Comparison of copper imine and amine podates: geometric consequences of podand size and donor type

Joanne L. Coyle, Anna Fuller, Vickie McKee and Jane Nelson

Chemistry Department, The Open University, Milton Keynes MK7 6AA, England, and Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, England

Correspondence e-mail: v.mckee@lboro.ac.uk

Received 11 August 2006
Accepted 28 August 2006
Online 12 September 2006

The imine podands tris[(2-nitrobenzylidene)aminoethyl]amine and tris[(2-nitrobenzylidene)aminopropyl]amine both stabilize copper(I), forming [tris[(2-nitrobenzylidene)aminoethyl]amine-κN]copper(I) perchlorate acetonitrile disolvate, [Cu(C27H27N7O6)ClO4]2CH3CN, (II), and [tris[(2-nitrobenzylidene)aminopropyl]amine-κN]copper(I) perchlorate, [Cu(C30H33N7O6)ClO4], (VI), respectively. The larger propyl-based ligand is a poorer fit for the Cu I ion. The reduced amine podand tris[(2-nitrobenzyl)aminoethyl]amine binds Cu II and the resulting compound, chloro[tris[(2-nitrobenzyl)aminoethyl]amine-κN]copper(II) chloride ethanol solvate, [Cu(C27H33N7O6)Cl]ClC2H5OH, (IV), shows both intra- and intermolecular hydrogen bonding, which gives rise to $RRS$ or $SSR$ conformations in the podand strands rather than the expected pseudo-threefold symmetry.

Comment

We have had a long-standing interest in the chemistry of both imine and amine cryptates derived from tris(aminoethyl)amine (tren) and tris(3-aminoisopropyl)amine (trpn) [see, for example, McKee et al. (2003) and Nelson et al. (1998)]. We have investigated some simple podate complexes derived from the same amines in order to clarify the geometric requirements associated with each (Coyle, 1999). A search of the Cambridge Structural Database (Version 5.27; Allen, 2002; Fletcher et al., 1996) showed that, although many tris(aminoethyl)amine/salicylate complexes have been investigated, surprisingly few simple podates with other substituted benzaldehyde derivatives have been structurally characterized to date. In this paper, we compare the structures of two Cu I podates, one derived from tris(aminoethyl)amine (tren) and one from tris(aminopropyl)amine (trpn), with the Cu II amine analogue of the smaller tren-based podate.

In podate and cryptate complexes with potential threefold symmetry, imine donors typically stabilize Cu I and are easily hydrolysed by Cu II (Harding et al., 1995; Arthurs et al., 2001). Reduction of the imine donors to the corresponding amines generates a site in which Cu I is activated to reaction with dioxygen, as shown elegantly by Suzuki, Schindler and their co-workers (Komiyama et al., 2004; Schatz et al., 2001). However, Cu II binds readily to the reduced ligands.
and perpendicular to the plane of the three \( sp^2 \)-hybridized imine donors); the interplanar angles are 71.6 (1), 73.5 (1) and 74.1 (1)° for the N11, N21 and N31 strands, respectively. In other words, the orientation of the conjugated nitrobenzylidene strands is determined by the orientation of the imine lone pairs. It is therefore not surprising that this geometry is common for tren-based imine podands in the absence of additional intra- or intermolecular interactions. There are no significant interactions between the cation and perchlorate anion or solvent molecules. The anion is disordered and was modelled with approximately 10% occupancy of the minor orientation (Fig. 1).

The amine podand, tris[2-nitrobenzylaminoethyl]amine, (III), was obtained by reduction of (I) with NaBH\(_4\), which reduced the imine groups but not the nitro substituents. Reaction of ligand (III) with CuCl\(_2\) in ethanol yielded the amine complex [Cu(III)Cl]Cl\(_2\)C\(_2\)H\(_5\)OH, (IV), as green crystals. The formula unit of (IV) is shown in Fig. 2. The geometry at the Cu\(^{\text{II}}\) ion is approximately trigonal–bipyramidal (Table 2), with the bridgehead tertiary amine and the coordinated Cl\(^{-}\) ion as apical donors. The coordination geometry is similar to that observed for the analogous Cu\(^{\text{II}}\) podate derived from benzaldehyde [tris(benzylaminoethyl)amine; Komiyama et al., 2004; Schatz et al., 2001].

Two of the nitro groups of (IV) are hydrogen bonded to the adjacent secondary amines (Table 3), but the third strand is different, with the amine (N31) hydrogen bonded to the ethanol solvent molecule. Consequently, the configuration at N31 is opposite to that at N11 and N21 (SRR in Fig. 2, although, since the structure is centrosymmetric, the RSS configuration is also present). This difference breaks the pseudo-threefold symmetry of the cation. The non-coordinated Cl\(^{-}\) ion Cl2 makes a relatively short hydrogen bond to the ethanol solvent molecule [3.105 (4) Å] and shows further interactions with N21 and with N11 of an adjacent molecule. The latter two interactions are long for hydrogen bonds to Cl\(^{-}\), at 3.302 (4) and 3.474 (4) Å, respectively (Steiner, 2002). However, both are bifurcated and involve coordinated amines. The resulting hydrogen-bond pattern links the structure in chains running parallel to the \( b \) axis (Fig. 3). The most notable

**Figure 1**
The structure of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The minor component of the disordered ClO\(_4\)^{-} ion is indicated by open bonds.

**Figure 2**
The structure of complex (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

**Figure 3**
A packing plot for complex (IV), viewed down the \( b \) axis. Hydrogen bonds are shown as dashed lines and the \( \pi-\pi \) interactions are indicated by open bonds linking ring centroids. Key: Cl atoms are shown cross-hatched, Cu atoms are shaded top left to bottom right, N atoms are dotted, and O atoms are shaded bottom left to upper right.
interaction between these chains is a $\pi-\pi$ interaction between
the C24–C29 ring and its symmetry equivalent by inversion
under $1 \times x, -y, 1 - z$; the rings are necessarily parallel, the
interplanar distance is 3.393 (4) Å and centroid-to-centroid
distance is 3.710 (4) Å.

Complex (VI), namely [tris(2-nitrobenzylidene)aminomethyl]amine|copper(I) perchlorate, is analogous to complex
(II), except that the longer tripodal amine tris(aminomethyl)amine (trpn) is used in place of tren. As for (II), the Cu
ion is stabilized in the $+1$ state and has trigonal–pyramidal
gometry (Fig. 4 and Table 4). However, the Cu$^+$ ion is
placed from the imine plane by 0.167 (1) Å towards the
bridgehead $[i.e. \text{in the opposite sense from complex (II)}]$. As
observed for complex (II), the requirement to coordinate the
Cu$^+$ ion to all four N-atom donors results in tilting of the C–
N atoms; the average angle is 114.4 (3)$^\circ$.

The three-dimensional ‘podand bite’ in the two Cu$^+$
complexes, (II) and (VI), can be compared by considering the
dimensions of the trigonal pyramid formed by the four N-atom
donors, with the tertiary amine (N1) at the apex and the imine
atoms N11, N21 and N31 in the basal plane. As mentioned
above, the Cu$^+$ ion is outside the pyramid in complex (II) and
inside for (VI). However, the Cu–N1 distances are identical
[2.196 (2) Å] and the Cu–N(imine) bonds are only marginally
different [mean values 2.003 (2) Å for (II) and 2.018 (2) Å for
(VI)]. The mean imine–imine distances in the basal plane are
similar [3.456 and 3.483 Å for (II) and (VI), respectively], but
the mean base–apex edges are significantly different
[2.842 (2) Å for (II) and 3.103 (2) Å for (VI)]. An indication of
steric strain in complex (VI) is given by the N–C–C and C–
C–C angles in the saturated chain between N1 and the imine
N atoms; the average angle is 114.4 (3)$^\circ$, compared with
110.5 (2)$^\circ$ for complex (II).

![Figure 4](image)

The structure of complex (VI), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

We have observed similar patterns in the geometry of Cu
ions in cryptand hosts derived from tren and trpn $[s.e. \text{for example, } \text{Farrar} \text{ et al. (1995)} \text{and } \text{Nelson et al. (1998)}]$, supporting the suggestion that steric constraints mean that the
larger podand has more difficulty accommodating bonding
between the Cu$^+$ ion and all four donors than the smaller
analogue. These results also go some way to explaining the
initially counterintuitive finding that, in the dinuclear imino-
cryptate series, the shortest internuclear distances between
cationic guests are found for the larger hosts (Drew $et$ $al.$, 2000;
Farrar $et$ $al.$, 1995; Nelson $et$ $al.$, 1998). In the case of the
cryptand ligands, the twist imposed on each strand by the
coordination of the imine donors shortens the distance
between the two metal binding sites.

**Experimental**

For the preparation of [Cu$^+$(II)]ClO$_4$·2CH$_3$CN, (II), tris(2-nitrobenzylidene)aminoethyl]amine, (I) (0.93 g, 1.7 mmol), was dissolved in dry deoxygenated acetoni-trile (30 ml) and a solution of
Cu(CH$_3$CN)$_3$ClO$_4$ (0.55 g, 1.7 mmol) in deoxygenated acetoni-trile
(20 ml) was added slowly with stirring. The red-brown solution was stirred for 30 min at 313 K and then cooled, during which time an orange crystalline product precipitated. This was filtered off and
dried under nitrogen, losing the acetoni-trile solvent in the process
(yield 0.70 g, 52%). Analytical results (available in the archived CIF)
are consistent with the stated composition for all compounds
reported here.

The amine podand tris(2-nitrobenzyl)aminoethyl]amine, (III),
was prepared by reduction of the imine analogue (Liu $et$ $al.$, 1992).
The imine (1) (2.15 g, 3.9 mmol) was dissolved in methanol (60 ml).
Na$_2$B$_4$O$_7$ (0.81 g, 4.0 mmol) was added, followed by NaBH$_4$ (0.65 g,
17.2 mmol) in small portions over a period of 30 min. The solution
was stirred for 2 h and then the solvent was removed on a rotary
evaporator. NH$_4$Cl (4 g, 76 mmol) in water (40 ml) was added and the
mixture was extracted with CHCl$_3$ (3 x 60 ml). The CHCl$_3$ solution
was washed with water, dried over MgSO$_4$ and filtered. Finally, the
solvent was removed under reduced pressure to yield the amine as a
pale-yellow oil (yield ca 88%). The IR spectrum of the oil confirmed
that the ligand had been successfully reduced. The imine stretch at ca
1630 cm$^{-1}$ was no longer present, but symmetric and antisymmetric
stretches of the nitro group at 1347 and 1526 cm$^{-1}$, respectively,
confirmed that the substituent remained unchanged. The amine
was used in the next step without further purification.

For the preparation of [Cu$^+$(III)]Cl·C$_2$H$_5$OH, (IV), the amine
ligand (III) (0.05 g, 0.09 mmol) was dissolved in ethanol (1.5 ml),
forming a pale-orange solution. On addition of a solution containing
CuCl$_2$ (0.013 g, 0.09 mmol) in ethanol (1 ml), a turquoise solution was
formed. Green crystals of (IV) were obtained on allowing the solu-
tion to stand (yield 0.03 g, 48%).

Ligand (V) was prepared by the dropwise addition of tris(3-
aminopropyl]amine (0.32 g, 1.7 mmol) in methanol (20 ml) with
stirring to nitrobenzaldehyde (0.77 g, 5.1 mmol) in methanol (20 ml).
The resulting solution was stirred at 313 K for 30 min and the volume
was then reduced to yield a yellow oil, viz. (V). The oil was dissolved in
deoxygenated acetoni-trile (30 ml) and Cu(CH$_3$CN)$_3$ClO$_4$ (0.55 g,
1.7 mmol) was added. A brown solution formed and dark-red crystals
of [Cu$^+$(V)]ClO$_4$·(VI), were obtained on allowing the solution to
stand (yield 0.69 g, 54%).
**Compound (II)**

**Crystal data**

\[ \text{[Cu(C_5H_4N_3O_6)]ClO}_4 \cdot 2\text{C}_2\text{H}_5\text{N} \]

- \( M_r = 790.65 \)
- Triclinic, \( P^\text{T} \)
- \( a = 11.178 (7) \text{ Å} \)
- \( b = 13.3595 (9) \text{ Å} \)
- \( c = 13.7998 (9) \text{ Å} \)
- \( \alpha = 111.627 (11) \)°
- \( \beta = 102.995 (11) \)°
- \( \gamma = 103.648 (11) \)°

Absorption correction: multi-scan

**Data collection**

Bruker SMART 1000 CCD area-detector diffractometer

- 15023 measured reflections
- 7856 independent reflections
- 6372 reflections with \( I > 2\sigma(I) \)

Refinement

Reefinement on \( \text{F}^2 \)

- \( wR(\text{F}^2) = 0.082 \)
- \( S = 1.02 \)
- 7856 reflections
- 480 parameters
- H-atom parameters constrained

**Selected geometric parameters (Å, °) for (II).**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1—N11</td>
<td>2.105 (4)</td>
<td>83.97 (16)</td>
</tr>
<tr>
<td>Cu1—N31</td>
<td>2.0326 (17)</td>
<td>127.92 (16)</td>
</tr>
<tr>
<td>N11—Cu1—N1</td>
<td>120.56 (6)</td>
<td>94.59 (8)</td>
</tr>
<tr>
<td>N31—Cu1—N1</td>
<td>118.25 (6)</td>
<td>85.48 (6)</td>
</tr>
</tbody>
</table>

**Compound (IV)**

**Crystal data**

\[ \text{[Cu(C_5H_3N_2O_7)]ClO}_4 \]

- \( M_r = 732.11 \)
- Monoclinic, \( P_2_1/c \)
- \( a = 13.183 (5) \text{ Å} \)
- \( b = 14.485 (6) \text{ Å} \)
- \( c = 16.914 (7) \text{ Å} \)
- \( \beta = 95.319 (7) \)°
- \( V = 3216 (2) \text{ Å}^3 \)

Absorption correction: multi-scan

**Data collection**

Bruker SMART 1000 CCD area-detector diffractometer

- 22643 measured reflections
- 5657 independent reflections

Refinement

Refinement on \( F^2 \)

- \( wR(F^2) = 0.090 \)
- \( S = 1.00 \)
- 7892 reflections
- 455 parameters
- H-atom parameters constrained

**Selected geometric parameters (Å, °) for (IV).**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1—N1</td>
<td>2.038 (4)</td>
<td>80.83 (5)</td>
</tr>
<tr>
<td>Cu1—N11</td>
<td>2.081 (4)</td>
<td>83.69 (5)</td>
</tr>
<tr>
<td>Cu1—N21</td>
<td>2.105 (4)</td>
<td>83.97 (16)</td>
</tr>
<tr>
<td>N1—Cu1—N11</td>
<td>80.83 (5)</td>
<td>83.69 (5)</td>
</tr>
<tr>
<td>N11—Cu1—N21</td>
<td>83.97 (16)</td>
<td>83.69 (5)</td>
</tr>
</tbody>
</table>

**Compound (VI)**

**Crystal data**

\[ \text{[Cu(C_5H_3N_2O_7)]ClO}_4 \]

- \( M_r = 750.62 \)
- Monoclinic, \( P_2_1/c \)
- \( a = 9.5361 (7) \text{ Å} \)
- \( b = 18.6870 (13) \text{ Å} \)
- \( c = 19.2567 (13) \text{ Å} \)
- \( \beta = 104.044 (11) \)°
- \( V = 3325.5 (4) \text{ Å}^3 \)

Absorption correction: multi-scan

**Data collection**

Bruker SMART 1000 CCD area-detector diffractometer

- 28475 measured reflections
- 7892 independent reflections

Refinement

Refinement on \( F^2 \)

- \( wR(F^2) = 0.082 \)
- \( S = 1.00 \)
- 7733 reflections
- 455 parameters
- H-atom parameters constrained

**Selected geometric parameters (Å, °) for (VI).**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1—N1</td>
<td>2.0124 (19)</td>
<td>80.83 (5)</td>
</tr>
<tr>
<td>Cu1—N11</td>
<td>2.0326 (17)</td>
<td>83.69 (5)</td>
</tr>
<tr>
<td>N1—Cu1—N11</td>
<td>80.83 (5)</td>
<td>83.69 (5)</td>
</tr>
<tr>
<td>N11—Cu1—N21</td>
<td>83.97 (16)</td>
<td>83.69 (5)</td>
</tr>
</tbody>
</table>

For all three compounds, H atoms were inserted in calculated positions and refined using a riding model. The constrained distances were 0.95, 0.99, 0.98, 0.93 and 0.84 Å for aryl, methylene, methyl, amine and alcohol H atoms, respectively. They were refined with
iso(H) = 1.2U\text{eq}(\text{carrier atom}). The value of R_{int} for complex (IV) is high (0.103) due to poor crystal quality resulting in broad diffraction peaks.

For all compounds, data collection: \textit{SMART} (Bruker, 1998); cell refinement: \textit{SMART}; data reduction: \textit{SAINT} (Bruker, 1998); program(s) used to solve structure: \textit{SHELXS97} (Sheldrick, 1997); program(s) used to refine structure: \textit{SHELXL97} (Sheldrick, 1997); molecular graphics: \textit{SHELXTL} (Sheldrick, 2001); software used to prepare material for publication: \textit{SHELXTL}.

The authors thank the Leverhulme Foundation, Unilever Research and Development and the Open University for support. They also acknowledge the use of the EPSRC Chemical Database Service at Daresbury.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3035). Services for accessing these data are described at the back of the journal.

References