

Conformational analysis of complexes of 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene and its 9-methyl derivative

José Pérez,^{*a} Luis García,^a A. Guy Orpen,^b M. Dolores Santana,^c Paloma Saez^c and Gabriel García^c

^a Departamento de Ingeniería Minera, Geológica y Cartográfica, Área de Química Inorgánica, Universidad Politécnica de Cartagena, 30203 Cartagena (Murcia), Spain.
E-mail: jose.perez@upct.es

^b School of Chemistry, University of Bristol, Cantocks Close, Bristol, UK BS8 ITS

^c Departamento de Química Inorgánica, Universidad de Murcia E-30071 Murcia, Spain

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The solid state conformations of complexes containing the ligands 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($\text{Me}_3[12]\text{N}_3$) and its 9-methyl derivative ($\text{Me}_4[12]\text{N}_3$) have been studied using principal component analysis. Three clusters of conformations are observed. The most populated has chair-like conformations in the two six-membered rings that do not contain the C=N bond. The coordination geometry in five-coordinate complexes containing the above ligands is always closer to square pyramidal than to trigonal bipyramidal. The synthesis and characterization of two new pentacoordinate nickel(II) complexes $[\text{Ni}(\text{Me}_3[12]\text{N}_3)(6\text{-Cl-2-pyridonato})][\text{ClO}_4]$ (**1**) and $[\text{Ni}(\text{Me}_4[12]\text{N}_3)(6\text{-Me-2-pyridonato})][\text{PF}_6]$ (**2**) are reported. The structures of both compounds have been elucidated by single crystal X-ray diffraction and show the square pyramidal coordination at the Ni atoms.

Introduction

Complexes of the triaza-macrocyclic ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($\text{Me}_3[12]\text{N}_3$) with Ni(II) and Cu(II) have been prepared by condensation of 4-azaheptane-1,7-diamine and two acetone residues, with elimination of two molecules of water.¹ In this manner it is possible to obtain di- μ -hydroxo-bridged complexes of Cu(II) and Ni(II) containing the $\text{Me}_3[12]\text{N}_3$ macrocycle. A considerable number of derivatives of the $(\text{Me}_3[12]\text{N}_3)\text{M}^{\text{II}}$ moiety with a variety of additional ligands have been prepared from these hydroxo complexes. For example, the hydroxo nickel(II) complex $[\text{Me}_3[12]\text{N}_3\text{Ni}(\mu\text{-OH})_2]^{2+}$ and its 9-methyl derivative $[\text{Me}_4[12]\text{N}_3\text{Ni}(\mu\text{-OH})_2]^{2+}$ react with a variety of organic acids, their anions acting as chelating ligands.^{3,4} Most coordination compounds of this macrocycle show a definite tendency to five-coordination.¹ On the other hand, the anions of 2-pyridones belong to the class of triatomic bridging ligands. The chief difference between the pyridones and the most of commonly used ligands, the carboxylates, is the presence of two different donor atoms. In pyridone ligands, one of two donor atoms lies within a ring and this restricts the direction of the bonds from that atom, so that the angles at the nitrogen prefer to be close to 120° and the metal atom to which the nitrogen is bound is within the plane of the ring. This means that the number of bonding modes of 2-pyridones is more restricted than for carboxylates, and they rarely act as chelating ligands.⁵ Derivatives of deprotonated 2-pyridones show at least seven coordination modes (see Chart 1). Winpenny *et al.* have reported polynuclear nickel complexes in which alteration of the pyridone from Hchp (6-chloro-2-hydroxypyridine) to Hmhp (6-methyl-2-hydroxypyridine) produces dramatic changes in the nature of the product.^{6,7} However, it has also been suggested that the presence of other ligands bonded to the metal atom could determine the bonding mode of the pyridone.^{8,9} Despite the

extensive work that has been achieved in this area, there is scarce information on mononuclear complexes of the first-row metals with pyridonates.¹⁰ In the context of our investigation on the reactivity of pentacoordinate hydroxo nickel(II) complexes derived from the $(\text{Me}_3[12]\text{N}_3)\text{Ni}(\text{II})$ fragment towards protic ligands, we have prepared mononuclear five-coordinate nickel complexes containing 2-pyridonates as chelating ligands. Moreover, the high thermodynamic and kinetic stability of macrocyclic complexes of transition metals has resulted in considerable interest in their use as catalysts. A number of ligands have also been used in attempts to study some biological processes in which metal complexes of macrocyclic ligands are involved.¹¹ Kinetic and thermodynamic studies of metallic complexes with this kind of ligand have been reported previously,¹² but less attention has been paid to the conformational characteristics in these compounds.

A few pentacoordinate nickel(II) complexes are known,¹³ subtle changes in the metal ion geometry causes dramatic changes in the magnetic properties in those complexes.¹⁴ Accordingly, in this paper, we report a detailed description of the crystal structures adopted by **1** and **2**, and a study of

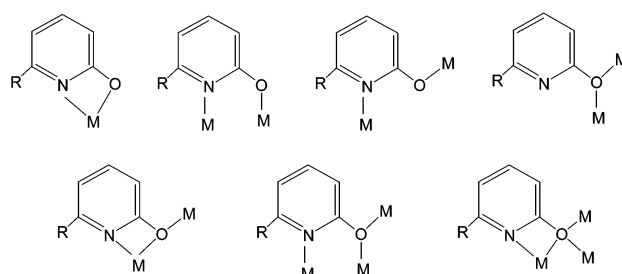


Chart 1

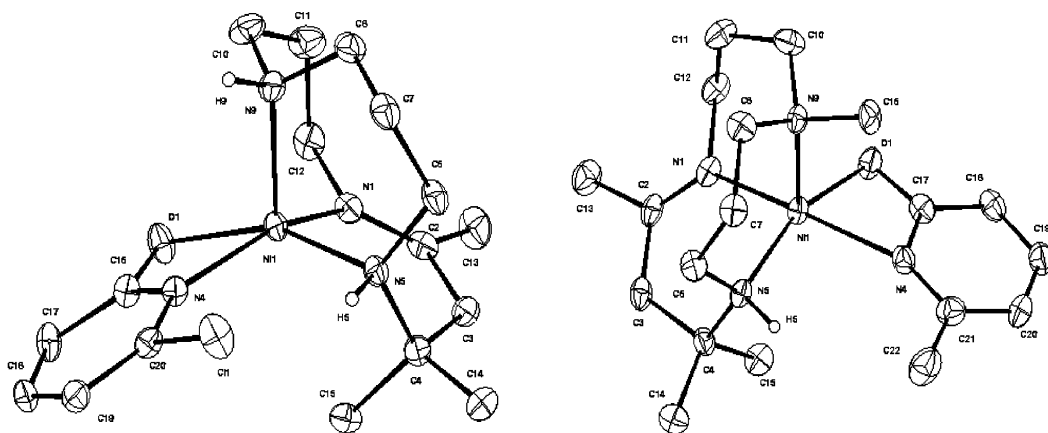


Fig. 1 Molecular structure of complexes **1** (left) and **2** (right). Displacement ellipsoids are drawn at the 50% probability level.

the conformations of the $(\text{Me}_3[12]\text{N}_3)\text{M}^{\text{II}}$ and $(\text{Me}_4[12]\text{N}_3)\text{M}^{\text{II}}$ moieties using principal component analysis is presented. We have also used data retrieved from the CSD and some newer data which have not been included yet. Our conformational study of pentacoordinate complexes is completed by details of the deviation in the geometry of coordination in these complexes with respect to the trigonal bipyramidal and square pyramidal ideals.

Experimental

General methods

Elemental analyses (C, H, N) were carried out with a Carlo Erba model EA 1108 microanalyzer. Infrared spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer from Nujol mulls between polyethylene sheets. The UV-vis spectra (in acetone) were recorded on a Hitachi 2000V spectrophotometer in the 300–800 nm range. ^1H NMR spectra of acetone- d_6 solutions were recorded on Bruker model AC 200E or Varian Unity 300 spectrometers. Fast atom bombardment (FAB) mass spectra were run on a Fisons VG Autospec spectrometer operating in the FAB^+ mode. All chemicals were purchased from Aldrich and were used without further purification. Solvents were dried and distilled by general methods before use. The complexes $[\text{Ni}(\text{Me}_3[12]\text{N}_3)(\mu\text{-OH})_2](\text{ClO}_4)_2$

and $[\text{Ni}(\text{Me}_4[12]\text{aneN}_3)(\mu\text{-OH})_2](\text{PF}_6)_2$ were prepared by procedures previously described.^{1,2}

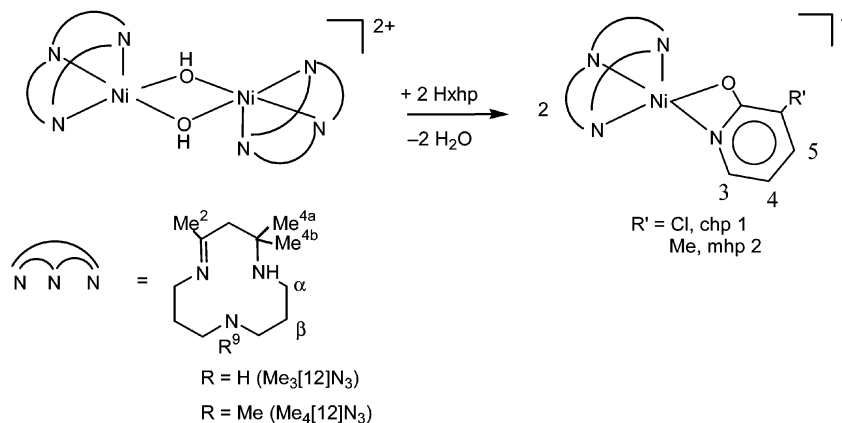
Synthesis of complexes **1** and **2**

Complex **1** was prepared by reaction of $[\text{Ni}(\text{Me}_3[12]\text{N}_3)(\mu\text{-OH})_2](\text{ClO}_4)_2$ (0.27 g, 0.35 mmol) with 6-Cl-2-hydroxypyridine (0.09 g, 0.70 mmol) in acetone. After stirring for 1 h, the solution was concentrated under reduced pressure and the addition of diethyl ether yielded **1** as a blue solid. Yield 72%. Anal. calc. for $\text{C}_{17}\text{H}_{28}\text{N}_4\text{O}_5\text{Cl}_2\text{Ni}$: C, 40.99, H, 5.67; N, 11.25; found: C, 40.79; H, 5.64; N, 11.05%. FAB-MS (+ve): m/z 397 (M^+). UV-vis (acetone), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 602 (162), 361 (297). Selected IR data (cm^{-1}): 3256, 3242 ($\nu_{\text{N-H}}$ mc), 1660 ($\nu_{\text{C=N}}$ mc), 1604, 1592, 1530. ^1H NMR (d_6 -acetone), δ : 317.9 (H_α , 2H), 233.4 (H_α , 2H), 229.1 (H_α), 101.2 (H_α), 64.1 (4-Me, 3H), 59.0 (H_β), 49.5 (H_β), 39.7 (H_α , 2H), 21.9 (4-Me, 3H), 10.7 (H_α), -9.8 (H_β), -13.3 (H_β , 2H), -13.5 (2-Me, 3H), -27.6 (H_β), -30.5 (H_β , 2H).

Complex **2** was prepared in a similar manner using $[\text{Ni}(\text{Me}_4[12]\text{N}_3)(\mu\text{-OH})_2](\text{PF}_6)_2$ (0.29 g, 0.32 mmol) and 6-Me-2-hydroxypyridine (0.07 g, 0.65 mmol). Yield 90%. Anal. calc. for $\text{C}_{19}\text{H}_{33}\text{N}_4\text{O}_5\text{PF}_6\text{Ni}$: C, 42.48, H, 6.19; N, 10.43; found: C, 42.33; H, 6.31; N, 10.29%. FAB-MS (+ve): m/z 391 (M^+). UV-vis (acetone), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 610 (172), 377 (291). Selected IR data (cm^{-1}): 3276 ($\nu_{\text{N-H}}$ mc), 1658 ($\nu_{\text{C=N}}$ mc), 1604, 1554. ^1H NMR (d_6 -acetone), δ : 291.9 (H_α , 2H), 218.8 (H_α), 207.0 (H_α), 117.4 (9-Me, 3H), 87.9 (H_α), 63.1 (4-Me,

Table 1 Crystal data and structure refinement details for compounds **1** and **2**

	1	2
Chemical formula	$\text{C}_{17}\text{H}_{28}\text{Cl}_2\text{N}_4\text{NiO}_5$	$\text{C}_{19}\text{H}_{33}\text{F}_6\text{N}_4\text{NiOP}$
Formula weight	498.04	537.17
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
$a, b, c/\text{\AA}$	13.4121(8), 9.0913(5), 18.3528(12)	9.2990(9), 10.5724(10), 12.8248(13)
$\alpha, \beta, \gamma/^\circ$	90, 104.904(5), 90	108.628(7), 95.446(7), 97.430(6)
$V/\text{\AA}^3$	2162.5(2)	1172.2(2)
Z	4	2
Radiation type	Mo-K α	Mo-K α
μ/mm^{-1}	1.18	0.96
Temperature/K	173.0(1)	173.0(1)
No. of measured, independent and observed [$F^2 > 2\sigma(F^2)$] reflections	7575, 3794, 2736	4263, 4023, 2661
$R(\text{int})$	0.0387	0.0500
$R1$ [$I > 2\sigma(I)$]	0.0384	0.0740
$wR2$ (all data)	0.1150	0.2570



Scheme 1

3H), 56.6 (H₃), 53.5 (H₅), 41.6 (H_α), 31.9 (H_α), 21.7 (4-Me, 3H), 16.6 (H_α), 7.6 (H₄), 6.4 (6-CH₃-hp, 3H), −8.4 (H_β), −10.7 (H_β), −13.3 (H_β), −15.1 (2-Me, 3H), −26.4 (H_β), −31.4 (H_β, 2H).

Data collection, structure solution and refinement

Single crystals of $[\text{Ni}(\text{Me}_3[12]\text{N}_3)(6\text{-Cl-2-pyridonato})][\text{ClO}_4]$ (**1**) and $[\text{Ni}(\text{Me}_4[12]\text{N}_3)(6\text{-Me-2-pyridonato})][\text{PF}_6]$ (**2**) were prepared by slow diffusion of diethyl ether into their acetone solutions. The crystals were mounted in inert oil and transferred to a Siemens P4 diffractometer. Details of cell data, data collection and structure refinement are given in Table 1. Fig. 1 shows the molecular structure of complexes **1** and **2**, with the atom-labelling schemes. Hydrogens atoms bonded to C atoms are omitted for clarity.

CCDC reference numbers 182499 and 182500. See <http://www.rsc.org/suppdata/nj/b2/b200164k/> for crystallographic data in CIF or other electronic format.

Structural analysis

The Cambridge Structural Database (CSD)¹⁵ v. 5.21 was searched for all the structures containing the fragment shown in Fig. 2. Bonds were assigned as being of any type and the stereochemistry at N₅ was fixed by constraining the M–C₆–C₄–N₅ improper torsion angle to be positive.

The April 2001 version (5.21) of the CSD, containing 233218 entries, was searched and 14 hits were obtained. In all cases, M = Cu or Ni. Two of the entries (HEWKEZ and KAYQEG) have two molecules in the asymmetric unit. The compounds

$[\text{Ni}(\text{Me}_4[12]\text{N}_3)(\text{acetohydroxamate-}O,O')][\text{PF}_6]$ (**3**),⁴ $\{[\text{Ni}(\text{Me}_3[12]\text{N}_3)_2(\mu\text{-oxamidato-}O,O',N,N')][\text{PF}_6]_2\}$ (**4**), $\{[\text{Ni}(\text{Me}_3[12]\text{N}_3)_2(\mu\text{-}N,N'\text{-diphenyloxamidato-}O,O',N,N')][\text{PF}_6]_2 \cdot 2\text{Me}_2\text{CO}\}$ (**5**), $\{[\text{Ni}(\text{Me}_3[12]\text{N}_3)_2(\mu\text{-dithiooxamidato-}S,S',N,N')][\text{PF}_6]_2\}$ (**6**) and complexes **1** and **2** were added to the dataset from the CSD and used in the study. The program PreQuest¹⁵ was used to create an in-house structural database in a format searchable by Quest. The intra-ring torsion angles of the three six-membered rings defined in Fig. 3 were tabulated for all 22 macrocycles in the dataset. In order to study the conformations of the triaza ligands in these complexes, the values of the torsions angles were transferred to Vista 2.1¹⁵ for statistical and graphical analysis.

Results and discussion

Synthetic and spectroscopic studies

The pentacoordinate pyridonate complexes of nickel(II) were prepared by an acid–base reaction between the corresponding hydroxo complex and 2-pyridone (1 : 2 molar ratio) in acetone, as shown in Scheme 1. The acidic proton of the pyridone is abstracted by the hydroxo complex providing the anion, which is trapped by the Ni([12]aneN₃) moiety with concomitant release of water. The IR spectra show bands attributable to the Me₃[12]aneN₃ and Me₄[12]aneN₃ ligands, $\nu(\text{NH})$ at $\sim 3260 \text{ cm}^{-1}$ and $\nu(\text{C}=\text{N})$ at $\sim 1660 \text{ cm}^{-1}$, and the two characteristic strong bands due to the ClO₄[−] (1100 and 620 cm^{-1}) and PF₆[−] (840 and 560 cm^{-1}) anions.³ The IR spectra also contain the

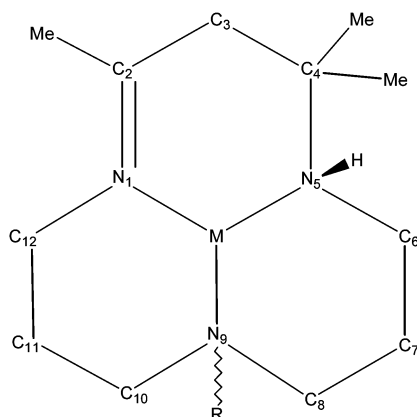


Fig. 2 Substructure used in CSD search. R = H or Me.

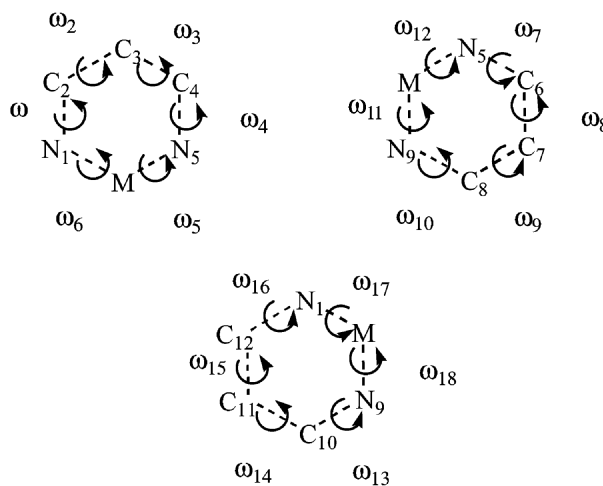


Fig. 3 Torsion angles used in the statistical analysis for ring 1 (top left), ring 2 (top right) and ring 3 (bottom).

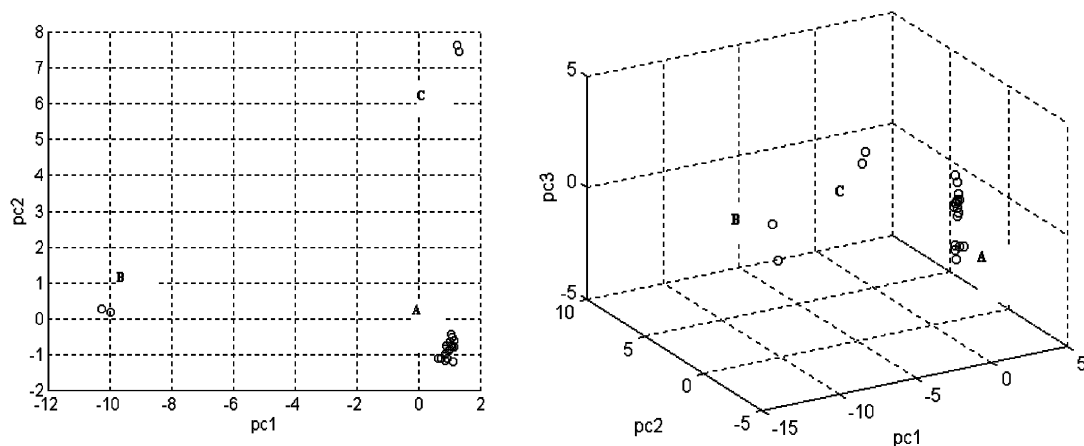


Fig. 4 Scatterplots for the scores on the most important components obtained by pca of $\text{Me}_3[12]\text{N}_3\text{M}$ and $\text{Me}_4[12]\text{N}_3\text{M}$ fragments.

expected absorptions attributable to the pyridonate ligands at ~ 1600 and 1550 cm^{-1} .¹⁶ The electronic spectra of the complexes in acetone solution are all similar and show bands in the 600 and 370 nm regions, which can be assigned to $^3\text{B}_1(\text{F}) \rightarrow ^3\text{E}(\text{F})$ and $^3\text{B}_1(\text{F}) \rightarrow ^3\text{A}_2, ^3\text{E}(\text{P})$ transitions, respectively.¹⁷ Both λ_{max} values and molar absorptivities are consistent with a pentacoordinate environment around $\text{Ni}(\text{II})$. The $^1\text{H-NMR}$ spectra for complexes **1** and **2** exhibit relatively sharp hyperfine shifted signals spanning from ~ 320 to -30 ppm. The spectra show the resonance line pattern commonly observed for $[12]\text{janeN}_3$ -macrocyclic ligands, as well as signals from the 2-pyridonate protons, assigned on the basis of previous studies of nickel macrocyclic complexes.¹⁰

Structures of complexes **1** and **2**

Fig. 1 shows the molecular structures of complexes **1** and **2**. In both compounds, the nickel atom is pentacoordinate, with an approximately square pyramidal coordination geometry. The degree of distortion towards trigonal bipyramidal geometry may be quantified using Reedijk's¹⁸ τ factor ($\tau = 0.03$ for **1** and 0.08 for **2**) where $\tau = 0$ for a square pyramid, and $\tau = 1$ for a trigonal bipyramid. The three nitrogen atoms of the triaza-macrocyclic occupy the apical position and two adjacent equatorial sites in the square-based pyramid; the other two basal positions are occupied by the chelating pyridonate group. The nickel atom is displaced out of the basal plane (N1, N5, O1, N4) towards atom N9 by $0.381(2)$ and $0.342(3)$ Å in **1** and **2**, respectively. Table 2 lists the bond lengths and

angles for the Ni atom in complexes **1** and **2**. In **1**, the bond distances from Ni to the three nitrogen atoms in the macrocycle are similar, while in **2**, the distance to the apical nitrogen is longer than to the basal ones. The bond angles defined by the atoms forming the square pyramid are similar in both complexes. The bond angles involving the N atoms of the macrocycle are similar to those found in complexes **3–6** (Table 2), but the geometry around the nickel atom shows great variation; for example, complexes **5** and **6** have $\tau = 0.48$ and 0.24 , respectively [the two largest bond angles in **5** are $175.2(1)$ and $146.2(1)^\circ$, in compound **6**, the two largest bond angles are $168.8(1)$ and $154.3(1)^\circ$].

In compound **1** each cationic complex is linked to a perchlorate anion by a hydrogen bond, $\text{N9-H9} \cdots \text{O}$, with a $\text{N9} \cdots \text{O}$ distance of $3.178(4)$ Å and a $\text{N9-H9} \cdots \text{O}$ angle of 166° . Around the chlorine atom in the pyridonate ligand, the shortest noncovalent contacts are $\text{N5-H5} \cdots \text{Cl1}$ [$2.713(3)$ Å] and $\text{C19}^i\text{-H19}^i \cdots \text{Cl1}$ [$2.848(4)$ Å; (i): $1-x, 1-y, -z$]. In compound **2**, the shortest distances between the cationic complex and the $[\text{PF}_6]^-$ anion are $\text{C15-H15C} \cdots \text{F6}$ [$2.361(3)$ Å], $\text{C3-H3B} \cdots \text{F1}^{\text{ii}}$ [$2.403(4)$ Å] and $\text{C6-H6B} \cdots \text{F1}^{\text{ii}}$ [$2.409(4)$ Å; (ii): $x, 1+y, z$].

Principal component analysis

Principal component analysis (pca) is a powerful technique for the study of high dimensional strongly correlated data-sets, such as torsion angles in ring and fused ring systems.¹⁹ It is therefore the method of choice for study of the 18 torsion angles of the three six-membered rings

Table 2 Selected bond lengths (Å) and angles ($^\circ$) for complexes **1–6**

	1	2	3	4	5	6
Ni–N1	1.995(3)	2.018(6)	2.036(6)	2.074(6)	2.042(2)	2.055(3)
Ni–N5	2.020(3)	2.017(6)	2.036(7)	2.042(7)	2.060(2)	2.059(3)
Ni–N9	2.017(3)	2.077(6)	2.064(7)	2.056(6)	2.026(3)	2.041(4)
Ni–N4	2.103(3)	2.144(6)	—	—	—	—
Ni–O1	2.074(3)	2.047(5)	—	—	—	—
N1–Ni–N5	93.3(1)	90.8(2)	90.9(3)	89.9(3)	93.2(1)	88.7(1)
N1–Ni–N9	93.8(1)	93.3(2)	93.1(3)	91.0(2)	94.7(1)	91.3(1)
N5–Ni–N9	101.9(1)	101.0(2)	102.3(3)	100.6(2)	101.0(1)	99.4(1)
N1–Ni–N4	152.8(1)	154.2(2)	—	—	—	—
N5–Ni–N4	99.1(1)	101.5(2)	—	—	—	—
N9–Ni–N4	107.0(1)	106.2(2)	—	—	—	—
N1–Ni–O1	95.5(1)	96.9(2)	—	—	—	—
N5–Ni–O1	154.7(1)	158.7(2)	—	—	—	—
N9–Ni–O1	101.2(1)	98.3(2)	—	—	—	—
N4–Ni–O1	64.0(1)	64.2(2)	—	—	—	—

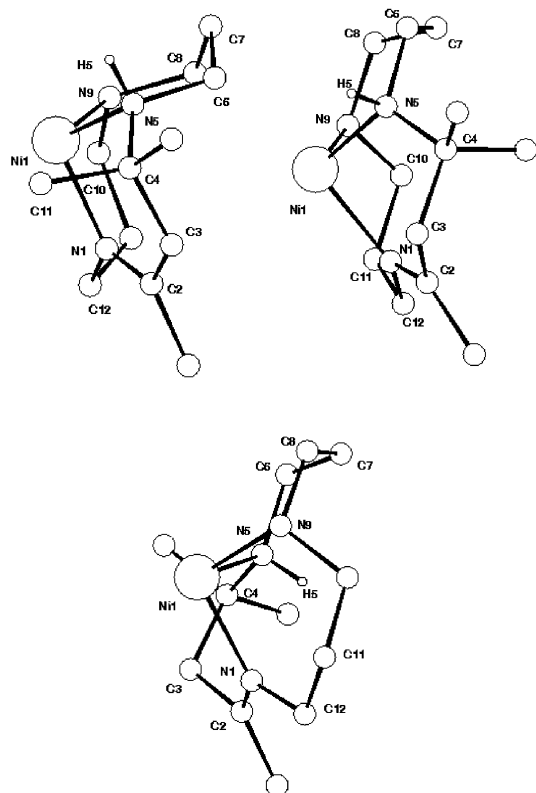


Fig. 5 Conformations of M(macrocycle) fragments for clusters **A** (top left), **B** (top right) and **C** (bottom).

defined in Fig. 3. The three most important principal components (pcs) display 99% of the total variance in the dataset, plots of the scores on these pcs are shown in Fig. 4.

There are 3 clusters of conformations **A–C**, Fig. 5 shows a typical M(macrocycle) fragment in each one. Clusters **A** and **B** are the same diastereomer (having the same configurations at N5, N9 and the metal); in this case, the H at N5 and the substituent at N9 are both *syn* to the metal. Cluster **C** contains a different diastereoisomer, having the mirror image arrangement at the metal as compared to that found in **A** or **B**; the hydrogen at N5 is *anti* to the metal but the substituent at N9 is *syn* to the metal, as in all the three clusters.

In cluster **A**, rings 2 and 3 (Fig. 3) have chair-like conformations, the torsion angles having the signs $-+-+--$ and $+--+-$ in rings 2 and 3, respectively. In cluster **B**, ring 2 has a chair conformation, with signs $+--+-$ (inverted with respect to those in cluster **A**), while ring 3 shows the signs $-+-+--$, corresponding to a twist conformation (see Fig. 5). In cluster **C**, ring 2 has a chair conformation similar to that in cluster **A**, while in ring 3, ω_{13} , ω_{14} , ω_{15} , ω_{17} have the signs $+--+-$, and ω_{16} and ω_{18} are close to zero (Fig. 5). Ring 1 (which contains the C=N double bond) has a more varied conformation and ω_3 is the torsion angle that most strongly links with the value of pc1 (structures **A** and **C** have ω_3 ca. $+50^\circ$, **B**-type structures have ω_3 ca. -75°).

Table 4 Values of the τ parameter and cluster membership for five-coordinate complexes

Refcode	τ	Cluster
1	0.03	A
2	0.08	A
3	0.05	A
4	0.12	A
5	0.48	B
6	0.24	A
BATSIY	0.14	A
CTMZCU10	0.27	A
HEWKEZ	0.20	A
HEWKEZ	0.20	A
JEFYEY	0.16	A
JEFYIC	0.16	A
KAYQAC	0.14	A
KAYQEG	0.11	A
KAYQEG	0.14	A
KAYQIK	0.09	A
MTZNIT	0.33	A
NOKHUQ	0.00	C
PAJZEF	0.29	A
RUSQOL	0.10	C
WELGUP	0.52	A

Complexes **1** and **2** belong to the most populated cluster (**A**). The conformations are almost equal in the corresponding rings of the two compounds, as can be seen from the ring puckering coordinates.²⁰ In complex **1**, the total puckering amplitudes are 0.634(3), 0.553(4) and 0.674(3) for rings 1, 2 and 3, respectively and $\theta = 130.0(3)$, $138.2(3)$ and $7.5(3)^\circ$ for these rings. For complex **2**, the total puckering amplitudes are 0.670(7), 0.565(9) and 0.680(7) for rings 1, 2 and 3, respectively and $\theta = 48.9(6)$, $37.9(5)$ and $172.2(7)^\circ$ for these rings. The value found for the θ parameter reveals a clear chair conformation in both compounds for ring 3, this is confirmed by the asymmetry parameters²¹ calculated for that ring (Table 3).

Metal coordination geometry in the five-coordinate complexes

Most of structures used in the previous section are pentacoordinate complexes, only two of the structures retrieved from the CSD (PIMHEY and VABNOB) show octahedral coordination. In order to complete the conformational analysis in those five-coordinated complexes, we have studied the variation in the geometry of coordination with respect to the ideal geometries: trigonal bipyramidal and square pyramidal. To do this, we have calculated the Reedijk's τ parameter; the results are shown in Table 4. As can be seen, the τ parameter spans the range 0–0.52. Thus, the coordination geometry in these species is closer to square pyramidal ($\tau = 0$) than to trigonal bipyramidal ($\tau = 1$). This fact is probably related to the narrow range of NMN bond angles in the M(macrocycle) fragment: the N1–M–N5, N5–M–N9 and N9–M–N1 angles typically cover the ranges 89–94, 99–105 and 90–96°, respectively, the only exceptions being the structures NOKHUQ and RUSQOL, which show values slightly outside this interval.

Table 3 Asymmetry parameters²¹ for ring 3 in **1** and **2**

	$\Delta C_5(\text{Ni})$	$\Delta C_5(\text{N1})$	$\Delta C_5(\text{C12})$	$\Delta C_2(\text{Ni–N9})$	$\Delta C_2(\text{N1–Ni})$	$\Delta C_2(\text{C12–N1})$
1	0.033(2)	0.008(2)	0.034(2)	0.033(2)	0.020(1)	0.017(1)
2	0.029(4)	0.010(4)	0.034(4)	0.031(3)	0.016(3)	0.019(3)

Conclusions

We have studied the conformations of complexes containing the ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene and its 9-methyl derivative. Principal component analysis reveals that the structures can be classified in three different conformation types. These types can be characterized by the conformations of two six-membered rings: that containing the metal and the nitrogen atoms in positions 5 and 9 in the macrocycle and the ring including the metal and the nitrogen atoms in positions 1 and 9. The most populated group (A) shows a chair conformation in these two rings. The other two conformation types represent different diastereomers of the M(macrocycle) fragment, and only the first ring shows a chair conformation.

In relation to the coordination geometry of five-coordinate complexes containing these macrocyclic ligands, we have quantified the arrangement around the metallic center and the preferred geometry is closer to square pyramidal than trigonal bipyramidal.

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