

Coordination chemistry of copper-(I) and -(II) with 2-pyridylmethyl substituted triazacyclohexanes

Randolf D. Köhn,* Zhida Pan, Mary F. Mahon and Gabriele Kociok-Köhn

Department of Chemistry, University of Bath, Bath, UK BA2 7AY.

E-mail: r.d.kohn@bath.ac.uk

Received 20th February 2003, Accepted 8th April 2003

First published as an Advance Article on the web 28th April 2003

The syntheses of several novel copper-(I) and -(II) compounds containing triazacyclohexanes with one or three 2-pyridylmethyl substituents are described. The molecular structures of $(2\text{-PyMe})_3\text{TACCuCl}_2$ **3**, $[(2\text{-PyMe})\text{Et}_2\text{-TACCuCl}_2]_2$ **4** and $[(2\text{-PyMe})_3\text{TACCu}^{\text{I}}(\text{BF}_4)]$ **5** have been determined by single crystal X-ray diffraction. The reactivity of **5** and $[(2\text{-PyMe})\text{Et}_2\text{TACCu}](\text{BF}_4)$ **7** towards dioxygen was investigated and a very stable oxidation product with a $\text{Cu}_4(\text{OH})_4$ cubane core could be obtained in high yield simply by exposing **7** to the atmosphere.

Introduction

Copper complexes are widely used as oxidation catalysts not only in laboratory research but also in industry.¹ For example, aerobic oxidation of 2,6-xyleneol with copper(I) in the presence of an N-donor ligand such as pyridine produces *p*-phenylene oxide polymer which is widely used as an engineering thermoplastic with the commercial name PPO. Other important cases include oxidation of ethylene to ethylene glycol, the Wacker process in which copper is required as a most effective co-catalyst, or the oxidative coupling of alkynes. Copper-dioxygen complexes are suggested to play an important role in these catalytic oxidation reactions, yet few such intermediates have been characterised.

In recent decades, a major interest in copper chemistry has been directed towards the study of copper-containing enzymes. Several copper(I) compounds have been described as low molecular weight model complexes for copper proteins involved in the activation of dioxygen.^{2–5} Some ligands used in these complexes are shown in Fig. 1. Treatment of a monomeric copper(I) complex containing a tripodal tetradentate ligand, $[(\text{TMPA})\text{Cu}(\text{MeCN})]^+$, with dioxygen at -85°C afforded a

thermally unstable *trans*-1,2-peroxo complex $\{[\text{Cu}(\text{TMPA})]_2(\text{O}_2)\}^{2+}$, whose structure was determined by X-ray diffraction.⁶ However, changes in the ligand backbone can result in reversible dioxygen binding, *e.g.* using the ligand Cyb.⁷ A common feature in many of these ligands is the 2-pyridylmethylamine motif.

During the last few years, we have been focusing on the coordination chemistry of readily available triazacyclohexanes, R_3TAC (*e.g.* see Scheme 1), with transition metals.^{8–10} Previously we have shown that copper(II) complexes of triazacyclohexanes can be prepared by the treatment of anhydrous CuCl_2 with R_3TAC . Recently, we have shown that these Cu(II) complexes can oxidise excess Me_3TAC to amidinium cations and that the resulting Cu(I) compounds are readily re-oxidised to Cu(II) by air¹¹ indicating that catalytic oxidation may be possible with these complexes. Moreover, we reported that the highly oxygen-sensitive copper(I) complexes obtained from the reaction of $[\text{Cu}(\text{MeCN})_4]^+$ and R_3TAC could be stabilised by the addition of PPh_3 to yield the more air stable adducts, $[(\text{R}_3\text{TAC})\text{Cu}(\text{PPh}_3)](\text{BF}_4)$, which were isolated and characterised by X-ray crystallography.⁸ Generally, the bonding in κ^3 -complexes of the triazacyclohexanes is weaker than in complexes of other

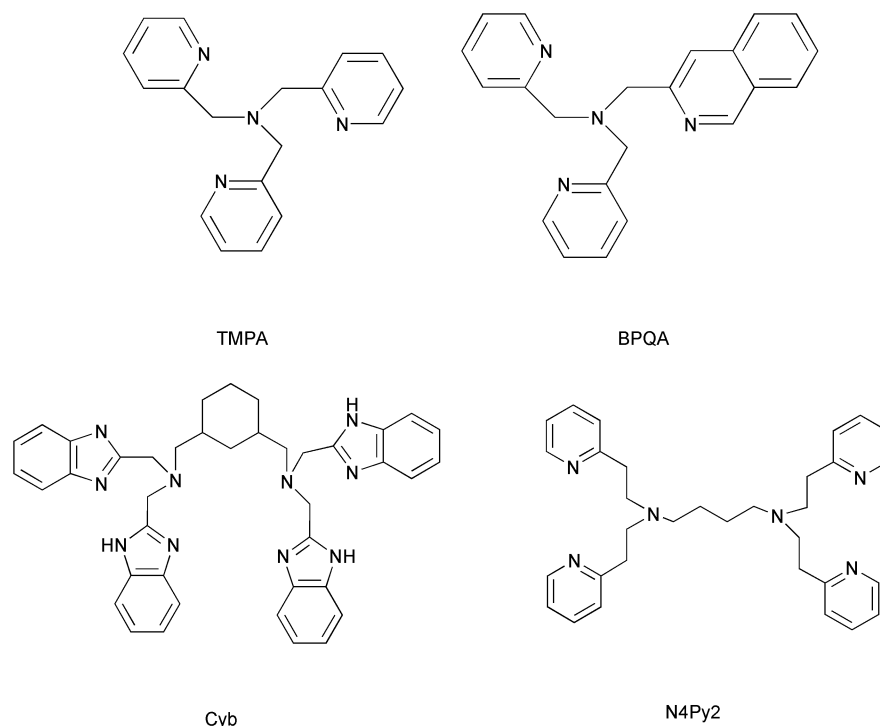
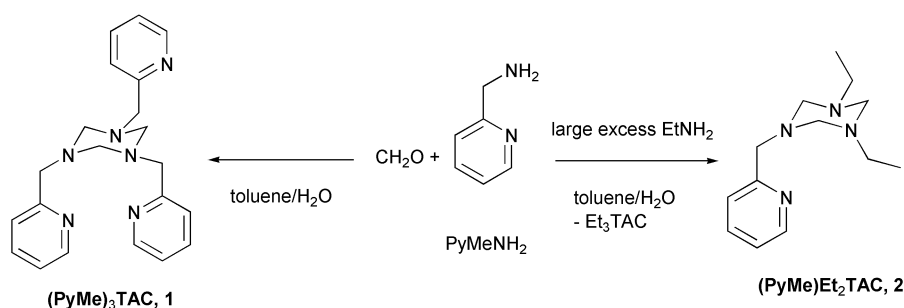
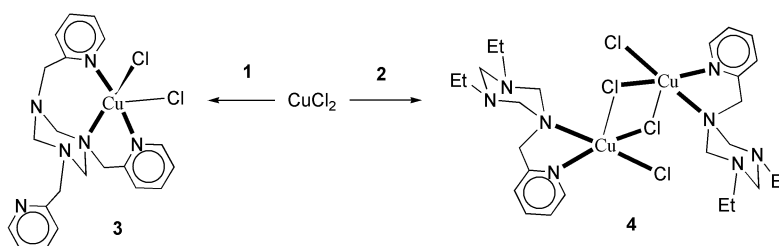


Fig. 1 Selected ligands used for the synthesis of copper-dioxygen complexes.



Scheme 1 Syntheses of pyridylmethyl-substituted ligands.



Scheme 2 Synthesis of the copper(II) complexes.

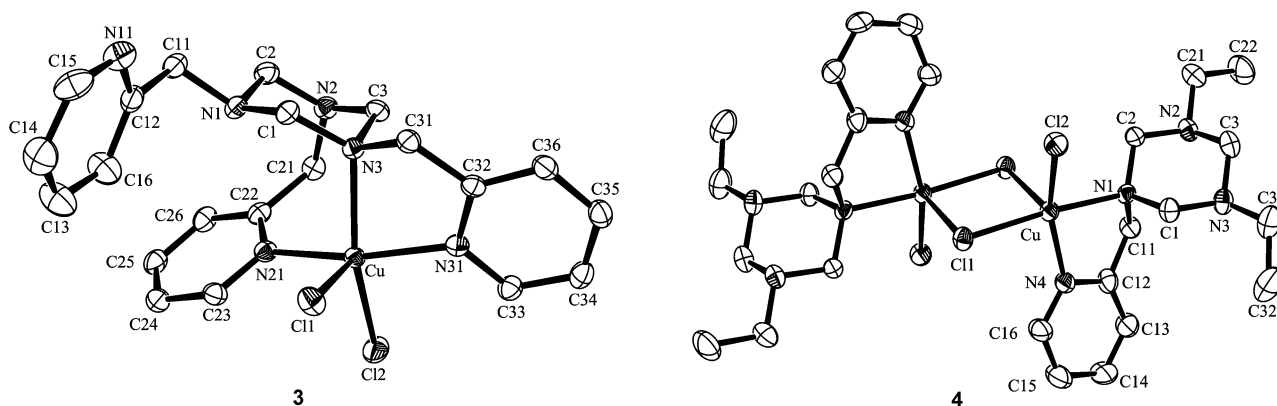


Fig. 2 ORTEP views of complexes 3 and 4. Ellipsoids are represented at the 50% probability level.

N_3 -ligands due to acute N–metal–N angles of about 60° . This weakness may be compensated by the introduction of pyridyl substituents into the triazacyclohexanes. Here we describe the syntheses of suitable new triazacyclohexanes, containing one or more 2-(aminomethyl)pyridine units as substituents, and explore their coordination chemistry to copper-(I) and -(II).

Results and discussion

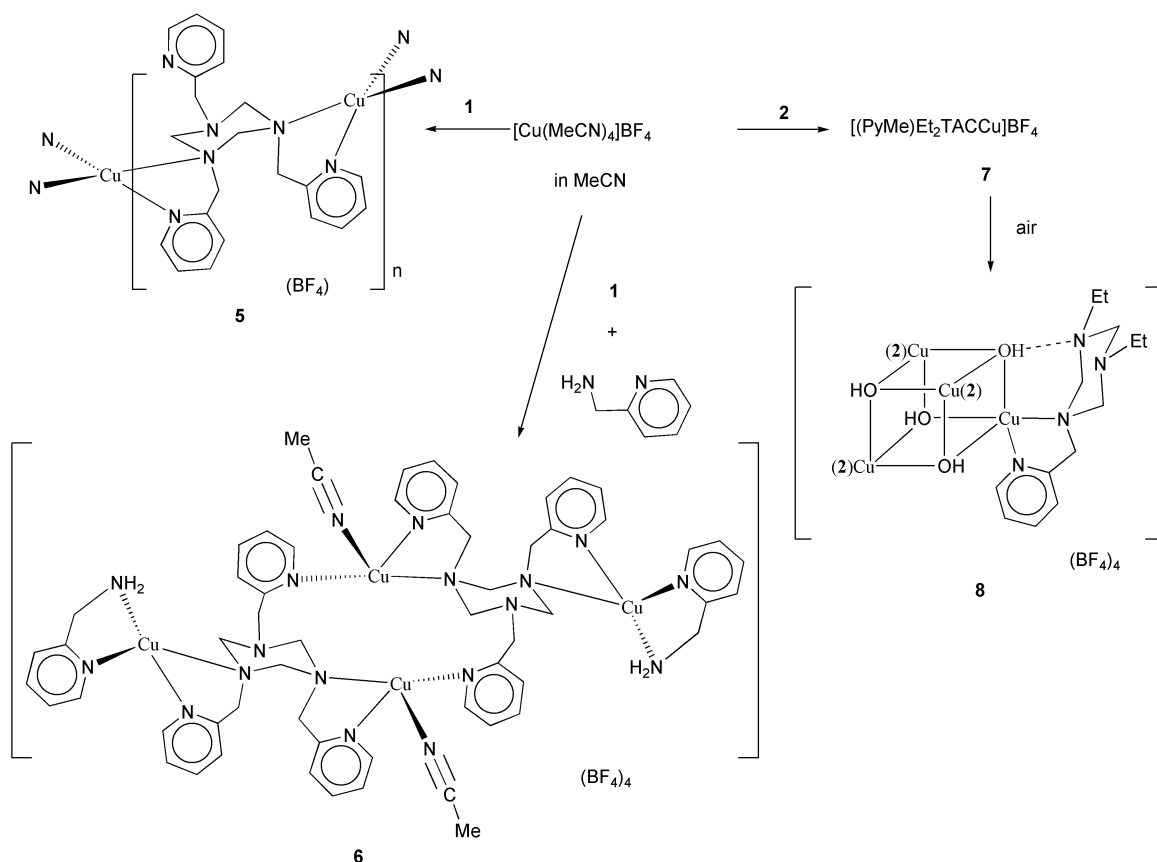
The pyridylmethyl substituted triazacyclohexanes, **1** and **2**, can be obtained according to Scheme 1. The isolation of **2** with two different substituents was achieved by first preparing a statistical mixture of triazacyclohexanes from PyMeNH₂ and EtNH₂. A large excess of EtNH₂ ensured that mostly Et₃TAC and some **2** was formed. The more volatile excess of Et₃TAC was removed under vacuum.

Synthesis of the copper(II) complexes

Treatment of anhydrous CuCl₂ in dichloromethane with an equimolar amount of ligand **1** forms a green solution (Scheme 2). After concentration of the solution by solvent removal, crystals of **3**, suitable for X-ray diffraction were obtained within a few hours. The molecular structure of **3** is shown in Fig. 2, and bonding of the pyridyl nitrogen atoms to copper occurs in preference to using all three nitrogen atoms of the triazacyclohexane. In particular, two pyridyl nitrogen atoms and one from the triazacyclohexane ring coordinate to the metal (Cu–N

1.990(2), 2.020(2), 2.141(2) Å respectively), while the third pyridine and the two other ring nitrogen atoms point away from the metal. The whole molecule exhibits a slightly distorted square-pyramidal geometry ($\tau = 0.112^{12}$) with one chlorine atom completing the basal plane and the other in the apical position (Cu–Cl 2.316(1) and 2.474(1) Å, respectively). The closely related TMAP complexes [Cu^{II}(TMAP)(H₂O)](ClO₄)₂ and [Cu^{II}(Me₃TMAP)Cl₂] reported by Tanaka *et al.* have similar bond lengths to those in **3** but have trigonal bipyramidal ($\tau = 0.97$) and intermediate geometries ($\tau = 0.53$), respectively.¹³

In an attempt to increase the number of triazacyclohexane nitrogen atoms binding to copper, preparation of a complex analogous to **3** using the ligand **2** which contains only one pyridyl substituent resulted in a green compound **4**, [(2-PyMe)-Et₂TACCuCl₂]₂ (Scheme 2). The molecular structure of this dinuclear complex is shown in Fig. 2 and selected bond lengths and angles are given in Table 1. The lattice contains both CH₂Cl₂ and EtNH₂ – the latter being residual from the ligand synthesis. No crystals could be grown in the absence of EtNH₂. Indeed, both **3** and **4** retained some CH₂Cl₂ even after pumping for several hours resulting in slightly low values for the elemental analyses. The coordination environment around the copper atom is a distorted square pyramid ($\tau = 0.31$) with two chlorine atoms, one pyridyl nitrogen and one ring nitrogen atom in the basal plane (Cu–Cl 2.248(16), 2.3034(15), and Cu–N 2.024(5), 2.095(5) Å, respectively). In the absence of additional pyridyl nitrogen atoms as in **3**, the metal in **4** chooses to bind a chlorine atom from a neighbouring complex (Cu–Cl



Scheme 3 Synthesis of Cu(I) complexes and their oxidation by air.

Table 1 Selected bond lengths [Å] and angles [°] in complexes **3** and **4**

3		4	
Cu–N(21)	1.9896(14)	Cu–N(4)	2.024(5)
Cu–N(31)	2.0200(15)	Cu–N(1)	2.095(5)
Cu–N(3)	2.1405(15)	Cu–Cl(2)	2.2477(16)
Cu–Cl(2)	2.3164(5)	Cu–Cl(1)	2.3034(15)
Cu–Cl(1)	2.4743(5)	Cu–Cl(1)#1	2.6258(16)
N(21)–Cu–N(31)	163.66(6)	N(4)–Cu–N(1)	81.3(2)
N(21)–Cu–N(3)	93.38(6)	N(4)–Cu–Cl(2)	156.13(17)
N(31)–Cu–N(3)	80.24(6)	N(1)–Cu–Cl(2)	92.42(14)
N(21)–Cu–Cl(2)	86.29(4)	N(4)–Cu–Cl(1)	93.44(15)
N(31)–Cu–Cl(2)	93.75(4)	N(1)–Cu–Cl(1)	174.77(14)
N(3)–Cu–Cl(2)	156.96(4)	Cl(2)–Cu–Cl(1)	92.41(6)
N(21)–Cu–Cl(1)	99.30(5)	Cl(2)–Cu–Cl(1)#1	107.33(6)
N(31)–Cu–Cl(1)	96.12(4)	Cl(1)–Cu–Cl(1)#1	89.37(5)
N(3)–Cu–Cl(1)	93.56(4)		
Cl(2)–Cu–Cl(1)	109.24(2)		

#1 atom related to asymmetric unit by $(-x + 2, -y, -z + 1)$ symmetry operator.

2.6258(16) Å) in preference to employing further nitrogen atoms of the triazacyclohexane and a chloride-bridged dinuclear complex is formed.

Synthesis of the Cu(I) complexes and their reaction with O₂

Previous work⁸ has shown that treatment of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ with substituted triazacyclohexanes leads to stable complexes only when the strong donor PPh_3 is added to give compounds of the type $[\kappa^3\text{-R}_3\text{TACCu}(\text{PPh}_3)](\text{BF}_4)$. NMR investigation of an acetonitrile solution without added phosphine showed the copper(I) complex existed only to a small extent. In order to obtain complexes that would still react with O₂, we investigated the reaction with $(2\text{-PyMe})_3\text{TAC}$ **3** containing the weaker pyridyl pendant donor substituent instead of added phosphine. Using completely degassed solvent, the reaction of

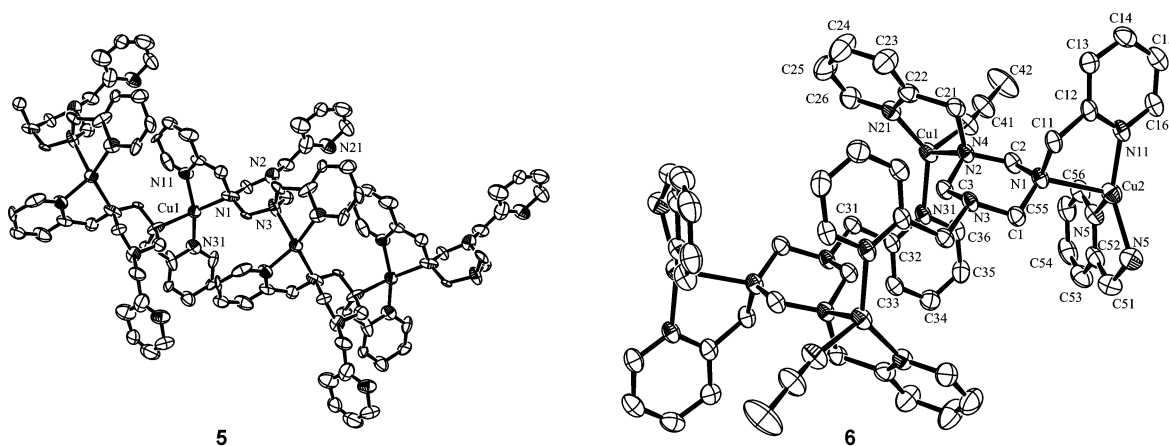
$[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ with **1**, in acetonitrile at room temperature, gave the pale yellow product $[(\text{PyMe})_3\text{TACCu}](\text{BF}_4)$ **5** (Scheme 3). Despite stringent efforts, only poor quality single crystals could be obtained by slow concentration of the reaction solution. However, the X-ray diffraction data were still adequate to unambiguously determine the coordination geometry and connectivity in **5**. The complex forms a linear polymeric structure as shown in Fig. 3. The copper(I) atom is tetrahedrally coordinated by one triazacyclohexane ring and its pendant pyridyl nitrogen from each of two different $(2\text{-PyMe})_3\text{TAC}$ ligands. Concomitantly, each ligand is coordinated to two copper atoms leaving the third triazacyclohexane and associated pyridyl nitrogen atoms uncoordinated. Thus, only two thirds of each ligand is used, while the remaining part is directed away from the metal centers.

Of the many attempts to obtain better crystals of **5** one attempt seemed initially successful. However, the crystal structure revealed that some 2-(aminomethyl)pyridine left from the preparation of **3** resulted in a break-up of the polymeric structure of **5** to give complex **6**, $[(\text{PyMe})_3\text{TAC}(\text{PyMeNH}_2)(\text{MeCN})\text{Cu}]_2(\text{BF}_4)_2$, as shown in Fig. 3. There are two different coordination environments for the metal. As in **5**, each copper is tetrahedrally coordinated by two pyridyl and two other nitrogen atoms and only two of the three 2-(aminomethyl)pyridine units of $(2\text{-PyMe})_3\text{TAC}$ chelate a copper atom. These two copper atoms are coordinatively saturated by one acetonitrile and pyridyl nitrogen atom from another ligand (Cu(1)) and by the two nitrogen atoms of 2-Py-CH₂NH₂ (Cu(2)). Thus, the crystal contains isolated tetranuclear units. The more accurate crystal data for **6** show a similar trend in the bond lengths and angles when compared to those estimated for **5** and hence can serve as a good model. The pyridyl nitrogen atoms (1.92–2.06 Å, see Table 2) are much closer to copper than the ring nitrogen atoms (2.21–2.42 Å). The bond angles between the nitrogen atoms of a 2-(aminomethyl)pyridine are necessarily acute (79–83°) and bond angles between two pyridyl nitrogen atoms are wide (126–157°). The severely distorted tetrahedral

Table 2 Selected bond lengths [Å] and angles [°] in complexes **5** and **6**

5		6	
Cu(1)–N(31)	1.924(13)	Cu(1)–N(4)	1.986(3)
Cu(1)–N(11)	1.988(12)	Cu(1)–N(21)	2.000(3)
Cu(1)–N(1)	2.221(14)	Cu(1)–N(31)	2.008(3)
Cu(1)–N(3)#1	2.406(14)	Cu(1)–N(2)	2.291(3)
		Cu(2)–N(11)	1.938(3)
		Cu(2)–N(5)	2.033(3)
		Cu(2)–N(51)	2.064(3)
		Cu(2)–N(1)	2.344(3)
N(31)–Cu(1)–N(11)	157.8(6)	N(4)–Cu(1)–N(21)	113.63(13)
N(31)–Cu(1)–N(1)	120.0(5)	N(4)–Cu(1)–N(31)	109.30(13)
N(11)–Cu(1)–N(1)	79.8(5)	N(21)–Cu(1)–N(31)	134.07(12)
N(31)–Cu(1)–N(3)#1	78.7(5)	N(4)–Cu(1)–N(2)	105.16(12)
N(11)–Cu(1)–N(3)#1	98.9(5)	N(21)–Cu(1)–N(2)	79.58(11)
N(1)–Cu(1)–N(3)#1	124.1(5)	N(31)–Cu(1)–N(2)	104.47(11)
		N(11)–Cu(2)–N(5)	146.42(14)
		N(11)–Cu(2)–N(51)	125.57(13)
		N(5)–Cu(2)–N(51)	83.08(14)
		N(11)–Cu(2)–N(1)	81.13(11)
		N(5)–Cu(2)–N(1)	112.54(12)
		N(51)–Cu(2)–N(1)	101.74(11)

#1 atom related to asymmetric unit by $(-x + 1/2, y + 1/2, -z)$ symmetry operator.

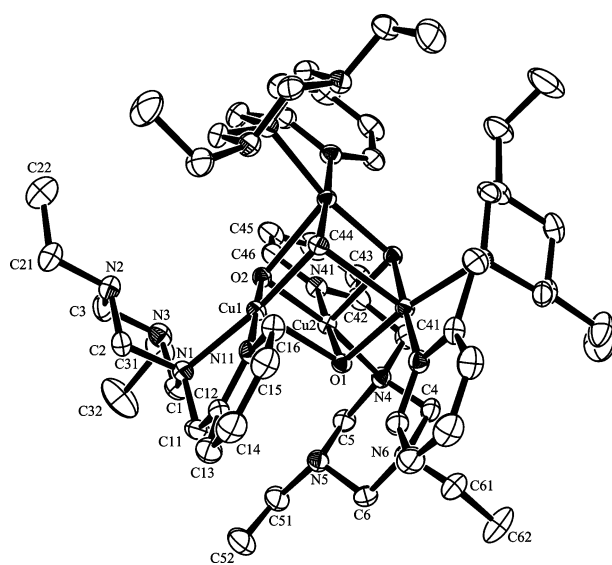
**Fig. 3** ORTEP plots of complexes **5** and **6**. Ellipsoids are represented at the 50% probability level. Labels for the carbon atoms in complex **5** are omitted for clarity.

geometry around Cu(2) may be due to π -stacking interactions between the nearly planar 2-(aminomethyl)pyridine–Cu units of neighbouring molecules in the crystal.

The ^1H and ^{13}C NMR spectra of a CD_3CN solution of **5** exhibit signals for a C_3 symmetrical ligand indicating fast exchange between bound and free 2-(aminomethyl)pyridines. These signals are broadened and a little shifted relative to the free ligand.

The reaction between complex **5** and O_2 in dichloromethane occurred very fast even at -70°C . The colour of the solution turned from pale yellow into deep violet quickly after exposure to air. When the whole system was warmed to room temperature, the violet solution gradually changed colour to green. Thus the initial product of the reaction with dioxygen is thermally unstable, and the structure has not as yet been identified.

Complex **7**, a yellow solid, was prepared by mixing $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ and **2** in the absence of oxygen. NMR and elemental analysis suggest a 1 : 1 complex, but we have not yet obtained suitable single crystals for a diffraction study. Exposure to air of an acetonitrile solution of complex **7** at room temperature overnight resulted in a colour change from pale yellow to deep green. Eventually, blue needle like crystals suitable for X-ray crystallography grew from this solution. These were identified as $[(2\text{-PyMe})\text{Et}_2\text{TAC}]\text{Cu}(\text{OH})_4(\text{BF}_4)_4$, **8**, and the structure is shown in Fig. 4. Complex **8** contains a $\text{Cu}_4(\text{OH})_4$ cubane core with eight short Cu–O distances of

**Fig. 4** Structure of complex **8**.

1.95(1) and four long ones of 2.31(1) Å (see Table 3). Each copper has a coordination number of five in square pyramidal geometry with the two nitrogen atoms of a triazacyclohexane ring and its associated pyridyl substituent ($\text{Cu}–\text{N}_{\text{TAC}}$ 2.05(1)

Table 3 Selected bond lengths [Å] and angles [°] in complex **8**

Cu(1)–O(2)	1.9412(14)	Cu(2)–O(2)	1.9646(13)
Cu(1)–O(1)#1	1.9635(13)	Cu(2)–N(41)	1.9874(18)
Cu(1)–N(11)	1.9881(17)	Cu(2)–N(4)	2.0529(17)
Cu(1)–N(1)	2.0567(17)	Cu(2)–O(2)#1	2.3032(13)
Cu(1)–O(1)	2.3254(13)	O(1)–Cu(1)#1	1.9635(13)
Cu(2)–O(1)	1.9483(14)	O(2)–Cu(2)#1	2.3032(13)
O(2)–Cu(1)–O(1)#1	86.89(6)	O(1)–Cu(2)–O(2)	87.10(6)
O(2)–Cu(1)–N(11)	177.28(6)	O(1)–Cu(2)–N(41)	177.71(6)
O(1)#1–Cu(1)–N(11)	95.34(6)	O(2)–Cu(2)–N(41)	94.74(6)
O(2)–Cu(1)–N(1)	96.62(6)	O(1)–Cu(2)–N(4)	97.14(6)
O(1)#1–Cu(1)–N(1)	171.49(6)	O(2)–Cu(2)–N(4)	170.10(6)
N(11)–Cu(1)–N(1)	81.38(7)	N(41)–Cu(2)–N(4)	81.25(7)
O(2)–Cu(1)–O(1)	77.80(5)	O(1)–Cu(2)–O(2)#1	77.84(5)
O(1)#1–Cu(1)–O(1)	85.20(5)	O(2)–Cu(2)–O(2)#1	85.54(5)
N(11)–Cu(1)–O(1)	100.80(6)	N(41)–Cu(2)–O(2)#1	100.92(6)
N(1)–Cu(1)–O(1)	103.10(6)	N(4)–Cu(2)–O(2)#1	104.07(6)

#1 atom related to asymmetric unit by $(-x + 1/2, y, -z + 1/2)$ symmetry operator.

and Cu–N_{py} 1.99(1) Å and two closely bound hydroxides in the square plane and a third long hydroxide bridge in apical position ($\tau = 0.11(2)$). Although only one (aminomethyl)pyridine of (PyMe)₃TAC is used in the bonding to copper, the triaza-cyclohexane is in the less stable all-equatorial conformation. This is partly due to hydrogen bonding interactions between one remaining ring nitrogen atom and a hydroxide bridge (N ⋯ O 2.73(2) Å). The synthesis of this very stable complex is reproducible and no decomposition of the crystals is observed after several days. Polynuclear transition metal compounds of this type have attracted much attention during the last few years due to their magnetic properties¹⁴ and a number of similar complexes containing the Cu₄O₄ cubane core have been investigated.^{15,16} Indeed, tetranuclear copper(II) complexes provide one of the simplest cases of a three-dimensional arrangement of metal ions, bridged through diamagnetic ligands. They are not only interesting because of their magnetic properties,¹⁷ but they also play a main role in catalysis, *e.g.* in the hydrolysis of peptides and DNA.¹⁸ The properties of **8** are currently being investigated.

Conclusions

Introduction of pyridyl substituents to triazacyclohexanes leads to the coordination of the 2-(aminomethyl)pyridine unit to copper(I) and -(II) rather than κ^3 -complexes of the triaza-cyclohexane even when only one pyridyl substituent is introduced. This leaves some amino groups unused for coordination and their ability to coordinate other metals is currently being investigated. The copper(I) complexes are readily oxidised in air and a Cu₄(OH)₄ cubane complex containing the unaltered ligand was isolated in one instance.

Experimental

General procedures

All manipulations of air- and moisture-sensitive complexes were carried out under an atmosphere of nitrogen or argon using standard Schlenk-line or glovebox techniques. Solvents were dried according to standard methods and collected by distillation. ¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury-400 or Bruker Avance-300 instruments. Elemental analysis was conducted on an Exeter Analytical Instruments CE-440 elemental analyser.

Synthesis of ligands **1** and **2**

(2-PyMe)₃TAC **1** and (2-PyMe)Et₂TAC **2** were prepared in a similar manner to other triazacyclohexanes.⁸ For the synthesis of **1**, equimolar amounts of 2-(aminomethyl)pyridine and

paraformaldehyde were stirred and heated in a mixture of toluene and water (5 : 1) for half an hour, and the water was co-distilled out completely by adding fresh toluene several times. The remaining toluene was removed under vacuum, giving **1** as a yellow oil in >90% yield.

For the synthesis of **2**, a large excess of EtNH₂ (molar ratio EtNH₂ : PyMeNH₂ = 20 : 1) was used and the by-product Et₃TAC was removed by distillation under high vacuum to give a 98% yield on a 5 g scale. Both **1** and **2** are yellow, viscous and high boiling liquids. **1**, ¹H NMR(CDCl₃, 300 MHz): δ 3.6 (s, 6H, ring-CH₂, $\Delta\nu_{1/2} = 6.4$ Hz), 3.85 (s, 6H, Py-CH₂-ring), 7.05, 7.45, 7.55, 8.5 (t, 4 × 3H, Py). ¹³C NMR(CDCl₃): δ 58.98 (Py-CH₂-ring), 74.26 (ring-CH₂), 122.34, 123.01, 136.78, 149.50, 159.21 (Py). **2**, ¹H NMR(CDCl₃, 300 MHz): δ 0.9 (t, 6H, -CH₃), 2.35 (t, 4H, -CH₂-), 3.30 (s, broad, 6H, ring-CH₂, $\Delta\nu_{1/2} = 23.2$ Hz), 3.63 (d, 2H, Py-CH₂-ring), 6.95, 7.30, 7.40, 8.35 (t, 4 × 1H, Py). ¹³C NMR(CDCl₃): δ 12.96 (-CH₃), 46.82 (-CH₂-), 59.00 (Py-CH₂-ring), 74.21, 74.26 (ring-CH₂), 122.21, 122.97, 136.65, 149.48, 159.27 (Py).

Synthesis of complexes **3** and **4**

CuCl₂ (0.78 g, 5.8 mmol) was suspended in 50 ml of dry CH₂Cl₂ and then **1** (2.09 g, 5.8 mmol) was added by syringe. Most of the CuCl₂ slowly dissolved. After 3 hours of stirring and another 2 hours of settling down, the deep green solution was decanted and reduced to half the volume, then cooled down to 4 °C, producing 0.61 g of crystals. Most of the solvent was removed from the mother solution and additional product was precipitated with excess hexane, washed with dry Et₂O, and dried *in vacuo* yielding a further 1.05 g of green **3** (58% yield in total). Elemental analysis: calcd. for C₂₁H₂₄N₆CuCl₂·0.2CH₂Cl₂: C 49.7, H 4.80, N 16.4; found C 49.9, H 4.91, N 16.3%.

Using the same method described for complex **3**, 1.78 g CuCl₂ (13 mmol) and 3.09 g **2** (13 mmol) gave 2.6 g green product **4** (53% yield). Elemental analysis: calcd. for C₁₃H₂₂N₄CuCl₂·0.3CH₂Cl₂: C 40.5, H 5.77, N 14.2; found C 40.2, H 5.57, N 14.2%.

Synthesis of complexes **5** and **7**

Copper(I) complexes are very sensitive to oxygen in solution. All chemicals used during the synthesis were carefully degassed by vacuum transfer and the reaction was performed under vacuum.

0.43 g [Cu(MeCN)₄]BF₄ (1.37 mmol) and 0.49 g ligand **1** (1.37 mmol) were dissolved in 50 ml dry acetonitrile and stirred overnight. The yellow solution was slowly concentrated to 20 ml under vacuum and single crystals of complex **5** were obtained eventually. Removal of all the solvent and drying *in vacuo* yielded 0.39 g (56% yield) of **5**. Elemental analysis: calcd.

Table 4 Crystal data, data collection and refinement parameters for **3**, **4**, **5**, **6** and **8**

Compound	3	4 ·2CH ₂ Cl ₂ ·EtNH ₂	5	6 ·2MeCN	8 ·MeCN·H ₂ O
Molecular formula	C ₂₁ H ₂₄ Cl ₂ CuN ₆	C ₃₀ H ₅₅ Cl ₈ Cu ₂ N ₉	C ₂₁ H ₂₄ BCuF ₄ N ₆	C ₆₂ H ₇₆ B ₄ Cu ₄ F ₁₆ N ₂₀	C ₅₄ H ₉₇ B ₄ Cu ₄ F ₁₆ N ₁₇ O ₅
<i>M</i> /g mol ⁻¹	494.90	952.51	510.81	1702.83	1665.89
Crystal colour	Green	Green	Pale yellow	Orange yellow	Turquoise
Crystal size/mm	0.2 × 0.18 × 0.18	0.63 × 0.4 × 0.2	0.15 × 0.13 × 0.08	0.33 × 0.20 × 0.15	0.5 × 0.25 × 0.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no.14)	<i>P</i> 2 ₁ / <i>a</i> (no.14)	<i>P</i> 2 ₁ / <i>a</i> (no.14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 13)
<i>a</i> /Å	8.5610(1)	9.3710(2)	18.6920(16)	10.4440(3)	14.9710(2)
<i>b</i> /Å	15.7360(3)	23.2990(5)	10.6070(6)	12.3160(4)	14.4640(2)
<i>c</i> /Å	15.8740(2)	9.9180(2)	24.0520(18)	15.6130(5)	16.7010(2)
<i>α</i> /°				89.6680(17)	
<i>β</i> /°	90.0570(7)	101.7720(10)	111.354(3)	76.0910(18)	90.8570(10)
<i>γ</i> /°				73.2270(12)	
<i>V</i> /Å ³	2138.48(5)	2119.90(8)	4441.3(6)	1862.08(10)	3616.04(8)
<i>Z</i>	4	2	8	1	2
<i>D</i> _c /g cm ⁻³	1.537	1.492	1.528	1.519	1.530
<i>μ</i> (Mo-K _α)/mm ⁻¹	1.293	1.542	1.039	1.220	1.258
<i>F</i> (000)	1020	984	2096	868	1720
Collected data	31384	27101	13703	23629	45486
Unique data [<i>I</i> > 2σ(<i>I</i>)]	4893 (<i>R</i> (int) = 0.059)	3732 (<i>R</i> (int) = 0.104)	7326 (<i>R</i> (int) = 0.2619)	6560 (<i>R</i> (int) = 0.071)	8281 (<i>R</i> (int) = 0.04)
Refined parameters	271	220	586	517	485
Min., max density/e Å ⁻³	-0.511, 0.717	-1.782, 1.950	-0.549, 1.493	-0.934, 0.636	-0.661, 0.939
<i>R</i> ₁ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0306	0.0818	0.1475	0.0515	0.0338
<i>wR</i> ₂ ^c (<i>I</i> > 2σ(<i>I</i>))	0.0755	0.2091	0.3040	0.01366	0.0859

^a $F_c^* = kF_c[1 + 0.001F_c^2/\sin(2\theta)]^{-1/4}$. ^b $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^c $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

for C₂₁H₂₄N₆CuBF₄: C 49.4, H 4.74, N 16.4; found C 49.5, H 4.79, N 16.5%. ¹H NMR (CD₃CN, 300 MHz): δ 3.50 (s, 6H, ring-CH₂, Δ*v*_{1/2} = 26.1 Hz), 3.90 (s, 6H, Py-CH₂-ring), 7.35, 7.45, 7.80, 8.60 (t, 4 × 3H, Py). ¹³C NMR(CD₃CN): δ 57.41 (Py-CH₂-ring), 73.23 (ring-CH₂), 123.18, 123.91, 137.30, 148.75, 156.56 (Py). ¹¹B NMR: δ 1.86 (s, BF₄).

Complex **7** was prepared with 0.65 g Cu(MeCN)₄BF₄ (2.07 mmol) and 0.48 g ligand **2** (2.07 mmol) in 30 ml MeCN. After the same treatment as described above and washing of the solid with oxygen-free hexane twice in the glove box, 0.33 g yellow product **7** was obtained in total 42% yield. ¹H NMR (CD₃CN, 300 MHz): δ 1.02 (t, 6H, -CH₃), 2.42 (t, 4H, -CH₂), 3.50 (s, 6H, ring-CH₂, Δ*v*_{1/2} = 11.6Hz), 4.19 (s, 2H, Py-CH₂-ring), 7.35, 7.45, 7.90, 8.50 (t, 4 × 1H, Py). ¹³C NMR(CD₃CN): δ 11.48 (-CH₃), 45.76 (-CH₂-), 57.05 (Py-CH₂-ring), 73.44, 73.52 (ring-CH₂), 123.72, 137.84, 148.58, 156.80 (Py). Elemental analysis: calcd. for C₁₃H₂₂N₄CuBF₄: C 40.6, H 5.76, N 14.5; found C 40.4, H 5.52, N 14.8%.

Exposure of the acetonitrile solution of complex **7** (0.17 g, 3.99 mmol) to air at room temperature overnight resulted in a colour change from pale yellow to deep green. The solution was concentrated and turquoise-blue crystals of **8** grew gradually to finally give 0.13 g of a solid (79% yield based on complex **7**). Elemental analysis: calcd. for C₅₄H₉₇N₁₇B₄F₁₆O₅Cu₄: C 38.9, H 5.87, N 14.3; found C 39.1, H 5.73, N 14.5%.

X-Ray crystal structure determinations

Intensity data were collected at 150 K on a Nonius Kappa CCD equipped with a low temperature device, using graphite monochromated Mo-K_α radiation (λ = 0.71070 Å) and processed using the Nonius Software.¹⁹ Empirical absorption corrections for **3** and **4** were applied using the SORTAV program for the Nonius area detector. For structure solution and refinement the programs SIR-97²⁰ and SHELXL97-2²¹ were used while illustrations were generated using ORTEP-3.²² Crystal parameters and details of the data collection, solution and refinement are summarised in Table 4.

Notes on the refinement: **4** crystallises with two molecules of CH₂Cl₂ and one molecule of EtNH₂ in the asymmetric unit. Bond lengths in the CH₂Cl₂ molecule were idealised and the terminal methyl group in EtNH₂ showed an unusually high temperature factor, probably indicative of some disorder which was not modelled. The EtNH₂ was refined isotropically. Weak

data in **5** led to high *R*-values and C5 and C11 were refined isotropically. The two independent molecules in the asymmetrical unit form infinite one dimensional chains along the *b*-axis. In **6** and **8** some of the BF₄ anions exhibited disorder. The co-crystallised CH₃CN solvent molecule in the asymmetric unit of **8** was found to be disordered about the crystallographic C₂ axis with 50% site occupancy.

CCDC reference numbers 204540–204544.

See <http://www.rsc.org/suppdata/dt/b3/b302037a/> for crystallographic data in CIF or other electronic format.

Acknowledgements

The authors wish to thank EPSRC for financial support.

References and notes

- N. Kitajima and Y. Moro-oka, *Chem. Rev.*, 1994, **94**, 737 and references therein.
- W. Kaim and J. Rall, *Angew. Chem.*, 1996, **108**, 47.
- K. D. Karlin, *J. Inorg. Biochem.*, 1997, **67**, 3.
- K. D. Karlin, *Science*, 1993, **261**, 701.
- E. Spodine and J. Manzur, *Coord. Chem. Rev.*, 1992, **119**, 171.
- K. D. Karlin, N. Wei, B. Jung, S. Kaderli and A. D. Zuberbühler, *J. Am. Chem. Soc.*, 1991, **113**, 5868; K. D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus and A. D. Zuberbühler, *J. Am. Chem. Soc.*, 1993, **115**, 9506.
- Y. Nishida, K. Takahashi, H. Kuramoto and S. Kida, *Inorg. Chim. Acta*, 1981, **54**, L103.
- R. D. Köhn, G. Seifert and G. Kociok-Köhn, *Chem. Ber.*, 1996, **129**, 1327 and references therein.
- R. D. Köhn, G. Kociok-Köhn and H. Haufe, *J. Organomet. Chem.*, 1995, **501**, 303.
- R. D. Köhn, Z. Pan, G. Kociok-Köhn and M. F. Mahon, *J. Chem. Soc., Dalton Trans.*, 2002, 2344.
- R. D. Köhn, G. Seifert, Z. Pan, M. F. Mahon and G. Kociok-Köhn, *Angew. Chem., Int. Ed.*, 2003, **41**, 804.
- $\tau = (\text{difference between two largest bond angles})/60$ for penta-coordinate complexes allows the assignment of square-pyramidal ($\tau = 0$) or trigonal-bipyramidal ($\tau = 1$) coordination geometry: A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
- H. Nagao, N. Komeda, M. Mukaida, M. Suzuki and K. Tanaka, *Inorg. Chem.*, 1996, **35**, 6809.
- (a) D. Gatteschi, R. Sessoli and A. Cornia, *Chem. Commun.*, 2000, 725; (b) A. Muller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239.

-
- 15 W. Haase, *J. Mol. Catal.*, 1984, **23**, 331.
- 16 (a) Y. S. Xie, H. Jiang, A. Chan, Q. L. Liu, X. L. Xu, C. X. Du and Y. Zhu, *Inorg. Chim. Acta*, 2002, **333**, 138; (b) M. Håkansson, C. Lopes and S. Jagner, *Inorg. Chim. Acta*, 2000, **304**, 178–183.
- 17 E. Ruiz, A. Rodriguez-Forteza, P. Alemany and S. Alvarez, *Polyhedron*, 2001, **20**, 1323–1327.
- 18 (a) T. Itoh, H. Hisada, T. Sumiya, M. Hosono, Y. Usui and Y. Fujii, *Chem. Commun.*, 1997, 677; (b) X. S. Tan, Y. Fujii, T. Sato, Y. Nakano and M. Yashiro, *Chem. Commun.*, 1999, 881.
- 19 Z. Otwinowski and W. Minor, DENZO-SMN Manual, University of Texas Southwestern Medical Center, Dallas, 1999.
- 20 SIR-97, A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.
- 21 G. M. Sheldrick, SHELXL97-2, Program for Crystal Structure Determination, Universität Göttingen, Germany, 1998.
- 22 ORTEP-3 for Windows, L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.