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

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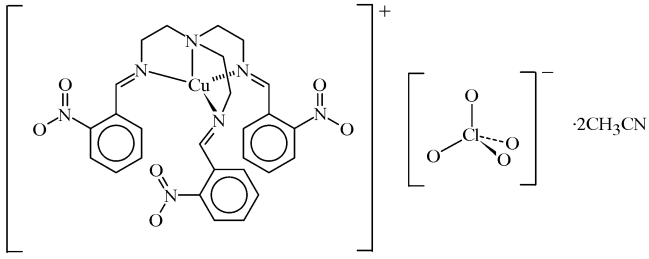
The imine podands tris[(2-nitrobenzylidene)aminoethyl]amine and tris[(2-nitrobenzylidene)aminopropyl]amine both stabilize copper(I), forming {tris[(2-nitrobenzylidene)aminoethyl]amine-κ^4N}copper(I) perchlorate acetonitrile disolvate, $[Cu(C_{27}H_{27}N_7O_6)]ClO_4\cdot 2CH_3CN$, (II), and {tris[(2-nitrobenzylidene)aminopropyl]amine-κ^4N}copper(I) perchlorate, $[Cu(C_{30}H_{33}N_7O_6)]ClO_4$, (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-κ^4N}copper(II) chloride ethanol solvate, $[Cu(C_{27}H_{33}N_7O_6)Cl]Cl\cdot C_2H_5OH$, (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.

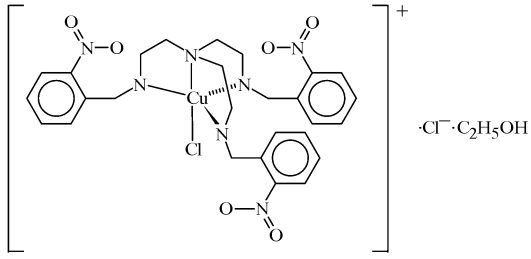
Comment

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.

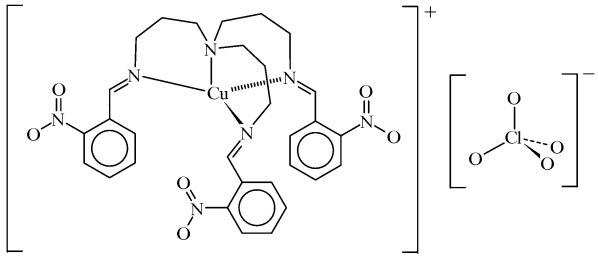
In podate and cryptate complexes with potential threefold symmetry, imine donors typically stabilize Cu^I and are easily hydrolysed by Cu^{II} (Harding *et al.*, 1995; Arthurs *et al.*, 2001). Reduction of the imine donors to the corresponding amines generates a site in which Cu^I is activated to reaction 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.



(II)



(IV)



(VI)

The structure of the imine podand tris[(2-nitrobenzylidene)aminoethyl]amine, (I), was reported recently (McKee *et al.*, 2006). Reaction of (I) with $Cu(CH_3CN)_4ClO_4$ in acetonitrile gave the Cu^I complex $[Cu(I)]ClO_4\cdot 2CH_3CN$, (II), as dark-brown crystals (Fig. 1). The Cu^I ion is coordinated to all four N atoms in an approximately trigonal–pyramidal geometry (Table 1), although the bonds to the imine N atoms [average 2.003 (2) Å] are significantly shorter than that to the bridgehead amine [Cu1—N1 = 2.196 (1) Å], and the Cu^I ion is 0.172 (1) Å out of the mean plane of the imine N atoms in the opposite direction to the bridgehead. The nitro groups are not involved in the coordination of the metal and the three strands are arranged fairly tightly about the approximate threefold axis. There are two important factors controlling this geometry, namely the essentially planar geometry at the imine N atoms [angle sums 359.9 (2), 359.9 (2) and 359.8 (2)° for atoms N11, N21 and N31, respectively] and the steric demands imposed by coordination of all four N donors of the ligand. These result in the C—N═C plane being tilted with respect to the 'default' orientation (parallel to the pseudo-threefold axis

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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).

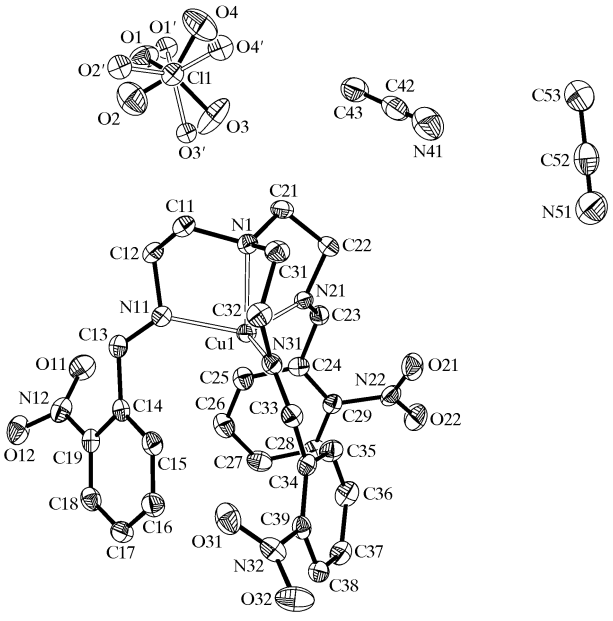

Figure 1
The structure of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The minor component of the disordered ClO_4^- ion is indicated by open bonds.

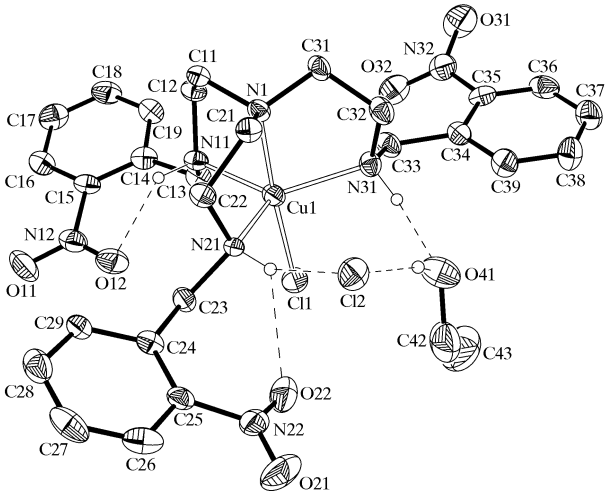

Figure 2
The structure of complex (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

The amine podand, tris[(2-nitrobenzyl)aminoethyl]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 $[Cu(III)Cl]Cl\cdot C_2H_5OH$, (IV), as green crystals. The formula unit of (IV) is shown in Fig. 2. The geometry at the Cu^I ion is approximately trigonal–bipyramidal (Table 2), with the bridghead tertiary amine and the coordinated Cl^- ion as apical donors. The coordination geometry is similar to that observed for the analogous Cu^{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

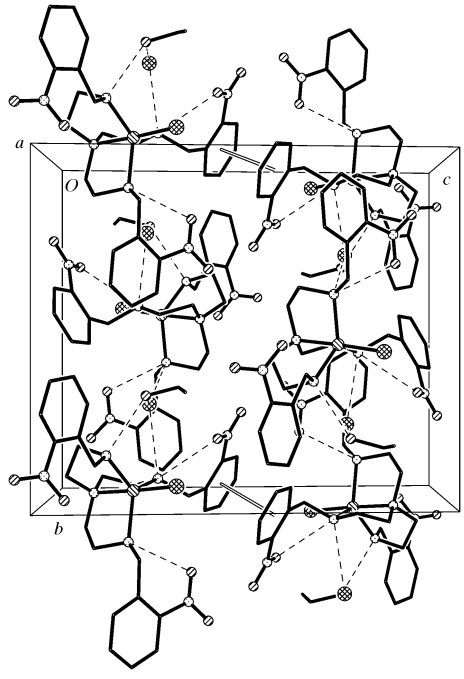

Figure 3
A packing plot for complex (IV), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines and the π–π interactions are indicated by open bonds linking ring centroids. Key: Cl atoms are shown cross-hatched, Cu atoms are shaded top left to bottom right, N atoms are dotted, and O atoms are shaded bottom left to upper right.

interaction between these chains is a π–π interaction between the C24–C29 ring and its symmetry equivalent by inversion under $(1-x, -y, 1-z)$; 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)aminopropyl]amine}copper(I) perchlorate, is analogous to complex (II), except that the longer tripodal amine tris(aminopropyl)amine (trpn) is used in place of tren. As for (II), the Cu ion is stabliized in the +1 state and has trigonal–pyramidal geometry (Fig. 4 and Table 4). However, the Cu^{I} ion is displaced from the imine plane by 0.167 (1) Å towards the bridgehead [*i.e.* in the opposite sense from complex (II)]. As observed for complex (II), the requirement to coordinate the Cu^{I} ion to all four N-atom donors results in tilting of the C—N═C planes relative to the plane of the three sp^2-hybridized imine donors. In complex (VI), however, this effect is much more pronounced [interplanar angles 34.9 (2), 36.3 (2) and 39.4 (2)° for atoms N11, N21 and N31, respectively].

The three-dimensional 'podand bite' in the two Cu^{I} 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^{I} 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) 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)°, compared with 110.5 (2)° for complex (II).

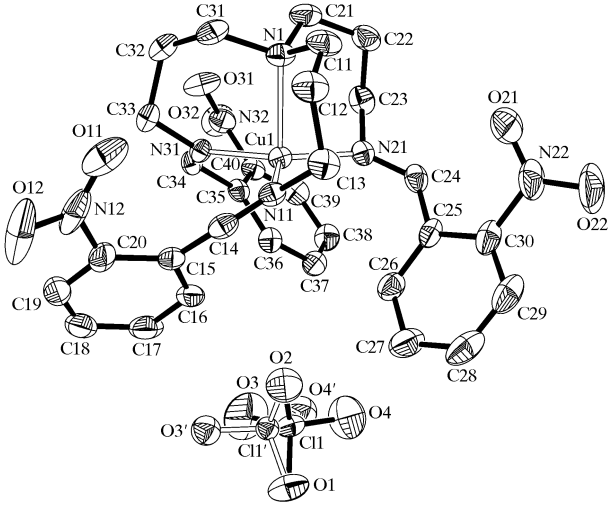

Figure 4
The structure of complex (VI), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

We have observed similar patterns in the geometry of Cu ions in cryptand hosts derived from tren and trpn [see, for example, Farrar *et al.* (1995) and Nelson *et al.* (1998)], supporting the suggestion that steric constraints mean that the larger podand has more difficulty accommodating bonding between the Cu^{I} 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 $[Cu^{I}(I)]ClO_4{\cdot}2CH_3CN$, (II), tris[(2-nitrobenzylidene)aminoethyl]amine, (I) (0.93 g, 1.7 mmol), was dissolved in dry deoxygenated acetonitrile (30 ml) and a solution of $Cu(CH_3CN)_4ClO_4$ (0.55 g, 1.7 mmol) in deoxygenated acetonitrile (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 acetonitrile 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 (I) (2.15 g, 3.9 mmol) was dissolved in methanol (60 ml). $Na_2B_4O_7$ (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_4Cl (4 g, 76 mmol) in water (40 ml) was added and the mixture was extracted with $CHCl_3$ (3 × 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 $[Cu^{II}(III)Cl]Cl{\cdot}C_2H_5OH$, (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 solution to stand (yield 0.03 g, 48%).

Ligand (V) was prepared by the dropwise addition of tris(3-aminoisopropyl)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 acetonitrile (30 ml) and $Cu(CH_3CN)_4{\cdot}ClO_4$ (0.55 g, 1.7 mmol) was added. A brown solution formed and dark-red crystals of $[Cu^{I}(V)]ClO_4$, (VI), were obtained on allowing the solution to stand (yield 0.69 g, 54%).

Compound (II)

Crystal data

$[Cu(C_{27}H_{27}N_7O_6)]ClO_4\cdot 2C_2H_3N$
M_r = 790.65
Triclinic, $P\overline{1}$
a = 11.1178 (7) Å
b = 13.3595 (9) Å
c = 13.7998 (9) Å
α = 111.627 (1)°
β = 102.995 (1)°
γ = 103.648 (1)°
V = 1737.8 (2) Å^3
Z = 2
D_x = 1.511 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.78 mm^{-1}
T = 150 (2) K
Tablet, brown
0.37 × 0.19 × 0.08 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.762, T_{max} = 0.941
15023 measured reflections
7856 independent reflections
6372 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.082
S = 1.02
7856 reflections
488 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.0079P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.025
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (II).

Cu1—N31	1.9974 (15)	Cu1—N11	2.0127 (16)
Cu1—N21	1.9981 (15)	Cu1—N1	2.1965 (15)
N31—Cu1—N21	120.56 (6)	N31—Cu1—N1	85.48 (6)
N31—Cu1—N11	118.99 (6)	N21—Cu1—N1	84.85 (6)
N21—Cu1—N11	118.25 (6)	N11—Cu1—N1	84.86 (6)

Compound (IV)

Crystal data

$[Cu(C_{27}H_{33}N_7O_6)Cl]Cl\cdot C_2H_6O$
M_r = 732.11
Monoclinic, $P2_1/c$
a = 13.183 (5) Å
b = 14.485 (6) Å
c = 16.914 (7) Å
β = 95.319 (7)°
V = 3216 (2) Å^3
Z = 4
D_x = 1.512 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 150 (2) K
Plate, green
0.23 × 0.21 × 0.07 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.819, T_{max} = 0.940
22643 measured reflections
5657 independent reflections
3256 reflections with $I > 2\sigma(I)$
R_{int} = 0.103
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.153
S = 0.98
5657 reflections
416 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (IV).

Cu1—N1	2.038 (4)	Cu1—N21	2.107 (4)
Cu1—N31	2.081 (4)	Cu1—Cl1	2.2547 (16)
Cu1—N11	2.105 (4)		
N1—Cu1—N31	84.44 (16)	N11—Cu1—N21	107.62 (15)
N1—Cu1—N11	83.97 (16)	N1—Cu1—Cl1	176.50 (12)
N31—Cu1—N11	127.92 (16)	N31—Cu1—Cl1	92.13 (12)
N1—Cu1—N21	84.35 (15)	N11—Cu1—Cl1	97.66 (11)
N31—Cu1—N21	121.43 (16)	N21—Cu1—Cl1	98.07 (11)

Table 3
Hydrogen-bond geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
N31—H31N···O41	0.93	2.13	2.998 (6)	154
N11—H11N···O12	0.93	2.29	2.882 (6)	121
N11—H11N···Cl2^{i}	0.93	2.63	3.474 (4)	152
N21—H21N···O22	0.93	2.46	3.023 (6)	119
N21—H21N···Cl2	0.93	2.48	3.302 (4)	147
O41—H41···Cl2	0.84	2.28	3.105 (5)	170

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Compound (VI)

Crystal data

$[Cu(C_{30}H_{33}N_7O_6)]ClO_4$
M_r = 750.62
Monoclinic, $P2_1/c$
a = 9.5361 (7) Å
b = 18.6870 (13) Å
c = 19.2367 (13) Å
β = 104.044 (1)°
V = 3325.5 (4) Å^3
Z = 4
D_x = 1.499 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 150 (2) K
Lath, red
0.47 × 0.17 × 0.13 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.704, T_{max} = 0.903
28475 measured reflections
7892 independent reflections
5773 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 28.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.112
S = 1.00
7892 reflections
455 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 2.0893P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 4
Selected geometric parameters (Å, °) for (VI).

Cu1—N21	2.0124 (19)	Cu1—N31	2.0326 (17)
Cu1—N11	2.0093 (18)	Cu1—N1	2.1965 (19)
N21—Cu1—N11	121.49 (8)	N21—Cu1—N1	94.59 (8)
N21—Cu1—N31	119.13 (7)	N11—Cu1—N1	94.67 (7)
N11—Cu1—N31	117.34 (7)	N31—Cu1—N1	95.00 (7)

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

$U_{iso}(H) = 1.2U_{eq}$(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: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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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.

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