ mol^{-1} of those for the isolated structures are italicized. [a] Isolated isomer **F** for which crystal structure has been determined.[17] [b] Isolated isomer **H** for which crystal structure has been determined.[18]

geometric isomers, when the two *N*-methyl centres have the same chirality, *i.e. RR* or *SS*, the molecules possess a real C_2 axis (through the centre of the en chelate). Therefore in these species the following pairs of conformers are equivalent: δ*λδ ≡ δ*δλ and λ*λδ ≡ λ*δλ (where the unique en ring is distinguished by an asterisk). For these two geometries, the forms with *N*-methyl groups of mixed chirality *RS* and *SR* are equivalent with respect to the *R* and *S* configurations, but this 'mixed configuration' does give rise to pairs of distinct conformers (since the *R* or *S* configuration does not stereospecifically determine the ring conformation). For example, for *RS* the conformations δ*λδ and δ*δλ are distinct, although these two conformations are equivalent for the *RR* and *SS* configurations.

For the *cis*(CH$_3$), *cis*(NH$_2$) geometry, in which there is no symmetry relationship between the positions of the two men rings, the caveat must be added that the molecule is viewed along the pseudo-C_3 axis with *both* N-*methyl groups directed towards the observer.*

The calculated steric energies for these isomers are listed in Table 2.

In assessing proportions of isomers, the steric energies require to be adjusted to take account of statistical inner-sphere entropy terms ($T\Delta S$). There is a statistical preference for isomers containing 'mixed' configurations of the chiral N-donors *RS* in the *trans*(CH$_3$), *cis*(NH$_2$) and *cis*(CH$_3$), *trans*(NH$_2$) forms (see above), and also for equivalent conformational forms such as δ*λδ ≡ δ*δλ. Therefore the theoretical predictions for the ratios of the most stable forms (at 80 °C, the temperature at which comparable experimental data are available) are, for the Λ absolute configuration, in order of decreasing stability (ΔG values in kJ mol^{-1}): **1** *cis*(CH$_3$), *trans*(NH$_2$)-*RR*-λ*δδ ('ΔG' = ΔH_{steric} = 58.5); **2** *cis*(CH$_3$), *trans*(NH$_2$)-*RR*-δ*δδ ('ΔG' = ΔH_{steric} = 60.4); **3** *trans*(CH$_3$), *cis*(NH$_2$)-*RR*-δ*δδ ('ΔG' = ΔH_{steric} = 61.8); **4** *trans*(CH$_3$), *cis*(NH$_2$)-*RS*-δ*δλ ['ΔG' = $\Delta H_{steric} + RT\ln(\frac{1}{2})$ = 62.9]; **5** *trans*(CH$_3$), *cis*(NH$_2$)-*RR*-(δ*λδ + δ*δλ) ['ΔG' = $\Delta H_{steric} + RT\ln(\frac{1}{2})$ = 64.4]; and **6** *cis*(CH$_3$), *cis*(NH$_2$)-*RS*-δ*δλ ('ΔG' = ΔH_{steric} = 67.6). On the presumption that conformational isomers of the same geometry/configuration would not be separated by normal crystallization and chromatographic procedures, the present calculations would predict that the ratio of the stereoisomer forms (**1** + **2**):(**3** + **5**):**4**:**6** would be 30:9:4:1 at 80 °C. In synthetic studies on the [Co(men)$_2$(en)]$^{3+}$ system[16] three isomers were obtained (designated **H**, **F** and **G**). These isomers remained distinct under basic conditions, which shows that they are of the three different geometries, since diastereoisomers *R*/*S* would interconvert in base by NH exchange, and en-type conformations are mobile in solution. Experimental ratios were obtained by chromatographic methods in basic media, where the three observed bands (**H**:**F**:**G** = *ca.* 36:5:1) would correspond to the proportions for the three possible geometries, each equilibrated to its most stable form. For comparison, it is therefore appropriate to present calculated ratios as the sums of the individual contributors within each of the three overall geometries: *i.e.* geometries *cis*(CH$_3$), *trans*(NH$_2$):*trans*(CH$_3$), *cis*(NH$_2$): *cis*(CH$_3$), *cis*(NH$_2$) = conformer forms numbered (**1** + **2**):(**3** + **4** + **5**):(**6**) = **H**:**F**:**G** = 30:13:1 at 80 °C.

Isomers **H** and **F** have been crystallized cleanly, but **G** has been characterized only in solution. The most abundant isomer **H** has been characterized by X-ray structural studies as *cis*(CH$_3$), *trans*(NH$_2$)-(Λ-*RR*-δ*δδ) + (Δ-*SS*-δ*λλ), with the unit cell containing the two different cations.[18] These molecules in **H** are pseudo-enantiomeric, differing only in the conformations of the en ring, and they correspond to the two conformers of the *cis*(CH$_3$), *trans*(NH$_2$)-Λ-*RR* diastereoisomer, δ*δδ and λ*δδ, which have the lowest calculated energies in this complete complex system. Their calculated energy difference of *ca.* 2 kJ mol^{-1} is not great, and crystal-packing forces are presumably decisive in determining the 1:1 occurrence of these conformers in the isolated material. The second most abundant isomer **F** has the structure *trans*(CH$_3$), *cis*(NH$_2$)-Λ-*RR*-δ*δδ,[17] which corresponds to the theoretically predicted next-most-stable diastereoisomer and conformation in the complete system.

The energy calculations have thus been able to predict correctly the three particular conformations (from the 72 possible) which have been isolated in the solid form, and moreover have been able to reproduce the experimental proportions of **H**:**F**:**G** with remarkable agreement.

The least-stable isomer **G** of those obtained experimentally must be of the geometry *cis*(CH$_3$), *cis*(NH$_2$). The calculated most stable conformer Λ-*RS*-δ*δλ is sufficiently lower in energy than the next most stable that this can be proposed as the structure for **G** with some confidence.

[Co(men)$_3$]$^{3+}$. Two geometry types are possible depending on the relative disposition of the *N*-methyl groups about the C_3 or pseudo-C_3 axis of the molecule. These are shown in Fig. 3, and are designated *fac* (facial) when all the *N*-methyl groups are located on one octahedral face and are all-*cis* to one another, and *mer* (meridional) when one of the *N*-methyl groups is located on an opposite octahedral face to the other two. For

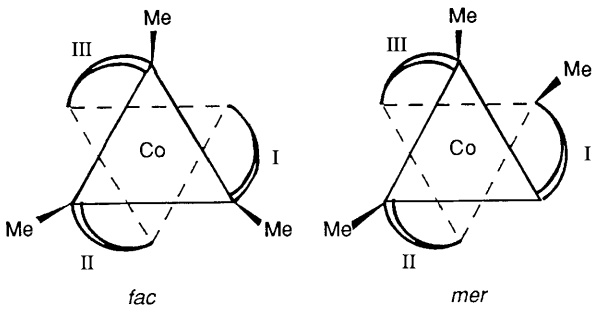

Fig. 3 Representations of the geometric isomers of the Λ-$[Co(men)_3]^{3+}$ cation, viewed down the (pseudo-)C_3 axis

designating the isomers, each molecule (Λ absolute configuration) is viewed along the (pseudo-)C_3 axis such that the *maximum number of* N-*methyl groups are directed towards the observer* on the near octahedral face (*i.e.* three for *fac* and two for *mer*). The rings are then listed in a *clockwise order*.

For the *fac* geometry there are only four possible configurational forms (diastereoisomers): *RRR*, *RRS*, *RSS* and *SSS*. In the *RRR* and *SSS* forms the ligands cannot be distinguished so that only four conformational isomers are possible for each form (δδδ, δλδ, λδλ and λλλ). In these instances with no unique men ring the order of listing the rings is irrelevant although the various types of parameter (*R*/*S* and δ/λ) must be written in the corresponding order. However the *RRS* and *SSR* isomers both have a men ring of unique configuration so that eight conformational isomers are possible: δ*δδ. δ*δλ, δ*λδ, λ*δδ, λ*λδ, λ*δλ. δ*λλ, λ*λλ. The parameters (δ/λ) for the unique men ring are designated with an asterisk, and are listed first.

For the *mer* geometry all of the chelate rings are distinct, so that there are eight possible diastereoisomer forms each of which can have eight separate conformational isomers. The ring designation commmences with the unique men ring (the *N*-methyl group on the remote octahedral face of the molecule), and the parameters (*R*/*S*, δ/λ) for this ring are designated with an asterisk, and are listed first. The eight internal diastereoisomers are therefore *R***RR*, *R***RS*, *R***SR*, *R***SS*, *S***RR*, *S***SR*, *S***RS*, *S***SS*, and each of these may exist as conformational isomers δ*δδ, δ*δλ, δ*λδ, λ*δδ, λ*λδ, λ*δλ, δ*λλ, λ*λλ.

Accordingly, there are a total of 88 possible geometric/configurational/conformational isomers for Λ-$[Co(men)_3]^{3+}$: they are listed in Table 3, along with their calculated steric energies.

Because all three ring *positions* are distinct in the *mer* but are identical in the *fac* geometries, the *mer* forms should show a statistical stabilization of $RT\ln(\frac{1}{3})$ over the *fac* forms. Further, the 'mixed' isomers (*RRS*, *SSR*) should be stabilized by a statistical factor of 3:1 over the *RRR* and *SSS* isomers for the *fac* (but not the *mer*) forms. After correction for these statistical factors (calculated at 25 °C), the most stable isomeric forms of Λ-$[Co(men)_3]^{3+}$ would be expected to be ['$\Delta G' = \Delta H_{steric} + RT\ln(\frac{1}{3})$, in kJ mol^{-1}]: **1** *mer*-*R***RS*-δ*δλ ('$\Delta G'$ = 83.4), **2** *mer*-*R***RR*-δ*λδ ('$\Delta G'$ = 87.1), **3** *mer*-*R***RS*-δ*λλ ('$\Delta G'$ = 87.8), **4** *mer*-*R***SR*-δ*λδ ('$\Delta G'$ = 90.6), **5** *mer*-*R***SR*-δ*δδ ('$\Delta G'$ = 90.9), **6** *mer*-*S***RR*-δ*λλ ('$\Delta G'$ = 91.8), **7** *mer*-*R***SS*-δ*λλ ('$\Delta G'$ = 92.9), **8** *mer*-*R***RS*-δ*δδ ('$\Delta G'$ = 93.6) and **9** *mer*-*R***SS*-δ*δλ ('$\Delta G'$ = 94.9). On the assumption that conformational isomers of the same geometry/configuration will not be separated experimentally (chromatography), the calculations predict that the order of geometric/configurational isomer stability will be *mer*-*R***RS* > *R***RR* > *R***SR* > *S***RR* > *R***SS* for the five most stable forms of Λ-$[Co(men)_3]^{3+}$. The experimental studies of the isomer stabilities[16] have realized three isomers (designated **A**, **B** and **C**) in the ratio 3:1:2 (at 25 °C). Isomers **A** and **C** have been determined as the *R***RR* and *R***RS* forms respectively, by X-ray structural studies.[17] While the prediction of isomer ratios in this case (**A**:**C** = 1:5) is not as satisfactory as with $[Co(men)_2(en)]^{3+}$ or for the $[Co(pn)_n(en)_{3-n}]^{3+}$ systems,[11] the selection of these two isomers (in the correct conformational form, see above) from 88 possible forms by the MM2 force field is a remarkable result. Further, the calculations allow prediction that the isolated isomer **B** should be diastereoisomer Λ-*R***SR*, and that two conformational forms δ*δδ and δ*λδ may be of comparable and highest stability. The reason for the particular stability of the *mer*-*R***RR* in complex **A** is not clear. It should be emphasized however that small changes in the free energies correspond to large changes in the relative proportions of the closely related forms of the molecule, and with these considerations the predictive value of calculations of this type within the complex systems reported here is quite striking.

Factors that are not readily accessible in calculations of this type are the differential effects on isomer stabilities of solvation and ion association. Cobalt(III) complexes containing amine ligands, like the present $[Co(men)_3]^{3+}$ and $[Co(men)_2(en)]^{3+}$ species, are known to undergo ion association with anions[20] utilizing the two groupings of three amine functions which are on opposite faces of the co-ordination octahedron. Since the CH_3 substituents are on the carbon skeleton of the rings in the $[Co(pn)_n(en)_{3-n}]^{3+}$ systems, it is possible that ion-association effects are similar for the isomers of each of these complex systems (n = 1–3) so that the relative free energies will not be greatly influenced by this factor. However, for the $[Co(men)_n(en)_{3-n}]^{3+}$ complexes the CH_3 substituent is on an N-donor atom and, dependent on its orientation, may have an influence on the interaction of the complex molecule with either solvent or anions. For this particular series of complexes such an effect is likely to become more significant in the sequence n = 1 < 2 < 3, so that its consequences may well be greatest for the $[Co(men)_3]^{3+}$ complex. Interestingly, it is only for this complex among all the $[Co(pn)_n(en)_{3-n}]^{3+}$ and $[Co(men)_n(en)_{3-n}]^{3+}$ systems studied that there is any noticeable discrepancy between the calculated and experimental thermodynamic ratios. Nevertheless, even in this least favourable case of these six systems studied, the two most stable geometric/conformational forms of the $[Co(men)_3]^{3+}$ species observed experimentally are among the three forms of the molecule calculated to be the most stable from 88 possible.

Structural Considerations.—The MM2 force-field calculations yield structural details of the minimized form of each conformer. Interconversions of ring conformations do not occur during the minimization, so that each calculation results in a lowest-energy form for the particular starting conformational isomer. The calculated and experimental structural data for the complexes are given in SUP 56800 for the complexes where X-ray crystal structures are available:[17,18] **F** = $[Co(men)_2(en)]^{3+}$, Λ-*trans*(CH_3), *cis*(NH_2)-*RR*-δ*δδ; **H** = $[Co(men)_2(en)]^{3+}$, Λ-*cis*(CH_3), *trans*(NH_2)-(*RR*-δ*δδ + *RR*-λ*δδ); **A** = $[Co(men)_3]^{3+}$, Λ-*mer*-*R***RR*-δ*λδ; and **C** = $[Co(men)_3]^{3+}$, Λ-*mer*-*R***RS*-δ*δλ. The molecular structures for the three complexes are shown in Figs. 4–7, which give the atom numbering schemes used.

Comparison of the geometric parameters for the crystal structures and minimized structures show that the correlations are very good.* Particular points of correlation are, first, the

* Summaries of comparisons: for **F**, root-mean-square (r.m.s.) differences for 17 bond lengths, 0.036 Å; for 31 bond angles, 1.60°; for 51 torsional angles, 16.08°; for all interatomic distances, 0.052 Å; for **H**, (*a*) r.m.s. differences for 17 bond lengths, 0.030 Å; for 31 angles, 1.69°; for 49 torsional angles, 2.01°; for all interatomic distances, 0.045 Å. (*b*) for 17 bond lengths, 0.022 Å; for 31 angles, 1.48°; for 49 torsional angles, 4.56°; for all interatomic distances, 0.041 Å; for **A**, r.m.s. differences for 18 bond lengths, 0.023 Å; for 33 bond angles, 0.97°; for 57 torsional angles, 7.11°; for all interatomic distances, 0.038 Å; for **C**, r.m.s. differences for 18 bond lengths, 0.027 Å; for 33 angles, 1.07°; for 57 torsional angles, *ca.* 3.00°; for all interatomic distances, 0.053 Å.

Table 3 Steric energies (kJ mol^{-1}) for the isomers of Λ-[Co(men)$_3$]$^{3+}$; superscript * designates the unique men ring

	Conformer							
Diastereoisomer	δ*δδ	δ*δλ	δ*λδ	λ*δδ	λ*λδ	λ*δλ	δ*λλ	λ*λλ
mer								
*R*RR*	96.2	111.2	89.8[a]	100.7	99.5	121.1	101.6	109.7
*R*SR*	*93.6*	108.2	*93.3*	106.5	104.0	118.7	114.8	128.9
*S*RR*	109.1	130.5	113.7	118.1	102.0	119.7	*94.5*	114.1
*R*RS*	*96.3*	86.1[b]	103.9	106.4	115.6	98.9	*90.5*	100.5
*S*RS*	125.8	135.9	111.2	109.5	117.0	100.4	111.8	104.1
*R*SS*	118.5	97.6	109.3	124.9	115.0	114.1	95.6	113.4
*S*SR*	120.5	126.6	118.2	110.3	103.0	122.8	140.0	130.1
*S*SS*	152.1	121.4	147.2	132.5	123.0	116.2	125.6	114.7
fac								
RRR	115.3	←	125.1	→	←	127.0	→	118.4
SRR	110.5	124.0	109.1	105.5	120.1	123.2	120.2	125.4
RSS	117.2	108.8	108.9	131.2	117.2	129.0	108.6	123.9
SSS	135.3	←	126.0	→	←	114.7	→	113.4

Energies within 7.5 kJ mol^{-1} of those for the isolated structures are italicized. [a] Isolated isomer **A** for which crystal structure has been determined.[17] [b] Isolated isomer **C** for which crystal structure has been determined.[17]

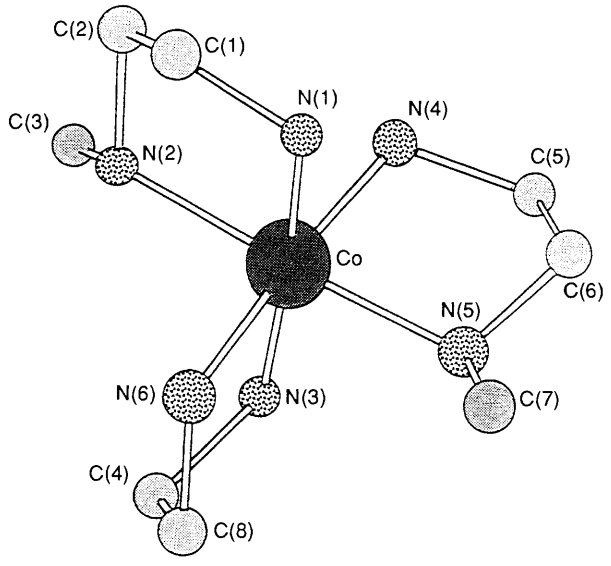

Fig. 4 Crystal structure[17] of **F**, Λ-[Co(men)$_2$(en)]$^{3+}$, *trans*(CH)$_3$, *cis*(NH$_2$)-*RR*-δ*δδ, showing atom numbering scheme used

MM2 force-field calculations have correctly accounted for the small (*ca.* 0.04 Å) Co–N bond-length increase observed for Co–NH(CH$_3$)– compared with Co–NH$_2$–. This effect is possibly caused by steric interactions involving the substituent methyl group, which elongate the Co–N bond and distort the tetrahedral geometry about the substituted N-donor atom. Restraining these N atoms to a strict tetrahedral arrangement in such calculations may reveal more about these particular interactions, but this was not undertaken in the present work.

Secondly, in the crystal structures of **A** and **C** there is a clear conformational distortion of the two δ rings, seen in Figs. 5 and 6 as a deviation from the expected parallel orientation of the C–C bonds relative to the pseudo-C_3 axis.* These distortions are duplicated in the calculated structure.

A discrepancy between the X-ray and calculated bond lengths is observed in some N–C and consistently in the (N)C–C(N) bonds, and the following factors may be involved. A deficiency of the present MM2 force field is that the parameters used for the N atoms are those of free amine groups, since MM2 force-field parameters do not exist for co-ordinated amines: undoubtedly, there will be perturbing electronic effects when amines are co-ordinated which will therefore reduce the accuracy of the parametrization. In addition, similar calculations involving O–C–C–O systems give minimized C–C bond lengths consistently longer than those observed in the same molecules in structural determinations.[21] This effect is unexplained, but it is clear that similar effects are observed in these analogous N–C–C–N systems. The correlation may be improved by adjustment of the parametrization relating to this grouping in the ligand. However, our aim in this and related studies[11] was to maintain a general force field in a comparison of its application to a variety of complex systems.

Conclusion

Where experimental thermodynamic and structural information is available for the various [Co(men)$_n$(en)$_{3-n}$]$^{3+}$ species the MM2 force-field calculations have shown a remarkable correlation. Because of the large number of closely related isomeric forms in each of these three complex systems, the results are encouraging for the predictive application of MM2 techniques to metal complex systems in which there are subtle differences between possible forms.

Experimental

The calculations used the MM2 force-field minimization program described previously.[11,22–24]

Starting structures were prepared by addition of methyl groups at standard bond lengths and angles to the cation in the [Co(en)$_3$]$_2$[HPO$_4$]$_3$·9H$_2$O structure of Duesler and Raymond.[25] The computer program CHEM 3D PLUS™ (Cambridge Scientific Computing, Boston, MA) was used for editing and manipulating initial structures and viewing final output. For each isomer minimized more than one starting geometry was used to reduce the possibility of conformations being hung in 'local energy minima'.

All of the organic parameters used in the force field derive

* When tris(bidentate) molecules involving five-membered chelate rings of the en type (*e.g.* en, pn) are viewed down the (pseudo-)C_3 axis the C–C bond of each ring is observed to be either roughly parallel ('lel') or oblique ('ob') to that axis. For the Λ absolute configuration of the metal the δ conformation is 'lel' and the λ conformation is 'ob'. For the enantiomeric Δ absolute configuration the λ conformation will be 'lel' and the δ conformation 'ob.'[11]

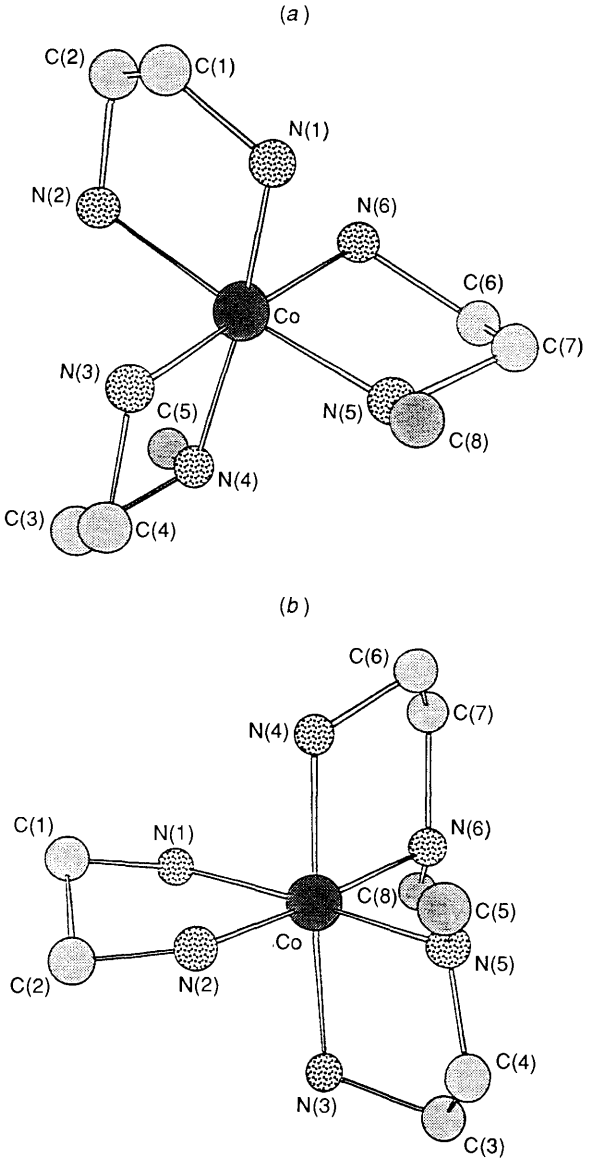

Fig. 5 Crystal structure[18] of **H**, $[Co(men)_2(en)]^{3+}$: (*a*) *cis*(CH_3), *trans*(NH_2)-Λ-*RR*-δ*δδ and (*b*) *cis*(CH_3), *trans*(NH_2)-Δ-*SS*-δ*λλ [≡*cis*(CH_3), *trans*(NH_2)-Λ-*RR*-λ*δδ], showing atom numbering scheme used

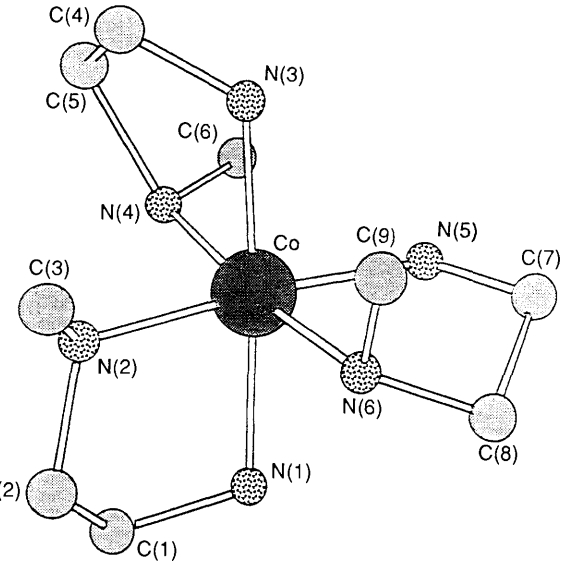

Fig. 6 Crystal structure[17] of **A**, Λ-$[Co(men)_3]^{3+}$, *mer*-*R***RR*-δ*λδ, showing atom numbering scheme used

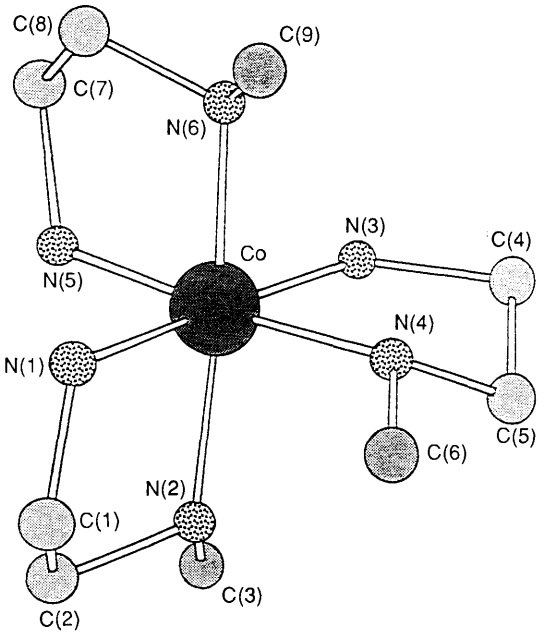

Fig. 7 Crystal structure[17] of **C**, Λ-$[(Co(men)_3]^{3+}$, *mer*-*R***RS*-δ*δλ, showing atom numbering scheme used

from the original work by Allinger.[22] Parameters containing the metal were taken in the first instance from the work by DeHayes and Busch[13] and Brubaker and Johnson,[19] and they were then adjusted to provide the best fits between MM2 minimized geometries and the available X-ray diffraction studies. The final parameters are*: non-bonding, cobalt(III) van der Waals radius, 2.30 Å; ε_0 = 0.711 kJ mol^{-1}; bond stretching, Co^{III}–N, K_{str} = 195.0 N m^{-1} molecule^{-1}, r_0 = 1.950 Å, bond moment = 0.0 D, cubic stretch constant = 2.000; valence angle deformation, N–Co^{III}–N, K_{bend} = 0.400 × 10^{-18} N Å rad^{-2} molecule^{-1}, θ_1 = 90.000°, θ_2 = θ_3 = 0.000°; Co^{III}–N–C, K_{bend} = 0.278 × 10^{-18} N Å rad^{-2} molecule^{-1}, θ_1 = 90.000°, θ_2 = θ_3 = 0.000°; H–N–Co^{III}, K_{bend} = 0.278 × 10^{-18} N Å rad^{-2} molecule^{-1}, θ_1 = 90.000°, θ_2 = θ_3 = 0.000°; torsional angle deformation, C–N–Co^{III}–N, V_1 = 0.000, V_2 = 0.000, V_3 = 0.000 kJ mol^{-1}; H–N–Co^{III}–N, V_1 = 0.000, V_2 = 0.000, V_3 = 0.000 kJ mol^{-1}; H–C–N–Co^{III}, V_1 = 0.000, V_2 = 0.000, V_3 = −2.174 kJ mol^{-1}; C–C–N–Co^{III}, V_1 = −0.836, V_2 = 3.051, V_3 = 3.344 kJ mol^{-1}.

The convergence criterion for minimization was taken to be $\Delta H_{steric} < 10^{-7}$ kJ mol^{-1} between successive iterations, and this usually required between 50 and 100 cycles (generally less than 5 min of time per isomer on either a DEC 10 or a CCI Power 32 minicomputer). For each isomer the calculations resulted in a minimum-energy geometry and the 'total steric energy', ΔH_{steric}, which is the sum of the component molecular mechanics potential-energy terms (non-bonded, bond-stretch, dipole–dipole, valence-angle bending, bend-stretch and torsional energies). Tables 1–3 summarize the calculated ΔH_{steric} values for the complexes considered. Complete listings of the contributing terms are included in SUP 56800.

* ε_0 = Energy parameter; θ_1 = ideal bond angle, θ_2 and θ_3 are higher-order terms in the potential function; V_1, V_2 and V_3 are the first three co-efficients of the Fourier series expansion which models the torsional energy of the system.[22,23]

Acknowledgements

The continuing interest and assistance of Dr. K. R. Adam (James Cook University of North Queensland) with aspects of

the molecular mechanics calculations is very gratefully acknowledged. This work was supported by the Australian Research Grants Scheme.

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Received 14*th February* 1990; *Paper* 0/00703J