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Trigonal prismatic metal complexes: a not so rare coordination geometry?†

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The solid state structures of two metal complexes of a hexamine macrobicyclic ligand, in which the metal ion has an exact trigonal prismatic geometry, have been determined. Theoretical calculations showed this is the most stable geometry for d^0 , d^{10} and high spin d^5 metal complexes of the ligand with M–N bond distances $> \sim 2.35$ Å.

All undergraduate chemistry students learn that six-coordinate metal complexes generally have octahedral geometries. In contrast, awareness of discrete six-coordinate complexes that instead have a trigonal prismatic geometry is much poorer. This is not surprising, as the number of such complexes is still relatively low.¹ One group of compounds that routinely exhibit exact or distorted trigonal prismatic geometries are organometallic species which contain d^0 or d^1 metal ions and pure σ -donor ligands, such as $[\text{Zr}(\text{CH}_3)_6]^{2-}$.^{1,2} Some tris(dithiolate) complexes (e.g. $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$ (Ph = C_6H_5)) are also trigonal prismatic,³ as is $[\text{Mn}(\text{acac})_2(\text{bpy})]$,⁴ and the Ti(IV), V(IV) and Fe(III) complexes of the macrobicycle TRENCAM, featuring three catecholate ligands.⁵

The only examples of trigonal prismatic complexes containing saturated amine ligands are $[\text{Cd}(\text{Me}_5\text{tricosane})](\text{PF}_6)_2$ and $[\text{Hg}(\text{Me}_5\text{tricosane})](\text{PF}_6)_2$ ($\text{Me}_5\text{tricosane}$ = 1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane).⁶ Single crystal X-ray crystallography confirmed the geometry of these isomorphous complexes in the solid state, whilst ¹H and ¹³C NMR spectroscopy indicated that the trigonal prismatic structure was retained in solution. In contrast, $[\text{Zn}(\text{Me}_5\text{-tricosane})](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ has a distorted octahedral solid state geometry,⁷ similar to that found for other metal complexes of

the same ligand.^{7–9} Another notable aspect of the solid state structures of the Cd(II) and Hg(II) complexes was that the configuration of the nitrogen atoms in the two trigonal caps were different, i.e. R_3S_3 . In contrast, for all octahedral complexes of $\text{Me}_5\text{tricosane}$ the nitrogen atoms have the same configuration, S_6 or R_6 , depending on whether the molecule is the Λ or Δ enantiomer.⁶ This is also true for all known solid state structures of metal complexes of related small cavity cage hexamine ligands such as sarcophagine (sar or 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane), and its derivatives.¹⁰

The above observations suggest $\text{Me}_5\text{tricosane}$ can adopt different conformations, including one that affords metal complexes with trigonal prismatic geometry under certain conditions. The related hexamine ligand $\text{Me}_8\text{tricosane}$ (1,5,5,9,13,13,20,20-octamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane) also appears to exhibit a degree of flexibility, as both six- and five-coordinate structures in which the ligand is bound to Cu(II) have been reported.¹⁰ We therefore decided to explore the generality of trigonal prismatic geometries amongst complexes of these expanded cavity hexamine ligands, by preparing the Zn(II), Cd(II) and Hg(II) complexes of $\text{Me}_8\text{tricosane}$, and determining their solid state structures.

Solutions containing $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$, or the corresponding Cd(II) or Hg(II) complexes, were obtained by mixing equimolar quantities of the free ligand and the metal nitrate salt in methanol under ambient conditions. Formation of the metal complexes was confirmed by electrospray ionization mass spectrometry, which we have shown previously provides simple, easy to interpret spectra of these systems.¹¹ Upon standing the nitrate salts of the complexes precipitated. Recrystallization from methanol/ethanol (Zn and Cd) or methanol/ H_2O (Hg) afforded crystals suitable for X-ray diffraction. Details of the crystallographic data collection and refinement processes may be found in the ESI.† Fig. 1 shows the solid state structures of the molecules viewed orthogonal to and directly along the C_3 axis of the molecules, while Table 1 provides selected bond lengths and the trigonal twist angles for each of the three metal cage complexes, as well as related com-

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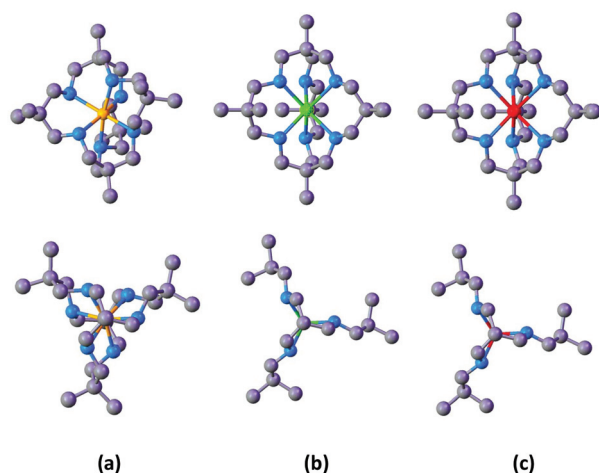


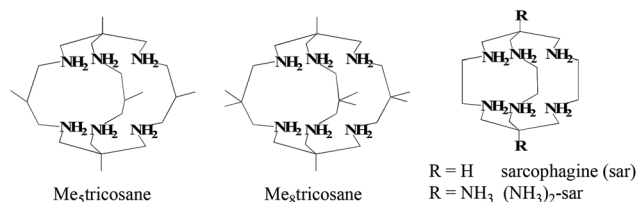
Fig. 1 Solid state structures viewed orthogonal to, and along the C₃ axis of: (a) [Zn(Me₈tricosane)]²⁺; (b) [Cd(Me₈tricosane)]²⁺ and (c) [Hg(Me₈tricosane)]²⁺. Coordinates taken from the Cambridge Crystallographic Database and displayed using Mercury 3.1. No hydrogen atoms shown. Grey spheres = carbon atoms; blue spheres = nitrogen atoms; orange sphere = zinc atom; green sphere = cadmium atom; red sphere = mercury atom.

Table 1 Metal–nitrogen bond distances and average trigonal twist angles (ϕ) for Zn, Cd and Hg(II) complexes

Structure	M–N range (Å)	ϕ (°)	Ref.
[Zn(Me ₈ tricosane)](NO ₃) ₂ ·H ₂ O	2.192(1)–2.260(1)	45.9	
[Zn(Me ₅ tricosane)](ClO ₄) ₂ ·0.5H ₂ O	2.196(2)–2.196(2)	60.7	7
[Zn(NH ₃) ₂ -sar](NO ₃) ₄ ·H ₂ O	2.181(3)–2.215(4)	28.6	6 and 12
[Zn(en) ₃](S ₂ O ₃)	2.09–2.29	^a	13
[Cd(Me ₈ tricosane)](ClO ₄) ₂ ·2H ₂ O	2.398(2)–2.408(2)	0	
[Cd(Me ₅ tricosane)](PF ₆) ₂ ·3H ₂ O	2.386(7)–2.400(7)	0	6
[Cd(NH ₃) ₂ -sar](NO ₃) ₄ ·H ₂ O	2.27(1)–2.34(1)	27.4	6 and 12
[Cd(en) ₃](S ₂ O ₃)	2.43(3)–2.46(3)	^a	14
[Cd(NH ₃) ₆]F ₂	2.336(2)–2.406(2)	51.3	15
[Hg(Me ₈ tricosane)](ClO ₄) ₂ ·2H ₂ O	2.433(2)–2.440(2)	0	
[Hg(Me ₅ tricosane)](PF ₆) ₂ ·3H ₂ O	2.39(2)–2.43(1)	0	6
[Hg(NH ₃) ₂ -sar](NO ₃) ₄ ·H ₂ O	2.32(2)–2.41(2)	25.8	6 and 12

^a Twist angle not available.

plexes of other hexaamine ligands.



The structure of the [Zn(Me₈tricosane)]²⁺ cation is very similar to that reported previously for [Zn(Me₅tricosane)]²⁺.⁶ In both cases the metal ion has a distorted octahedral geometry, with the configurations of all six nitrogen atoms identical to each other for a given enantiomeric configuration of chelate

erings. Furthermore both zinc complexes have skewed boat conformations for the three rings forming the “straps” connecting the two trigonal “caps” of the molecule. For [Zn(Me₈tricosane)]²⁺ the degree of distortion from a regular octahedral geometry is greater, with its trigonal twist angle of 45.9° being further from the theoretical value for a perfect octahedron (60°) than that for [Zn(Me₅tricosane)]²⁺ (60.7°). In addition, for [Zn(Me₈tricosane)]²⁺ two N–Zn–N angles are 167.65(5)°, while the third is 171.64(7)°. In contrast, for [Zn(Me₅tricosane)]²⁺ the same three N–Zn–N bond angles (179.3(2), 178.8(2) and 176.90(10)°) are all very close to the value of 180° for a regular octahedron. The Zn–N bond distances in [Zn(Me₈tricosane)]²⁺ are similar to those of other Zn(II) hexaamine complexes (Table 1).

Scrutiny of Fig. 1 shows that the [Cd(Me₈tricosane)]²⁺ and [Hg(Me₈tricosane)]²⁺ cations have higher symmetry than the Zn(II) analogue, owing to the former complexes having exact trigonal prismatic geometries (twist angle = 0°). The cadmium and mercury molecules show M–N bond distances comparable to those of other hexaamine complexes of these metal ions (Table 1). In contrast to the Zn complex, the configuration of the three nitrogen atoms in one cap is different to that of the remaining three, and the six-membered rings in the straps exhibit chair conformations. In order to accommodate trigonal prismatic geometries for the cadmium and mercury complexes, three of the N–M–N angles are heavily distorted away from 180°. For the cadmium complex the relevant bond angles are 136.34(6), 134.71(6) and 136.90(6)°, while for the mercury structure they are 136.50(8), 134.76(8) and 137.04(8)°.

The geometries of the Cd(II) and Hg(II) complexes of Me₈-tricosane are in stark contrast to the distorted octahedral geometries reported for the corresponding complexes of (NH₃)₂-sar, or for [Zn(Me₈tricosane)]²⁺. However, they are identical to those reported previously for [Cd(Me₈tricosane)]²⁺ and [Hg(Me₈tricosane)]²⁺. This suggests that the trigonal prismatic geometry may be a standard structural motif for complexes of expanded hexaamine cage ligands, when coordinated to metal ions without significant electronic demands, and optimum M–N bond distances greater than a threshold value. Scrutiny of the M–N bond distances in Table 1 provides insight as to what this threshold M–N bond distance might be. Since neither [Zn(Me₅tricosane)]²⁺ or [Zn(Me₈tricosane)]²⁺ have trigonal prismatic geometries, the threshold must be greater than ~2.26 Å. In contrast, all the M–N bond distances for the Cd(II) and Hg(II) complexes of these ligands are within the range 2.39–2.44 Å. This therefore suggests the threshold M–N bond distance for a trigonal prismatic complex is probably ≥ 2.30 Å.

In order to better understand the factors that determine the geometry of the metal coordination sphere in these systems, we have performed a range of DFT calculations (see ESI† for details of computational methods). Initially the effect of varying the trigonal twist angle on the total energy of the Zn(II), Cd(II) and Hg(II) complexes of Me₈tricosane was explored. The results of these calculations are presented in Fig. 2. In order to facilitate comparison of the data obtained for the different complexes, the lowest energy calculated for

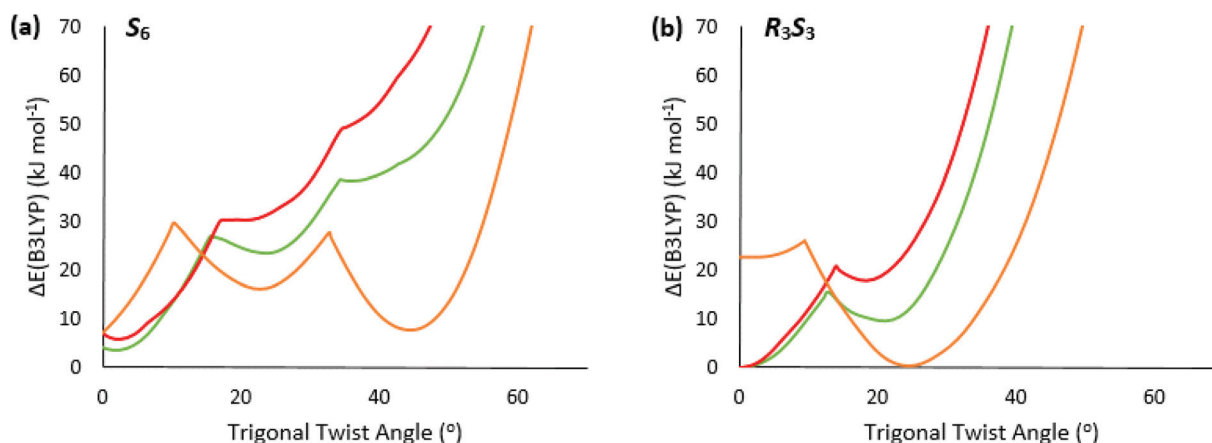


Fig. 2 Effect of trigonal twist angle on the potential energy surfaces of metal complexes of $\text{Me}_8\text{tricosane}$: (a) complexes with an S_6 set of nitrogen atom configurations; and (b) complexes with an R_3S_3 set of nitrogen atom configurations. Orange = $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$; green = $[\text{Cd}(\text{Me}_8\text{tricosane})]^{2+}$ and red = $[\text{Hg}(\text{Me}_8\text{tricosane})]^{2+}$.

each complex was set to 0 kJ mol^{-1} . For each metal complex, two initial ligand geometries were used. The first was that observed in the X-ray structure of $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$, and had overall D_3 symmetry, with all six nitrogen atoms exhibiting an identical, S configuration (*i.e.* S_6). The second initial geometry was that present in the solid-state structure of the mercury complex. In these cases all nitrogen atoms in a single cap had the same configuration, however the opposite cap had a catoptric set of nitrogen configurations (R_3S_3), resulting in overall C_{3h} symmetry.

In each potential energy surface there is at least one discontinuity corresponding to a change in conformation of the rings in one of the caps of the ligand. These changes in ring conformation alter the chirality of the caps, from λ to δ (Fig. 3) or *vice versa*,¹⁶ and result in three different overall (pseudo) symmetries. For example, in Fig. 2a, the potential energy surface for $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$ molecules with a S_6 set of nitrogen atom configurations exhibits δ chirality in both caps at very low twist angles. When the twist angle is increased to 11° a discontinuity is observed. This is a result of the conformation of the three rings in one of the caps changing, resulting in the cap's chirality changing to λ , and an overall change in symmetry of the molecule to C_3 . When the twist angle is increased further to 33° , the chirality at the second cap changes owing to identical conformational changes to the rings in that cap, which result in the molecule now having overall D_3 symmetry. For $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$ molecules with a R_3S_3 set of nitrogen atom configurations (Fig. 2b), the potential energy surface only shows one discontinuity. This is because at low twist angles the energetically most preferred structure already has caps with opposing chirality. Once the twist angle is increased to 10° a change in conformation occurs to the rings in one of the caps resulting in δ chirality for both. There is no change to the C_3 symmetry of the molecule as a result of the change in ring conformations. The potential energy surfaces for the two different geometries of the cadmium and mercury complexes of $\text{Me}_8\text{tricosane}$ show the same number of discontinuities as

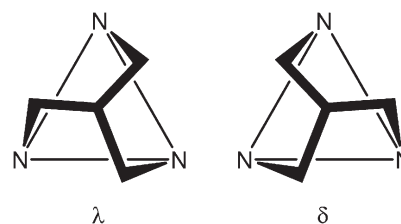


Fig. 3 Illustration of chirality in the caps of cage complexes (exaggerated for clarity).

the corresponding forms of $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$, again reflecting the possibility of molecules with either the same or different chirality in the two caps.

The potential energy surfaces correctly predict that the most stable geometry for $[\text{Cd}(\text{Me}_8\text{tricosane})]^{2+}$ and $[\text{Hg}(\text{Me}_8\text{tricosane})]^{2+}$ is trigonal prismatic, with an R_3S_3 set of nitrogen atom configurations, and a twist angle of exactly 0° , as observed in their crystal structures. When the initial geometry imposed on these complexes had an S_6 set of nitrogen atom configurations, the calculations again showed energy minima at twist angles very close ($<5^\circ$) to that for a trigonal prismatic geometry. This confirms that this geometry is strongly preferred for the Cd(II) and Hg(II) complexes of $\text{Me}_8\text{tricosane}$.

Surprisingly, the calculations predicted that a structure with an R_3S_3 set of nitrogen atom configurations would be energetically more stable for $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$, than a structure with D_3 symmetry and S_6 set of nitrogen atoms, as observed in the solid state structure. In this context it is noteworthy that the difference between the energy minima for the R_3S_3 and S_6 forms of the zinc complex was less than 8 kJ mol^{-1} . Re-optimising these structures with different functionals (PBE and TPSS) reduced the energy difference to less than 4 kJ mol^{-1} . This low energy barrier may be overcome by packing forces in the solid state.

The relationship between the metal–nitrogen bond distances of metal complexes of $\text{Me}_8\text{tricosane}$, and their trigonal twist angles, was investigated by an additional set of DFT calculations, the results of which are presented in Fig. 4. These calculations determined the lowest energy structures of theoretical metal complexes of $\text{Me}_8\text{tricosane}$ with a wide range of metal ions (see ESI† for list), including those with and without crystal field stabilisation (CFSE). Fig. 4 shows that most metal complexes with CFSE have calculated structures with trigonal twist angles consistent with a geometry that is close to octahedral, or a distorted octahedron. Two metal complexes, featuring V(III) and V(IV), did however exhibit twist angles $<7^\circ$, suggesting that experimentally they might be found to instead have trigonal prismatic geometries. The reasons for this are presently unclear, as the expected M–N bond distances in these complexes are not dissimilar to those of any of the other metal complexes with CFSE.

In contrast to the above, the vast majority of metal complexes without CFSE were predicted to have structures with twist angles $<5^\circ$, suggesting that experimentally they will have trigonal prismatic structures. The only exceptions to this were the complexes with Zn(II) and Mg(II), which instead had calculated structures with twist angles of $\sim 25^\circ$. The reasons for this are not known, however this result is consistent with the experimental observation of $[\text{Zn}(\text{Me}_8\text{tricosane})]^{2+}$ adopting a distorted octahedral geometry. Fig. 4 also suggests that the trigonal prismatic geometry will be universally adopted by all metal complexes which have M–N distances $>2.35 \text{ \AA}$. This prediction is consistent with the experimental solid state structures for $[\text{Cd}(\text{Me}_8\text{tricosane})]^{2+}$ and $[\text{Hg}(\text{Me}_8\text{tricosane})]^{2+}$. We are currently exploring the general validity of the above prediction, by synthesising and characterising the solid state structures of additional complexes of $\text{Me}_8\text{tricosane}$ with metal ions expected to form M–N bond distances longer than the threshold value.

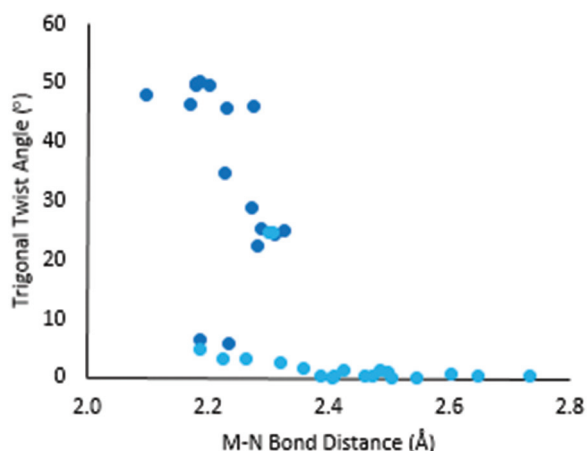


Fig. 4 Effect of metal–nitrogen bond distance on trigonal twist angle of metal complexes of $\text{Me}_8\text{tricosane}$: light blue = metal complexes without crystal field stabilisation energy (d^0 , high-spin d^5 and d^{10}); dark blue = metal complexes with crystal field stabilisation energy (all other configurations).

In order to explore the generality of the trigonal prismatic geometry for complexes of hexamine cage ligands with large metal ions without any CFSE, we also performed DFT calculations on the Zn(II), Cd(II) and Hg(II) complexes of $\text{Me}_5\text{tricosane}$. The potential energy surfaces obtained by examining the effects of varying the trigonal twist angle on the total energy of these systems are presented in Fig. S1.† The energy minima for the surface of the Zn(II) complex was found for the ligand with an S_6 set of nitrogen atom configurations, and occurred at a twist angle very close to 60° . Both observations are consistent with the experimental solid state structure of this complex. Similarly the energy minima for the Cd(II) and Hg(II) complexes of $\text{Me}_5\text{tricosane}$ occurred when the twist angle was 0° , and the ligand had an R_3S_3 set of nitrogen atom configurations. Interestingly the potential energy surfaces for all three metal complexes with an S_6 set of nitrogen atom configurations had a different shape than the $\text{Me}_8\text{tricosane}$ analogues. In the case of complexes of $\text{Me}_5\text{tricosane}$, the total energy increases at twist angles less than $\sim 40^\circ$. In contrast, the total energy for the metal complexes of $\text{Me}_8\text{tricosane}$ decreased at twist angles $<10^\circ$ (Fig. 2a), resulting in values close to 0 kJ mol^{-1} . The relationship between the preferred metal–nitrogen bond distance and trigonal twist angle was also investigated for metal complexes of $\text{Me}_5\text{tricosane}$ (Fig. S2†). This suggested that the trigonal prismatic geometry would be adopted by metal complexes with M–N distances $>2.36 \text{ \AA}$.

Overall, the results presented here show that when steric factors favouring formation of octahedral complexes are diminished, owing to lengthening of M–N bonds, there are greater opportunities for observing trigonal prismatic complexes with d^{10} metal ions. It must be remembered, however, that at long M–N distances the trigonal prismatic geometry does not become more stable than the octahedron, in the absence of any other factors. Therefore the observation of exact trigonal prismatic geometries for the Cd(II) and Hg(II) complexes of both $\text{Me}_5\text{tricosane}$ and $\text{Me}_8\text{tricosane}$ suggests there are other significant influences present. The most likely is a high degree of pre-organisation of the structure of these ligands in favour of forming metal complexes with a trigonal prismatic geometry. Such pre-organisation was noted to be a feature of the structure of $[\text{Me}_5\text{tricosaneH}_2](\text{CF}_3\text{SO}_3)_2$ in the solid state.⁶

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