

A polymorph of tetrakis(acetonitrile- κ N)copper(I) tetrafluoridoborateJan W. Bats,^{a*} Tonia Kretz^b and Hans-Wolfram Lerner^b^aInstitut für Organische Chemie, Universität Frankfurt, Max-von-Laue-Strasse 7, D-60438 Frankfurt am Main, Germany, and ^bInstitut für Anorganische Chemie, Universität Frankfurt, Max-von-Laue-Strasse 7, D-60438 Frankfurt am Main, Germany

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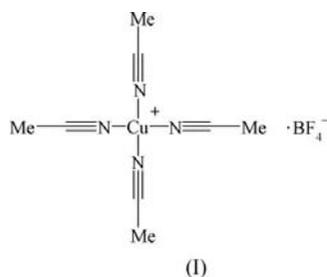
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A $P2_12_12_1$ polymorph of the title compound, $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$, is reported. The crystal structure is very similar to the structure of the $Pna2_1$ polymorph reported by Jones & Crespo [*Acta Cryst.* (1998), C54, 18–20]. The anions and one of the three independent cations occupy similar positions in both polymorphs. Two of the four symmetry-related positions of the other two cations are also identical in the two polymorphs, and the other two positions are related by mirror symmetry. The crystal used for the structure determination contained a volume fraction of 0.088 (7) of the $Pna2_1$ polymorph.

Comment

Recently, we have produced copper(II) complexes with N,N,N',N' -tetramethylethylenediamine (tmeda) or 1,1,4,7,7-pentamethyldiethylenetriamine as starting materials in the synthesis of hydroquinone-based dinuclear Cu^{II} complexes (Margraf *et al.*, 2005). The title compound, (I), was obtained as a minor by-product in the preparation of $[\text{Cu}(\text{tmeda})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ from tmeda and $\text{Cu}(\text{BF}_4)_2$ in acetonitrile. We report here the crystal structure of (I).



The asymmetric unit of (I) contains three independent pairs of cations and anions. The molecular structure with the atomic numbering scheme is shown in Fig. 1. Each Cu atom has a tetrahedral coordination of acetonitrile ligands. The N—Cu—N angles range from 105.69 (15) to 112.98 (15)^o and

the Cu—N bond lengths vary between 1.971 (3) and 2.020 (4) Å, with an average length of 1.994 (4) Å. The BF_4^- anions also have a tetrahedral conformation. The B—F bond distances range from 1.341 (6) to 1.418 (6) Å, with an average value of 1.377 (7) Å. The BF_4^- anions show rather large librational motion. The average B—F distance, corrected for libration, is 1.415 (7) Å. The crystal packing of (I) is shown in Fig. 2. The cations are connected to the anions by 26 different intermolecular C—H...F contacts with H...F distances less than 2.75 Å. The shortest H...F distances are 2.36, 2.37, 2.41 and 2.42 Å. There are also two intermolecular C—H...N contacts with H...N distances of 2.61 and 2.64 Å.

The crystal structure of a polymorph of (I) has been reported by Jones & Crespo (1998). Surprisingly, the cell constants reported for that polymorph are almost identical to those observed in the present study; the a , b and c axes are, respectively, 0.01, 0.05 and 0.06 Å shorter in the present determination. This difference may result from small differences in the temperatures of the measurements or from small experimental errors in the Bragg angles. Thus, at first glance, it appears that the same crystal structure has been determined in both studies. The space group reported by Jones & Crespo, however, is $Pna2_1$, while in our study we found $P2_12_12_1$. Moreover, starting with the fractional coordinates of Jones & Crespo, the structure could not be refined with our reflection data to a low R value. For a direct comparison of the crystal packing in the two structures, the structure of Jones & Crespo has been transferred to the nonstandard setting $Pc2_1n$. The resulting crystal packing is shown in Fig. 3. The resemblance to the packing shown in Fig. 2 is striking, apart from an origin shift of $(0,0,\frac{1}{4})$. The difference between the packings of the two polymorphs can only be seen on close inspection. For this purpose, the packing diagrams in Figs. 2 and 3 have been divided into segments. The segments labelled A and A' contain the cation with atom Cu1 and the three independent BF_4^- anions. The anions are positioned directly over three of the terminal methyl groups of this cation. The molecules within

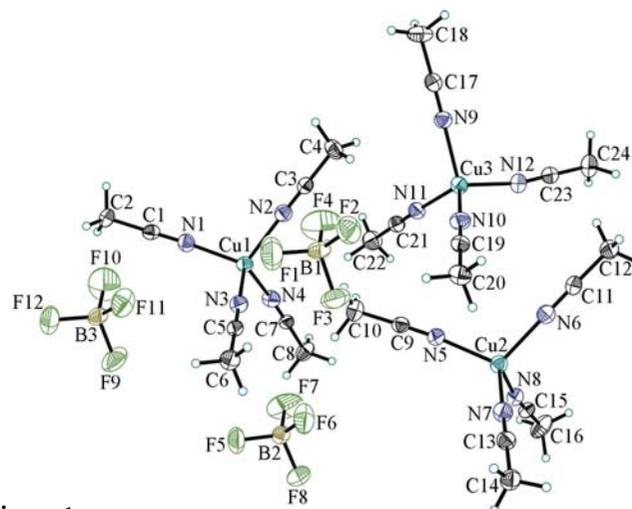


Figure 1

The structure of the three independent cations and anions of (I), shown with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

these segments show pseudo-mirror symmetry, with atoms Cu1, B1, F2, F4, N2, N3, C3, C4, C5 and C6 approximately on a pseudo-mirror plane perpendicular to the *b* axis. The segments labelled *B* and *B'* contain the cations with atoms Cu2 and Cu3. The two independent cations are related by a pseudo-twofold screw axis about $(x, \frac{1}{4}, \frac{1}{4})$ in Fig. 2 and about $(x, \frac{1}{4}, 0)$ in Fig. 3. The arrangement of these cations in each segment is extended in the *b*-axis direction by a crystallographic screw axis. The atoms in segment *B* are related to the atoms in segment *B'* by an additional screw axis in the $P2_12_12_1$ polymorph but by a glide plane in the $Pc2_1n$ polymorph. The structure of the latter polymorph can be derived from the structure of the title compound if the atoms in segment *B'* are replaced by their mirror image about the *a* axis.

From the close similarity of the two polymorphs, the question arises whether the crystal could be a mixture of the

two polymorphs. In that case, the observed intensities would be the sum of the contributions from two crystal structures: $F^2(\text{obs}) = xF^2(P2_12_12_1) + (1 - x)F^2(Pc2_1n)$. Using the observed reflections, *x* was calculated by a least-squares procedure as 0.912 (7). Thus, the crystal used for the structure determination contains a volume fraction of 0.088 (7) of the second polymorph. A similar calculation, using the observed reflections of the $Pc2_1n$ polymorph, showed the crystal used by Jones & Crespo to contain a volume fraction of 0.044 (7) of the $P2_12_12_1$ polymorph.

A number of isomorphous crystal structures of related compounds have been reported, for example, $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (Bowmaker *et al.*, 2004), $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (Jones & Bembenek, 1993), $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (Aly *et al.*, 2004), $[\text{Zn}(\text{CH}_3\text{CN})_4]\text{SO}_4$ (Yang *et al.*, 2004) and $[\text{Li}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (Yokota *et al.*, 1999). All these structures have the space group $Pna2_1$. No isomorphous structure has been reported for the $P2_12_12_1$ polymorph. A crystal structure with the space group $P2_12_12_1$ and also having $Z' = 3$ has been reported for $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6 \cdot \text{CH}_3\text{CN}$ (Black *et al.*, 1995; Dakin *et al.*, 2000). The crystal packing of this compound, however, differs from the packing of the title compound.

Experimental

N,N,N',N'-Tetramethylethylenediamine (1.16 g, 10 mmol) was added under stirring to a solution of $\text{Cu}(\text{BF}_4)_2$ (2.91 g, 10 mmol) in dry acetonitrile. After a few days of slow evaporation, blue crystals of $[\text{Cu}(\text{tmeda})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ and colourless crystals of (I) were obtained (yield 5%).

Crystal data

$[\text{Cu}(\text{C}_2\text{H}_3\text{N})_4]\text{BF}_4$	$V = 4020.4 (7) \text{ \AA}^3$
$M_r = 314.57$	$Z = 12$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 8.3184 (7) \text{ \AA}$	$\mu = 1.66 \text{ mm}^{-1}$
$b = 20.2887 (15) \text{ \AA}$	$T = 156 (2) \text{ K}$
$c = 23.822 (3) \text{ \AA}$	$0.50 \times 0.34 \times 0.32 \text{ mm}$

Data collection

Siemens SMART 1K CCD diffractometer	13482 independent reflections
Absorption correction: numerical (<i>SHELXTL</i> ; Sheldrick, 2008)	11521 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.467$, $T_{\max} = 0.638$	$R_{\text{int}} = 0.041$
54515 measured reflections	1189 standard reflections
	frequency: 1200 min
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{\text{max}} = 1.84 \text{ e \AA}^{-3}$
$wR(F^2) = 0.142$	$\Delta\rho_{\text{min}} = -0.99 \text{ e \AA}^{-3}$
$S = 1.15$	Absolute structure: Flack (1983),
13482 reflections	5847 Friedel pairs
501 parameters	Flack parameter: 0.265 (15)
H-atom parameters constrained	

H atoms were positioned geometrically and refined as riding [C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$]. Friedel opposites were not merged. The value of the Flack (1983) parameter showed the crystal to be an inversion twin. The volume fraction of the major polymorph included in the crystal was calculated by minimizing the sum $\sum w[F_o^2 - xF_{c1}^2 - (1-x)F_{c2}^2]^2$, where F_o , F_{c1} and F_{c2} are the observed

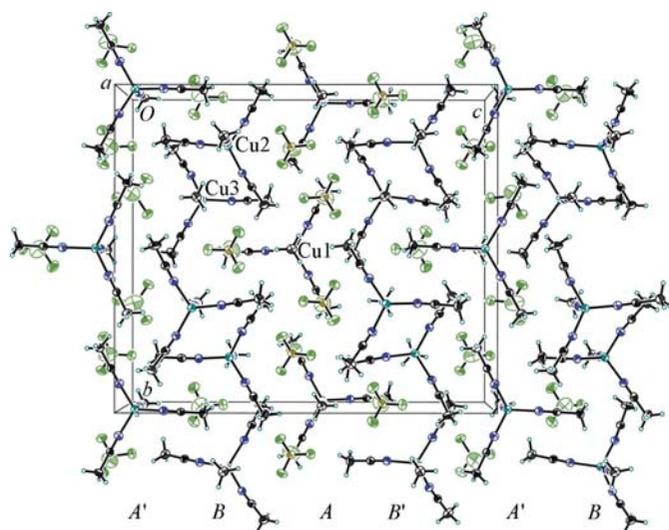


Figure 2
The crystal packing of the $P2_12_12_1$ polymorph of (I), viewed down the *a* axis.

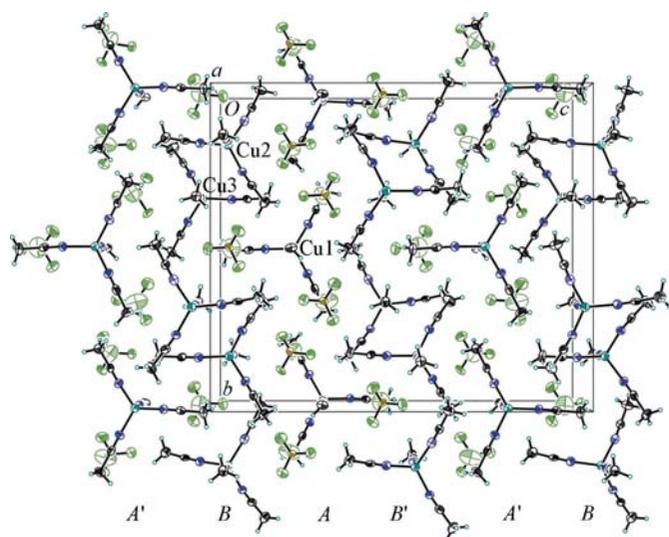


Figure 3
The crystal packing of the $Pc2_1n$ polymorph of (I), viewed down the *a* axis.

structure factor and the calculated structure factors for the $P2_12_12_1$ and $Pc2_1n$ polymorphs, respectively, and $w = \sigma^{-2}(F_o^2)$. The resulting formula is $x = \sum w(F_o^2 - F_c^2)(F_{c1}^2 - F_{c2}^2) / \sum w(F_{c1}^2 - F_{c2}^2)^2$. The R values and structural parameters reported in this work are based on a refinement using the original intensities, which contain a small contribution of the second polymorph.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3075). Services for accessing these data are described at the back of the journal.

References

- Aly, A. A. M., Walfort, B. & Lang, H. (2004). *Z. Kristallogr. New Cryst. Struct.* **219**, 489–491.
- Black, J. R., Levason, W. & Webster, M. (1995). *Acta Cryst.* **C51**, 623–625.
- Bowmaker, G. A., Gill, D. S., Skelton, B. W., Somers, N. & White, A. H. (2004). *Z. Naturforsch. Teil B*, **59**, 1307–1313.
- Dakin, L. A., Ong, P. C., Panek, J. S., Staples, R. J. & Stavropoulos, P. (2000). *Organometallics*, **19**, 2896–2908.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Jones, P. G. & Bembek, E. (1993). *Z. Kristallogr.* **208**, 213–218.
- Jones, P. G. & Crespo, O. (1998). *Acta Cryst.* **C54**, 18–20.
- Margraf, G., Bats, J. W., Wagner, M. & Lerner, H.-W. (2005). *Inorg. Chim. Acta*, **358**, 1193–1203.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Siemens (1995). *SMART* (Version 4.05) and *SAINT* (Version 4.05). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Yang, H.-L., Yang, F. & Zhu, H.-L. (2004). *Z. Kristallogr. New Cryst. Struct.* **219**, 329–330.
- Yokota, Y., Young, V. G. & Verkade, J. G. (1999). *Acta Cryst.* **C55**, 196–198.