

Studies on d¹⁰ Metal Complexes of Expanded Hexaamine Cage Ligands

L.J. Alcock,¹ G. Cavigliasso,² R. Stranger,² A. Willis,² J. Hook,³ S. F. Ralph¹

UNIVERSITY OF WOLLONGONG



¹School of Chemistry, University of Wollongong, Wollongong, NSW, 2522; lja847@uowmail.edu.au

²Research School of Chemistry, Australian National University, Canberra, ACT, 0200

³NMR Facility, Mark Wainwright Analytical Centre, University of New South Wales, Kensington, NSW, 2052

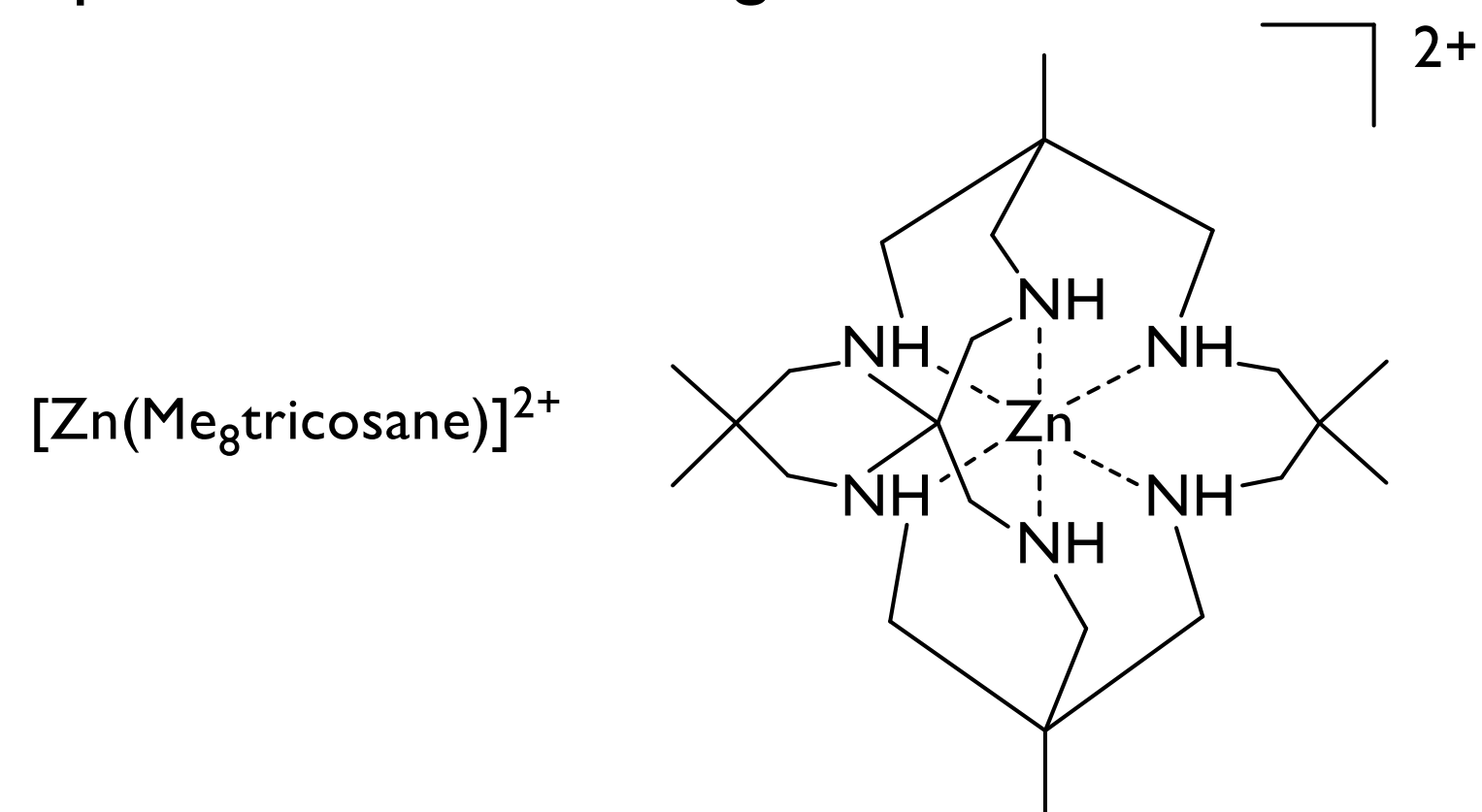


Australian National University



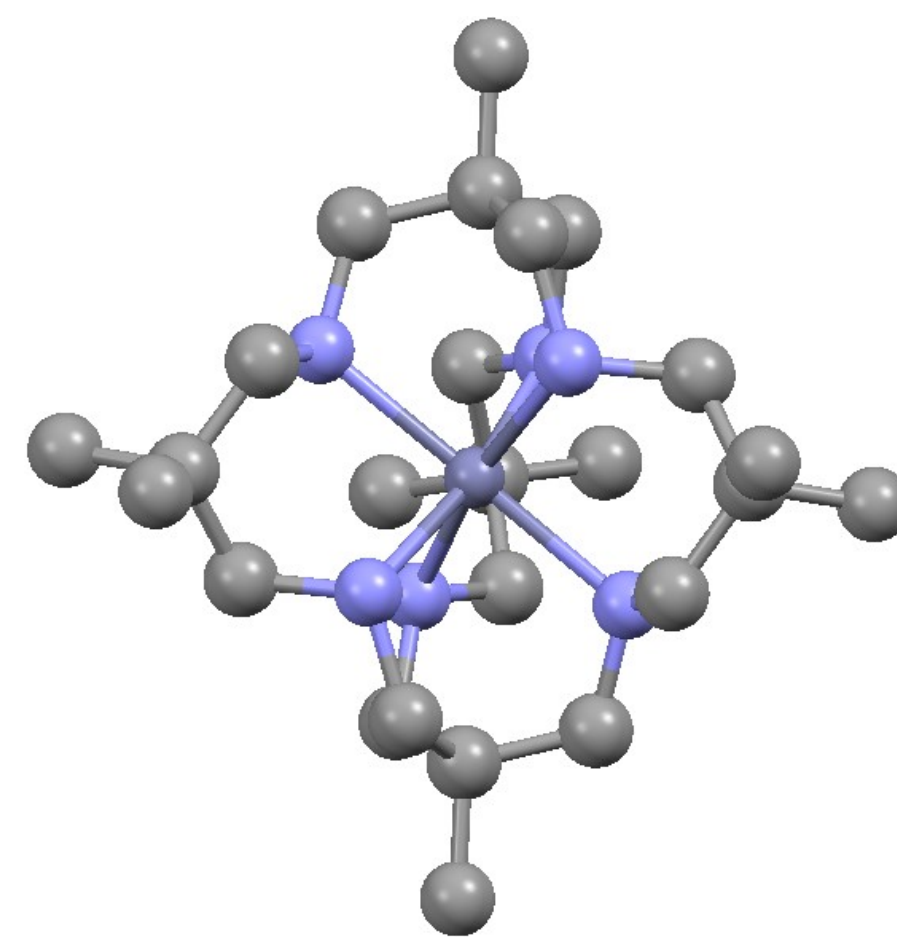
Background

We are investigating the solution and solid state structures of transition metal complexes of the expanded hexaamine cage ligand Me₈tricosane. Of particular interest are complexes of Zn²⁺, Cd²⁺ and Hg²⁺. Their d¹⁰ configurations yields no net crystal field stabilisation energy, allowing for the adoption of metal complexes with different geometries.

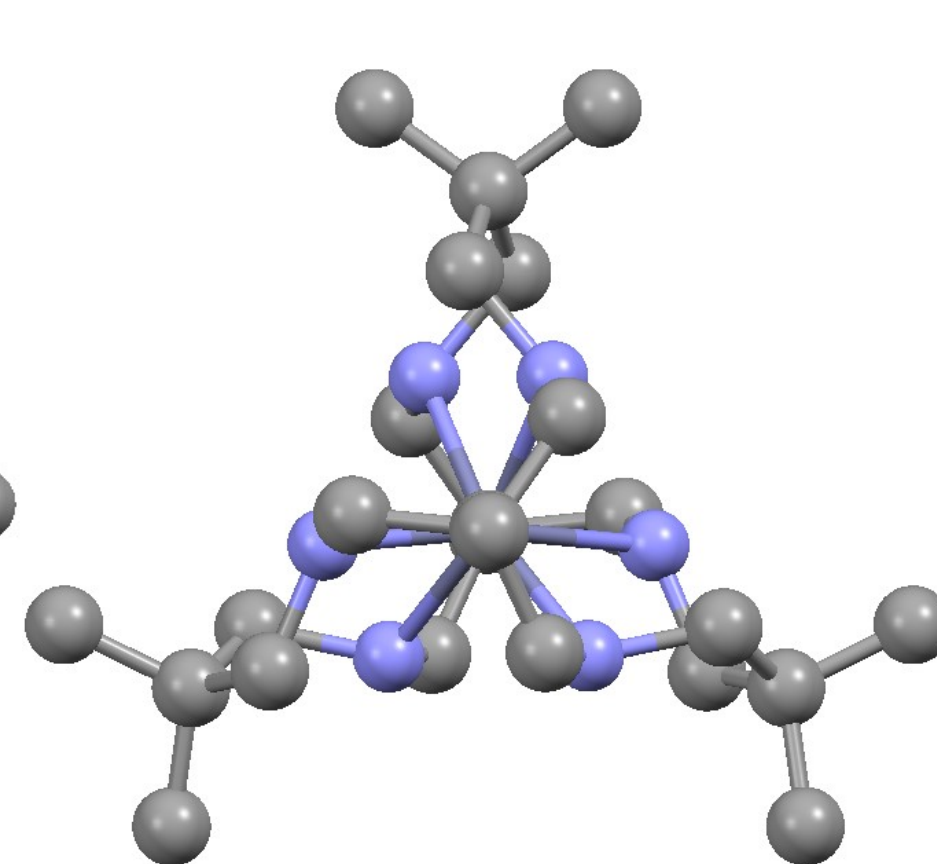


[Zn(Me₈tricosane)]²⁺ Crystal structure, viewed:

Perpendicular to the C₃ axis

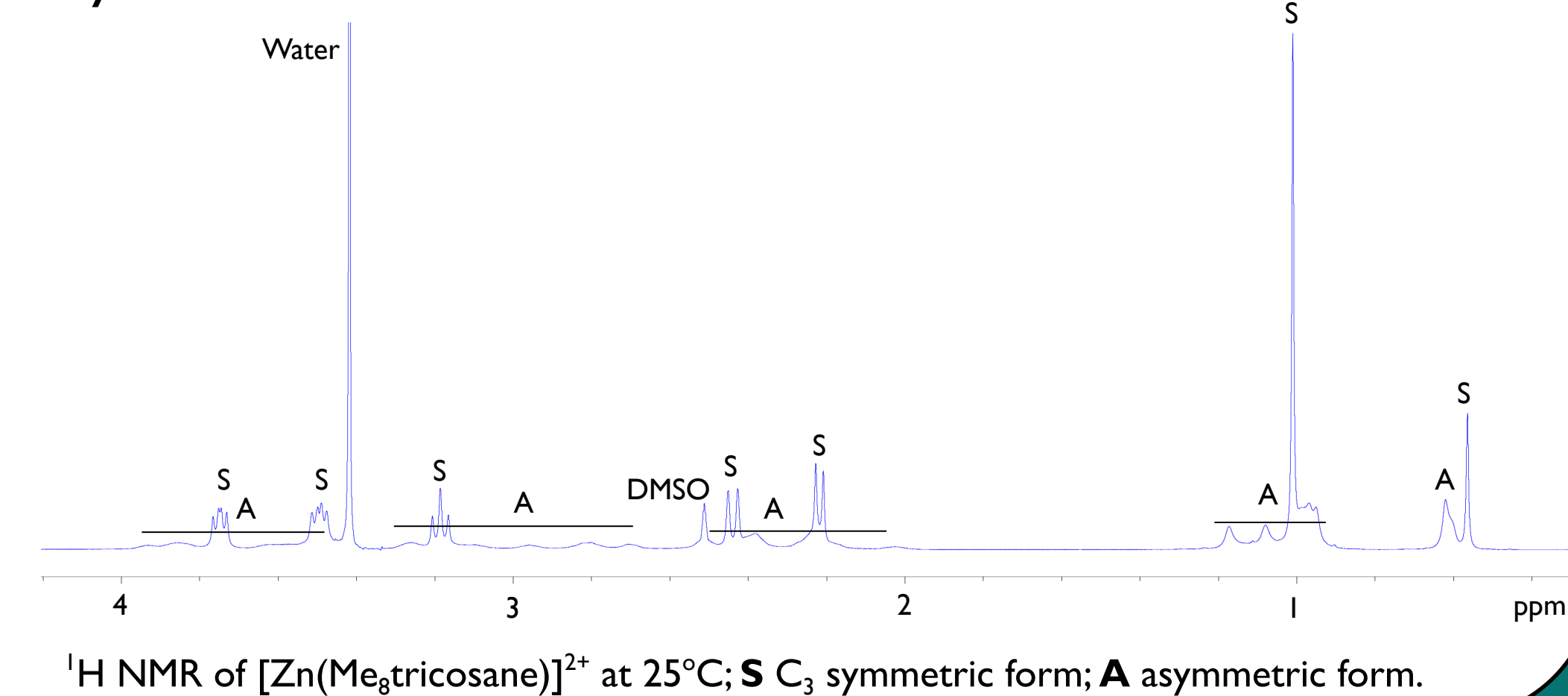


Along the C₃ axis



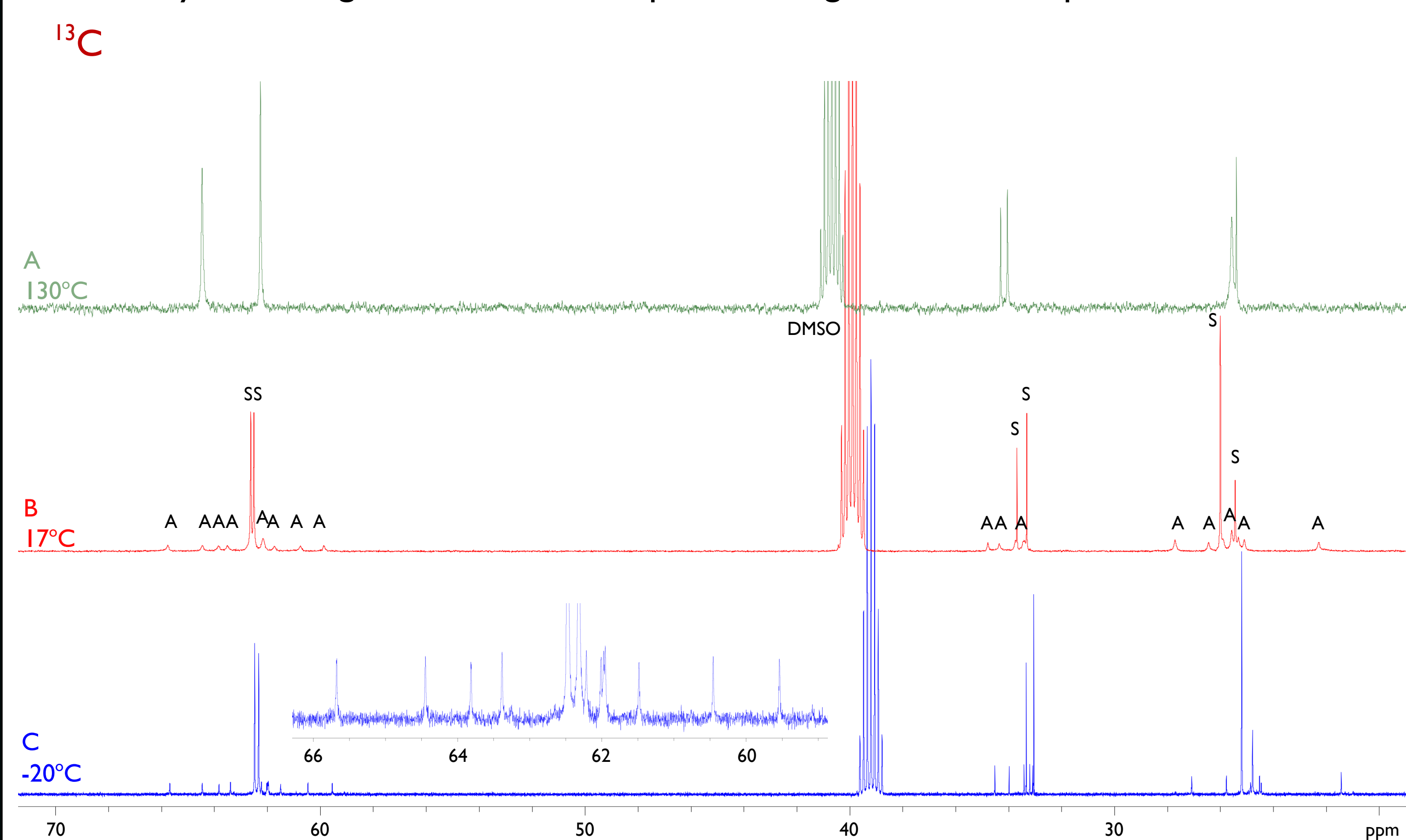
The solid state structure of [Zn(Me₈tricosane)]²⁺ shows that the Zn²⁺ ion has a distorted octahedral coordination geometry, with the nitrogen atoms in either the S₆ or R₆ configuration.

However, the room temperature ¹H and ¹³C NMR spectra of [Zn(Me₈tricosane)]²⁺ provide evidence for the existence of more than one conformation in solution. The ¹H spectrum below shows sharp, high-intensity, resonances from a C₃ symmetric form **S**, and broad low-intensity resonances for an asymmetric form **A**.



[Zn(Me₈tricosane)]²⁺

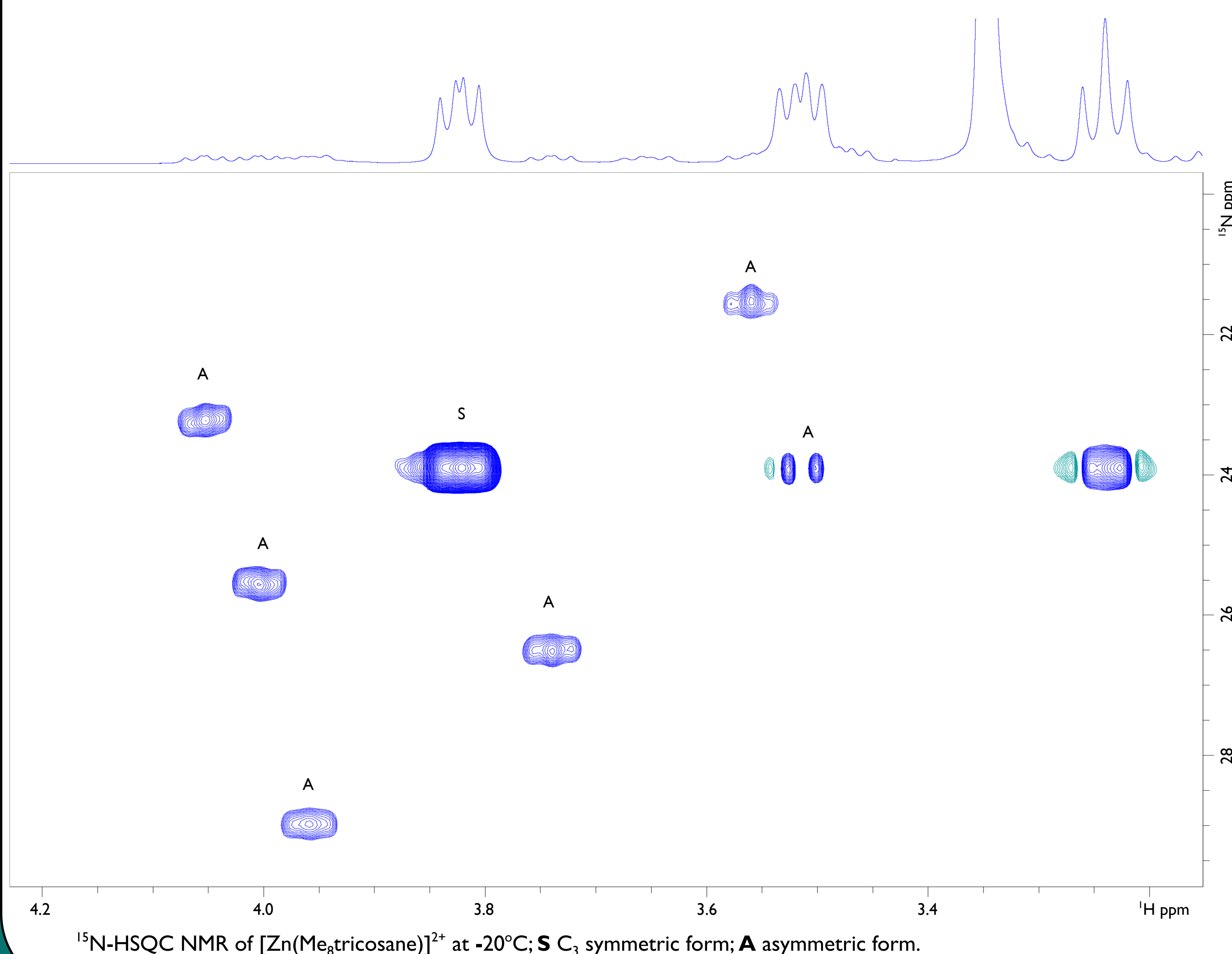
Further evidence for two interconverting forms of [Zn(Me₈tricosane)]²⁺ in solution was obtained by recording ¹H and ¹³C NMR spectra at high and low temperatures.



¹³C NMR of [Zn(Me₈tricosane)]²⁺ at: **A** 130°C, **B** 17°C and **C** -20°C. Similar to the ¹H spectrum above, the resonances visible at 17°C indicate most of the complex is present in a form with C₃ symmetry **S**. The spectrum simplifies at high temperature to what would be expected for a complex with average D₃ symmetry, while at low temperatures the broad signals sharpen and resolve allowing the asymmetric conformation **A** to be easily discerned.

At low temperature the ¹³C NMR of [Zn(Me₈tricosane)]²⁺ shows resonances for each carbon in the asymmetric conformation. This result can also be observed clearly in its ¹⁵N HSQC NMR spectrum at -20°C. A single intense signal corresponding to the six equivalent amine nitrogen atoms of the symmetric form **S** is evident, along with six other resonances due to the asymmetric form **A**.

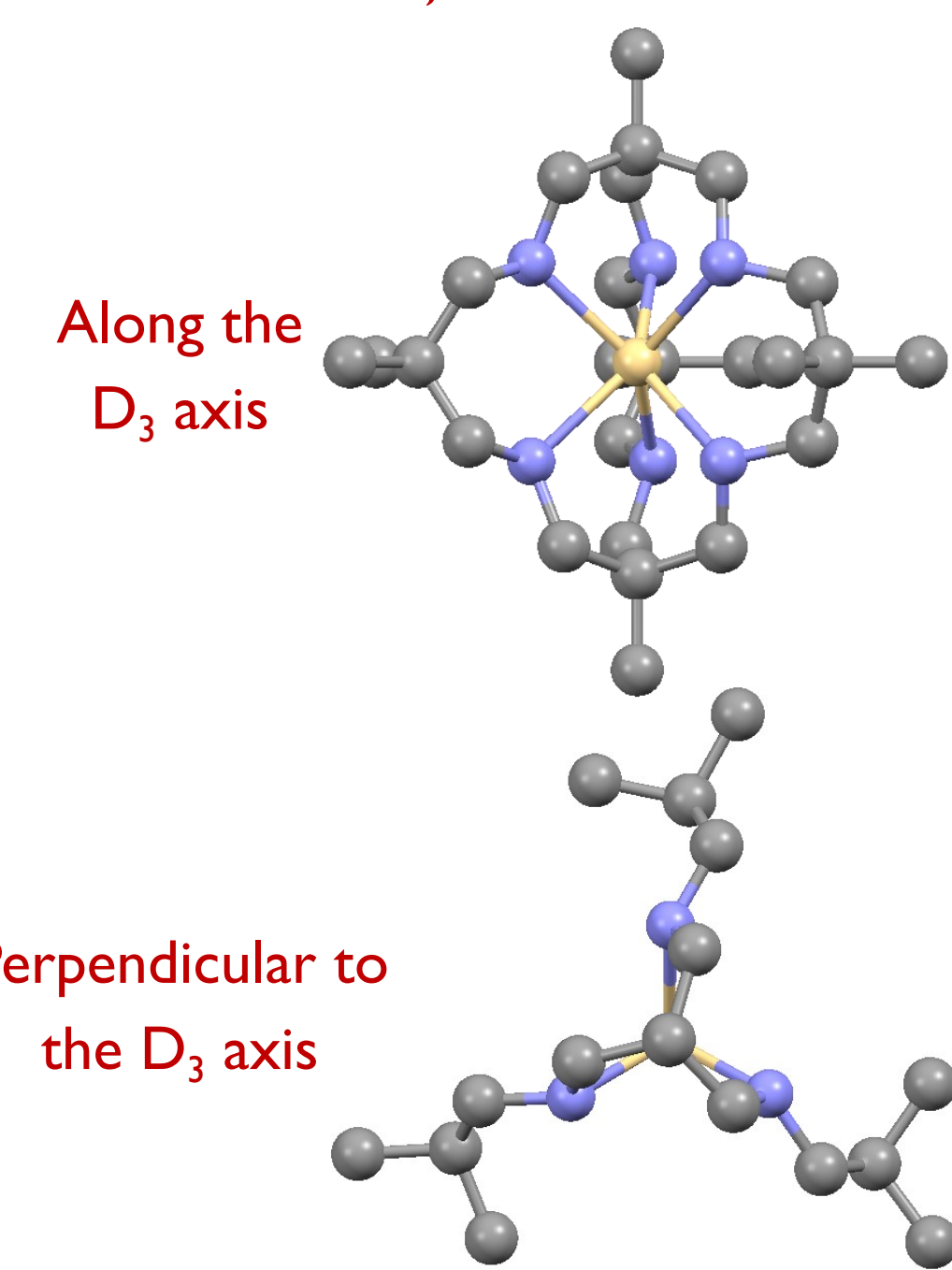
¹⁵N-HSQC



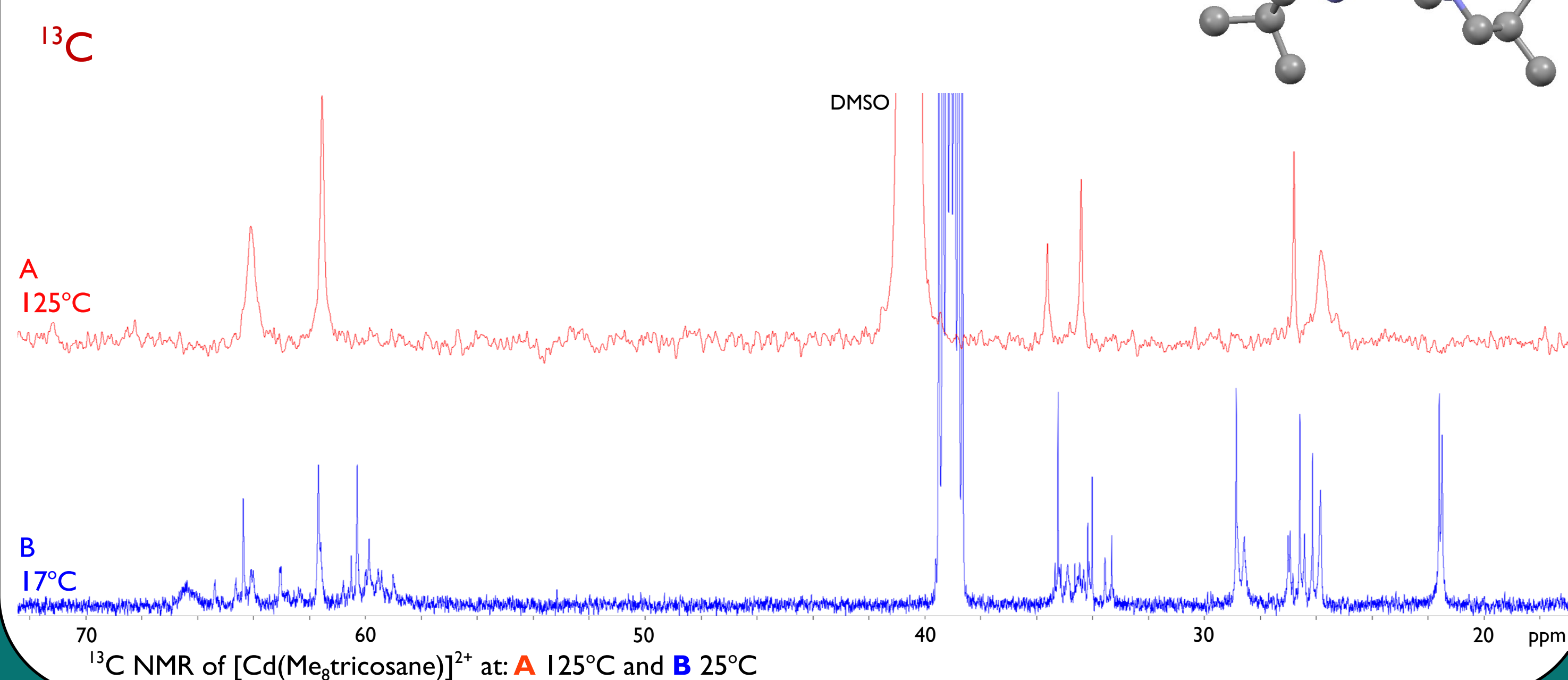
[Cd(Me₈tricosane)]²⁺

The solid state structure of [Cd(Me₈tricosane)]²⁺ shows the Cd²⁺ adopts the rare trigonal prismatic geometry, with nitrogens in the configuration R₃S₃. Despite this high degree of symmetry the room temperature ¹H and ¹³C NMR spectra show resonances consistent with the presence of two or more conformations, at least one of which is asymmetric. At high temperatures these resonances converge and simplify to give the spectrum expected for a complex with D₃ symmetry. The same behaviour (solid state and solution) is also observed for [Hg(Me₈tricosane)]²⁺.

[Cd(Me₈tricosane)]²⁺ Crystal structure, viewed:

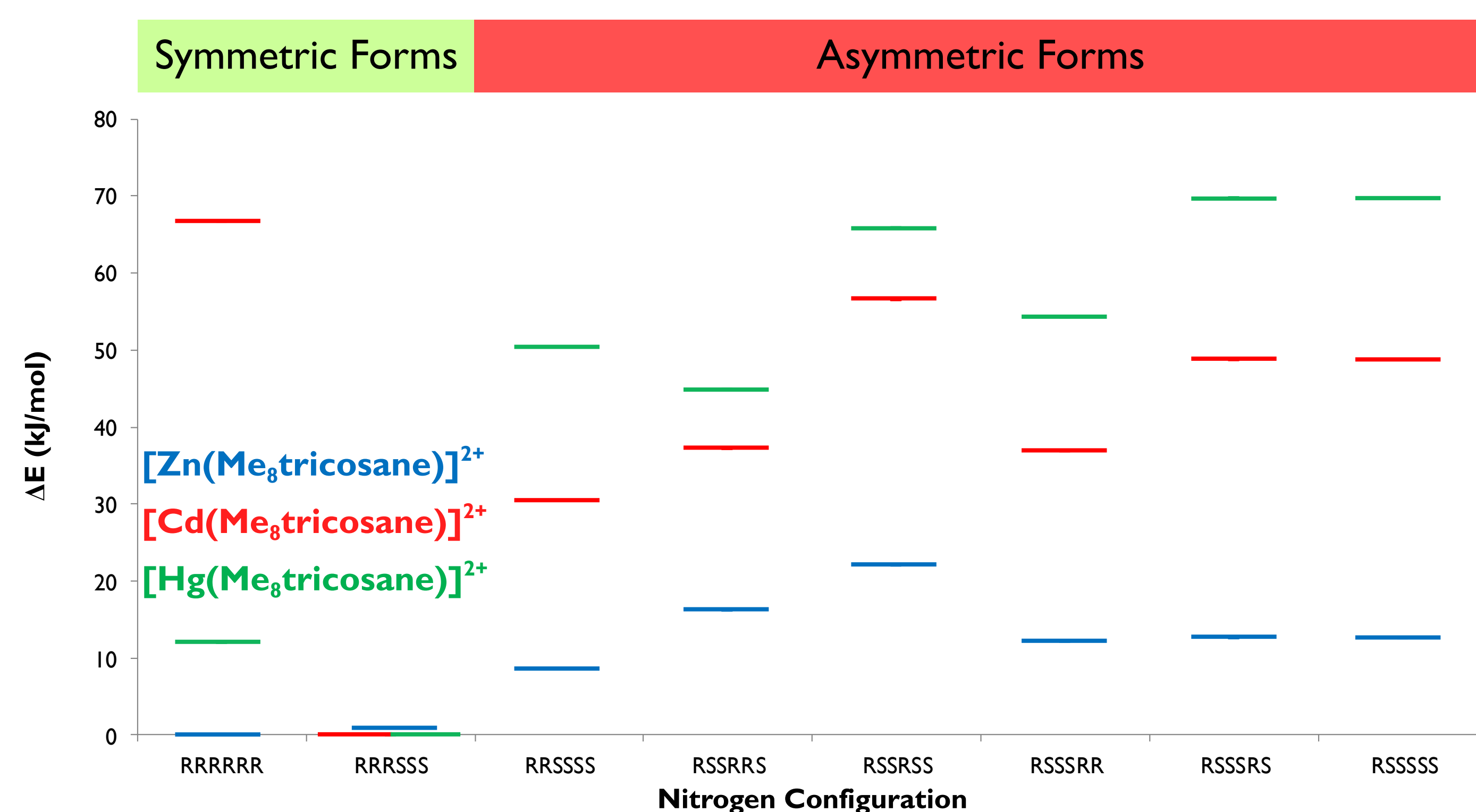


Perpendicular to the D₃ axis



Comparison of stereoisomers by DFT

Computational methods allow us to compare the conformations observed in crystal structures to those with a combination of R and S configurations for the nitrogens which result in an overall lower symmetry.



Plot of the single point energy of [M(Me₈tricosane)]²⁺ (M = Zn, Cd, Hg) for varying nitrogen configuration. Energy measured relative to that for the configuration observed in the crystal structure. [Zn(Me₈tricosane)]²⁺ has asymmetric structures with nitrogen configurations that have energies close to that of the symmetric form, while [Cd(Me₈tricosane)]²⁺ and [Hg(Me₈tricosane)]²⁺ have few. More work is required to determine the energy barrier between interconversion of these forms, as well as to identify the influence of ring configuration.