

Preparations and structures of nickel(II) compounds of 2,9-*rac*-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane

Neil F. Curtis^{a,*}, Martyn P. Coles^a, Jan Wikaira^b

^a School of Chemical and Physical Sciences, Victoria University of Wellington, Box 600, Wellington 6140, New Zealand

^b Department of Chemistry, University of Canterbury, Box 8400, Christchurch 8410, New Zealand

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ABSTRACT

The imine functions of 3,10-*rac*-[(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II)]²⁺ are reduced by NaBH₄ in water forming the 2*RS*,7*SR*, 9*RS*,14*SR*-, [Ni(*rac-rac*-1-*L*)]²⁺, and 2*RS*,7*SR*,9*RS*,14*RS*-[Ni(*rac-meso*-*L*)]²⁺, isomeric [(2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II)] cyclic tetraamine cations. The structures of [Ni(*rac-rac*-1-*L*)](ClO₄)₂, [Ni(*rac-rac*-1-*L*)]ZnCl₄, [Ni(*rac-rac*-1-*L*)](acac)ClO₄ and [Ni(*rac-meso*-*L*)](ClO₄)₂·H₂O were determined by X-ray diffractometry. The perchlorate and tetrachlorozincate salts of the cation [Ni(*rac-rac*-1-*L*)]²⁺ have near twofold symmetry about the nickel(II) ion, normal to the NiN₄ plane, with “basket” cyclam nitrogen configuration I (1*RS*,4*RS*,8*RS*,11*RS*). The C2 and C9 methyl substituents are axially oriented to the same side of the plane as the four NH groups, with the axially oriented components of the C5 and C12 *gem*-dimethyl groups oriented to the other side. The salt [Ni(*rac-rac*-1-*L*)](NCS)₂ has uncoordinated thiocyanate ions. The compound [Ni(*rac-rac*-1-*V*-*L*)](acac)ClO₄, with pentane-2,4-dionate chelate, has the macrocycle in configuration 1*RS*,2*SR*,4*RS*,7*RS*,8*RS*,9*SR*,11*RS*,14*RS*, folded along N4–Ni–N11, with methyl substituents on C2 and C9 equatorially oriented. The [Ni(*rac-meso*-*L*)]²⁺ cation was isolated as the *trans*-dithiocyanato compound, [Ni(*rac-meso*-III-*L*)](NCS)₂, which was converted into the square-planar perchlorate salt [Ni(*rac-meso*-III-*L*)](ClO₄)₂·H₂O, with configuration 1*RS*,2*SR*,4*SR*,7*SR*,8*SR*,9*SR*,11*RS*,14*RS*. This cation has the C2 methyl substituent axially and the C9 substituent equatorially oriented.

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1. Introduction

Isomeric 3,10-*meso*- and 3,10-*rac*- [(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II)] perchlorate salts, orange [Ni(*meso*-Me₈[14]diene)](ClO₄)₂ and yellow [Ni(*rac*-Me₈[14]diene)](ClO₄)₂, were first prepared by reaction of [tris(*rac*-propane-1,2-diamine)nickel(II)] perchlorate with acetone. The salt *meso*-[(3,5,7,7,10,12,14,14-octamethyl-1,8-diaza-4,11-diazonia-cyclotetradec-4,11-diene)] perchlorate was later prepared by reaction of *rac*-propane-1,2-diamine mono hydroperchlorate with acetone or mesityl oxide, see Fig. 1 [1–5].

Reduction of both imine functions of each of the *meso*- or *rac*-diene macrocycles potentially generates three diastereoisomeric 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecanes. The isomers formed by reduction of the *rac*-diene are here labelled by the Chan Ingold Prelog (CIP) [6] configurations of the chiral centres present; first the C2, C9 pair which are *rac* for these compounds, then the C7, C14 pair, which can be *meso* or *rac*, leading

to the isomers *rac-rac*-1 (2*RS*,7*SR*,9*RS*,14*RS*), *rac-rac*-2 (2*RS*,7*RS*,9*RS*,14*RS*) and *rac-meso* (2*RS*,7*SR*,9*RS*,14*RS*) as shown in Fig. 2.

When coordinated the amines have four chiral nitrogen centres in addition to the two pairs of chiral carbon centres, which can, in principle, occur in five configurations, I–V, first characterised for cyclam [7]. Combining the carbon and nitrogen chiral centres gives a total of 20 possible configurations for the coordinated C2,C9-*rac*-amines, occurring as enantiomeric pairs. These stereo-isomeric cations vary in energy, and usually occur with the lowest energy nitrogen configuration, though metastable higher energy isomers can often be prepared. Isomerisation of these to the stable configuration is often very slow in neutral or non-aqueous solution, but usually rapid in a basic environment.

Reduction of the imine functions of [H₂(*meso*-Me₈[14]diene)](ClO₄)₂ by NaBH₄ was first reported by Tait and Busch, who described the isolation of *meso*- and *rac*-isomeric cyclic tetraamines [8]. Further studies of this reduction were published by Lee et al. [9], Bembi et al. [10] and Lin et al. [11]. The last group isolated and structurally characterised the *meso-meso*-1-*L* (2*RS*,7*SR*,9*SR*,14*RS*) and *meso-rac*-*L* (1*RS*,7*SR*,9*SR*,14*RS*) amines as

* Corresponding author. Tel.: +64 4 463 6514.

E-mail address: neil.curtis@vuw.ac.nz (N.F. Curtis).

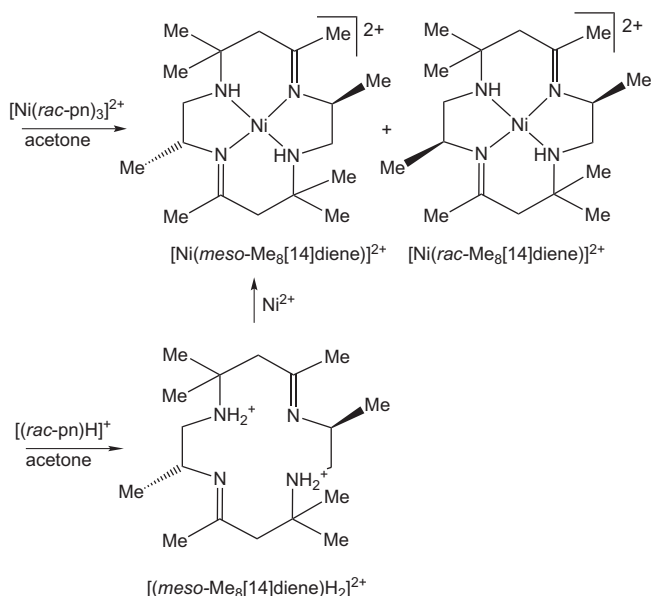


Fig. 1. The preparations of [(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,12-diene)nickel(II)] compounds.

hydrates and their nickel(II) and copper(II) cations as perchlorate salts.

No crystalline perchlorate salt was isolated when resolved [H(*l*-propane-1,2-diamine)]ClO₄ was reacted with acetone or mesityl oxide [3]. However, Tait and Busch reported, without experimental details, the NaBH₄ reduction of Me₈[14]diene “formed from *R*-propane-1,2-diamine”, and that they “had isolated five isomeric cyclic amine compounds of nickel(II), in the ratio of 60:15:18.5:1.2:1.8, all of which, because of the mode of synthesis, contain carbon atoms 2 and 9 having *R* chirality” [12]. Since only three isomeric cyclic tetraamines, with configurations *rac-rac-1*, *rac-rac-2* or *rac-meso* can be formed by reduction of the *rac*-diene (see Fig. 3), some of the reported compounds are probably nitrogen configuration isomers. ¹H NMR studies of the major product were reported, including detailed deuteration experiments, which established the configuration as *rac-rac-1-I-L* and of details of the conformation of this cation [12,13]. The structure of [Ni(*R-R-1-I-L*)](ClO₄)₂ was later determined [15], with configuration 1*S*,2*R*,4*S*,7*S*,8*S*,9*R*,11*S*,14*S* (the reported configuration is incorrect). The cation has C₂ symmetry, with the macrocycle in the “basket” nitrogen configuration I, with the four NH groups oriented

to the same side of the N₄ plane as the axially oriented C2 and C9 methyl substituents, with both chair conformation six-membered chelate rings tilted to the other side of the N₄ plane.

Cyclic tetraamine compounds have been prepared by reduction, by NaBH₄ or by catalytic hydrogenation, of the imine functions of [(tetraazacyclotetradecadiene)nickel(II)] compounds. Reduction of the imine functions of [(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II)] [15] and [(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradec-4,14(1)-diene)nickel(II)] [16] yielded the *rac*- and *meso*-cyclic tetraamine cations, which were separated by formation of sparingly soluble compounds with chelates by one of the isomers.

The reduction of the imine functions of 3,10-*rac*-[(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II)]²⁺ potentially generates the three isomeric cations [Ni(*rac-rac-1-L*)]²⁺, [Ni(*rac-rac-2-L*)]²⁺ and [Ni(*rac-meso-L*)]²⁺, see Fig. 3. The reduction, isolation and structural characterisation of the resultant cyclic tetraamine nickel(II) compounds are now reported. The similar reduction of [3,10-*meso*-(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II)], which forms the nickel(II) cations of all three possible C2,C9-*meso*-isomeric amines, will be reported subsequently [17].

2. Results

The imine functions of [*C-rac*-(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II)] perchlorate are readily reduced by NaBH₄ in water, forming cyclic tetraamine cations. As the reduction proceeds orange coloured [Ni(*rac-rac-1-I-L*)](ClO₄)₂ (structures 1A and 1B) crystallises. The tetrachlorozincate salt of this cation was also prepared and structurally characterised as structure 2. The thiocyanate salt of this cation is orange in colour, with singlet ground state nickel(II), with the IR of the thiocyanate ion (Section 4) indicating that it is not coordinated.

No precipitate of water insoluble chelate compounds formed when pentane-2,4-dione or oxalate was added to the solution after reduction, as observed for the hexamethyl homologues [15,16]. However, the compound [Ni(*rac-rac-V-L*)(acac)]ClO₄, characterised as structure 3, with the macrocycle folded to accommodate the acac[−] chelate, was prepared under non-aqueous conditions, using the method reported for [Ni(teta)(acac)]ClO₄ (teta = *meso*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II)) [18]. This compound is quite soluble in water, forming a yellow dissociated solution.

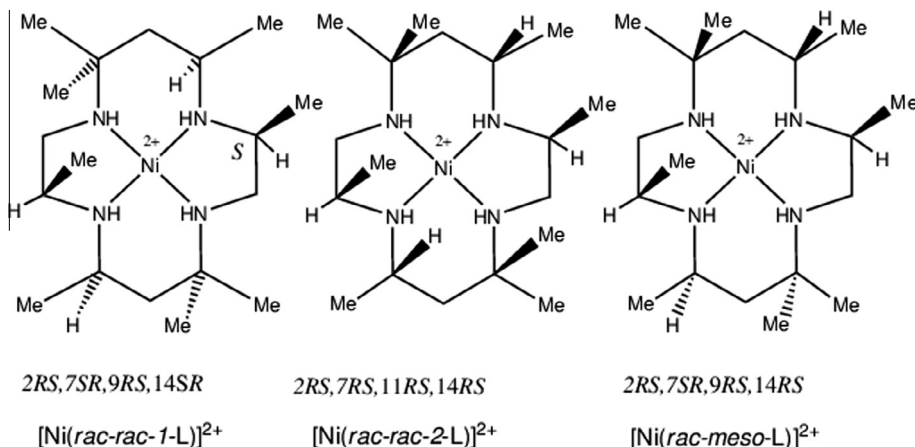


Fig. 2. Configurations of [(2,9-*rac*-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II)].

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