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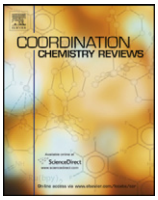

Review

Configurational isomerism of 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane and its compounds

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ABSTRACT

The cyclic tetraamine 2,5,5,7,9,12,12,14-Octamethyl-1,4,8,11-tetraazacyclotetradecane can occur as six-diasterioisomers which are best characterised by the Cahn Ingold Prelog (CIP) priority rules. When coordinated, the nitrogen centres can occur in five configurations, resulting in 30 possible configurations. The configuration of the amines and their metal-ion compounds are unambiguously defined by the CIP configuration of the four carbon and four nitrogen chiral centres present. The chemistry of these cyclic tetraamines, and their metal-ion compounds is reviewed, with emphasis on structural studies, which permit unambiguous assignment of configuration. The literature reporting the preparations and properties of 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane and its compounds contains confusing and incorrect configuration assignments.

1. Introduction

The diamine-dimine azamacrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, *trans*-Me_6[14]diene, and its 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetrane cyclic tetraamine reduction products, *meso*- and *rac-trans*-Me_6[14]ane, often labelled as tet*a* and tet*b*, have been extensively studied and many compounds reported, with the C.D.C. data base [1] including over 380 structure determinations. The octamethyl homologues 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, *trans*-Me_8[14]diene, and its 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane cyclic tetraamine reduction products, *trans*-Me_8[14]ane, have been less studied, with relatively few compounds reported. With the four chiral carbon centres for the amine, increased to eight for coordination compounds when the four chiral coordinated nitrogen centres are included, these amines exhibit a variety of configurational isomerism. There remains considerable ambiguity and confusion in the literature about this isomerism that is here clarified by consideration of X-ray diffraction crystal structures. NMR spectra, which have been commonly used to assign configurations for these compounds, indicate the number of unique carbon atoms, particularly of methyl groups, and also equatorial/axial orientation of the methyl substituents, but generally do not permit unambiguous assignment of configuration. Mis-interpreted NMR spectra have led to much confusion in the literature about the configurations of these compounds, so assignments of configuration based on NMR spectra will generally not be considered in this review. Details of X-ray structure determinations of all relevant compounds are listed in Table 1, The C.D.C. c.i.f. codes of reported structures are shown in the legends to the figures, or where there is no figure, in the text. Reported applications and non-structural studies of these compounds are listed in the final sections.

2. 3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienes

Isomeric *C-meso*- and *C-rac*-(3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)nickel(II) perchlorate salts, orange [Ni(*C-meso-N-meso*-Me_8[14]diene)]$(ClO_4)_2$ and yellow [Ni(*C-rac-N-rac*-Me_8[14]diene)]$(ClO_4)_2$, were first prepared by reaction of tris(*rac*-propane-1,2-diamine)nickel(II) perchlorate with acetone, see Fig. 1 [2–4]. The isomers were separated by fractional crystallisation from water, the *C-rac*-isomer salt being appreciably more soluble than the *C-meso*-isomer salt. The structures of the *C-rac-N-rac*-isomer as the perchlorate salt {c.i.f. QQQCHD and 855026} [5–7] and the *C-meso-N-meso*-isomer as the thiocyanate salt{c.i.f. XAZLEQ} [8] have been determined.

The tetraazamacrocycle salt *C-meso*-(3,5,7,7,10,12,14,14-octamethyl-4,11-diaza-1,8-diazonium-cyclotetradec-4,11-diene) perchlorate, [(*C-meso*-Me_8[14]diene)H_2]$(ClO_4)_2$, is formed by reaction of [(*rac*-propane-1,2-diamine)H]ClO_4 with acetone, see Fig. 1 [3,9].

Metal ion compounds are readily formed from this salt, and the structures of [Cu(*C-meso-N-meso*-Me_8[14]diene)]$(ClO_4)_2$ {c.i.f. HIDHEH} [10], *trans*-[Co(*C-meso-N-meso*-Me_8[14]diene)Cl_2]ClO_4{c.i.f. PELJOF} [11], [Co(*C-meso-N-meso*-Me_8[14]diene)]ClO_4 {c.i.f. KIKDUD} [12] and [Pd(*C-meso-N-meso*-Me_8[14]diene)][Pd$(NCS)_4$] {c.i.f. MOJBIX} [13] have been structurally characterised, see Table 1.

3. 2,5,5,7,9,12,12,14-Octamethyl-1,4,8,11-tetrazacyclotetradecanes

3.1. Configurations of the isomeric amines

Reduction of both imine functions of the *meso*- and *rac*-diene macrocyles generates three diastereoisomeric 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecanes for each, shown in Fig. 2.

The isomerism of these cyclic tetraamines, and their compounds, has been discussed, and structural assignments made, largely from NMR spectra, but with some degree of confusion and several mis-assignments. The situation has not been helped by the use of varying atom-numbering schemes for the macrocycles, arising from using "2,9-dimethyl" or "3,10-dimethyl" numbering. Consistentency with I.U.P.A.C. rules [14], which requires 3,10-dimethyl for the 4,11-dienes and 2,9-dimethyl for the tetraamines, is used in this publication. Dimensions quoted apply to the structures renumbered to comply with the I.U.P.A.C. rules. In some cases authors have labelled species according to the axial or equatorial orientation of the methyl substituents of coordination compounds, though for a particular isomer the orientations depend on both the coordinated nitrogen configuration, and on the macrocycle conformation, so do not provide unambiguous identification of isomer configuration. Empirical isomer labels, with inconsistent usages by different authors, have not helped. The isomer labels as used in the original publications are here used when referring to compounds described in the publication, without any implication as to the configuration present. The idiosyncratic atom labelling which is commonly reported for crystal structures has not helped.

For ions or molecules with chiral centres the Chan Ingold Prelog chiral priority rules (CIP) [15] provide unambiguous identification of configuration. The diastereoisomers of these cyclic tetraamines will here be labelled according to the chirality of the 2,9 and 7,14 enantiomeric pairs of chiral centres as *meso* or *rac*, first the C2 and