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Four Ni^{II} complexes with the new cyclam–methylimidazole ligand 1-[(1-methyl-1*H*-imidazol-2-yl)-methyl]-1,4,8,11-tetraazacyclotetradecane

Ariel G. De Candia,[a] Matias Molnar,[a] Leonardo D. Slep[a]* and Ricardo Baggio[b]*

[a]INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina, and [b]Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: slep@qi.fcen.uba.ar, baggio@cnea.gov.ar

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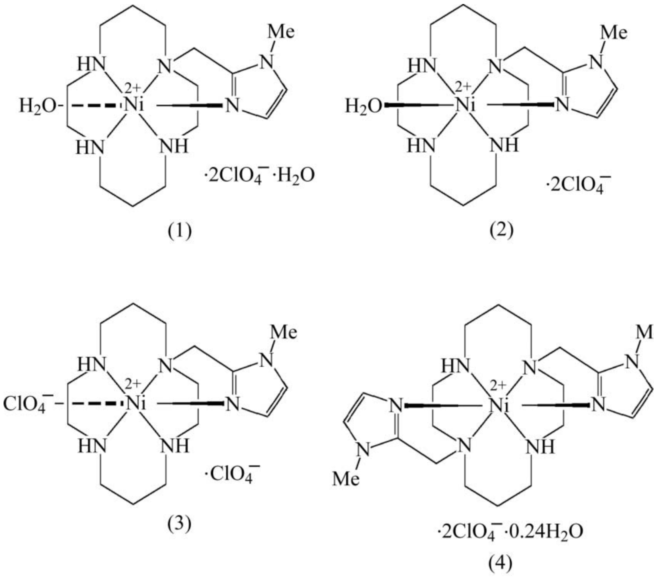
Although it has not proved possible to crystallize the newly prepared cyclam–methylimidazole ligand 1-[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane ($L^{\rm Im1}$), the *trans* and *cis* isomers of an Ni^{II} complex, namely *trans*-aqua{1-[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane}nickel(II) bis(perchlorate) monohydrate, $[Ni(C_{15}H_{30}N_6)(H_2O)](ClO_4)_2\cdot H_2O$, (1), and *cis*-aqua{1-[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane}nickel(II) bis(perchlorate), $[Ni(C_{15}H_{30}N_6)(H_2O)](ClO_4)_2$, (2), have been prepared and structurally characterized. At different stages of the crystallization and thermal treatment from which (1) and (2) were obtained, a further two compounds were isolated in crystalline form and their structures also analysed, namely *trans*-{1-[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane}(perchlorato)nickel(II) perchlorate, $[Ni(ClO_4)(C_{15}H_{30}N_6)]ClO_4$, (3), and *cis*-{1,8-bis[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane}nickel(II) bis(perchlorate) 0.24-hydrate, $[Ni(C_{20}H_{36}N_6)](ClO_4)_2\cdot 0.24H_2O$, (4); the 1,8-bis[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane ligand is a minor side product, probably formed in trace amounts in the synthesis of $L^{\rm Im1}$. The configurations of the cyclam macrocycles in the complexes have been analysed and the structures are compared with analogues from the literature.

Comment

Macrocyclic polyamines such as cyclam and cyclen, bearing potentially coordinating pendant arms, are useful in applications such as diagnostic medicine, waste-water treatment and others, due to the stability conferred on their metallic complexes by the additional donor groups in the pendant arms (Curtis, 2003). This stability is especially important in processes where the release of free metals is particularly undesirable, as in, for instance, the majority of medical treatments. A paradigmatic example can be found in the administration of the gadolinium cation as a contrast agent for magnetic resonance imaging (MRI), a process where the stability of the tetraacetate cyclen (DOTA) complex of the Gd^{III} cation, *viz.* $Gd(DOTA)H_2O$, has made the complex, and some of its derivatives, a 'must' for the safe and successful use of the technique (Schwietert & McCue, 1999; Yam & Lo, 1999; Caravan *et al.*, 1999).

Complexes of substituted macrocyclic polyamines are also interesting from a purely structural point of view, in particular due to the many different ring conformations attainable, as well as the diversity in binding modes provided by the functionalized side arms (Bosnich *et al.*, 1965; De Candia *et al.*, 2007).

There are a large number of reported ligands of this type, with a wide range of pendant side groups, and, consistent with the above-mentioned stability, the majority of their complexes are clathrates [Cambridge Structural Database (CSD), Version 5.32; Allen, 2002].



Scheme 1

Exploring further the substantial body of chemistry already based on the cyclam macrocycle, we have prepared a new cyclam–methylimidazole ligand, 1-[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane ($L^{\rm Im1}$). Crystallizing the free ligand has proved impossible so far. However, we succeeded in obtaining the *trans* and *cis* isomers of an Ni^{II} complex, *viz.* *trans*-$[Ni(L^{\rm Im1})(H_2O)](ClO_4)_2\cdot H_2O$, (1), and *cis*-$[Ni(L^{\rm Im1})(H_2O)](ClO_4)_2$, (2), reported herein. At different stages of the crystallization and thermal treatment processes (see *Experimental* for details), another two compounds were obtained in crystalline form and their structures are also reported here, *viz.* *trans*-$[Ni(ClO_4)(L^{\rm Im1})]ClO_4$, (3), and *cis*-$[Ni(L^{\rm Im2})](ClO_4)_2$, (4) (where $L^{\rm Im2}$ is 1,8-bis[(1-methyl-

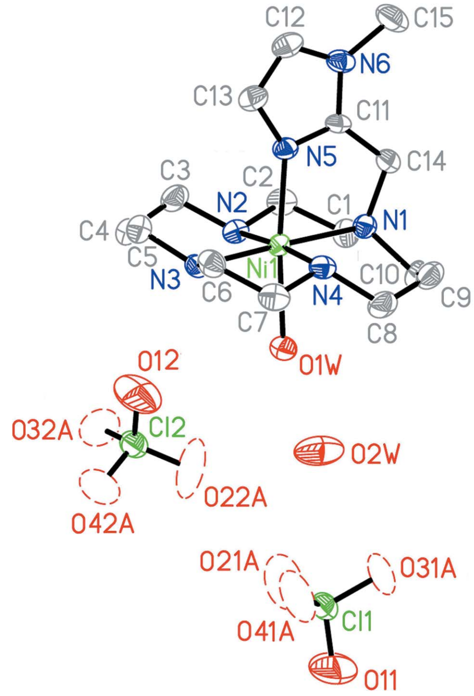


Figure 1
The molecular structure of (1), with displacement ellipsoids drawn at the 35% probability level. The major components of the disordered perchlorate anions are shown with broken lines. The minor component(s) and H atoms have been omitted for clarity.

1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane, a minor side product probably formed in trace amounts during the synthesis of L^{Im1}).

The structures of (1)–(4) (Figs. 1–4) all have a central $\mathrm{Ni^{II}}$ cation chelated by a cyclam ring (four N atoms), the common fifth ligand being the imidazole N atom. They differ in the sixth ligand completing the octahedral coordination of atom Ni1, this being water in (1) and (2), a perchlorate anion in (3) and a second imidazole N atom in (4). All four structures present perchlorate groups as either isolated counter-ions or a coordinated ligand, and invariably this fragment is disordered, as a result of which the quality of the refinement is in most cases diminished.

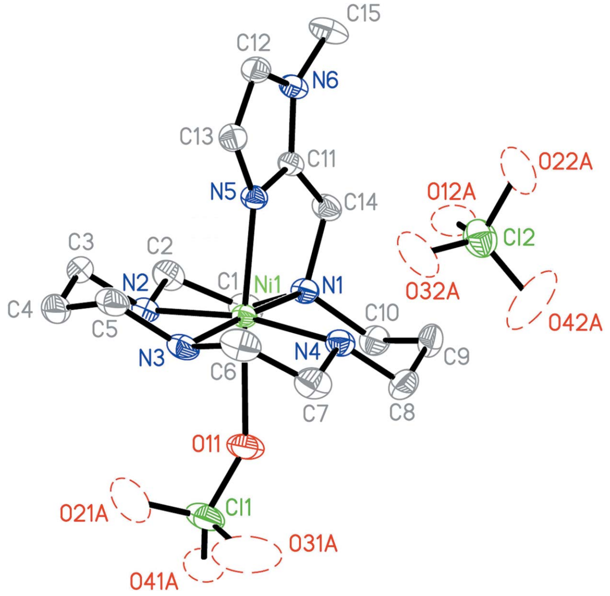


Figure 3
The molecular structure of (3), with displacement ellipsoids drawn at the 35% probability level. The major components of the disordered perchlorate anions are shown with broken lines. The minor component(s) and H atoms have been omitted for clarity.

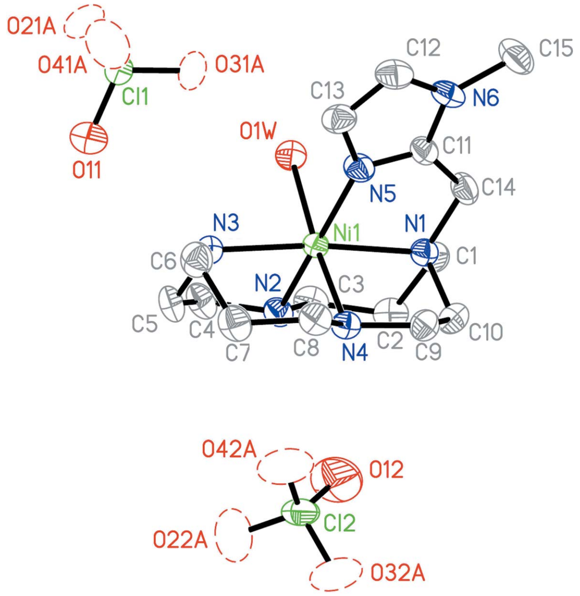


Figure 2
The molecular structure of (2), with displacement ellipsoids drawn at the 35% probability level. The major components of the disordered perchlorate anions are shown with broken lines. The minor component(s) and H atoms have been omitted for clarity.

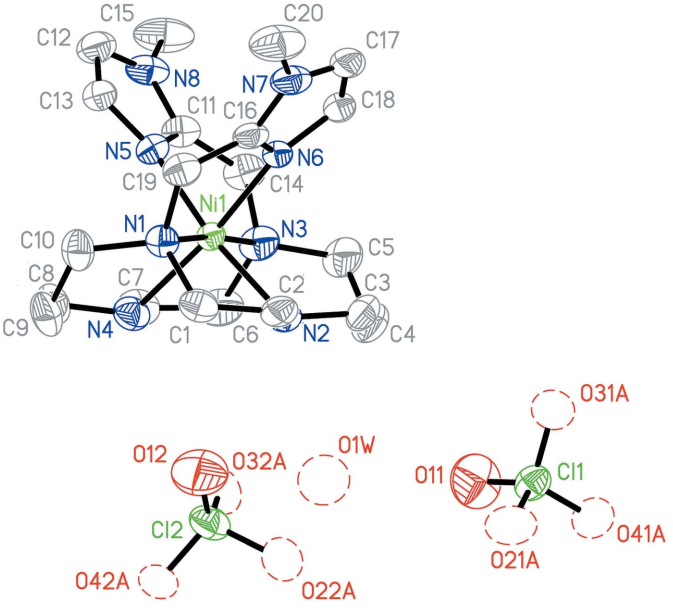


Figure 4
The molecular structure of (4), with displacement ellipsoids drawn at the 35% probability level. The major components of the disordered perchlorate anions are shown with broken lines. The minor component(s) and H atoms have been omitted for clarity.

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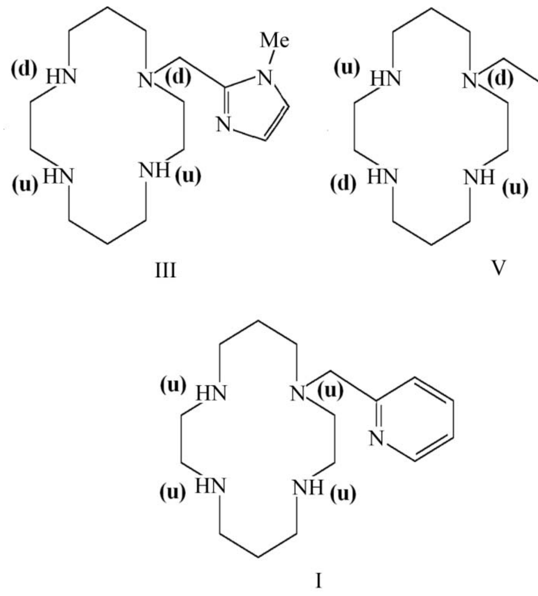
Chelation of the Ni^{II} cation by the four cyclic N atoms of the cyclam unit is achieved in two different fashions in these compounds, which can be described by the relative orientations of the Ni1/N1–N3 and Ni1/N1/N4/N3 mean planes. The dihedral angles are 3.9 (2) and 7.7 (2)° in (1) and (3), respectively, describing a fairly planar arrangement of the cyclam macrocycle, and angles of 79.6 (2) and 81.5 (2)° in (2) and (4), respectively, describing a 'butterfly-like' conformation. This is closely associated with the way the two extra ligands bind the cation, *viz. trans* in (1) and (3), and *cis* in (2) and (4). The similarities and differences in the coordination parameters are related to these differences in ligand conformation, as well as to the character of the sixth ligand, as reflected in the comparison of the geometric data given in Table 1. The bond angles are split into two groups, those in the first and third column of Table 1 (the '*trans*' moieties), and those in the second and fourth columns ('*cis*'), with the differences within each group being smaller than those between groups. The Ni—N bond distances fall between 2.046 (3) and 2.144 (3) Å, in the range expected for high-spin Ni^{II}—N bonds.



Scheme 2

As described by Bonisch *et al.* (1965), the designation '*trans*' does not fully characterize these complexes since the cyclic ligand has a number of possible distinct configurations. Bonisch and co-workers analysed the principles which apply to any cyclic tetradentate ligand whose donor atoms are tetrahedral when coordinated, and concluded that, in the case of cyclam, each N atom when coordinated is an asymmetric centre. Five distinct non-enantiomeric combinations can be produced. Thus, they proposed a simple description of the five different possible configurations of a cyclam macrocycle upon chelation (named I to V in their paper) by stating the directions, either up (**u**) or down (**d**), which the N substituents adopt (in our case, either H atoms or the methylimidazole arm). According to this classification, in (1) and (3) the group adopts a *trans* type III configuration (see Scheme 2), while in (2) and (4) the *cis* form is preferred, described by Bonisch and co-workers as V.

Similar Ni^{II} complexes with closely related monosusbtituted cyclam derivatives have been reported in the literature. El Ghachtouli *et al.* (2006) described two structures, (II) and (III) therein, having 2-methylpyridine as a pendant arm and CH_3CN and H_2O, respectively, occupying the sixth coordination sites, and which present coordination analogous to that of (1) and (2). But while their compound (III) shares with our (2) the same *cis*-V cyclam configuration (Bonisch classification), compound (II) of El Ghachtouli and co-workers adopts a *trans*-I configuration (all up, see Scheme 2). A search of the CSD shows that the configuration found in (1) occurs slightly more frequently than that displayed by (II), appearing with a 60:40 relative frequency.

The disordered perchlorate groups, in addition to providing charge balance, act as acceptors in generally weak hydrogen bonds having the cyclam N—H and water O—H groups as donors (Tables 2–5). The result is an arrangement with the Ni–cyclam units isolated from each other in space but interconnected by a dense network of these perchlorate-mediated interactions.

The redox behaviour of the configurational isomers (1) and (2) was investigated in aqueous solution by means of cyclic voltammetry experiments. The oxidation of the *trans* isomer, (1), is quasi-reversible and occurs at $E_{1/2} = 0.77$ V. In contrast, and analogous with what is observed in the closely related derivatives reported by El Ghachtouli *et al.* (2006), the oxidation of the *cis* isomer, (2), is irreversible ($E_{ox} = 1.03$ V) and after several scans leads to the exclusive formation of (1).

Experimental

The compounds 2-(chloromethyl)imidazole hydrochloride and 1,4,8,11-tetraazacyclotetradecane (cyclam) were prepared according to previously published procedures (Jones, 1949; Barefield, 1975). All other reagents employed were obtained commercially and used as supplied.

For the synthesis of 1-[(1-methyl-1*H*-imidazol-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane (L^{Im1}), cyclam (2.50 g, 12.5 mmol) was partially dissolved in hot (388 K) dimethylformamide (DMF, 60 ml) and the suspension stirred vigorously. 2-(Chloromethyl)imidazole hydrochloride (0.7 g) dissolved in DMF (32 ml) was added dropwise over a period of 4 h. The reaction mixture was heated at 388–393 K for an extra hour and then allowed to cool to 277 K. The unreacted cyclam separated as white needles, which were removed by filtration. The solution was concentrated to 15 ml at room temperature under reduced pressure and treated with water (10 ml) and KOH (4 *M*), raising the pH to 11.5. This solution was extracted with $CHCl_3$ (10 × 50 ml). The organic extracts were evaporated to dryness, leaving a colourless oily residue.

Purification of this residue was achieved by chromatography on a column (diameter 4 cm and length 15 cm) packed with silica gel 40 (35–70 mesh) in a CH_2Cl_2–MeOH (9:1 *v*/*v*) mixture. The column was first eluted with the same solvent mixture to remove some non-macrocyclic contaminants, then with CH_2Cl_2–MeOH–NH_3 (5:5:1 *v*/*v*/*v*) to remove polysubstituted cyclam species and finally with CH_2Cl_2–MeOH–NH_3 (2:2:1 *v*/*v*/*v*) to elute the monosubstituted derivative.

Acta Cryst. (2012). C**68**, m121–m126 De Candia *et al.* • $[Ni(C_{15}H_{30}N_6)(H_2O)](ClO_4)_2 \cdot H_2O$ and three analogues **m123**

Table 1
Selected geometric parameters (Å, °) for (1), (2), (3) and (4).

Atom *X* is O1*W* for (1) and (2), O11 for (3) and N6 for (4).

Bond or angle	(1)	(2)	(3)	(4)
Ni1—N1	2.120 (5)	2.144 (6)	2.124 (3)	2.144 (3)
Ni1—N2	2.071 (5)	2.085 (6)	2.059 (3)	2.098 (3)
Ni1—N3	2.068 (5)	2.094 (6)	2.068 (3)	2.144 (3)
Ni1—N4	2.073 (5)	2.088 (6)	2.046 (3)	2.099 (3)
Ni1—N5	2.083 (5)	2.051 (6)	2.077 (3)	2.068 (3)
Ni1—*X*	2.268 (4)	2.222 (6)	2.359 (3)	2.073 (3)
N1—Ni1—N2	85.7 (2)	92.7 (2)	85.85 (11)	83.84 (12)
N1—Ni1—N3	178.4 (2)	173.9 (2)	176.57 (12)	174.60 (12)
N1—Ni1—N4	95.0 (2)	84.6 (2)	95.69 (12)	92.39 (12)
N1—Ni1—N5	81.2 (2)	81.9 (2)	82.30 (11)	102.34 (11)
N1—Ni1—*X*	90.92 (18)	92.6 (2)	86.83 (10)	81.60 (11)
N2—Ni1—N3	94.4 (2)	83.5 (2)	92.83 (12)	92.52 (12)
N2—Ni1—N4	175.0 (2)	97.6 (2)	169.98 (12)	96.10 (13)
N2—Ni1—N5	92.4 (2)	169.5 (3)	95.16 (11)	171.31 (12)
N2—Ni1—*X*	84.89 (18)	85.9 (2)	84.06 (11)	88.20 (12)
N3—Ni1—N4	84.8 (2)	91.2 (2)	85.07 (13)	84.01 (13)
N3—Ni1—N5	100.3 (2)	102.6 (2)	100.98 (11)	81.72 (12)
N3—Ni1—*X*	87.54 (18)	91.8 (2)	89.89 (11)	102.32 (13)
N4—Ni1—N5	92.5 (2)	90.9 (3)	94.86 (11)	89.80 (12)
N4—Ni1—*X*	90.17 (19)	175.6 (2)	86.15 (12)	172.22 (13)
N5—Ni1—*X*	171.89 (19)	85.3 (2)	169.13 (10)	86.69 (11)

Table 2
Hydrogen-bond geometry (Å, °) for (1).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O32*A*^{i}	0.91	2.37	3.198 (13)	151
N3—H3···O12	0.91	2.17	3.053 (8)	162
O1*W*—H1*WA*···O2*W*	0.85	1.99	2.790 (7)	156
O1*W*—H1*WB*···O22*B*	0.85	2.19	3.041 (15)	176
O1*W*—H1*WB*···O22*A*	0.85	2.38	3.163 (15)	153
O2*W*—H2*WA*···O11^{ii}	0.85	2.18	3.034 (11)	179
O2*W*—H2*WB*···O21*B*	0.85	2.26	3.107 (19)	175
O2*W*—H2*WB*···O21*A*	0.85	2.01	2.855 (18)	174

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Removal of the solvent *in vacuo* yielded 0.90 g (66%) of the oily product, $L^{\rm Im1}$.

For the synthesis of [Ni($L^{\rm Im1}$)(H_2O)](ClO_4)$_2$, $L^{\rm Im1}$ (150.4 mg, 0.51 mmol) dissolved in water (3 ml) was added dropwise and with constant stirring to a solution of Ni(ClO_4)$_2$·6H_2O (189.7 mg, 0.52 mmol) in water (3 ml). The resulting pink solution was heated at 343 K for 80 min and then concentrated in a rotary evaporator to yield a microcrystalline pink–violet solid, which was collected by filtration, washed with chilled water and dried *in vacuo* (yield 220 mg, 0.39 mmol, 75%). Elemental analysis, found: C 31.6, N 14.7, H 5.6%; calculated for [Ni($L^{\rm Im1}$)(H_2O)](ClO_4)$_2$ ($C_{15}H_{32}Cl_2N_6NiO_9$): C 31.6, N 14.7, H 5.7%.

This material was redissolved in water and the solution was allowed to evaporate slowly, yielding three consecutive crops of crystals, all of them suitable for single-crystal X-ray diffraction (XRD) studies. The first crop was a pink crystalline material which, upon XRD analysis, proved to be the *cis*-[Ni($L^{\rm Im1}$)(H_2O)](ClO_4)$_2$ isomer, (2). A second crop consisted of a very small number of pale-pink crystals which were found to be *cis*-[Ni($L^{\rm Im2}$)](ClO_4)$_2$, (4), where $L^{\rm Im2}$ is a minor side product, probably formed in trace amounts during the synthesis of $L^{\rm Im1}$. Further evaporation of the mother liquors finally gave another pink crystalline solid which was identified by X-ray diffraction as the *trans*-[Ni($L^{\rm Im1}$)(H_2O)](ClO_4)$_2$ isomer, (1).

Table 3
Hydrogen-bond geometry (Å, °) for (2).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O11	0.91	2.32	3.140 (9)	150
N4—H4···O42*A*	0.91	2.16	3.068 (15)	173
N4—H4···O42*B*	0.91	2.24	3.12 (2)	161
O1*W*—H1*WA*···O12^{i}	0.85 (1)	2.29 (3)	3.098 (10)	161 (7)
O1*W*—H1*WB*···O31*B*	0.85 (1)	2.04 (4)	2.86 (2)	163 (9)
O1*W*—H1*WB*···O31*A*	0.85 (1)	2.06 (7)	2.740 (13)	137 (8)

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

The thermal *cis–trans* conversion between (2) and (1) (see *Comment*) was followed spectrophotometrically. For that purpose, compound (2) (λ/nm^{-1} [ε/M^{-1} cm^{-1}] = 344 [13], 544 [10], 788 (*sh*) [6], 833 (*sh*) [7], 942 [9]) was dissolved in water and the solution heated at 363 K for several hours, following the course of the process by changes in the electronic spectrum. The experiments show a *cis* → *trans* [(2) → (1)] conversion, as indicated by the appearance of new UV–vis features which are compatible with those found for isomer (1) (λ/nm^{-1} [ε/M^{-1} cm^{-1}] = 335 [13], 515 [9], 721 [3], 803 [2], 961 [5]). This thermal isomerization process was also followed by cyclic voltammetry measurements and suggests that *trans*-[Ni($L^{\rm Im1}$)(H_2O)](ClO_4)$_2$ is the thermodynamically stable isomer. Solutions kept at 363 K for longer periods of time (4–5 days) followed by slow evaporation of the solvent yielded single crystals of a major product identified by X-ray diffraction as *trans*-[Ni(ClO_4)($L^{\rm Im1}$)]ClO_4, (3).

Compound (1)

Crystal data

[Ni($C_{15}H_{30}N_6$)(H_2O)](ClO_4)$_2$·H_2O
M_r = 588.09
Monoclinic, $P2_1/c$
a = 14.596 (3) Å
b = 10.995 (2) Å
c = 16.192 (3) Å
β = 107.96 (3)°
V = 2471.9 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.06 mm^{-1}
T = 294 K
0.18 × 0.16 × 0.12 mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{\rm min}$ = 0.98, $T_{\rm max}$ = 0.99
8284 measured reflections
4852 independent reflections
2770 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.077

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.136
S = 1.23
4852 reflections
362 parameters
452 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.51 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.91 e Å^{-3}

Compound (2)

Crystal data

[Ni($C_{15}H_{30}N_6$)(H_2O)](ClO_4)$_2$
M_r = 570.08
Orthorhombic, $P2_12_12_1$
a = 9.428 (5) Å
b = 16.047 (5) Å
c = 16.060 (5) Å
V = 2429.7 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.08 mm^{-1}
T = 294 K
0.32 × 0.30 × 0.20 mm

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Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{\min} = 0.98$, $T_{\max} = 0.99$
8056 measured reflections
4312 independent reflections
3342 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.153$
$S = 1.07$
4312 reflections
362 parameters
720 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}
Absolute structure: Flack (1983), 1601 Friedel pairs
Flack parameter: 0.14 (3)

Compound (3)

Crystal data

$[\mathrm{Ni(ClO_4)(C_{15}H_{30}N_6)]ClO_4}$
$M_r = 552.06$
Monoclinic, $P2_1/c$
$a = 16.665$ (5) Å
$b = 9.696$ (5) Å
$c = 13.936$ (5) Å
$\beta = 92.849$ (5)°
$V = 2249.0$ (16) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.16$ mm^{-1}
$T = 294$ K
0.12 × 0.12 × 0.10 mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{\min} = 0.98$, $T_{\max} = 0.99$
23451 measured reflections
4403 independent reflections
2878 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.092$
$S = 0.90$
4403 reflections
356 parameters
732 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.92$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Compound (4)

Crystal data

$[\mathrm{Ni(C_{20}H_{36}N_6)](ClO_4)_2\cdot 0.24H_2O}$
$M_r = 650.50$
Orthorhombic, *Pbca*
$a = 13.7285$ (12) Å
$b = 19.2330$ (18) Å
$c = 21.171$ (2) Å
$V = 5589.9$ (9) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.95$ mm^{-1}
$T = 294$ K
0.22 × 0.16 × 0.16 mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{\min} = 0.98$, $T_{\max} = 0.99$
40257 measured reflections
5489 independent reflections
3936 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.151$
$S = 1.08$
5489 reflections
479 parameters
934 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 4
Hydrogen-bond geometry (Å, °) for (3).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O21*B*	0.91	2.29	3.140 (13)	155
N4—H4···O12*B*	0.91	2.15	3.035 (14)	165
N4—H4···O12*A*	0.91	2.15	2.997 (15)	154

Table 5
Hydrogen-bond geometry (Å, °) for (4).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*C*···O12	0.91	2.27	3.123 (8)	156

All H atoms attached to C and N atoms were placed at calculated positions, with aromatic C—H = 0.95 Å, methylene C—H = 0.97 Å, methyl C—H = 0.96 Å and N—H = 0.91 Å, the N—H group having been identified previously in difference Fourier maps. The O—H groups showed varying behaviours and were accordingly treated differently in the refinements of (1)–(4). In (1) and (2) they were found in difference maps, and while those in (2) could be refined successfully with restraints [O—H = 0.85 (1) Å and H···H = 1.35 (3) Å], those in (1) would not refine properly. They were thus kept at their original positions as found in the difference map, corrected to an idealized O—H distance of 0.85 Å. Structure (3) does not include any solvent or ligand water molecules. In (4), the O—H atoms could not be located in the difference map and were accordingly not included in the model. In all cases, H atoms were assigned $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(host) [or $1.5U_{\rm eq}$(host) for methyl].

All the perchlorate anions showed some kind of disorder, which was treated through the use of split models, in most cases in the form of a rotation around a nondisordered Cl—O bond. Similarity restraints were used for Cl—O and O···O distances, as well as for displacement parameters. For the first three structures, a simple twofold splitting was enough, with occupancies of 0.53 (3):0.47 (3) for (1), 0.62 (3):0.38 (3) and 0.61 (3):0.39 (3) for (2), and 0.48 (2):0.52 (2) for (3). In the case of (4), a threefold splitting was required, with occupancies of 0.405 (18):0.405 (18):0.190 (18). All four structures were refined in a homogeneous way, with similarity restraints applied to perchlorate geometries (s.u. values: Cl—O = 0.010 Å and O···O = 0.015 Å). Continuity in anisotropic displacement parameters for neighbouring atoms (except metallic centres) were also applied (*SHELXL* instructions DELU 0.01 and SIMU 0.02). An isolated peak in structure (4) was satisfactorily refined as a partially occupied solvent water molecule [occupancy factor 0.248 (15)].

Although (2) is metrically tetragonal, the $R_{\rm int}$ values indicate unequivocally that the diffraction pattern has orthorhombic symmetry [$R_{\rm int}$(tetragonal $4/m$) 0.31; $R_{\rm int}$(tetragonal $4/mmm$) 0.41; $R_{\rm int}$(orthorhombic mmm): 0.06]. In addition, in this same structure, the Flack (1983) parameter refined to 0.14 (3), thus suggesting the presence of a significant fraction of an inversion twin, even if far removed from being a racemate. The noncentrosymmetric character is clearly in line with $|E|$ statistics [mean values for $|E^*E - 1|$: 0.740 (experimental), 0.968 (centrosymmetric) and 0.736 (noncentrosymmetric)].

For all compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008);

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software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3274). Services for accessing these data are described at the back of the journal.

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