178. A Molecular-Mechanics Analysis of Complexes of the Sexidentate Macrocycles *cis*- and *trans*-6,13-Dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine

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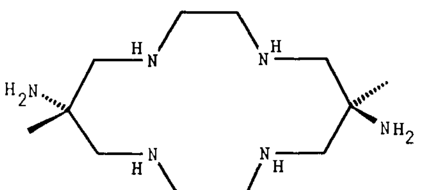
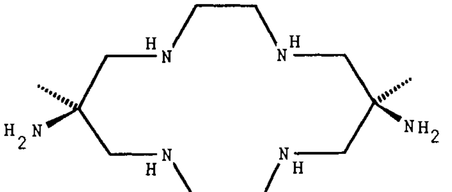
Molecular-mechanics calculations of the sexidentate coordinated complexes of the pendant arm macrocyclic hexaamines *trans*- (L^1) and *cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^2) reveal that the *trans*-isomer shows a preference toward small metal ions, whereas the L^2 may coordinate a wider range of metal ions without significant intramolecular strain. Conformational disorder in previously reported crystal structures of complexes of L^1 is interpreted, and predictions for some, as yet, unknown complexes of L^2 are made.

Introduction. – In recent years, it has been shown [1–6] that sexidentate coordination of the pendant arm macrocyclic hexaamine *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1) to a range of octahedral metal ions results in exceptionally short M–N bond lengths in comparison with other hexaamine complexes. In addition, the d–d electronic maxima of all sexidentate coordinated transition-metal complexes of L^1 have been found to lie at higher energies than other hexaamine analogues. In some cases, the metal$^{III/II}$ redox couples were also shifted to exceptionally negative values. We have only recently isolated the *cis*-isomer of L^1, (L^2), and the crystal structure of its Cd^{II} complex [7] revealed that metal ion 'compression' had not occurred in contrast to earlier reported complexes of L^1.



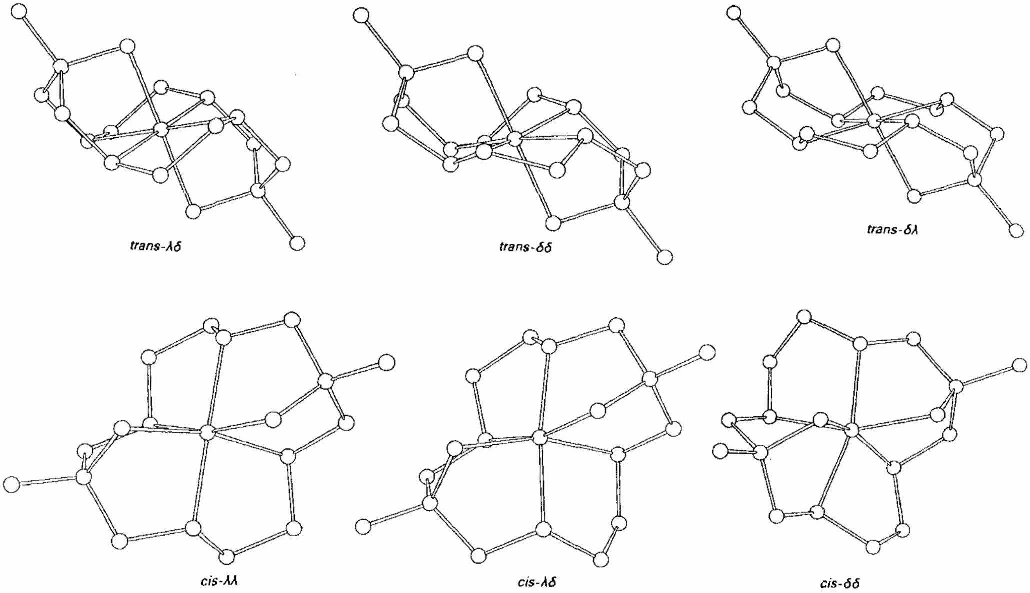
L^1



L^2

To understand the observed contracted coordination spheres imposed by L^1, and also to explain the present and predict future structures of complexes of L^2, we have undertaken a molecular-mechanics study of the sexidentate complexes of both L^1 and L^2. Molecular mechanics is a technique particularly well suited to modelling structures of relatively simple coordination compounds [8–11] where satisfactory force fields are available. In the past, it has been used successfully to predict thermodynamic data relating to hexaaminecobalt(III) complexes, such as isomer distributions and Co$^{III/II}$ redox couples [12–14]. It is imperative that the force field models the metal-ligand interactions as accurately as possible, if one wishes to predict thermodynamic data with any degree of accuracy. In this paper, we will be primarily concerned with an analysis and prediction of the structural features of sexidentate coordinated complexes of L^1 and L^2 using a recently published [15] force field for transition-metal complexes.

The rigid nature of the two ligands, when coordinated as sexidentates, restricts the conformational freedom of the macrocycle. In fact, there exist only three nondegenerate conformations of the complexes of each ligand (*Fig. 1*). The *trans-δδ*-conformer of L^1 is chiral and is, thus, degenerate with its enantiomer, *trans-λλ*, whereas the other two *trans*-conformers are centrosymmetric. All three conformers of the L^2 complexes are chiral. The conformer *cis-λδ* is degenerate with its conformational isomer *cis-δλ*, whereas the *cis-λλ*- and *cis-δδ*-conformers are geometric isomers of their enantiomeric twins (*Δ* and *Λ* isomers). The only conformers that have been identified in crystal structures of sexidentate complexes of L^1 and L^2 are *trans-λδ*, *trans-δδ*, and *cis-λλ*. Herein, we report a molecular-mechanics analysis of all conformers of [ML^1]$^{n+}$ and [ML^2]$^{n+}$ with particular emphasis on the preferences of particular conformers for metal ions of various sizes. Predictions are made regarding as yet unobserved conformations of both ligands and some crystal structures of complexes containing L^1 are reanalyzed.


trans-λδ *trans-δδ* *trans-δλ*

cis-λλ *cis-λδ* *cis-δδ*

Fig. 1. *The nondegenerate conformations of sexidentate complexes of L^1 and L^2*

Experimental. – Molecular-mechanics calculations were performed with the strain-energy minimization program MOMEC87 [16]. The model has been described in [15]. The component of the force field describing intraligand forces is based on earlier force fields for organic compounds [17], and has been combined with the relevant parameters describing metal–ligand interactions, namely the M–N force constant and the strain-free

M–N bond length. This force field has been published in detail in [15]. The strain-minimization routine was applied to each conformer, until the shift in the positional coordinates of all atoms was less than 0.005 Å.

Starting coordinates were either obtained from crystallographic data (for experimentally observed conformers) or from molecules that had been 'constructed' with the graphics program SMILE [18]. Drawings of all molecules were produced with the plotting program ORTEP [19] in conjunction with SMILE.

Results and Discussion. – 1. *'Sphere-Radius' Calculations.* Ideal 'hole sizes' of planar tetraaza macrocycles have, in the past, been calculated in several ways [20–22]. Our approach for octahedral hexaaza macrocycles [23] has been to fix all six M–N bond lengths to the same value and minimize the intraligand strain energy. The minimized strain energy is then ploted as a function of the M–N bond length (*i.e.* the radius of the coordination sphere). In other words, the strain energy is independent of the metal ion in question, and moreover the M–N interaction makes no contribution to the strain energy. Fixing all six M–N bond lengths to the same value is not entirely representative of the known structures of L^1, where a slight elongation of the M–N (primary amine) bonds is invariably found. Nevertheless, this simplification is necessary, if meaningful comparisons between complexes of the two isomeric forms of the macrocycle are to be made.

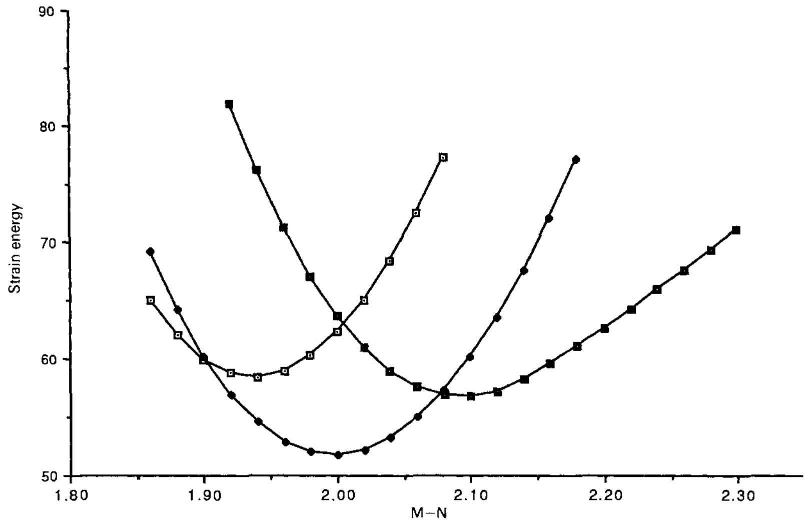


Fig. 2. *Plot of ligand strain energy* [kJ/mol] *as a function of coordination sphere radius* [Å] *for* $[ML^1]^{n+}$.
□: *trans-λδ*, ■: *trans-δδ*, ◆: *trans-δλ*.

Plots of strain energy *vs.* 'sphere radius' for the three conformers of L^1 are shown in *Fig. 2.* There is clearly a large difference in the preference of each conformer for metal ions of various sizes. The *trans-λδ*-conformer is most stable for the smallest metal ions, the *trans-δδ*-conformer is the most stable within the range $1.94 < r < 2.08$ Å, and the *trans-δλ*-conformer is favored, when the M–N bond length exceeds *ca.* 2.10 Å. As mentioned above, only the *trans-λδ*- and *trans-δδ*-conformers have been observed in the X-ray crystal structures of complexes of L^1. It is apparent from *Fig. 2* that only large metal ions will force the complex into the *trans-δλ*-conformation.

The ligand strain energies of the three conformers of $[ML^2]^{n+}$ as functions of metal-ion size are plotted in *Fig. 3.* The three curves display quite flat minima in contrast with the conformers of $[ML^1]^{n+}$. It is also apparent that, for all metal-ion radii, the *cis-λλ*-conformer is the most stable. It is clear that the *cis-δδ*-conformer will almost certainly never be found, but the *cis-λδ*-conformer might possibly be observed as the two curves are quite close in energy. The minimum energy of the *cis-λλ*-conformer is found at a sphere radius of 2.40 Å, which is comparable with the average Cd–N bond lengths determined in the structure of $[CdL^2]^{2+}$, where the *cis-λλ*-conformation was identified [7].

2. *Crystal Structures of Complexes of L^1.* Although the plots in *Figs. 2* and *3* are illustrative of the preferences of each conformer for metal ions of various sizes, they cannot be used to predict relative energies of each conformer in any real complex. As mentioned above, the metal–ligand interactions are not included in the analysis for the purpose of generality. Moreover, the constraint of all M–N bonds being equal is not an exact representation of the known structures of both L^1 and L^2. If any quantitative information is to be obtained with respect to the relative strain energies of complexes of these ligands, then each conformer must be refined with a force field appropriate to the metal ion at hand. The force field for hexaaminecobalt(III) complexes is now fairly well established [24]; and in conjunction with our recently developed force field for hexaamine complexes of other metal ions [15], we have performed a conformational analysis of sexidentate coordinated complexes of L^1 and L^2. At present, crystal structures of sexidentate Co^{III} [2], Fe^{III} (low spin) [5] [25], Cr^{III} [4], Ni^{II} [1], Zn^{II} [6], and Rh^{III} [3] complexes of L^1 are extant. The structure of the *cis*-isomer L^2 as its Cd^{II} complex is the sole example, to date, of a complex of this ligand [7].

The minimized strain energies of the *trans-λδ*-, *trans-δδ*-, and *trans-δλ*-conformers of the complexes of L^1 are presented in *Table 1*. The refined M–N bond lengths for each conformer are also presented in comparison with the crystallographic values. Disorder of the macrocyclic five-membered chelate rings was observed in the crystal structures of the

Table 1. *Comparison of Experimental and Strain-Energy-Minimized M–N Bond Lengths* [Å] *and Total Strain Energies* [kJ/mol] *for the Three Conformers of* $[ML^1]^{n+}$

	Crystal structure	*trans-λδ*	*trans-δδ*	*trans-δλ*
$Co^{III}–N_{eq}$	1.937	1.938	1.953	1.977
$Co^{III}–N_{ax}$	1.946	1.946	1.951	1.958
E_T		114.77	116.79	144.25
$Fe^{III}–N_{eq}$	1.972	1.965	1.981	2.005
$Fe^{III}–N_{ax}$	1.984	1.978	1.983	1.992
E_T		90.91	89.98	111.33
$Rh^{III}–N_{eq}$	2.045	2.025	2.043	2.066
$Rh^{III}–N_{ax}$	2.056	2.050	2.058	2.068
E_T		69.02	54.14	57.41
$Cr^{III}–N_{eq}$	2.040	2.017	2.040	2.071
$Cr^{III}–N_{ax}$	2.067	2.051	2.063	2.076
E_T		68.66	54.23	57.17
$Ni^{II}–N_{eq}$	2.070	2.024	2.060	2.108
$Ni^{II}–N_{ax}$	2.125	2.091	2.112	2.134
E_T		75.88	59.14	57.10
$Zn^{II}–N_{eq}$	2.100	2.056	2.100	2.156
$Zn^{II}–N_{ax}$	2.210	2.161	2.190	2.218
E_T		95.44	73.45	64.08

Fe^{III}, Cr^{III}, and Rh^{III} complexes of L^1, with the C-atoms refining to positions between those defined by λ or δ conformations of the rings. However, the disorder was not the same in each structure. For example, the five-membered rings in the structures of $[RhL^1]^{3+}$ and $[CrL^1]^{3+}$ refined to planar geometries (*i.e.* a 1:1 average of λ and δ conformers), whereas disorder in both structures of $[FeL^1]^{3+}$ was less severe (*ca.* 4:1 ratio of conformers). The question is then: of what is the disorder actually an average? It is clear that either a 1:1 mixture of *trans*-$\lambda\lambda$- and *trans*-$\delta\delta$-conformers or of *trans*-$\lambda\delta$- and *trans*-$\delta\lambda$-conformers would result in the observed planar conformation of the macrocyclic five-membered rings. With the aid of molecular mechanics, it is possible to interpret the disorder. In all structures of L^1, the M–N bond lengths were precisely determined despite the disorder in the five-membered chelate rings. Therefore, matching the crystallographically determined M–N bond lengths with like values predicted by molecular mechanics allows one to assign the actual structure.

a) *$[CoL^1]^{3+}$*. The present strain-energy-minimized structure of $[CoL^1]^{3+}$ in the *trans*-$\lambda\delta$-conformation reproduces the X-ray crystal structure [2] as has been noted previously [8] with a slightly different force field, and also the strain energy in this conformer is less than those of the other two. There was no disorder found in the crystal structure of this complex, and indeed the *trans*-$\lambda\delta$-conformer was identified.

b) *$[FeL^1]^{3+}$*. Two structures of this complex have been published, one of the triperchlorate [25] and the other being the perchlorate dichloride salt [5]. In both structures, disorder was identified in the above-mentioned five-membered chelate rings, however, the perchlorate dichloride structure was refined with partial occupancies of the five-membered chelates. As mentioned above, it is still unclear what the observed disorder represents. The calculated Fe–N bond lengths and the minimized strain energies of the three possible conformers of $[FeL^1]^{3+}$ suggest that the observed structures are mixtures of the *trans*-$\lambda\delta$- and the *trans*-$\delta\delta$-conformers. The Fe–N bond lengths of both conformers are quite similar, so conformational disorder in the crystal lattice would not be expected to affect the precision of the experimentally determined bond lengths. The calculated Fe–N bond lengths of the *trans*-$\delta\lambda$-conformer are not consistent with the crystal structure, nor would one expect this conformer to be observed when one considers its strain energy relative to the other two conformers. The strain energies of the *trans*-$\lambda\delta$- and *trans*-$\delta\delta$-conformers of $[FeL^1]^{3+}$ are virtually the same so the observed mixture of these species in the crystal lattice is, with retrospect, not surprising.

c) *$[CrL^1]^{3+}$ and $[RhL^1]^{3+}$*. These two complexes contain metal ions of similar sizes, and their structures are, therefore, rather similar. In both crystal structures [3] [4], the five-membered chelate rings averaged to planar geometries. When one examines the calculated M–N bond lengths of the three conformers of both complexes, it is clear that the observed structures were actually averages of the enantiomeric *trans*-$\lambda\lambda$- and *trans*-$\delta\delta$-conformers, and not averages of the *trans*-$\lambda\delta$- and *trans*-$\delta\lambda$-conformers. The *trans*-$\delta\delta$-conformers of both $[CrL^1]^{3+}$ and $[RhL^1]^{3+}$ are also predicted to be the most stable of the three possibilities on the basis of strain energy.

d) *$[NiL^1]^{2+}$ and $[ZnL^1]^{2+}$*. The crystal structures of both complexes [1] [6] identified *trans*-$\delta\delta$-conformations, with no disorder of the five-membered chelate rings. The strain-energy-minimized structures of the *trans*-$\delta\delta$-conformers reproduce the observed structures within acceptable limits. However, it is apparent that the experimentally observed structures of both $[NiL^1]^{2+}$ and $[ZnL^1]^{2+}$ are not predicted by molecular mechanics to be the most stable conformations, but instead one might anticipate, in each case, the observation of *trans-δλ*-conformers.

It is one of the fundamental assumptions in our calculations that no intermolecular interactions are considered in the minimization of strain energy within a complex ion. It is well known that the H-bonding between complex cations and H_2O molecules or with anions within the crystal lattice can result in unpredictable and often incalculable distortions of the coordination sphere – so-called 'crystal packing effects'. A pertinent example of this is the structure of $[ZnL^1](ClO_4)_2 \cdot H_2O$ where the *trans*-Zn–N bond lengths to the pendant primary amines are 2.200(5) and 2.228(4) Å instead of being equivalent [6], as one might have expected. When the whole unit cell is examined, it is apparent that a H-bond between the H_2O molecule and one pendant primary amine H-atom breaks the symmetry of the complex cation. A more serious and even less calculable problem is the selective crystallization of one particular conformer – not necessarily the most stable one. The strain energy minimized structure of $[ZnL^1]^{2+}$ refines to the expected C_2 symmetry in the absence of any other forces. It is clear that one cannot always expect molecular mechanics to accurately predict crystal structures, and thus the model may sometimes fall short in prediction of observed conformations solely on the basis of calculated intramolecular strain energies.

3. *Predictions for Structures of L^2.* There is clearly not a great deal that one can say at this juncture regarding the sole crystal structure of a complex of L^2, that is $[CdL^2]^{2+}$, without a force field for Cd^{II} hexaamines. There are few structures of hexaaminecadmium(II) complexes in the literature. In fact, it is not without some qualification that the structure of $[CdL^2]^{2+}$ may be labeled as being that of a hexaamine complex, since weak bonds are formed between the metal center and one O-atom of each perchlorate anion. We have not pursued a hexaamine force field for Cd^{II} complexes, since the paucity of available structural data concerning these systems makes such a force field untenable.

However, the opportunity exists to calculate the structures of several transition-metal complexes of L^2 prior to their syntheses. The strain-energy-minimized structures of sexidentate coordinated complexes of L^2 have been determined, and the predicted metal-ligand environment (of each conformer) is presented in *Table 2*. In all cases, the refined *cis-λλ*-conformer was found to be the most stable. The calculations do not rule out the possibility of the *cis-λδ*-conformer being observed in some cases, since the refined strain energies were not greatly different from those of the *cis-λλ*-conformers. The *cis-δδ*-conformers invariably refined to strain energies greatly in excess of the other two conformations of L^2, and one would not expect this geometry to be observed.

Table 2. *Strain-Energy-Minimized M–N Bond Lengths* [Å] *and Strain Energies* [kJ/mol] *for the Three Conformers of* $[ML^2]^{n+}$

	cis-λλ	*cis-λδ*	*cis-δδ*		*cis-λλ*	*cis-λδ*	*cis-δδ*
Co^{III}–N	1.947–1.961	1.947–1.964	1.945–1.970	Cr^{III}–N	2.071–2.085	2.066–2.078	2.050–2.077
E_T	120.32	127.08	154.86	E_T	49.32	53.82	72.46
Fe^{III}–N	1.978–1.992	1.982–1.994	1.976–1.997	Ni^{II}–N	2.138–2.156	2.124–2.150	2.092–2.149
E_T	92.96	99.44	123.69	E_T	46.21	52.23	72.38
Rh^{III}–N	2.064–2.075	2.061–2.071	2.050–2.068	Zn^{II}–N	2.244–2.260	2.222–2.257	2.183–2.268
E_T	49.71	54.03	72.59	E_T	43.02	51.20	73.96

4. *Preferred Geometries of Complexes of L^1 and L^2.* Examination of the strain-energy-minimized structures of sexidentate coordinated complexes of L^1 and L^2 reveals that the ligands accommodate metal ions of various sizes in quite different ways. All observed and calculated structures of sexidentate complexes of L^1 reveal virtually centrosymmetric complex cations regardless of the metal ion. As the metal ion increases in size, the observed angle between the pendant N-atom, the metal center and the secondary amine N-atom (defining the same five-membered chelate ring) is contracted from 85.0° ([CoL^1]$^{3+}$, *trans-λδ*) to 80.0° ([ZnL^1]$^{2+}$, *trans-δδ*). Concomitant with this is an increase in the axial elongation of the M–N bond lengths with increasing metal-ion size. All crystal structures within this series, reveal that the *trans-N–M–N* bond angles remain between 176 and 180°, in keeping with the approximate center of symmetry at the metal. As anticipated, the strain-energy-minimized structures of all three conformations of [ML^1]$^{n+}$ refined to symmetrical molecules. Qualitatively, it may be seen that this axial elongation must lead to an eventual breaking of the M–N bonds to the primary amines at the point, when the metal ion becomes too large to coordinate all six N-donors. This has been observed in the Cd^{II} complex of L^1, where sexidentate coordination of the ligand could not be achieved, but instead quadridentate coordination of the four secondary amines in a planar arrangement was observed [7].

By contrast, the complexes of L^2 may undergo a distortion from octahedral symmetry toward trigonal prismatic geometry in order to accommodate larger metal ions. The relatively flat potential-energy curves exhibited by the conformers of L^2 (*Fig. 3*) demonstrate that the ligand does not enforce any particular geometry, nor does it have a distinct preference for metal ions of any particular size. It appears that the governing factor determining the degree of trigonal twist in complexes of L^2 is the strain free M–N bond length of the metal ion concerned. This may be seen by examination of the strain-energy-minimized structures of complexes of L^2, where the *cis-λλ*-conformer is considered in

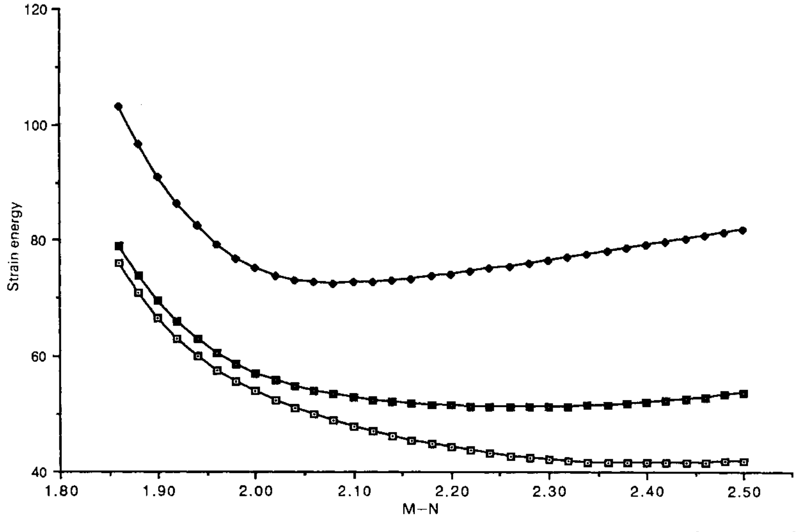


Fig. 3. *Plot of ligand strain energy* [kJ/mol] *as a function of coordination sphere radius* [Å] *for* $[ML^2]^{n+}$. □ : *cis-λλ*, ■ : *cis-λδ*, ◆ : *cis-δδ*.

each case. For the present discussion, the angle by which the two facial sets of N-donors (defined by the fused five-membered chelate rings) are staggered is defined as the trigonal twist angle, *i.e.* 60° for octahedral and 0° for trigonal prismatic geometry. It was found that the distortion toward trigonal prismatic geometry increased with the size of the metal ion, regardless of the M–N force constant: 57.6° for $[CoL^2]^{3+}$; 57.6° for $[FeL^2]^{3+}$; 33.2° for $[RhL^2]^{3+}$; 32.3° for $[CrL^2]^{3+}$; 25.6° for $[NiL^2]^{2+}$ and 17.1 for $[ZnL^2]^{2+}$. The crystal structure of $[CdL^2]^{2+}$ revealed a large distortion toward trigonal prismatic geometry [7], where the observed twist angle was 21.3°. Finally, it is worth noting that the minimized strain energies of all but the Co^{III} complex of L^2 were less than or comparable with those of the corresponding most stable conformer of L^1. Therefore, on steric grounds, syntheses of the above-mentioned complexes of L^2 should not be difficult, since almost all of the isomeric complexes of L^1 are predicted to be less stable, but nevertheless have been synthesized in good yields *via* relatively simple procedures.

Conclusions. – The results presented herein provide a quantitative analysis of the observed conformational isomerism of sexidentate complexes of the *trans*-isomer L^1. It has been shown that, in addition to reproducing crystallographically determined geometries of complexes of L^1, it is possible to unravel conformational disorder in some structures that would have otherwise remained unresolved. It has also been possible to predict the structures, and strain energies, of several complexes of L^2 prior to their synthesis. An important prediction that has emerged from the calculations is that sexidentate complexes of L^2 will not exhibit short M–N bond lengths, unlike the isomeric $[ML^1]^{n+}$ complexes. However, the sexidentate complexes of L^2 are predicted to exhibit considerable trigonal twist distortions when metal ions larger than the 'hypersmall' Co^{III} and Fe^{III} are involved. In addition, our calculations have revealed that L^2 may coordinate a much greater range of metal ion sizes with impurity, whereas L^1 shows a distinct preference for smaller metal ions.

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REFERENCES

[1] N. F. Curtis, G. J. Gainsford, T. W. Hambley, G. A. Lawrance, K. R. Morgan, A. Siriwardena, *J. Chem. Soc., Chem. Commun.* **1987,** 295.

[2] P. V. Bernhardt, T. W. Hambley, G. A. Lawrance, *J. Chem. Soc., Dalton Trans.* **1989,** 1059.

[3] P. V. Bernhardt, T. W. Hambley, G. A. Lawrance, *J. Chem. Soc., Dalton Trans.* **1990,** 983.

[4] P. V. Bernhardt, P. Comba, N. F. Curtis, T. W. Hambley, G. A. Lawrance, M. Maeder, A. Siriwardena, *Inorg. Chem.* **1990,** *29,* 3208.

[5] P. V. Bernhardt, P. Comba, T. W. Hambley, G. A. Lawrance, *Inorg. Chem.* **1991,** *30,* 942.

[6] P. V. Bernhardt, G. A. Lawrance, M. Maerder, M. Rossignoli, T. W. Hambley, *J. Chem. Soc., Dalton Trans.* **1991,** 1167.

[7] P. V. Bernhardt, P. Comba, T. W. Hambley, G. A. Lawrance, K. Várnagy, *J. Chem. Soc., Dalton Trans.* **1991,** in press.

[8] T. W. Hambley, *Inorg. Chem.* **1988,** *27,* 2496.

[9] G. R. Brubaker, D. W. Johnson, *Coord. Chem. Rev.* **1984,** *53,* 1.

[10] R. D. Hancock, *Prog. Inorg. Chem.* **1989,** *37,* 187.

[11] P. Comba, in 'Stereochemistry of Organometallic and Inorganic Compounds', Ed. I. Bernal, Vol. 16, 1992, in press.

[12] P. Comba, T.W. Hambley, L. Zipper, *Helv. Chim. Acta* **1988,** *71,* 1875.

[13] P. Comba, M. Maeder, L. Zipper, *Helv. Chim. Acta* **1989,** *72,* 1029.

[14] A.M. Bond, T.W. Hambley, M.R. Snow, *Inorg. Chem.* **1985,** *24,* 1920.

[15] P.V. Bernhardt, P. Comba, submitted to *Inorg. Chem.*

[16] T.W. Hambley, 'MOMEC87, a Fortran Program for Strain Energy Minimization', School of Chemistry, The University of Sydney, Australia, 1987.

[17] N.L. Allinger, *J. Am. Chem. Soc.* **1977,** *99,* 8127.

[18] D. Eufri, A. Sironi, *J. Mol. Graphics* **1989,** *7,* 165.

[19] C.K. Johnson, 'ORTEP, A Thermal Ellipsoid Plotting Program', Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

[20] L.Y. Martin, L.J. De Hayes, L.J. Zompa, D.H. Busch, *J. Am. Chem. Soc.* **1974,** *96,* 4047.

[21] R.D. Hancock, G.J. McDougall, *J. Am. Chem. Soc.* **1980,** *102,* 6553.

[22] M.G.B. Drew, S. Hollis, P.C. Yates, *J. Chem. Soc., Dalton Trans.* **1985,** 1829.

[23] P. Comba, *Inorg. Chem.* **1989,** *28,* 426.

[24] T.W. Hambley, C.J. Hawkins, J.A. Palmer, M.R. Snow, *Aust. J. Chem.* **1981,** *34,* 45.

[25] P.V. Bernhardt, T.W. Hambley, G.A. Lawrance, *J. Chem. Soc., Chem. Commun.* **1989,** 553.