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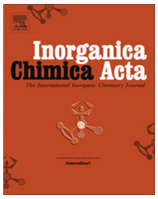

(3,5,7,7,12,14,14-Heptamethyl-1,4,8,11-tetraazacyclotetradec-4-11-diene)nickel(II) revisited and some (2,5,5,7,12,12,14-heptamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) compounds

Neil F. Curtis [a,*], Jan Wikaira [b], Raymond Butcher [c]

[a] School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington 6140, New Zealand
[b] Department of Chemistry, University of Canterbury, Christchurch 8410, New Zealand
[c] Department of Chemistry, Howard University, Washington DC 20059, USA

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ABSTRACT

The reported preparation of (3,5,7,7,12,14,14-heptamethyl-1,4,8,11-tetraazacyclotetradec-4-11-diene)nickel(II) perchlorate, [Ni(Me$_7$[14]diene)](ClO$_4$)$_2$, by reaction with acetone of equimolar mixtures of [Ni(en)$_3$](ClO$_4$)$_2$ and [Ni(*rac*-pn)$_3$](ClO$_4$)$_2$ has been investigated. A crystal isolated from this reaction has half the cation sites occupied by [Ni(Me$_7$[14]diene)]$^{2+}$ cations and half by [Ni(Me$_6$[14]diene)]$^{2+}$ cations. A tetracyanonickelate salt prepared from this has 72% of the cation sites occupied by the heptamethyl cation. Reduction of the mixed-macrocycle nickel(II) cations, [Ni(Me$_{6/7}$[14]diene)]$^{2+}$, with NaBH$_4$ in water forms (cyclic tetraamine)nickel(II) cations. The *meso*-2*RS*,7*RS*,14*SR*-[Ni(Me$_7$[14]ane)]$^{2+}$ and 7*RS*,14*SR*-[Ni(Me$_6$[14]ane)]$^{2+}$ cations and the *rac*-2*RS*,7*RS*,14*RS*-[Ni(Me$_7$[14]ane)]$^{2+}$ and 7*R*,14*R*-[Ni(Me$_6$[14]ane)]$^{2+}$ cations generally co-crystallise as *meso* or *rac* salts, some with stoichiometric formulae. The structures of [Ni(*meso*-Me$_{6/7}$14]ane)][ZnCl$_4$], [Ni(*rac*-Me$_{6/7}$[14]ane)](ClO$_4$)$_2$ and [Ni(*meso*-Me$_6$[14]ane)] [Ni(*rac*-Me$_{6/7[}$14]ane)(acac)](ClO$_4$)$_3$ compounds were determined. Structures of [Ni(*meso*-Me$_6$[14]ane)][ZnCl$_4$] and [Ni(*rac*-Me$_6$[14]ane)(acac)]ClO$_4$ were determined for comparison. An equimolar mixture of [H(en)](ClO$_4$)$_2$ and [H(pn)](ClO$_4$)$_2$ reacted with acetone to form a tetraaza macrocycle salt, from which a cobalt(III) compound [Co(Me$_{6/7}$[14]diene)(acac)](ClO$_4$)$_2$ with ca. 23% of the cation sites occupied by the heptamethyl cation was prepared and structurally characterised.

1. Introduction

Reaction of tris(ethane-1,2-diamine)nickel(II) perchlorate with acetone, over a period of days at ambient temperatures, forms a mixture of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II) perchlorate, [Ni(*trans*-Me$_6$[14]diene)](ClO$_4$)$_2$ (which can occur as interconvertable N-*meso*- and N-*rac*-isomers) and [5,7,7,12,12,14-(hexamethyl-1,4,8,11-tetraazacyclotetradec-4,14(1)-diene)nickel(II)] perchlorate, [Ni(*cis*-Me$_6$[14]diene)](ClO$_4$)$_2$, see Fig. 1 [1]. The reaction of tris(*rac*-propane-1,2-diamine)nickel(II) perchlorate with acetone is much slower, occurring over days at 110 °C, or weeks at ambient temperatures, to form a mixture of non-interconvertable 3,10-*meso*- and 3,10-*rac*-(3,5,7,7,10,12,12,14-octamethyl-1,4-8,11-tetraazacyclotetradec-7,14-diene)nickel(II) perchlorates, *meso*- and *rac*-[Ni(*trans*-Me$_8$[14]diene)](ClO$_4$)$_2$, see Fig. 1 [1–5]. Structures with C-*meso*-N-*meso* and C-*rac*-N-*rac* configurations have been reported [5]. The compounds in this communication all have *trans*-configurations, so this label will be omitted from formulae.

A reaction of equimolar proportions of tris(ethane-1,2-diamine) and tris(*rac*-propane-1,2-diamine)nickel(II) perchlorates with acetone was reported to occur over a period of days at ambient temperatures, to form an orange coloured crystalline product. This was assigned as a 3,5,7,7,12,14,14-heptamethyl homologue of the previous compounds, [Ni(Me$_7$[14]diene)](ClO$_4$)$_2$, incorporating one ethane-1,2-diamine and one propane-1,2-diamine residue, see Fig. 1 [6]. The chemistry of the hexa- and octa-methyl macrocyclic compounds has been extensively studied [1,5], but that of this heptamethyl homologue has received no attention for over 40 years, and even the formation of this cation has not been confirmed. This issue is now addressed.

The Me$_6$[14]diene and *meso*-Me$_8$[14]diene macrocycles are also formed as the salts [H$_2$(Me$_6$[14]diene)](ClO$_4$)$_2$ or [H$_2$(*meso*-Me$_8$[14]diene)](ClO$_4$)$_2$ by reaction of mono-protonated salts of ethane-1,2-diamine or *rac*-propane-1,2-diamine with acetone [1,4,5,7–10]. The possibility that reaction of a mixture of these salts

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* Corresponding author.

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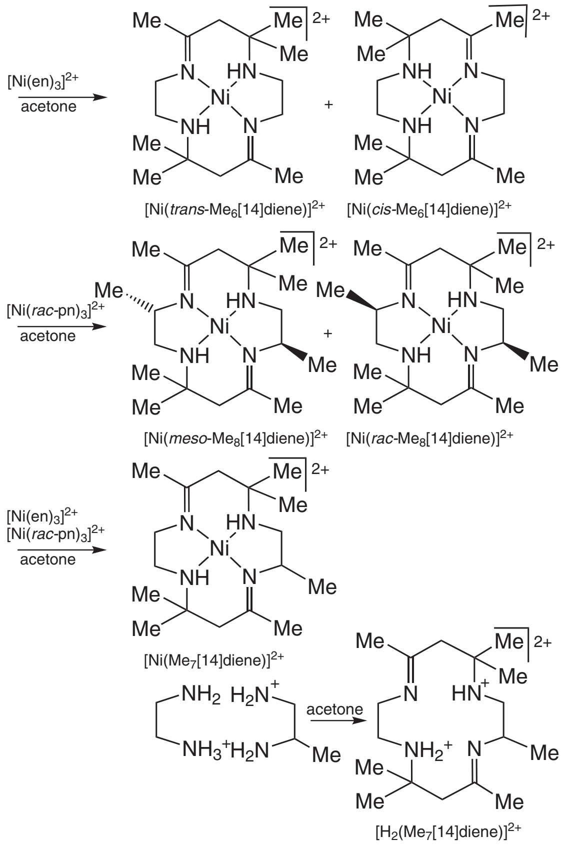

Fig. 1. Some reactions of ethane-1,2-diamine and propane-1,2-diamine compounds of nickel(II) and protons with acetone.

with acetone could form the heptamethyl homologue has been investigated.

2. Results

The structures of 14 compounds resulting from these studies have been determined by X-ray crystallography. The compounds often occur with co-crystallised hexa- and hepta-methyl substituted macrocycle cations and will be designated as "hexa/heptamethyl" or "$Me_{6/7}[14]$", with "mac" used as a generic label for the diene macrocycles and "macH" for the cyclic tetraamines formed by reduction of the imine functions. The cell parameters and *R*-factors for the structures are included in Tables 1 and 2, or in the legends to the figures for the compounds. The Supplementary Tables 1–4 show crystallographic details, Tables 5–7 show selected dimensions of the structures, which are all similar to those of related compounds. Tables 8–10 show displacements of atoms from selected planes and Table 11 shows hydrogen bonds.

2.1. ((3),5,7,7,12,14,14-Hexa/heptamethyl-1,4,8,11-tetraazacyclotetradec-4-11-diene)nickel(II) compounds

The reported reaction of an equimolar mixture of tris(ethane-1,2-diamine)- and tris(*rac*-propane-1,2-diamine)nickel(II) perchlorate salts with acetone [6] was revisited. An acetone solution of the mixture changes colour from blue to orange over a period of days at ambient temperatures. Well-formed orange crystals begin to separate after about 3 days and continue to deposit for weeks. These have an IR spectrum similar to that of $[Ni(\textit{rac-trans}[14]diene)](ClO_4)_2$, but with differences in the detail of the fingerprint region which is unchanged on recrystallisation. A crystal which separated early in the reaction was characterised, without recrystallization, as structure 1.

2.1.1. Structure 1. 1RS,(3SR),8RS-((3),5,7,7,12,14,14-Hexa/heptamethyl-1,4,8,11-tetraazacyclotetradec-4-11-diene)nickel(II) perchlorate

The asymmetric unit consists of a square-planar $[Ni(mac)]^{2+}$ cation, shown in Fig. 2, and two perchlorate ions. The nickel(II) ion is coordinated by a 1,4,8,11-tetraazacyclotetradec-4,11-diene macrocycle, with obvious methyl substituents at ring positions 5, 7, 7, 12, 14 and 14.

The axially oriented groups, C72 and C142 are oriented to the same side of the NiN_4 plane, with N1–H and N8–H oriented to the other side, indicating the N-*rac*-configuration. Residual electron density at the axial substitution position for ring site 3 oriented to the side of the NiN_4 plane opposite to C72 and C142, was refined with free s.o.f., as methyl group $(C31)H_3$, with resultant s.o.f. of 0.475(13). The H-atom H3B of the hexamethyl macrocycle was located and refined as a separate SHELXL PART, with complementary s.o.f. The s.o.f. of this group, and that of the complementary H3B, was fixed at 0.5 with no significant change in the *R* factors. There was no anomaly near the C10 ring position, excluding the alternative possibility that the crystal included 25% of the $[Ni(\textit{rac}\text{-}Me_8[14]diene)]^{2+}$ cation. The crystal thus apparently contains equal proportions of $[Ni(Me_7[14]diene)]^{2+}$ and $[Ni(Me_6[14]diene)]^{2+}$ cations, co-crystallised. The configuration of the heptamethyl component is 1*S*,3*R*,8*S*-(*rac*-1-Me_7[14]diene) of Fig. 3.

The N_4 group is tetrahedrally twisted (±0.065(1), with Ni1 0.03(1) Å from the best N_4 plane). The six atoms of each of the imine functions are co-planar, within the uncertainties. The displacement of C31 from the N1···Ni1···N4 plane is 1.863(4) Å.

The perchlorate ion including Cl1 is located axially with respect to the nickel(II) ion, with Ni1···O14 = 3.055(3) Å. Disorder of the perchlorate ion including Cl2 was modelled with two sets of four O-atom sites, three pairs with s.o.f. of 0.5 and a pair with s.o.f. of 0.75 and 0.25, respectively. This disorder is apparently related to occupancy of the C31 site as C31···O23($-x$, $1-y$, $1-z$) = 2.91(1) Å.

The crystal is not isostructural with $[Ni(\textit{rac}\text{-}Me_6[14]diene)](ClO_4)_2$ [P b c a; *a*, 19.759(3); *b*, 17.016(3); *c*, 13.661(3) Å] [15–17] or $[Ni(\textit{rac}\text{-}Me_8[14]diene)](ClO_4)_2$ [P 41 21 2; *a*, 8.7177(5); *b*, 8.7177(5); *c*, 33.184(2) Å] [18,19]. The cell volume of 2300.0(2) $Å^3$ is between the values for the hexamethyl compound (2243.4 $Å^3$) and the octamethyl compound (2521.9(2) $Å^3$). The hexamethyl compound does not have the perchlorate ion disorder observed for this structure, though that of the octamethyl compound is even more disordered [5].

2.1.2. Other $[Ni(Me_{6/7}[14]diene)]^{2+}$ salts

In attempts to separate the hexa- and heptamethyl cations, the crystallisation of salts with various counter-ions was investigated. Only salts with large anions such as perchlorate or the tetrahalozincates could be readily crystallised and these appeared to crystallise homogeneously. An exception was observed for the tetracyanonickelate salt, which formed both yellow and orange crystals. The orange crystals when stood under (m)ethanol converted to grey-green crystals, as is characteristic of orange $[Ni(\textit{rac-trans}\text{-}Me_6[14]diene)][Ni(CN)_4]$ H_2O, which converts to chain polymeric $[–Ni(\textit{meso-trans}\text{-}Me_6[14]diene)\text{-}\mu\text{-}NC\text{-}Ni(CN)_2\text{-}CN–]$ H_2O under these conditions [20], while the yellow crystals were unchanged. A fragment of a large well-formed yellow crystal was characterised as structure 2.