

# An expanded cavity hexamine cage for copper(II)

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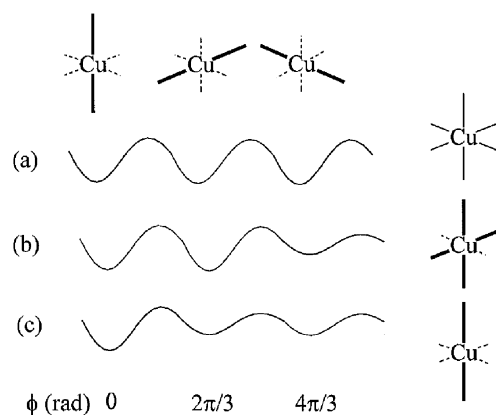
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The crystal structure of the bicyclic hexamine complex  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{fac-Me}_5\text{-tricosane-N}_6 = \text{facial-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane}$ ) at 100 K defines an apparently tetragonally compressed octahedral geometry, which is attributed to a combination of dynamic interconversion and static disorder between two tetragonally elongated structures sharing a common short axis. This structure is fluxional at 60 K and above as shown by EPR spectroscopy. Aqueous cyclic voltammetry reveals that a remarkably stable  $\text{Cu}^{\text{I}}$  form of the complex is stabilised by the encapsulating nature of the expanded cage ligand.

## Introduction

Structural distortions characteristic of six coordinate copper(II) complexes are usually ascribed to the Jahn–Teller effect.<sup>1–4</sup> For six coordinate  $d^9$  metal ions with identical ligands there is an inherent tetragonal distortion (usually a tetragonal elongation) that removes the orbital degeneracy of the  $^2E_g$  ( $O_h$ ) electronic ground state.

If the complex cation crystallises on a site of special symmetry (e.g. a three-fold axis), this underlying tetragonal distortion will be masked by an averaging of three mutually orthogonal orientations shown in Fig. 1(a) *i.e.* the complex ion will *appear* to be octahedral or trigonal. But if *one* of these three orientations is *destabilized*



**Fig. 1** Circular cross-sections of the “Mexican Hat” potential energy surface for a  $\text{Cu}(\text{II})$  ion in an octahedral ligand field. The three geometries on the far right hand side show the *apparent* (crystallographically-derived) structure arising from the average of (from top to bottom) (a) three degenerate structures (e.g. trigonal site symmetry), (b) two degenerate structures (e.g. two degenerate tetragonally elongated structures) or (c) a single non-degenerate tetragonally elongated structure. The *elongated* coordinate bonds are shown in bold while the short axes are shown in broken lines.

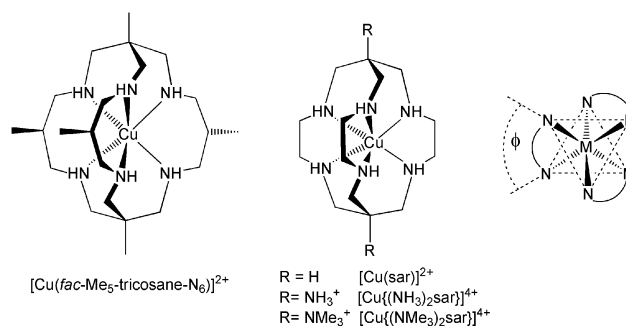
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relative to the other two in the solid state, then the complex will occupy a site of lower symmetry and the geometry will *appear* tetragonally *compressed* through averaging of the two degenerate lower energy structures in Fig. 1(b)<sup>3</sup> Only in the third case, shown in Fig. 1(c) where one of the three ideally degenerate structures is favoured by lattice forces, will the true underlying tetragonally elongated molecular structure emerge from an X-ray crystallographic analysis. In order to unequivocally characterize the geometry of an individual  $\text{Cu}(\text{II})$  complex, spectroscopic measurements, which can probe the instantaneous structure of the complex, are a vital addition to any crystallographic analysis.

Complexes of the expanded macrobicyclic hexamines such as  $\text{fac-Me}_5\text{-tricosane-N}_6$  (facial-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane, Chart 1) are few<sup>5–8</sup> in comparison with their more thoroughly studied smaller cavity sarcophagine (or  $\text{sar} = 3,6,10,13,16,19\text{-hexaazabicyclo[6.6.6]icosane}$ ) relatives.<sup>9–11</sup> Both types of cage ligands usually encapsulate six-coordinate metal ions in a hexadentate binding mode. Typically,  $\text{sar}$  complexes exhibit  $D_3$  symmetry (although  $C_3$  or  $C_2$  symmetry are possible in certain conformations), whereas  $\text{fac-Me}_5\text{-tricosane-N}_6$  complexes possess  $C_3$  symmetry in all reported examples; the methyl-substituted six-membered chelate rings break the two-fold symmetry seen in the (five-membered chelate ring)  $\text{sar}$  analogues.



**Chart 1**

$\text{Cu}(\text{II})$  is an interesting case. Although it readily forms six-coordinate complexes, in almost all known cases two of the six-coordinate bonds are inherently weaker than the remaining

four due to the Jahn–Teller effect. In this work, we report the structural and spectroscopic characterisation of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)\cdot\text{H}_2\text{O}$ , as well as its electrochemical behaviour. We show that the physical and structural properties of this complex contrast with those of its smaller sar analogues.

## Experimental

**CAUTION:** Perchlorate salts are potentially explosive. Although we have experienced no problems with the compounds reported herein, they should only be handled in small quantities, never scraped from sintered glass frits and never heated in the solid state.

### Synthesis

The template synthesis of the ligand *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> as its Co(III) complex  $[\text{Co}(\text{fac-Me}_5\text{-tricosane-N}_6)]\text{Cl}_3\cdot 6\text{H}_2\text{O}$  has been reported.<sup>5</sup>

**Facial-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo-[7.7.7]tricosane hexahydrochloride hexahydrate, *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub>·6HCl·6H<sub>2</sub>O.** The complex  $[\text{Co}(\text{fac-Me}_5\text{-tricosane-N}_6)]\text{Cl}_3\cdot 6\text{H}_2\text{O}$  (1.03 g, 1.54 mmol) was dissolved in water (20 cm<sup>3</sup>), Zn dust (0.42 g, 6.42 mmol) added and the mixture stirred under N<sub>2</sub> for 30 min. While stirring continuously under N<sub>2</sub>, a degassed aqueous HCl solution (8 mol dm<sup>-3</sup>, 20 cm<sup>3</sup>) was introduced dropwise, and this was followed by another addition of degassed HCl (8 mol dm<sup>-3</sup>, 20 cm<sup>3</sup>) after the effervescence had subsided. The cloudy yellow solution was then heated to 70 °C for 90 min and slowly the colour of the solution turned to an intense blue as  $[\text{CoCl}_4]^{2-}$  was generated, indicative of dissociation of the Co(II) cage complex. Finally, the blue solution was cooled to 20 °C and added to water (420 cm<sup>3</sup>) in air. The now pale pink solution containing the protonated free ligand as well as divalent aqua/chloro Co and Zn species was sorbed onto a column of Dowex 50W-X2 resin (5 × 2 cm, H<sup>+</sup> form), which was washed with water (100 cm<sup>3</sup>) and then with 1 mol dm<sup>-3</sup> HCl (50 cm<sup>3</sup>) to remove the zinc(II) and cobalt(II) species. The metal-free polyamine (the major product) eluted from the column with 4 mol dm<sup>-3</sup> HCl (50 cm<sup>3</sup>) as a faint-yellow band, along with some pinkish cobalt(II) impurities. The eluate was evaporated to dryness, redissolved in conc. HCl solution (~10 mol dm<sup>-3</sup>, 2 cm<sup>3</sup>), then precipitated by slow addition of MeOH and then EtOH, and finally cooling in ice to afford an off-white precipitate. The first crop collected, after washing with EtOH and Et<sub>2</sub>O and drying in air yielded 0.53 g (48%). Microanalysis: Found C 36.8; H 9.5; Cl 29.2; N 11.1. C<sub>22</sub>H<sub>66</sub>Cl<sub>6</sub>N<sub>6</sub>O<sub>6</sub> requires C 36.5; H 9.2; Cl 29.4; N 11.6%. <sup>13</sup>C NMR (D<sub>2</sub>O, pD ca. 10): δ 17.23 (CH<sub>3</sub>–CH); 22.24 (CH<sub>3</sub>–Cq); 31.30 (CH); 37.04 (Cq); 56.04, 56.21 (CH<sub>2</sub>).

***fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> (free base).** *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub>·6HCl·6H<sub>2</sub>O (1.0 g, 1.38 mmol) was dissolved in water (2 cm<sup>3</sup>) and adsorbed on a column of Dowex 1-X8 resin (10 × 2 cm), which had previously been converted to its OH<sup>-</sup> form and washed thoroughly with water. The ligand solution was washed well into the resin bed several times with a small head of water, and then eluted from the column using a MeOH/water eluent containing sufficient MeOH to maintain ligand solubility. The eluate was evaporated to dryness leaving a colourless residue that was soluble in MeOH

at 20 °C and slightly soluble in hot MeCN, but poorly soluble in water. The residue was recrystallised from MeCN to give colourless rectangular plates that were collected, washed with Et<sub>2</sub>O and dried in air (yield 0.49 g, 89%). Microanalysis: Found C 66.4; H 12.5; N 20.9. C<sub>22</sub>H<sub>48</sub>N<sub>6</sub> requires C 66.6; H 12.2; N 21.2%. <sup>1</sup>H NMR (CD<sub>3</sub>OD): 0.81 (s, 6H, CH<sub>3</sub>–Cq); δ 0.91 (d, 9H, *J* = 6.7 Hz, CH<sub>3</sub>–CH); 1.96 (m, 3H, X region of ABX system, *J*<sub>AX</sub>, *J*<sub>BX</sub> given below, additional *J* = 6.7 Hz, CH); 2.32, 2.36, 2.72, 2.75 (AB system, 12H, |*J*<sub>AB</sub>| = 11.6 Hz, |*v*<sub>A</sub> – *v*<sub>B</sub>| = 118 Hz, CH<sub>2</sub>–Cq); 2.45–2.56 (8 lines, 12H, AB region of ABX system, |*J*<sub>AB</sub>| = 12.1 Hz, |*v*<sub>A</sub> – *v*<sub>B</sub>| = 1.9 Hz, *J*<sub>AX</sub>, *J*<sub>BX</sub> = –1.21, 13.57 Hz, CH<sub>2</sub>–CH). <sup>13</sup>C NMR (CD<sub>3</sub>OD): δ 17.80 (CH<sub>3</sub>–CH); 24.25 (CH<sub>3</sub>–Cq); 33.85 (CH); 38.96 (Cq); 58.29 (CH<sub>2</sub>–CH); 59.21 (CH<sub>2</sub>–Cq).

**$[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ .** Equimolar quantities of *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> and CuCl<sub>2</sub>·2H<sub>2</sub>O were reacted in EtOH to yield an immediate blue solution of the  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  cation. This was isolated as either the perchlorate or tetrafluoroborate salt by addition of excess NaClO<sub>4</sub> or NaBF<sub>4</sub> and slow evaporation (yield ~70%, first crop). Microanalysis: (perchlorate salt) found C, 36.4; H, 7.3; N, 11.4. C<sub>22</sub>H<sub>48</sub>CuCl<sub>2</sub>·N<sub>6</sub>O<sub>8</sub>·4H<sub>2</sub>O requires C, 36.1; H, 7.7; N, 11.5%; (tetrafluoroborate salt) found C, 39.1; H, 7.4; N, 12.2. C<sub>22</sub>H<sub>52</sub>B<sub>2</sub>F<sub>8</sub>N<sub>6</sub>CuO<sub>2</sub> requires C, 39.5; H, 7.8; N, 12.6%. Recrystallisation of the perchlorate salt from water afforded light blue crystals of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$  suitable for X-ray diffraction.

### Physical methods

<sup>1</sup>H and proton-decoupled <sup>13</sup>C NMR spectra were acquired at 20 °C using a Varian VXR-300 spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to SiMe<sub>4</sub>, with the internal standards in CD<sub>3</sub>OD being CD<sub>3</sub>OD (δ 49.0 ppm) for <sup>13</sup>C and CD<sub>2</sub>HOD (δ 3.30 ppm) for <sup>1</sup>H spectra. For <sup>13</sup>C experiments in D<sub>2</sub>O 1,4-dioxane (δ 67.4 ppm) was used as an internal reference. Electron paramagnetic resonance spectra were measured with a Varian V-4502 spectrometer employing a V-4561 34.99 GHz microwave bridge. The sample temperature was varied with an Oxford ESR9 helium flow cryostat. This was run at high He flow rates (ca. 2.5 dm<sup>3</sup> h<sup>-1</sup>) and calibrated by a carbon resistor in the sample position. Temperature uncertainty in the sample was ca. 0.3 K. The samples were either 1 mmol dm<sup>-3</sup> frozen solutions in DMF–H<sub>2</sub>O (1 : 2) or powders where the EPR active Cu(II) complex was diluted into the EPR silent Zn(II)<sup>8</sup> host. The magnetic moment of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)\cdot\text{H}_2\text{O}$  was determined at 296 K using a vibrating magnetometer. Cyclic voltammetry was performed with a Bioanalytical Systems BAS100 electrochemical analyser employing a glassy carbon working electrode, Ag/AgCl reference and Pt counter electrode. The solution contained 1 mmol dm<sup>-3</sup> analyte and the supporting electrolyte was 0.1 mol dm<sup>-3</sup> NaCl. The electrochemical cell was purged with nitrogen prior to measurement.

### Crystallography

Data were collected at 100 K on an Oxford Diffraction Xcalibur S CCD diffractometer employing graphite-monochromated Mo-Kα radiation. Data reduction and absorption correction were performed with the instrument's CrysAlis software package and also the WinGX<sup>12</sup> suite of programs. The structure was solved

with SHELXS and refined by full-matrix least-squares analysis with SHELXL.<sup>13</sup> A thermal ellipsoid drawing of the complex cation was produced with ORTEP3,<sup>14</sup> while the view illustrating a superposition of the two components to disorder was drawn with PLATON.<sup>15</sup>

The structure was complicated by disorder in both cation and the anions. The complex cation is rotationally disordered about a non-crystallographic two-fold axis bisecting the metal centre and one of the methyl groups attached to the six-membered chelate rings. In other words the two contributors share common positional parameters for the Cu atom, the six N-donors, the five methyl groups and the two quaternary C-atoms in each cap. The occupancies of the two contributors were refined complementarily (converging to a ratio of 84 : 16). The three groups of chemically distinct bonds within the disordered component of the cation (CH<sub>3</sub>-CH, CH<sub>2</sub>-CH and CH<sub>2</sub>-NH) were each restrained and refined with a common C-C or C-N bond length. The bond lengths converged to distances consistent with their bond order and type. Both perchlorate anions were disordered. One anion (containing Cl1) was disordered over two different sites (with 2 positions for each Cl- and O-atom) while the other was disordered about 4 orientations each sharing a common Cl atom (Cl2). Tetrahedral restraints were imposed on the perchlorate anions during refinement.

**Crystal data.** [Cu(*fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, C<sub>22</sub>H<sub>50</sub>-CuN<sub>6</sub>Cl<sub>2</sub>O<sub>9</sub>, *M* = 677.1, *a* = 10.1288(2), *b* = 17.4431(3), *c* = 17.6656(3) Å, β = 99.828(2)°, *V* = 3075.3(1) Å<sup>3</sup>, *D*<sub>c</sub> = 1.462 g cm<sup>-3</sup>, *T* = 100 K, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14, variant of *P*2<sub>1</sub>/*c*), *Z* = 4, μ(Mo-Kα) = 9.4 cm<sup>-1</sup>. 25 895 reflections measured to 2θ = 50° of which 5404 were unique (*R*<sub>int</sub> = 0.0327), 3851 observed with *I* > 2σ(*I*). *R*<sub>1</sub> = 0.060 (obs. data), *wR*<sub>2</sub> = 0.1890 (all data).

CCDC reference number 628563.

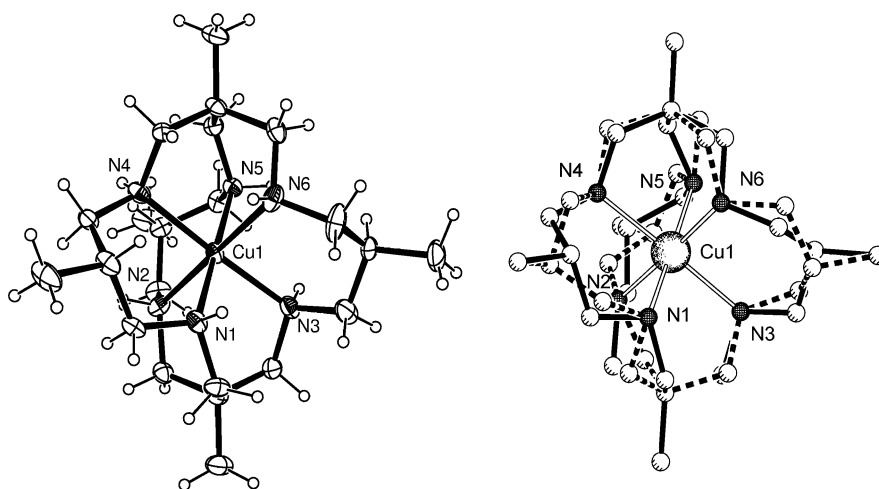
For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617153b

## Results and discussion

Complexation of Cu(II) by the hexadentate ligand *fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub> was straightforward and the compound could be isolated as the tetrafluoroborate or perchlorate salts. The room temperature magnetic moment of [Cu(*fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>)](ClO<sub>4</sub>)·H<sub>2</sub>O (μ<sub>eff</sub> 1.82 μ<sub>B</sub>) is similar to that found for other Cu(II) cage complexes [Cu(sar)]SO<sub>4</sub> (μ<sub>eff</sub> 1.91 μ<sub>B</sub>, 300 K) and [Cu{(NH<sub>3</sub>)<sub>2</sub>sar}]Cl<sub>4</sub>·6H<sub>2</sub>O (μ<sub>eff</sub> 1.92 μ<sub>B</sub>, 300 K),<sup>10</sup> each being consistent with a d<sup>9</sup> electronic ground state (μ<sub>eff</sub> 1.73 μ<sub>B</sub>, spin only). Dissolution of [Cu(*fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub> in 5 mol dm<sup>-3</sup> HCl results in complete release of Cu(II) (*k*<sub>obs</sub> 2.2 × 10<sup>-4</sup> s<sup>-1</sup>, 298 K); a rate approximately four-fold more rapid than dissociation of [Cu(sar)]<sup>2+</sup> under the same conditions.<sup>16</sup> However, as expected, both molecules are much more kinetically stable than the [Cu(en)<sub>3</sub>]<sup>2+</sup> ion in acidic aqueous solution (*k*<sub>obs</sub> ≫ 10<sup>4</sup> s<sup>-1</sup>).

The crystal structure of [Cu(*fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O was determined. As mentioned in the Experimental section, the structure was complicated by disorder in both the complex cation and the perchlorate anions. The cation can be modelled as two complex ions in the same conformation but which are related by a non-crystallographic two-fold axis passing through the Cu atom and the methyl group attached to the six-membered chelate rings on the right hand sides of both drawings in Fig. 2. The two contributors to the disorder share the same CuN<sub>6</sub> atomic coordinates. The ligand conformation is the same seen in the Cr(III),<sup>7</sup> Pt(IV)<sup>6</sup> and Co(III),<sup>5</sup> Zn(II) and Ni(II) complexes<sup>8</sup> of *fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>. The isomorphous Zn(II) and Ni(II) complexes (perchlorate salts) exhibit a similar cation disorder<sup>8</sup> to that seen here.

The crystal structure of [Cu(*fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O also reveals an apparently tetragonally compressed CuN<sub>6</sub> coordination sphere; one pair of *trans* Cu-N bonds (to N1 and N5) is significantly shorter than the remaining four. The *cis* N-Cu-N angles are all close to 90°. A relatively small trigonal twist angle of the CuN<sub>6</sub> moiety is found (φ = 67°; compared

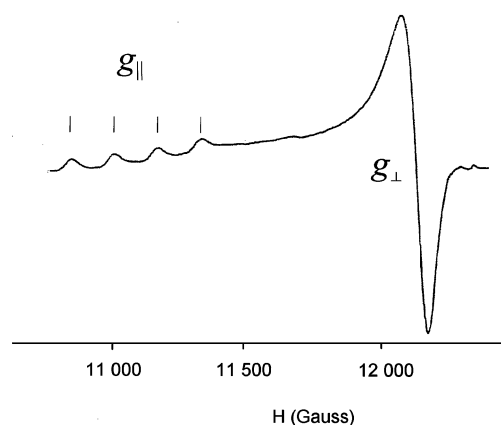


**Fig. 2** View of the [Cu(*fac*-Me<sub>5</sub>-tricosane-N<sub>6</sub>)]<sup>2+</sup> complex cation (30% ellipsoids). Left, ORTEP plot of major contributor (84%); right, PLATON superposition of both contributors to the disorder in the same orientation as shown in ORTEP view (H-atoms omitted for clarity). Coordinate bond lengths (Å) and angles (°): N(1)-Cu(1) 2.088(3), N(2)-Cu(1) 2.194(4), N(3)-Cu(1) 2.198(4), N(4)-Cu(1) 2.224(4), N(5)-Cu(1) 2.075(3), N(6)-Cu(1) 2.231(4); N(5)-Cu(1)-N(1) 178.25(12), N(5)-Cu(1)-N(2) 95.52(11), N(1)-Cu(1)-N(2) 86.20(12), N(5)-Cu(1)-N(3) 91.49(14), N(1)-Cu(1)-N(3) 88.79(13), N(2)-Cu(1)-N(3) 89.57(12), N(5)-Cu(1)-N(4) 86.42(13), N(1)-Cu(1)-N(4) 93.26(13), N(2)-Cu(1)-N(4) 92.10(12), N(3)-Cu(1)-N(4) 177.44(11), N(5)-Cu(1)-N(6) 87.20(12), N(1)-Cu(1)-N(6) 91.07(13), N(2)-Cu(1)-N(6) 177.12(13), N(3)-Cu(1)-N(6) 91.29(12), N(4)-Cu(1)-N(6) 87.14(12).

with  $60^\circ$  for ideal trigonal antiprismatic and  $0^\circ$  for trigonal prismatic—see Chart 1).<sup>†</sup> By comparison, the crystal structure of  $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ <sup>11</sup> reveals a much larger trigonal twist distortion ( $\phi = 28^\circ$ ), coupled with a tetragonal elongation.

EPR spectroscopy has been traditionally the most effective tool for elucidating the true ground state electronic configuration of mononuclear Cu(II) complexes.<sup>17</sup> Briefly, in the  $d^9$  electronic configuration of a six-coordinate Cu(II) complex, the single unpaired electron will reside in either the  $d_{x^2-y^2}$  orbital for tetragonally elongated complexes (more common), or the  $d_{z^2}$  orbital for a tetragonally compressed geometry. For magnetically dilute systems (no exchange coupling) exhibiting pseudo-axial symmetry, a  $d_{x^2-y^2}$  ground state will give rise to an EPR spectrum with  $g_{\parallel} (g_z) > g_{\perp} (g_x = g_y)$ . Hyperfine coupling between the unpaired electron and the  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  nuclei (both  $I = 3/2$ ) should split the  $g_{\parallel}$  and  $g_{\perp}$  resonances into four lines each separated by their respective hyperfine coupling constants  $A_{\parallel}$  and  $A_{\perp}$ ; for tetragonally elongated geometries it is usual that  $A_{\parallel} \gg A_{\perp}$ . The ordering of the  $g$  values is reversed for tetragonally compressed structures and a so-called 'inverse' EPR spectrum is found ( $g_{\parallel} < g_{\perp}$ ).<sup>3,17</sup>

The frozen solution EPR spectrum of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  (DMF– $\text{H}_2\text{O}$  1 : 2, 40 K) is shown in Fig. 3. A classic axial EPR spectrum is seen comprising two sets of resonances where the magnetic field is either parallel with or perpendicular to the unique axis. Spin Hamiltonian values of  $g_{\parallel} = 2.25$  ( $A_{\parallel} = 160$  G) and  $g_{\perp} = 2.06$  were obtained;  $A_{\perp}$  was too small to enable its resolution from the broad peak around 12 000 G. These values are clearly consistent with a tetragonally elongated structure and not the 'apparent' compressed structure that is suggested by the crystal structure analysis. The spin Hamiltonian values may be compared with those obtained for the smaller cavity homologues  $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}]^{4+}$  and  $[\text{Cu}\{(\text{NMe}_3)_2\text{sar}\}]^{4+}$  ( $g_z = 2.22$  ( $A_z = 130$  G),  $g_y = 2.11$ ,  $g_x = 2.07$  which show rhombic symmetry) under the same experimental conditions.<sup>11</sup>

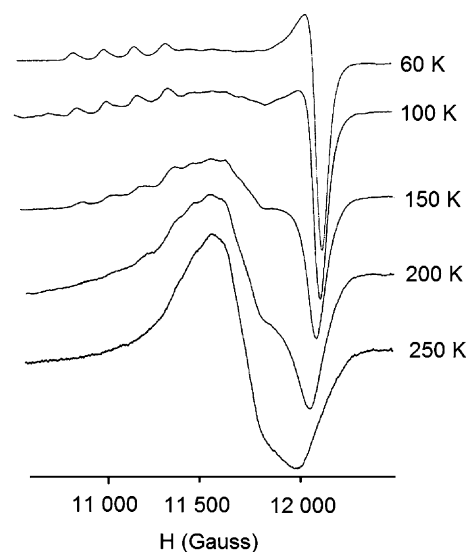


**Fig. 3** Q-Band (34.96 GHz) EPR spectrum of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2$  in a DMF– $\text{H}_2\text{O}$  1 : 2 glass at 40 K. The  $g_{\parallel}$  and  $g_{\perp}$  transitions are indicated and the hyperfine coupling constant  $A_{\parallel}$  is derived from the equal separation of the vertical bars centred at  $g_{\parallel}$ .

<sup>†</sup> In this case  $\phi > 60$  indicates that the pairs of donor atoms connected by each chelate ring are pushed further apart by the trigonal twist. The opposite is the case in the smaller cavity sar cages ( $\phi < 60^\circ$ ) where the less flexible five-membered chelate rings bring the connected pairs of donor atoms closer towards an eclipsed conformation ( $\phi = 0^\circ$ ).

The EPR spectra of tetragonally elongated six-coordinate Cu(II) complexes (with weakly bound axial ligands) are very sensitive to distortions of the coordinate angles away from their ideal values of  $90^\circ$  (*cis*) and  $180^\circ$  (*trans*).<sup>18</sup> It is known that distortions away from an ideal tetragonal structure lower  $A_{\parallel}$  and raise  $g_{\parallel}$ ; a linear relationship between these two parameters has been identified in a number of different ligand systems.<sup>18,19</sup> In the present systems, the most relevant ligand-derived distortion is due to the trigonal twist imposed on the six-coordinate geometry by the constraints of the cage. Trigonal twist distortions away from an ideal trigonal antiprism ( $\phi = 60^\circ$ ) are most significant in the smaller cages  $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}]^{4+}$  and  $[\text{Cu}\{(\text{NMe}_3)_2\text{sar}\}]^{4+}$  ( $\phi = 28^\circ$ ). By contrast, the trigonal twist distortion in  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  ( $\phi = 67^\circ$ ) is modest and the N–Cu–N coordinate angles are all close to  $90^\circ$  or  $180^\circ$ . Similar trigonal twist angles have been identified in other hexaazabicyclo-tricosane homologues bearing the same N-based isomeric configuration *e.g.* Rh(III),<sup>20</sup> Co(III),<sup>5</sup> Zn(II)<sup>8</sup> and Cr(III).<sup>7</sup>

The 60 K solid state EPR spectrum of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  diluted (1%) into the lattice of its EPR silent, isomorphous Zn(II) analogue<sup>8</sup> (Fig. 4, top) is also consistent with a tetragonally elongated Cu(II) $\text{N}_6$  geometry. The same spin Hamiltonian parameters found in the frozen solution spectrum were obtained. Upon warming to 100 K, minor features apparent at 60 K at 11 750 G become more intense and continue to grow as the temperature is raised until they dominate the spectrum at 250 K. The set of four lines centred at  $g_{\parallel} = 2.25$  at low temperature shift to higher field until they merge with the dominant resonance centred at 11 750 G. Above 200 K hyperfine coupling is gradually lost altogether and the spectrum approaches that of an isotropic system at room temperature. The solid state EPR spectra of undiluted  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2$  is devoid of any hyperfine coupling at all temperatures due to exchange between neighbouring paramagnetic centres and was of no diagnostic value.



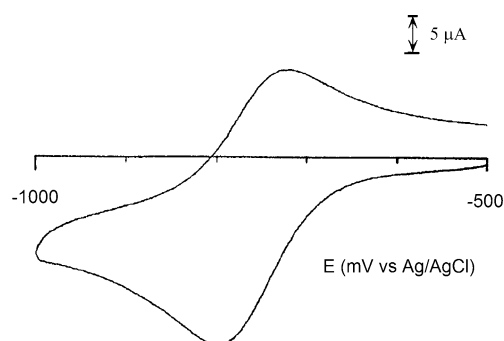
**Fig. 4** Q-Band (34.96 GHz) powder EPR spectra of 1%  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2$  diluted into  $[\text{Zn}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2$  at (from top to bottom) 60 K, 100 K, 150 K, 200 K and 250 K.

The temperature dependence of the powder EPR spectra is indicative of thermally activated dynamic interconversion (on the

EPR timescale) between the three orthogonal structures shown in Fig. 1(b). Given that dynamic behaviour is already apparent at 60 K (minor peaks around 11 750 G) the classical barrier height between the potential wells in Fig. 1(b) may be estimated to be less than  $40 \text{ cm}^{-1}$ . In a sense this interconversion in the solid state (on a timescale shorter than the EPR transition) has a similar result as molecular tumbling in fluid solutions by removing the anisotropy of the spectrum.

In aqueous solution  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  exhibits two weak d-d transitions at 616 nm ( $\epsilon = 59 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and a lower energy (NIR) and particularly broad maximum at 1 330 nm ( $\epsilon = 6 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). A charge transfer band at 270 nm ( $\epsilon = 5 610 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) is also seen. The two weaker bands are characteristic of a tetragonally distorted Cu(II) cage complex, although the nature of the distortion (elongation or compression) cannot be deduced from these data.<sup>11</sup> On the basis of our EPR data, the  $\text{CuN}_6$  chromophore is certainly tetragonally elongated. Thus, the NIR band is due to an electronic transition between the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals (split by the Jahn–Teller distortion). The 616 nm band is due to an overlap of transitions from the three lowest energy d orbitals (all of similar energy) to the half filled  $d_{x^2-y^2}$  orbital. The 616 nm band is at significantly higher energy and has a lower extinction coefficient than found for the smaller Cu(II) cage complexes such as  $[\text{Cu}\{(\text{NH}_3)_2\text{sar}\}]^{2+}$  (658 nm,  $\epsilon = 140 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).<sup>11</sup> This is qualitatively consistent with the observed angular distortions seen in the smaller cavity cage complexes, which lower the effective ligand field strength of the hexaamine.

Cyclic voltammetry of an aqueous solution of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  is shown in Fig. 5. A quasi-reversible Cu(II/I) couple is found at  $E^0 -0.76 \text{ V vs Ag/AgCl}$  ( $\Delta E_p = 84 \text{ mV}$ ) at  $100 \text{ mV s}^{-1}$ . However, at slower scan rates the ratio of the anodic to cathodic peak currents drops considerably below unity ( $i_a/i_p = 0.43$  at  $20 \text{ mV s}^{-1}$ ). This is indicative of an irreversible chemical reaction following reduction to the monovalent state. This is most likely dissociation of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^+$  and the sweep rate dependence of  $i_a/i_p$  was used to provide an estimation for the half-life of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^+$  under these conditions as ca. 2 s. The lifetime of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^+$  is about 3 orders of magnitude greater than that of  $[\text{Cu}(\text{sar})]^+$  ( $t_{1/2}$  ca. 1 ms) which was generated by pulse radiolysis reduction of the divalent complex.<sup>21</sup>



**Fig. 5** Cyclic voltammogram of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (pH 6, sweep rate  $100 \text{ mV s}^{-1}$ ).

At voltammetric sweep rates higher than  $100 \text{ mV s}^{-1}$  the peak-to-peak separation  $\Delta E_p$  increases and the peaks broaden. This may

be due to conformational changes accompanying reduction and re-oxidation that become rate limiting to electron transfer (so-called conformational gating). Although the solution structure of  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  is now well established, we can only speculate on the geometry of the Cu(I) analogue formed electrochemically. A coordination number of 6 for Cu(I) would be unusual. Crystallographically characterised six-coordinate Cu(I) complexes are rare<sup>22,23</sup> (excluding metal–metal bonded systems) and one of these two examples is a coordination polymer. A coordination number lower than 6 is likely upon reduction in line with the usual low coordination numbers of Cu(I) complexes, but bond breaking and reforming upon reduction and oxidation should still be facile if the Cu(I) ion is confined to remain inside the cage. Reversible or quasi-reversible Cu(II/I) electrochemistry is more typical of conformationally flexible  $\text{CuN}_4$  systems where the ligand can alter its conformation to accommodate the larger Cu(I) ion, even to the point of adopting a pseudo-tetrahedral geometry.<sup>24,25</sup>

## Conclusions

We have shown that expansion of the cavity size going from the smaller sar cage to *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> leads to some interesting contrasts between their respective coordination chemistries. Although the expanded size of the *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> cage has until now been associated with a lengthening of the coordinate bonds and a concomitant weakening of the ligand field relative to the smaller cavity sar analogues,<sup>5</sup> the present study has shown that this is not a general feature. The Cu(II) complex of *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> features a stronger ligand field as a consequence of its relatively small trigonal twist distortion. Despite an apparent tetragonally compressed geometry emerging from the crystal structure analysis, spectroscopy has shown that  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+}$  is another example of a truly tetragonally elongated Cu(II) complex whose true structure has eluded crystallographic characterisation. At 60 K and above the powder EPR spectrum indicates that dynamic interconversion between the two more stable minima in Fig. 1(b) is significant. The crystal structure performed at 100 K then must be interpreted as being dynamic but is further complicated by cation disorder between two (non-interconvertible) diastereomers. Notwithstanding the ligand disorder, a model may be proposed comprising a 1 : 1 disorder of two tetragonally elongated structures where the short N1–Cu1–N5 axis is common to both forms but the remaining two axes (one long and one short) are effectively disordered. Thermal ellipsoid librational analyses of apparently symmetrical or tetragonally compressed Cu(II)N<sub>6</sub> complexes have met with mixed success.<sup>26,27</sup> The main conclusion is that, once more, crystallographic characterisation of any Cu(II) complex with six chemically equivalent ligands must be viewed with caution.

Of particular note was the quasi-reversible  $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^{2+/+}$  couple ( $t_{1/2}$   $[\text{Cu}(\text{fac-Me}_5\text{-tricosane-N}_6)]^+ \sim 2 \text{ s}$ ), which contrasts with the smaller cavity sar complexes where the cuprous oxidation state survives for only milliseconds. The larger cavity of the expanded *fac-Me*<sub>5</sub>-tricosane-N<sub>6</sub> cage may be better able to accommodate the large Cu(I) ions within its confines and hence dissociation is sufficiently delayed that quasi-reversible electrochemistry can be observed. This is a subtle consequence

of the significantly larger and less trigonally twisted  $N_6$  cavity provided by the interesting  $Me_5$ -tricosane- $N_6$  cage.

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