Geometrical isomerism in octahedral complexes arising from the presence of a fused ring on a triaza macrocycle

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The chiral 2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane (L^1), an analogue of 1,4,7-triazacyclononane, (L^2) that has a *trans*-cyclohexane ring fused to the tacn framework, forms *bis* complexes with a wide range of metal ions where two geometric forms may exist depending on the relative locations of the substituent cyclohexane units. For the crystal structure of bis(*RR*-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane)nickel(II) nitrate, two macrocyclic ligands each occupy a face on opposite sides of the metal-centred octahedron, with the cyclohexane rings, when viewed down an axis passing through the centre of these faces and the metal, arranged in an *anti* disposition. However, the crystal structure of bis(*RR*-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane)chromium(III) perchlorate shows the cyclohexane rings disposed in the alternate *syn* arrangement. Isomerism is defined simply by the spatial disposition of macrocycle substituents. Isomeric preference has been probed by a molecular mechanics analysis, including an energy profile analysis as one macrocycle is rotated relative to the other. The force field calculations predict very small differences between isomers, but a large barrier to interconversion by a twist mechanism. Complexation of L^1 with a range of labile metal(II) ions has been probed by determination of apparent stability constants *via* spectrophotometric titrations. In general, formation constants of L^1 complexes are similar to or even slightly higher than the unsubstituted 1,4,7-triazacyclononane (L^2) analogues, consistent with no strong steric influence of the fused cyclohexane rings in L^1 and with differences in properties reflecting minor electronic effects and ligand flexibility differences resulting from substitution.

Introduction

We,[1–3] and others,[4–12] have been examining macrocycles incorporating cyclohexane rings fused to a macrocycle framework, which introduce chirality, bulk and some rigidity to the ligand system. These factors may be exploited in molecular recognition and metal ion binding or when complexes are employed for chiral catalysis, since rigidity (or flexibility and elasticity) and chirality are important factors in these applications.[13] Recently, we reported the synthesis and some coordination chemistry of the chiral fused-ring cyclic triamine L^1, which can bind facially to octahedral metal ions.[2] The simplest and most studied example of a cyclic polyamine capable of coordinating facially to an octahedral complex is the triazamacrocycle 1,4,7-triazacyclononane (tacn,[1] L^2). The coordination chemistry of this molecule has been comprehensively investigated, especially by Wieghardt and coworkers.[14] The cyclic triamine L^2 forms complexes with metal ions which exceed in thermodynamic stability those of related acyclic tri-amines, assigned to the favourable entropy effects arising from the endodentate conformation of the cyclic ligand limiting rearrangement on coordination. Coordination to octahedral ions occurs dominantly by facial coordination involving all three secondary amines, although chelation by two donors only is required in square-planar complexes. The range of complexes described involving L^2 and its N-alkylated analogues is both extensive and diverse.[14,15]

The chtacn (2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane, L^1) analogue of tacn (1,4,7-triazacyclononane, L^2) can form pseudo-octahedral *bis* complexes where, in terms of a view down a pseudo-C_3 axis passing through the centre of the two opposite octahedral faces where the two tridentate ligands are coordinated and the metal, the two cyclohexane rings can be

L^1   **L^2**
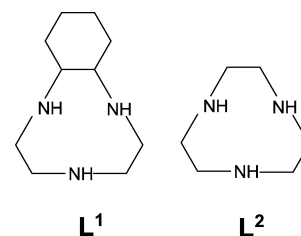
located in either *anti* (or *trans*) or *syn* (or *cis*) dispositions.† Previously, only the *anti* arrangement has been characterised, found in the cobalt(III) complex, so exemplification of this potential form of isomerism was not forthcoming.[2] Now, we present evidence from X-ray structural studies of chromium(III) and nickel(II) complexes that both the *syn* and *anti* dispositions can form and are observed for these ions respectively. The preferences of octahedral metal ions for these forms have been probed *via* a molecular mechanics analysis. Further, the influence of the fused cyclohexane ring on the stability of metal(II) complexes of L^1 has been probed by determination of apparent stability constants by a spectrophotometric titration method, and the results are compared with those reported for the unsubstituted L^2.

Experimental

Syntheses

The polyamine macrocycle (L^1) was prepared by a variation of

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† We use the *anti*/*syn* nomenclature here to avoid confusion with the *trans*/*cis* nomenclature conventionally used for the 1,2-substitution on the cyclohexane ring itself.

the well-studied Richman–Atkins procedure,[16–20] as described previously.[2] Syntheses of octahedral metal complexes have earlier been performed successfully with either racemic, *RR*- or *SS*-*trans*-L[1], with products differing in chiroptical properties only;[2] here, the *RR*-*trans*-L[1] has been employed exclusively.

Crystals of the bis(chtacn)nickel(II) and bis(chtacn)chromium(III) ions suitable for X-ray crystallography were obtained by slow evaporation of dilute solutions from water in the presence of added excess counterions, which yielded crystals of formulae [Cr(*RR*-L[1])₂]Cl₃ and [Ni(*RR*-L[1])₂](NO₃)₂.

Circular dichroism spectroscopy

Spectra were recorded on solutions of complexes in water or 1 : 1 water : DMSO with concentrations in the range 0.005–0.01 $dm^3 mol^{-1}$ using a Jasco J710 CD spectrometer in the range 300–800 nm.

Stability constant determinations

All solutions were made using CO_2-free MilliporeQ water and fresh metal salt solutions were prepared prior to each series of measurements. Potentiometric titrations were carried out under nitrogen in a sealed double jacketed glass cell using a Metrohm 665 automated burette and a Metrohm 605 digital pH meter fitted with a Metrohm 665 combined glass electrode. Standard NBS buffers, pH 6.86 (KH_2PO_4, $NaHPO_4$) and pH 4.01 ($KHC_4H_4O_6$), were used to calibrate the electrode; thus proton activities 10^{-pH} were used for [H⁺]. All measurements were fully automated under control of a computer. Titrations were performed at 25.0 ± 0.1 °C in constant ionic strength ($I = 0.5$, KCl) aqueous solutions under purified nitrogen. Solutions of ligand (6×10^{-4} M) alone and in the presence of 0.9 or 0.5 equivalents of metal ion were titrated with at least 83 increments (of 4×10^{-6} L) of 0.4 M NaOH. The solutions contained initially four equivalents of acid, sufficient to protonate the number of basic sites present and provide one equivalent of excess acid, to ensure titrations commenced in the acidic region. Equilibrium constants were calculated from potentiometric data with a TURBO BASIC version of the program TITFIT.[21]

Spectrophotometric titrations were performed under computer control in a similar manner but using a 1 cm spectrophotometer cell in a thermostatted holder of a Hitachi spectrophotometer as the titration vessel, and including a micro-magnetic stirrer bead and micro-pH electrode in the cell. Solutions of ligand (~6×10^{-4} mol dm^{-3}) alone and in the presence of 0.9 or 0.5 equivalents of metal ion were titrated with from 83 to 100 increments (of 4×10^{-6} mol dm^{-3}) of 0.4 mol dm^{-3} NaOH. The spectra recorded and stored following addition of each aliquot were examined collectively using a second-order global analysis modelling method described recently to produce formation constants as well as spectra of component species.[22] For each system, each titration was repeated at least three times, with good reproducibility (± 0.05 log units) in the stability constants.

X-Ray crystallography

A pale pink (Ni) or yellow (Cr) prism-like crystal was attached to a thin glass fibre and mounted on a Bruker SMART 1000 CCD diffractometer employing graphite monochromated MoKα radiation generated from a sealed tube. An empirical absorption correction determined with SADABS[23] was applied to the data, and there was no crystal decay. The data integration and reduction were undertaken with SAINT and XPREP,[24] and subsequent computations were carried out with the teXsan,[25] WinGX[26] and XTAL[27] graphical user interfaces. The data reduction included the application of Lorentz and polarisation corrections. The structures were solved by direct methods with SIR97,[28] and extended and refined with SHELXL-97.[29]

The asymmetric unit of the Ni structure contains a complex molecule and two nitrate counterions. The non-hydrogen atoms were modelled with anisotropic displacement parameters, and a riding atom model was used for the hydrogen atoms. An ORTEP[30] depiction of the molecule is provided in Fig. 1. The absolute structure was established with the Flack parameter[31] refining to 0.002(9). The asymmetric unit of the Cr structure contains two crystallographically independent complex molecules and six chloride counterions. Additionally there are fourteen sites treated as water oxygen sites, and six of these have partial occupancies refined and then fixed. No hydrogens were included in the model for the water sites. In general the non-hydrogen atoms were modelled with anisotropic displacement parameters and a riding atom model with group displacement parameters was used for the hydrogen atoms. The partially occupied sites were modelled isotropically. An ORTEP[30] depiction of the molecule is provided in Fig. 2. The absolute structure was established with the Flack parameter[31] refining to 0.01(3).
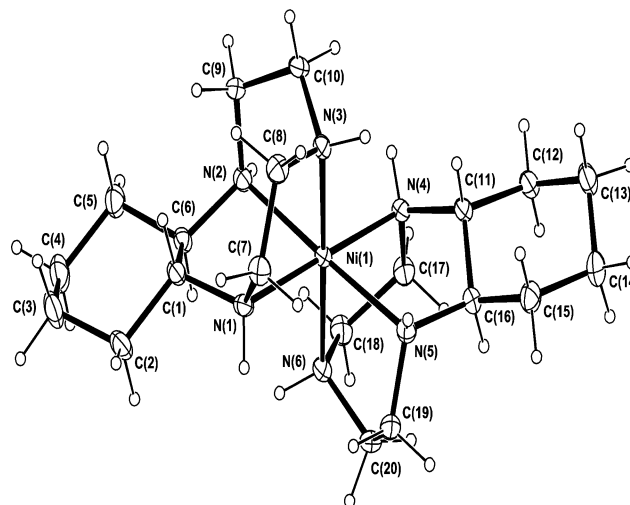

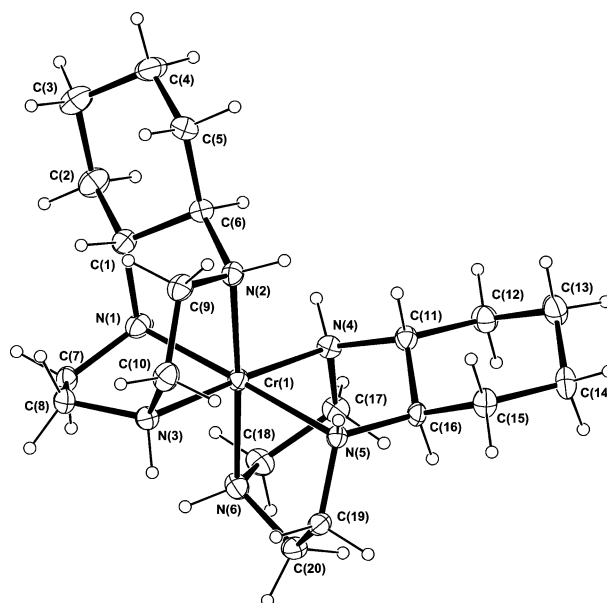**Fig. 1** A view of the [Ni(*RR*-L[1])₂]²⁺ cation, including atom numbering.

Fig. 2 A view of the [Cr(*RR*-L[1])₂]³⁺ cation, including atom numbering.

[Ni(*RR*-L[1])₂](NO₃)₂. Formula $C_{20}H_{42}N_8NiO_6$, *M* 549.33, monoclinic, space group $P2_1$(#4), *a* 8.590(2), *b* 11.754(3), *c* 12.725(3) Å, *β* 103.509(4)°, *V* 1249.3(6) Å³, D_c 1.460 g cm^{-3}, *Z* 2, crystal size 0.181 by 0.112 by 0.074 mm, colour pale pink,

	Ni(II)	Cr(III)[a]	Co(III)[b]
M–N(1)	2.1119(18)	2.091(5)	1.976(7)
M–N(2)	2.1356(19)	2.098(5)	1.976(8)
M–N(3)	2.1067(17)	2.073 (5)	1.948(5)
M–N(4)	2.1153(17)	2.086(5)	1.975(8)
M–N(5)	2.1390(19)	2.105(4)	1.977(7)
M–N(6)	2.1043(18)	2.074(4)	1.948(5)
N(2)–M–N(5)	178.03(6)	98.49(17)	176.0(4)
N(2)–M–N(1)	82.08(7)	82.44(18)	84.8(2)
N(5)–M–N(1)	99.64(7)	178.6(2)	98.1(4)
N(2)–M–N(4)	96.83(7)	100.2(18)	92.4(4)
N(5)–M–N(4)	81.48(7)	82.46(17)	84.8(2)
N(1)–M–N(4)	177.44(7)	98.40(19)	176.0(4)
N(2)–M–N(3)	81.86(7)	82.88(17)	85.3(3)
N(5)–M–N(3)	97.38(7)	97.11(18)	92.3(3)
N(1)–M–N(3)	82.60(7)	82.0(2)	85.2(4)
N(4)–M–N(3)	99.56(7)	176.92(19)	97.4(3)
N(2)–M–N(6)	98.75(7)	176.66(19)	97.4(3)
N(5)–M–N(6)	82.09(7)	82.76(19)	85.1(4)
N(1)–M–N(6)	94.93(7)	96.26(19)	92.3(3)
N(4)–M–N(6)	82.93(7)	83.02(18)	85.3(3)
N(3)–M–N(6)	177.36(8)	93.90(19)	176.1(7)

[a] Data for one of two complex cations in the unit cell. [b] Data amended from ref. 2.

|	Co(III)	Cr(III)	Ni(II)
Calculated (*anti*)	131.57	92.80	87.03
Calculated (*syn*)	127.86	89.82	84.80
Calculated (L^2)	102.75	68.05	63.55
Observed (X-ray structure)	*anti*	*syn*	*anti*

across a series of complexes, and hence the crystal structures of additional octahedral compounds, namely chromium(III) and nickel(II), were completed. As described below, the chromium and nickel complexes isolated adopt *syn* and *anti* geometries respectively. Previously, positional disorder was observed in the *bis*(*R*-2-methyl-1,4,7-triazacyclononane)cobalt(III) ion;[35] however, all possible positional isomers for the methyl groups were present in the crystal and could not be resolved. With the much larger and fused ring cyclohexane unit, a preference occurs and isomers are observed.

The origins of a preference are not immediately clear, since the approximate planes which include the ligands and 'sandwich' the metal ion between them would seem sufficiently separated as to produce minimal non-bonded interactions, which would seem to suggest that the selection may be the result of kinetic rather than thermodynamic factors in formation or be driven by solubility differences. To probe this, and assuming the absence of possible specific packing effects in the crystal lattice, molecular mechanics modelling was pursued. Differences in calculated energies between isomers (Table 2) are small (< 4 kJ mol^{-1}), suggesting the isomers should in most cases co-exist. The primary source of energy differences between isomers for each metal is calculated to arise in the non-bonded interactions, but the difference is still only of the order of ~3 kJ mol^{-1}, even for the smallest Co(III) ion for which closest approach of the ligand planes would occur. Indeed, and perhaps counter-intuitively, the *syn* isomers exhibit the smaller non-bonded interaction energies, presumably due to greater attractive non-bonded contributions. While two of the three structurally characterised complexes match the predicted thermodynamically stable product, a match is not necessarily anticipated since the calculated energy differences are small. The isomers formed and isolated here are presumably kinetic products, since the energy differences predicted between the two geometric forms would seem insufficient to direct the assembly towards a single thermodynamic product.

However, for these relatively inert complexes, no low energy path to interconversion between the *syn* (*cis*) and *anti* (*trans*) geometries in the solid state or solution should exist, with interconversion only permissible *via* a trigonal twist mechanism about the pseudo-C_3 axis, or else *via* a partial dissociation mechanism with rearrangement within the transition state. While both types are known for inert octahedral systems, they are typically slow reactions. The absence of evidence from NMR spectroscopy for any interconversion over period of hours with the diamagnetic cobalt(III) complex supports the view that the isomer isolated is inert to rearrangement in solution. The inert chromium(III) is anticipated to behave similarly; while nickel(II) is more labile, we see no evidence of high spin–low spin equilibration which, if present, could be taken as support for facile dissociation processes.

Force field calculations including bis(1,4,7-triazacyclo-nonane) complexes have been reported previously,[36] but were focussed on defining ideal distances and angles. Here, we have probed the influence of rotation of one macrocycle in its coordination plane relative to the other, analysed *via* force field calculations by monitoring the strain energies of conformers as the twist angle between the two cyclohexane units was varied over 180°. For this molecule, which lacks a proper C_3 axis, this

habit prism, temperature 294(2) K, λ(MoKα) 0.71069 Å, μ(MoKα) 0.829 mm^{-1}, $T_{min,max}$ 0.886, 1.000, $2\theta_{max}$ 52.82°, *hkl* range −10 10, −14 14, −15 15, N 11997, N_{ind} 5026 (R_{merge} 0.0261), N_{obs} 4676 ($I > 2\sigma(I)$), N_{var} 316, residuals $R_1(F)$ 0.0258, $wR_2(F^2$,all) 0.0634, GoF(all) 1.011, $\Delta\rho_{min,max}$ −0.208, 0.329 e$^-$ Å^{-3}.

[Cr(RR-L^1)$_2$]Cl$_3$.xH$_2$O. Model formula C$_{20}$H$_{42}$Cl$_3$CrN$_6$O$_{4.875}$, M 602.95, orthorhombic, space group $P2_12_12$(#18), a 18.936(4), b 29.495(5), c 11.545(2) Å, V 6448(2) Å^3, Z 8, crystal size 0.169 by 0.134 by 0.134 mm, colour yellow, habit prism, temperature 294(2) K, λ(MoKα) 0.71073 Å, μ(MoKα) 0.638 mm^{-1}, $T_{min,max}$ 0.937, 1.000, $2\theta_{max}$ 56.60°, *hkl* range −25 25, −39 39, −15 15, N 78427, N_{ind} 15616 (R_{merge} 0.0605), N_{obs} 10662 ($I > 2\sigma(I)$), N_{var} 572, $R_1(F)$ 0.0665, $wR_2(F^2$,all) 0.1947, GoF(all) 1.568, $\Delta\rho_{min,max}$ −0.452, 1.277 e$^-$ Å^{-3}.

Selected bond lengths and angles are listed in Table 1. The atomic numbering scheme is illustrated in Fig. 1 and 2.

CCDC reference numbers 195129 and 195130.

See http://www.rsc.org/suppdata/dt/b3/b303515h/ for crystallographic data in CIF or other electronic format.

Molecular mechanics

The strain energy minimisation program MOMEC97[32] adapted to HyperChem® using a force field described previously[33] was employed for molecular mechanics.

Results and discussion

The molecule L^1 forms octahedral complexes of cobalt(III), chromium(III) and nickel(II) with two chiral L^1 molecules co-ordinated as tridentate ligands to two opposite octahedral faces. The only substituted chiral analogue of the parent cyclic triamine L^2 previously reported was the *R*-2-methyl-1,4,7-tri-azacyclononane.[34] The pseudo-octahedral bis(L^1) metal complexes can in principle exist in two geometric isomers (*syn* and *anti*), where the isomerism arises from the presence of C-substitution on the macrocycle framework leading to two forms when two ligands are coordinated. Prior to this study, only the cobalt(III) complex had been structurally characterised in our initial report, and was found in the *anti* geometry.[2] It was of some interest to discover if this was the only geometry found

was achieved by defining the angle between projected lines joining pairs of secondary amines adjacent to the cyclohexane rings as the relevant angle defining the rotation about the pseudo-C_3 axis; for an angle of 0°, the two rings are in the *anti* arrangement whereas for an angle of 120° they are in the *syn* arrangement. The rotation angle was constrained to an initial value and then varied stepwise by 5° intervals. The *syn* and *anti* forms are both octahedral geometries, but as the angle is varied the geometry shifts to and through a higher energy trigonal geometry, illustrated for the Co(III) system in Fig. 3. It is more common to employ the standard trigonal twist angle, defined by the projection of a N–M bond from one face onto the plane of the other octahedral face. However, because of the non-ideal character of each facially-bound triamine macrocycle due to inequivalent M–N distances and compressed intraligand N–M–N angles, the twist angles projected for each nitrogen differ by as much as 17°, making definition *via* the twist angle problematical. Distortion is enhanced by a tilting of the two triaza-nitrogen planes slightly away from parallel as twisting towards the trigonal position occurs. The tilting, which is calculated to vary with rotation angle (but is of no more than 4°) is directed away from the cyclohexane rings, and presumably relates in part to non-bonded repulsions between protons on opposite cyclohexane carbons, which appear greatest in the trigonal arrangements.
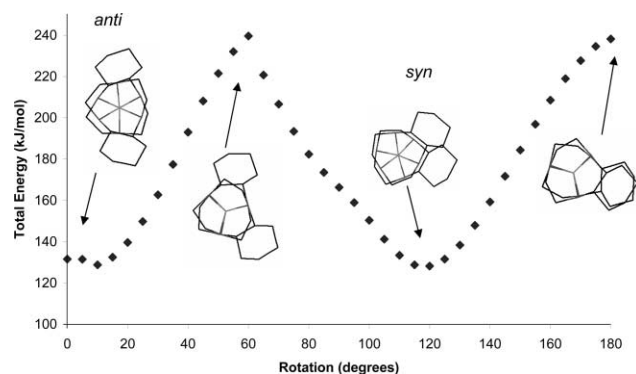
Fig. 3 Calculated energy profile from molecular mechanics for a rotation of one ring relative to the other, performed about the pseudo-trigonal axis on $[Co(L^1)_2]^{2+}$ with the cyclohexane units in the chair conformation. Models of the low-energy and high-energy forms are included in the figure.

The highest energy maxima occur in the trigonal prismatic geometries, and the large energy differences between octahedral and trigonal prismatic forms represents the barrier to isomerization through a non-dissociative twist mechanism, and indicates that it is not a facile process, consistent with earlier observations for the cobalt(III) system. Similar profiles are observed with each metal ion. However, the barrier to trigonal twisting is substantially lower for Ni(II) (53 kJ mol^{-1}) compared with Co(III) (100 kJ mol^{-1}), consistent with the usual faster isomerization rates in nickel complexes. It should be noted that this twist, as computed, does not include electronic factors that relate to changes in ligand field parameters from octahedral to trigonal prismatic, but only steric ones. Further, it is notable that the lowest energy *anti* form is slightly twisted (from between 5–10°) away from the ideal position. This is consistent with structural observations. For the *bis*(R-2-methyl-1,4,7-tri-azacyclononane)cobalt(III) ion it was found that one triangle of nitrogen donors was twisted slightly clockwise from the perfectly aligned position by ~7.6° with respect to the lower one.[35] The rotation direction appeared to be determined by the steric effects of the hydrogen atoms. For the unsubstituted $[Ni(L^2)_2]^{2+}$ itself, a small trigonal twist of ~4° was also observed.[37] This effect is not seen in the crystal structure of $[Co(L^1)_2]^{3+}$ where a crystallographic two-fold axis operates,[2] but does occur in the $[Ni(L^1)_2]^{2+}$ structure.

Table 3 Stability constants for metal(II) complexes of L^1 and comparative data for L^2

System	(L^1)	(L^2)[39]	(L^2)[40]	(L^2)[38]
pK_{a1}	11.12	10.42	10.47	10.68
pK_{a2}	6.94	6.82	6.80	6.86
$Zn^{2+} + L$	12.22	11.62	11.3	11.7
$ZnL^{2+} + L$	8.9	—	9.2	10.0
$Cd^{2+} + L$	10.05	—	9.5	9.5
$CdL^{2+} + L$	8.3	—	8.4	8.4
$Cu^{2+} + L$	16.28	15.52	15.4	15.1
$CuL^{2+} + L$	12.6	—	12.0	12.0
$CuL^{2+} + OH^-$	8.8	8.25	—	—
$Ni^{2+} + L$	12.85	16.24	12.4	13.6
$NiL^{2+} + L$	7.3	—	6.8	11.8
$NiL^{2+} + OH^-$	6.87	—	—	—
$NiL(OH)^+ + OH^-$	10.94	—	—	—

We have also examined the rotation of one ring relative to the other for two different forms: the experimentally observed and usually energetically preferred form with the cyclohexane ring in the chair conformation, and an alternative with the ring in a skew-boat arrangement. In the latter, the skewed cyclohexane rings are disposed slightly more away from the plane of the donors, influencing non-bonded interactions between the rings. Calculated energy differences between the *syn* and *anti* forms in the skew-boat structure are essentially zero, implying that there are no significant differences in non-bonded interactions between the two rings in either isomer. Given the distance separating the two donor planes of any 'sandwich' structure, this is not surprising. The absence of any differences in low-energy and high-energy wells in modelling the analogous unsubstituted tacn (L^2) system helps to validate the process employed. What is notable is that the energy barrier calculated for twisting for L^2 is actually higher than for L^1 (107 *versus* 100 kJ mol^{-1} for the Co(III) system), reflecting a 'tighter' coordination in the former and supporting the concept of ligand flexibility and elasticity playing a role in complexes.[13]

The bis complexes of the analogues L^1 and L^2 are predicted to be energetically similar but not identical. Moreover, electronic factors and bonding would not be identical–donor basicity alone varies slightly, as shown here by variations in determined pK_a values—so some differences in physical properties are expected. Previously, we have observed by comparison of the electronic spectra and metal-centred redox properties of bis(triamine)metal complexes of L^1 and L^2, consistent small differences which were presumed to arise from the introduced cyclohexane ring fused to the macrocycle ring adjacent to two of the nitrogen donors in L^1. The differences in physical properties would seem most likely to reflect minor electronic, rather than steric effects. Differences in the pK_a values of the two ligands (Table 3) indicate different amine basicities presumably resulting from substitution on the parent tacn ring, with inductive effects increasing basicity; the electronic influences reflected in these differences are likely to likewise influence physical properties of their complexes. It was therefore of interest to explore the capacity of L^1 as a ligand further, particularly with respect to labile metal ions systems as distinct from the more inert complexes. Consequently, apparent stability constants were determined with a number of metal(II) ions (Table 3). The overall stability constant (β_2) for formation of $[M(L^1)_2]^{2+}$ with Zn (21.1), Cd (18.35), Cu (28.9) and Ni (20.15) are similar to those reported for the tacn (L^2) analogue (Table 3),[38–40] and the first-row elements follow the Irving–Williams series. The similarities support force field calculations that infer that steric effects of the cyclohexane ring are not substantial. Three different determinations reported for tacn differ slightly, but in most cases the values are slightly lower

than those determined here for chtacn. The small differences may arise from the higher rigidity of the fused-ring macrocycle or simply as a result of solvation differences between the more hydrophobic L^1 and L^2, although the effects are not sufficient to warrant deep analysis. It is apparent that L^1 is an as effective a ligand for labile metal ions as L^2. It is most likely that both minor and opposing electronic and steric effects are involved, with the consequence being a ligand that behaves very much like its unsubstituted parent.

The distinction between introduction of rigidity on the macrocycle framework as opposed to including the donor atoms is notable. The latter leads to substantial, but not necessarily appropriate, changes to the complexation properties of the ligand; for example, an exceptionally rigid bispidone-based macrocycle with four tertiary nitrogen donors is very difficult to bind to metal ions,[41] since rigidity makes it unable to introduce metal ions *via* stepwise substitution of aqua ligands. Introduction of substituents on the framework clearly does not present such problems, although the addition of a cyclohexane ring does freeze one five-membered ring into a fixed conformation, introducing a form of rigidity. However, such substitution also influences the binding capacity of the ligand much less than for substitution involving the donor atoms; achieving a compromise presents a challenge for synthetic design.

The complex cation in the $[Ni(RR\text{-}L^1)_2](NO_3)_2$ structure displays a distorted octahedral geometry, and has the cyclohexane groups located *anti* to one another. There are no obvious steric reasons for this arrangement being preferred. Bond lengths and angles are as expected, although the Ni–N(2) and Ni–N(5) bonds [2.138(2) and 2.139(2) Å] are slightly longer than the other pairs of bonds [Table 2, average Ni–N 2.108 Å]. Intraligand N–M–N angles are compressed to near 82°, whereas interligand angles between the pairs of macrocycles are opened out to around 98°, reflecting the small 'bite' of the macrocycle on the octahedral face. The $[Ni(L^2)_2]^{2+}$ structure has been reported,[37] and in that case the Ni–N distances are equivalent within experimental error, with an average Ni–N distance of 2.105(4) Å, compared with an average of 2.120(2) Å observed here in the L^1 structure. Notably, the difference resides entirely in the amines adjacent to the cyclohexane units. $[Ni(L^2)_2]^{2+}$ also shows compressed intraligand N–Ni–N angles (av. 82.8°) and concomitant expanded interligand angles (av. 97.3°).

The most obvious feature of both the Ni(II) and earlier Co(III) structures is that the cyclohexane rings are disposed in an *anti* arrangement. Unlike the Ni(II) and Co(III) structures, where one pair of M–N bonds differ from the remainder, the Cr(III) in the $[Cr(RR\text{-}L^1)_2]Cl_3$ structure lies in a slightly more distorted octahedral environment where all Cr–N distances differ (Table 1, average 2.09(4) Å). This outcome may relate in part to the different *syn* arrangement of the cyclohexane rings compared with the *anti* arrangements found for Co(III) and Ni(II), but the unit cell of the $[Cr(L^1)]^{3+}$ ion also contains two non-equivalent but closely related complex cations. Nevertheless, the average Cr–N distance to nitrogens adjacent to the fused ring (2.093(4) Å) is slightly longer than to the other nitrogen (2.078(4) Å). Intraligand N–M–N angles are compressed to near 82°, whereas interligand angles are opened out to around 98°, as for the nickel(II) case. Although the analogous L^2 structure is not reported, Cr–N distances in structures such as $[Cr_2(L^2)_2(OH)_3]^{3+}$ are all equivalent and on average comparable (av. 2.089(4) A)[42] to those found here. Overall, the trend in bond lengths for L^1 complexes of Co(III) < Cr(III) < Ni(II) follows the usual pattern for hexaamines, and the average M–N distances are not unusual and comparable with those of L^2.

The ligand L^1 contains two asymmetric carbon centres and has been prepared as RR and SS isomers *via* the resolved cyclohexanediamine precursor.[2] Since the imposition of rotational strength on metal d–d transitions by ligands containing

asymmetric centres is well established,[43] it was of interest to examine the chiroptical properties of complexes of L^1. Even unidentate asymmetric amines can impose a modest circular dichroism, with $\Delta\varepsilon$ −0.35 for S-(cyclohexyl)ethylamine, although variation in the size of $\Delta\varepsilon$ with substituents is substantial.[44] Asymmetric chelated amine ligands impose a much stronger Cotton effect than unidentate ligands due to the additional influence of chiral conformations of chelate rings, with some bands exhibiting $\Delta\varepsilon > 1$; significant solvent or electrolyte dependence is also frequently observed.[45] The present complexes present four asymmetric centres from the two tridentate macrocycles to a metal, and a significant induced Cotton effect was anticipated. Previously, large Cotton effects were observed in cobalt(III) and chromium(III) complexes of the acyclic ligand RR,RR-1,3-bis(2′-aminocyclohexylamino)-2-methylpropan-2-amine, also based on the same chiral cyclohexanediamine parent,[46] and for R-2-methyl-1,4,7-triazacyclononane as the bis cobalt(III) complex.[34] The latter displayed the largest ring-conformation optical activity reported at the time. To exemplify the imposition of rotational strength on metal centres from L^1, the CD of the complexes of d^5 Fe(III), d^6 Co(III) and d^8 Ni(II) were recorded (Fig. 4).
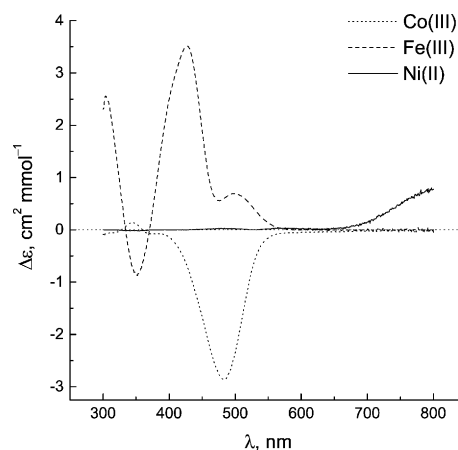
Fig. 4 Solution circular dichroism spectra of $[M(L^1)_2]^{n+}$ (M = Co(III), Fe(III) and Ni(II)) with S,S-(Co), R,R-(Fe) and S,S-(Ni) chirality of the chtacn ligand.

The circular dichroism of the cobalt(III) has been described by us earlier;[2] the $S,S(+)$ isomer has been examined here and exhibits a very strong Cotton effect under the $^1A_{1g} \longrightarrow {}^1T_{1g}$ envelope at 484 nm ($\Delta\varepsilon$ −2.88 cm^2 mmol^{-1}) and a weaker transition of opposite sign under the high energy $^1A_{1g} \longrightarrow {}^1T_{2g}$ envelope at 345 nm ($\Delta\varepsilon$ +0.133 cm^2 mmol^{-1}). The position of the CD maximum at lower energy to the absorption maximum of 469 nm can be interpreted as the Cotton effect arising dominantly from the $^1A_1 \longrightarrow {}^1E$ component, consistent with general observations for cobalt(III) hexaamines. The nickel(II) ion in an octahedral field has three spin-allowed bands $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$. The dominant Cotton effect is seen under the magnetic-dipole-allowed lowest energy band near 800 nm ($\Delta\varepsilon$ +0.78 cm^2 mmol^{-1}), close to the position of the electronic spectrum maximum of 812 nm; the inability of the CD spectrometer to record above 800 nm frustrated attempts to check for any lower energy component. The sign for this largest Cotton effect is opposite to that found for the cobalt(III) analogue, although the same isomer is involved. Several weaker bands are also found in the CD spectrum at higher energy under the other transition envelopes (575 nm, $\Delta\varepsilon$ +0.032; 480 nm, $\Delta\varepsilon$ +0.025; 350 nm, $\Delta\varepsilon$ −0.0175 cm^2 mmol^{-1}). The Fe(III) complex exhibits large Cotton effects at 499 nm ($\Delta\varepsilon$ +0.692), 426 nm ($\Delta\varepsilon$ +3.52), 352 nm ($\Delta\varepsilon$ −0.871) and 304 nm ($\Delta\varepsilon$ +2.56), which are most likely associated in turn with the four spin-allowed transitions under an octahedral field $^2T_{2g} \longrightarrow {}^2A_{2g}$ (observed in Fe(L^1)$_2^{3+}$ at 512 nm) $^2T_{2g} \longrightarrow {}^2T_{1g}$ (at 435 nm),

$^2T_{2g} \longrightarrow {}^2E_g$ (at 347 nm) and $^2T_{2g} \longrightarrow {}^2A_{1g}$ (at ~300 nm). The CD spectra of low-spin iron(III) hexaamines are rare (indeed, we believe this may be the first reported), since few examples of stable, well-characterised systems have appeared.[47] What is apparent is that significant Cotton effects occur, comparable in size to those found with Co(III); similar ion sizes, bond distances and stereochemistry presumably contribute to this outcome.

The sensitivity of CD spectra to chelate ring conformation suggests it could be applied to probe the presence of more subtle conformational variations, like probing for both *syn* and *anti* forms of the bis complex in solution under conditions where variations may occur, such as at various stages during sample dissolution or crystallisation. The CD spectra of L^1 complexes show a marked sensitivity to minor changes in the solution environment; for example, addition of Na_2SO_4 to a concentration of only 0.02 mol dm^{-3} causes a diminution in the major Cotton effect of the cobalt(III) complex by ~10%. However, this type of effect is not uncommon in the CD of chelate complexes generally.[43] Minor species also contribute to uncertainty; for example, solutions of the more labile nickel(II) may contain, albeit as minor components, ML species with inherently different spectra to that of the dominant ML_2 species. Such masking effects make using CD for probing conformer variation problematical, and we found no conclusive evidence we can ascribe to the coexistence of *syn* and *anti* forms in solution.

The presence of a cyclohexane ring fused onto the basic tacn framework clearly influences the coordination chemistry involving this ligand somewhat, although influences are clearly less than for substitution involving the donor groups despite the bulk of the cyclohexane unit and the loss of flexibility resulting from fusing the two rings. The ability of this somewhat more rigid and chiral tacn analogue to form 1 : 2 complexes with octahedral metal ions has been established, and aspects of the coordination chemistry of these revealed. The identification of geometric isomers resulting from dispositions of the cyclohexane units has been illustrated. This type of isomerism should also be present with two fused rings about the tacn core, and we are currently extending our studies to examine the effect of increasing the number of fused rings around the core.

Acknowledgments

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