Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Material

Syntheses

Synthesis of [Zn(Me$_8$tricosane)]$^{2+}$

Me$_8$tricosane (49.81 mg) was dissolved in ethanol (5 mL) with stirring, $Zn(NO_3)_2.6H_2O$ (41.88 mg) was separately dissolved in ethanol (5 mL). To assist in dissolution of the ligand, both solutions were heated in a water bath (~40 ^oC) for 1 h. The solutions were then combined, with no immediate changes being observed. The reaction mixture was then stirred and heated for a further 1 h. Subsequent evaporation of the solution in air produced crystals of the zinc complex suitable for X-ray analysis.

Synthesis of [Cd(Me$_8$tricosane)]$^{2+}$

Me$_8$tricosane (49.7 mg) was dissolved in ethanol (5 mL) with stirring, $Cd(NO_3)_2.4H_2O$ (39.9 mg) was separately dissolved in ethanol (5 mL). To assist in dissolution of the ligand, both solutions were heated in a water bath (~40 ^oC) for 1 h. The solutions were then combined, with no immediate changes being observed. The reaction mixture was then stirred and heated for a further1 h. When the solution was allowed to evaporate in air a large number of small crystals were produced. Recrystallisation of this solid from hot water produced crystals of the cadmium complex suitable for X-ray analysis.

Synthesis of [Hg(Me$_8$tricosane)]$^{2+}$

Me$_8$tricosane (50.7 mg) was dissolved in ethanol (5 mL) with stirring. $Hg(NO_3)_2.H_2O$ (43.1 mg) was separately dissolved in water (5 mL). To assist in dissolution of the ligand, both solutions were heated in a water bath (~40 ^oC) for 1 h. The solutions were then combined, and a white suspension formed immediately. The suspension was then stirred and heated for 1 h, with no further changes observed. Subsequently allowing the solution to evaporate in air produced crystals of the mercury complex suitable for X-ray analysis.

Crystallography

For all three metal complexes, X-ray data were collected using a Nonius KappaCCD diffractometer at 200 K using Mo Kα radiation, l = 0.71073Å, and COLLECT software (Nonius B.V.).[1] Data reduction and cell refinement were accomplished using DENZO/SCALEPACK.[2] The structures were solved with SIR92,[3] and refined by full-matrix least-squares analysis using the program CRYSTALS.[4] Molecular structure diagrams were produced from the CIF files using the program Mercury.

[Zn(Me$_8$tricosane)](NO$_3$)$_2$.H$_2$O

The crystallographic asymmetric unit for the zinc complex consisted of one-half of a $[Zn(C_{25}H_{54}N_6)]^{2+}$ cation, a nitrate anion and one-half of a water molecule of crystallisation. The other half of the dication, and the second half the water molecule, were generated by crystallographic two-fold rotation symmetry operations.

H atoms attached to C were included at calculated positions. Subsequent difference electron density maps showed peaks attributable to the H atoms of the amine groups and the one unique H atom of the water molecule. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93 – 0.98 Å, N-H = 0.86Å and O-H = 0.82Å) and with $U_{iso}(H)$ in the range 1.2 – 1.5 times U_{eq} of the parent atom. In the final refinement the H atoms' coordinates were refined without restraints or constraints.

[Cd(Me$_8$tricosane)](NO$_3$)$_2$.2H$_2$O

The cadmium complex had an asymmetric unit which consisted of one-half of a $[Cd(C_{25}H_{54}N_6)]^{2+}$ cation, a nitrate anion and a water molecule of crystallisation. The other half of the dication was generated by a crystallographic mirror symmetry operation. There were two overlapping images of the nitrate anion.

Two sites were used for each atom and restraints were imposed on bonding distances and angles and on displacement parameters. The relative occupancies were refined appropriately. H atoms attached to C were included at calculated positions. Subsequent difference electron density maps showed peaks attributable to the H atoms of the amine groups and the water molecule. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93 – 0.98 Å, N-H = 0.86Å and O-H = 0.82Å) and with U_{iso}(H) in the range 1.2 – 1.5 times U_{eq} of the parent atom. In the final refinement the coordinates of H atoms attached to N and O were refined (with restraints for the water molecule) but H atoms attached to C ride on the atom to which they are respectively bonded. The lar

The largest feature in the final difference electron density map is a large peak (2.03 e^{-} $Å^{-3}$) at (0.571, 0.250, 0.780) which is 2.08 Å from Cd1 and is at the centre of a square face of the trigonal bipyrmaidal coordination sphere. It equates approximately to an O atom with occupancy 0.12. We can attach no chemical explanation to its existence. The next largest features in the final difference map are all less than 0.47 e^{-} $Å^{-3}$ and are located randomly through the structure.

[Hg(Me$_8$tricosane)](NO$_3$)$_2$.2H$_2$O

For the mercury complex the asymmetric unit consisted of one-half of a $[Hg(C_{25}H_{54}N_6)]^{2+}$ cation, a disordered nitrate anion and one water molecule of crystallization. The other half of the dication was generated by a crystallographic mirror symmetry operation.

Two images of the nitrate group were identified (N50, O51, O52, O53; N54, O55, O56, O57) and the atom sites were refined with appropriate restraints imposed on distances, angles and displacement parameters. The relative occupancies of the two images were then refined. All H atoms bonded to C were included at calculated positions. Subsequent difference electron density maps showed peaks attributable to the H atoms of the amine groups. The H atoms of the water molecules were not located and are not included in the structure. H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C-H in the range 0.93 – 0.98 Å and N-H = 0.87 Å) and with U_{iso}(H) in the range 1.2 – 1.5 times U_{eq} of the parent atom. In the final refinement the H atoms on C ride on the atoms to which they are respectively bonded, and the H atoms bonded to N were refined without restraints or constraints.

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5. P. R. Edgington, P. McCabe, C. F. Macrae, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. Van De Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.

Supplementary Table 1. Crystallographic collection and refinement data.

	$[Zn(Me_8tricosane)](NO_3)_2.H_2O$	$[Cd(Me_8tricosane)](NO_3)_2.2H_2O$	$[Hg(Me_8tricosane)](NO_3)_2.2H_2O$
formula	$C_{27}H_{56}N_8ZnO_7$	$C_{25}H_{58}N_8CdO_8$	$C_{25}H_{58}N_8HgO_8$
Fw	646.15	711.18	799.38
crystal system	monoclinic	orthorhombic	orthorhombic
space group	*C*2/*c*	*Pnma*	*Pnma*
a/Å	10.4071 (2)	18.6325 (4)	18.6126 (3)
b/Å	17.2603 (4)	16.3963 (3)	16.4042 (2)
c/Å	17.7437 (4)	10.5649 (2)	10.5731 (2)
β/deg	105.3125 (15)		
V/Å^3	3074.15 (12)	3227.62 (11)	3228.23 (9)
Z	4	4	4
T/K	200	200	200
μ/mm^{-1}	0.85	0.73	4.83
$R[F^2 > 2\sigma(F^2)]$	0.032	0.033	0.026
$wR(F^2)$	0.081	0.083	0.058

Computational Methods

All DFT calculations were performed using Gaussian 09 Revision A02[1] with the SDDall basis set and the B3LYP density functional.

For all calculations the following z-matrix was used to define the MN_6 region:

```
M
X 1 1.0
N 1 BN 2 AA
N 1 BN 2 AA 3 D1
N 1 BN 2 AA 3 D2
N 1 BN 2 AB 3 DN
N 1 BN 2 AB 4 DN
N 1 BN 2 AB 5 DN
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The initial positions of all other atoms are defined in Cartesian coordinates.

For calculations contributing to Figure 2 and Figure S1 (potential energy surfaces) the starting geometry for complexes with a S_6 set of nitrogen atom configurations was that of the $[Zn(Me_{5/8}tricosane)]^{2+}$ crystal structure. Similarly, the starting geometry for complexes with a R_3S_3 set of nitrogen configurations was that of the $[Hg(Me_{5/8}tricosane)]^{2+}$ crystal structure. Partial optimisations were performed with the trigonal twist angle (parameter DN in the z-matrix above) held constant. Once an optimisation completed the final geometry was used as the initial geometry for the next calculation, with the value of the trigonal twist angle increased or decreased by 1° as appropriate.

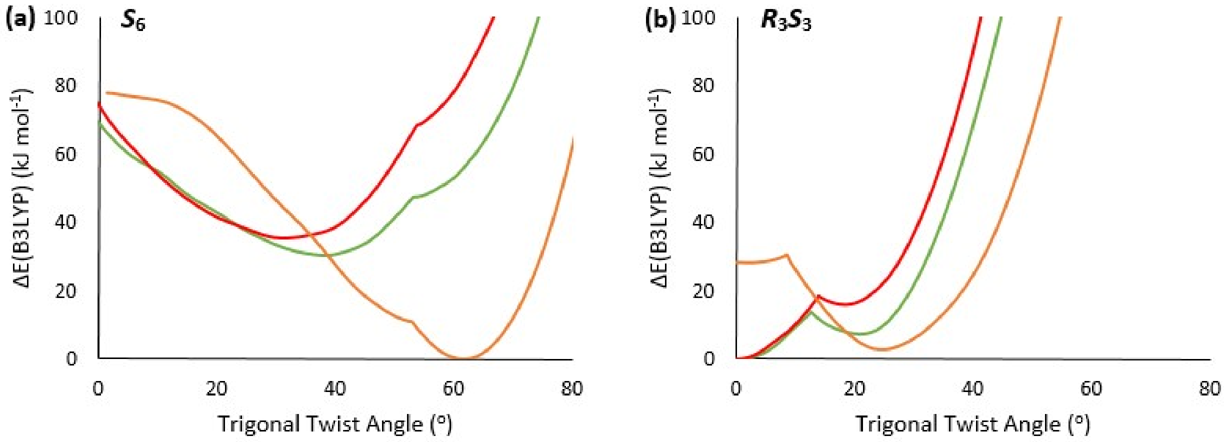

Figure S1. Effect of trigonal twist angle on the potential energy surfaces of metal complexes of Me$_5$tricosane: (a) complexes with an S_6 set of nitrogen atom configurations; and (b) complexes with an R_3S_3 set of nitrogen atom configurations. Orange = [Zn(Me$_5$tricosane)]$^{2+}$; green = [Cd(Me$_5$tricosane)]$^{2+}$ and red = [Hg(Me$_5$tricosane)]$^{2+}$.

For calculations contributing to Figure 4 and Figure S2 (dependence of twist angle on M-N bond distance) starting geometries were utilised corresponding to each of the minima observed in the corresponding potential energy surfaces (For Me$_5$tricosane: S_6 δδ, S_6 δλ, R_3S_3 δλ, R_3S_3 λλ. For Me$_8$tricosane: S_6 δδ, S_6 δλ, S_6 λλ, R_3S_3 δλ, R_3S_3 δδ). In all cases the coordinates of the initial geometry matched that of [Zn(Me$_{5/8}$tricosane)]$^{2+}$ as optimised with that geometry. The identity of the metal ion, charge and multiplicity were changed and the geometry of the resulting theoretical complex optimised. Of the resulting optimised geometries, parameters corresponding to the structure with the lowest electronic energy (E(B3LYP)), of the structural configurations examined, were plotted. This process was repeated across 38 metal ions.

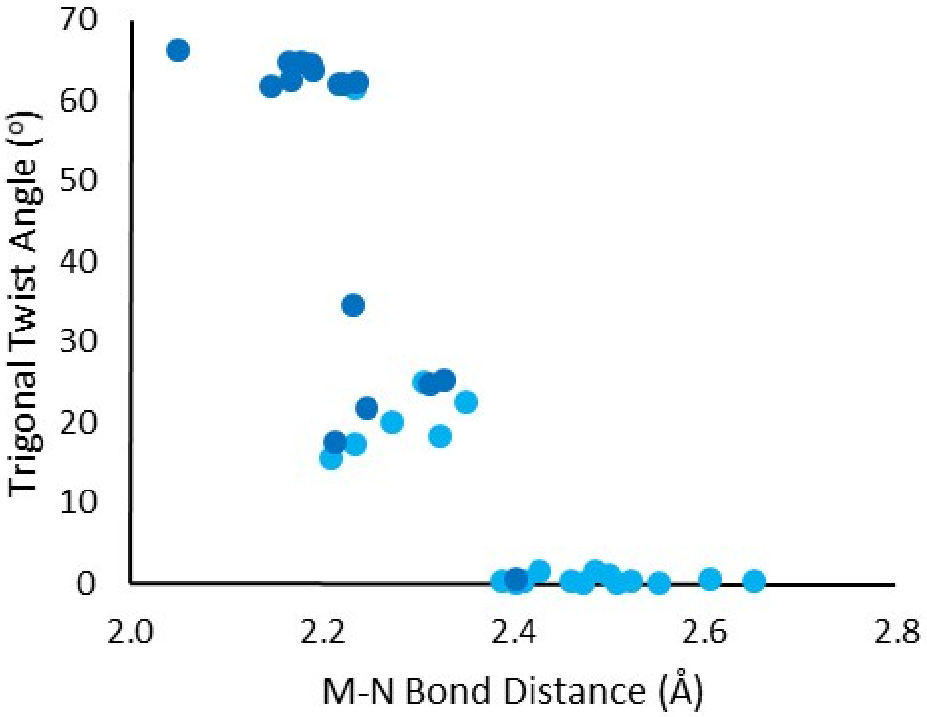

Figure S2. Effect of metal-nitrogen bond distance on trigonal twist angle of metal complexes of Me_5tricosane: light blue = metal complexes without crystal field stabilisation energy (d^0, high-spin d^5 and d^{10}); dark blue = metal complexes with crystal field stabilisation energy (all other configurations).

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