Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# A second polymorph of *cyclo*-tetrakis{$\mu_2$-[(dimethylamino)methyl]phenyl-$\kappa^3C^2$:$C^2$,*N*}copper tetrahydrofuran solvate

**Duncan M. Tooke,* Martin Lutz and Anthony L. Spek**

Bijvoet Centre for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Correspondence e-mail: d.m.tooke@chem.uu.nl

**Key indicators**

Single-crystal X-ray study
*T* = 100 K
Mean $\sigma$(C–C) = 0.003 Å
Disorder in solvent or counterion
*R* factor = 0.019
*wR* factor = 0.045
Data-to-parameter ratio = 18.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

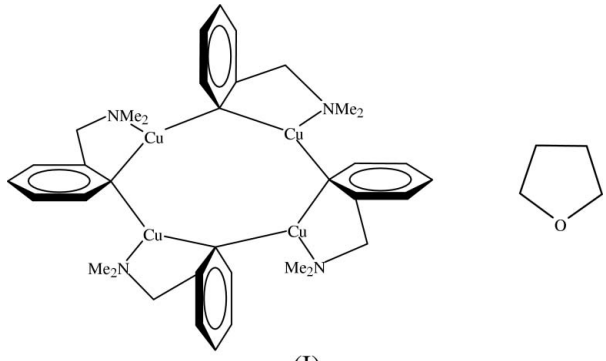


Received 12 May 2005
Accepted 24 May 2005
Online 31 May 2005

The structure of the title compound, $[Cu_4(C_9H_{12}N)_4]\cdot C_4H_8O$, has previously been reported in the monoclinic space group *C*2/*c*. We report here the structure of a second polymorph which crystallizes in the orthorhombic space group $P2_12_12_1$. The copper complex is located at a general position but exhibits local $S_4$ symmetry.

## Comment

The structure of the title compound, (I), has previously been reported crystallizing in the monoclinic space group *C*2/*c*, (II) (Janssen *et al.*, 1996). The asymmetric unit of (II) contains one half of the copper complex, the other half being identical by a twofold rotation, and one half-weight tetrahydrofuran (THF) molecule. The THF was found to be disordered about the twofold rotation axis. The solvent-free metal complex has also been reported, in space group $P2_1/c$, (III) [Spek & van Koten, 2004; Cambridge Structural Database (Version 5.26) and *Conquest* (Version 1.7) (Allen, 2002) refcode IQOTOX].




(I)

The title compound, (I), is a second polymorph of the *C*2/*c* structure (Fig. 1) and crystallizes in the orthorhombic space group $P2_12_12_1$. The asymmetric unit consists of one complete copper complex and a single disordered THF molecule. The overall crystal structure is quite different from that of the previous polymorph, (II). In (II), the complex and the THF lie on a twofold rotation axis, with the THF molecules lying in the cavities of adjacent copper complexes (Fig. 2). In (I), however, whilst the complexes now line up roughly parallel to the *a* axis, the THF no longer sits between pairs of complexes and is instead displaced to the side (Fig. 3).

The structure of the copper complex is essentially the same as previously reported, with the Cu atoms forming a 'butterfly' arrangement. The Cu—C and Cu—N bond lengths are comparable with those in (II), as are the Cu—C—Cu bond angles, which are once again very acute, at between 70.33 (8) and 72.14 (9)°. The Cu···Cu distances in (II) are very short, at

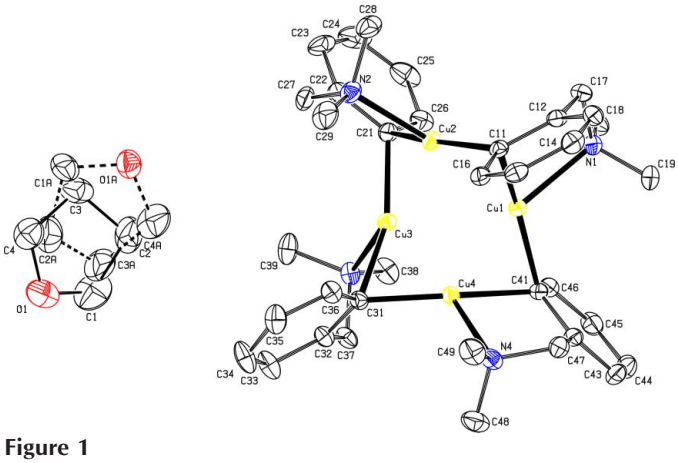



**Figure 1**
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Both disorder components are shown.

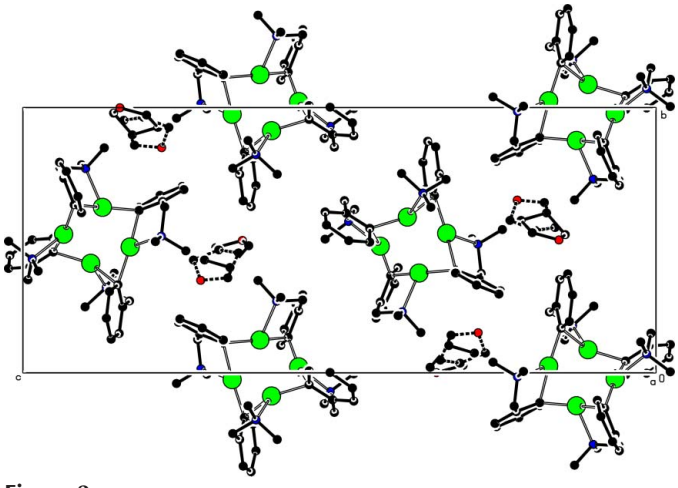



**Figure 2**
A packing diagram for the $P2_12_12_1$ polymorph, (I), viewed along the *a* axis. The THF molecule is disordered over two positions, with relative occupancies of 73% and 27%; dashed lines indicate the minor disorder component.

2.3728 (3) and 2.3885 (3) Å. Polymorphs (I) and (III) also have very short Cu···Cu distances for Cu atoms that are adjacent in the metallocycle, at between 2.3773 (4) and 2.4118 (4) Å for (I), and between 2.372 (2) and 2.396 (2) Å for (III). However, in both cases, opposite Cu atoms have longer Cu···Cu distances, with one distinctly longer than the other [3.0065 (4) and 3.3810 (4) Å in (I), and 3.040 (2) and 3.380 (3) Å in (III)].

As a consequence of the different packing, the intermolecular Cu···Cu distances are different for the three crystal structures: in (I), the shortest Cu···Cu distance is 8.1780 (4) Å, in (II) it is 8.0630 (6) Å, and in (III) it is 6.508 (2) Å.

## Experimental

The title compound was obtained unintentionally during an attempt to synthesize a mixed Cu–Li complex. It was recrystallized from THF, yielding pale-yellow crystals of (I) suitable for X-ray diffraction.

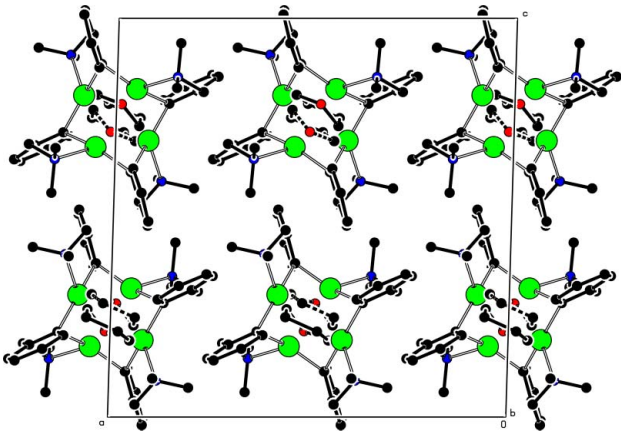



**Figure 3**
A packing diagram for the *C*2/*c* polymorph, (II), viewed along the *b* axis. The THF molecule is disordered about the twofold axis.

*Crystal data*

$[Cu_4(C_9H_{12}N)_4]\cdot C_4H_8O$
$M_r$ = 863.05
Orthorhombic, $P2_12_12_1$
$a$ = 9.4952 (2) Å
$b$ = 13.2026 (3) Å
$c$ = 31.5269 (6) Å
$V$ = 3952.25 (14) Å$^3$
$Z$ = 4
$D_x$ = 1.450 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 53905 reflections
$\theta$ = 1.3–27.5°
$\mu$ = 2.16 mm$^{-1}$
$T$ = 100 (2) K
Block, pale yellow
0.42 × 0.24 × 0.15 mm

*Data collection*

Bruker Nonius KappaCCD area-detector diffractometer
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*MULABS*; Blessing, 1995)
$T_{min}$ = 0.59, $T_{max}$ = 0.72
53905 measured reflections
9022 independent reflections
8758 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.047
$\theta_{max}$ = 27.5°
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = -40 \rightarrow 40$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.045
$S$ = 1.04
9022 reflections
496 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 1.2769P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$
Absolute structure: Flack (1983), with 3956 Friedel pairs
Flack parameter: −0.013 (6)

All H atoms were placed in geometrically idealized positions, with C—H distances in the range 0.95–0.99 Å, and constrained to ride on their parent atoms, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H atoms and 1.2$U_{eq}$(C) for all other H atoms. The THF molecule was refined using a disorder model, with relative occupancies of 73.1 (4)% and 26.9 (4)%.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

The authors thank the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-

NWO) for their support. Many thanks are due also to Claudia Kronenburg and Gerard van Koten (Utrecht University) for the synthesis of the compound.

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307-326. New York: Academic Press.
Janssen, M. D., Corsten, M. A., Spek, A. L., Grove, D. M. & van Koten, G. (1996). *Organometallics*, **15**, 2810–2820.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Spek, A. L. & van Koten, G. (2004). Private communication to the Cambridge Structural Database.