

Pseudo-merohedrally twinned tetrakis(1*H*-imidazole- κ N³)-bis(*N*-nitrocyanamidato- κ N)-copper(II)

Jesús García Díaz,^a Jozef Kožíšek,^{b*} Marek Fronc,^b Anton Gašal,^b Ingrid Svoboda^c and Vratislav Langer^d

^aDepartment of Materials, Technological Institute of Morelia, Michoacán, México, ^bDepartment of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, ^cStrukturforschung, FB11 Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany, and ^dDepartment of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden
Correspondence e-mail: kozisek@cvt.stuba.sk

Received 7 January 2005

Accepted 14 February 2005

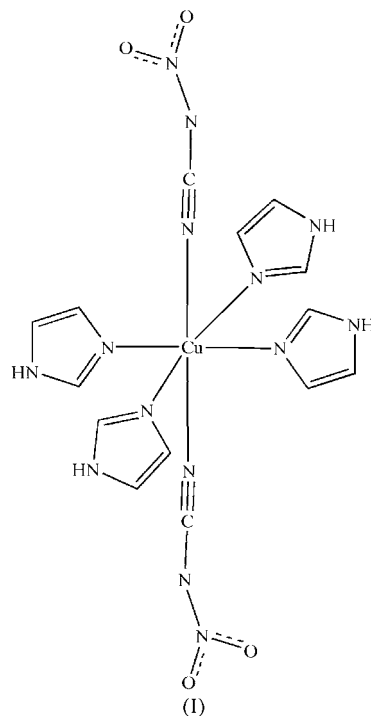
Online 11 March 2005

Crystals of the title complex, [Cu(CN₃O₂)₂(C₃H₄N₂)₄], the structure of which has been determined by single-crystal X-ray diffraction at 304 K, appear to be pseudo-merohedrally twinned. Transformation to a monoclinic *C*-centred cell was necessary in order to derive the twin law. Twin refinement in a triclinic unit cell significantly reduced the *R* value. The asymmetric unit of the triclinic cell consists of one molecule in a general position and two half entities with the Cu atom on a centre of inversion. The coordination of the Cu atom is quasi-octahedral, with four imidazole N-atom donors in the equatorial plane and two cyano N atoms from the *N*-nitrocyanamidate anion in axial positions. Owing to symmetry in the centrosymmetric molecules, the *trans* imidazole ligands are parallel, while those in the non-centrosymmetric molecule make angles of 22.8 (2) and 77.9 (2)°.

Comment

Non-linear pseudohalides, such as dicyanamide, N(CN)₂⁻, tricyanomethanide, C(CN)₃⁻, nitrosodicyanomethanide, ONC(CN)₂⁻, and nitrocyanoamide (*nca*), O₂NN(CN)⁻, exhibit a rich variety of bonding modes for coordination in 3*d* complexes (Jäger *et al.*, 1997; Hvastijová *et al.*, 1998; Kohout *et al.*, 2000; Potočník *et al.*, 2001, 2002; Kožíšek *et al.*, 2002; Díaz *et al.*, 2003). A comparison of bond distances for compounds of the type [M(NL)₄(NO₂NCN)₂] [where *M* = Co, Ni and Cu, and NL is a neutral ligand, such as *iz* (imidazole), *pz* (pyrazole) or *meiz* (1- or 5-methylimidazole)] found in the Cambridge Structural Database (CSD; Version 1.6, 2003 release; Allen, 2002) is shown in Table 3. For Ni and Cu compounds, neutral ligands were found in the equatorial plane

and anionic (*nca*) ligands in axial positions. In all previously solved crystal structures, except for CSD refcode OFILEU, (Hvastijová *et al.*, 2001) the molecules are centrosymmetric.



Cell reduction for the crystal structure of the title compound, (I), revealed that the cell could be transformed to a monoclinic *C*-centred one, but *R*_{int} and *R*_σ [defined as the sum of $\sigma(F^2)$ divided by the sum of F^2] were significantly better for the triclinic case (0.0301 and 0.0375, respectively)

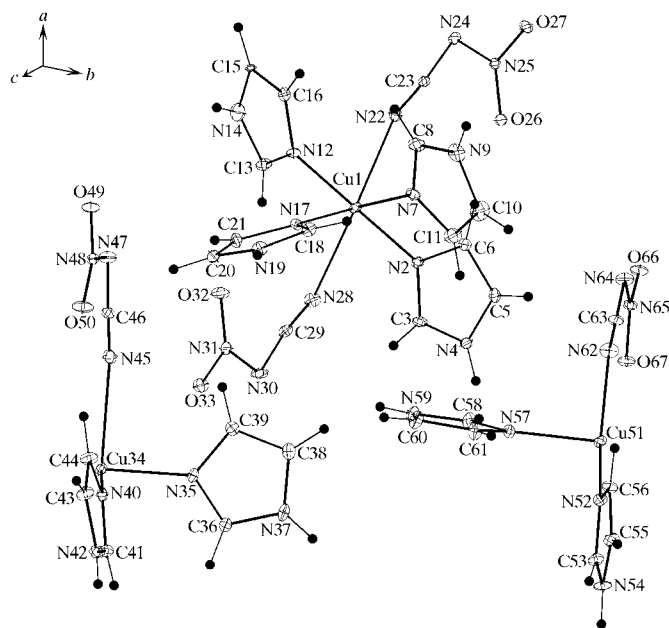


Figure 1
The atom-numbering scheme of (I). Displacement ellipsoids are shown at the 50% probability level.

than for a monoclinic lattice (0.0570 and 0.0483). The structure could be solved in the triclinic space group $P\bar{1}$ only, with many difficulties. During refinement, large positional shifts led to unreasonable molecular geometry, and additional peaks appeared in the difference map. This behaviour is typical of merohedral and pseudo-merohedral twins, which are formed when the metric symmetry of the unit cell is higher than that of its contents. Under these conditions, a matrix product (monoclinic to triclinic) \times (inversion) \times (triclinic to monoclinic) = $(001/\frac{1}{2}0/\frac{1}{2}0) \times (\bar{1}00/0\bar{1}0/00\bar{1}) \times (0\bar{1}\bar{1}/0\bar{1}\bar{1}/\bar{1}00)$ (matrices written by rows) can be expressed as TWIN 1 0 0 0 0 1 0 1 0 in the *SHELXL97* code (Sheldrick, 1997). The volume ratios of the twins refined to 0.5627 (8):0.4373 (8).

An interesting feature of the title compound is the presence of one non-centrosymmetric and two centrosymmetric molecules in the crystal structure (Fig. 1). Although the differences in Cu–N_{NL} bond distances are small, it might be supposed that the orientation of the imidazole ligands (and thus the interaction of π -electron density with Cu^{II} *d*-orbitals) could increase the asymmetry at the Cu^{II} centre, the most pronounced distortion being in the axial direction [2.509 (3) and 2.570 (3) Å]. It can be seen that all Cu–N_{iz} distances that are perpendicular to the *N*-nitrocyanoamide/Cu^{II}/imidazole ‘plane’ are significantly shorter than the Cu–N_{iz} distances in the ‘plane’ [Cu1–N7 = 1.998 (3) Å, Cu1–N17 = 2.002 (3) Å, Cu34–N35 = 2.015 (3) Å and Cu51–N57 = 2.005 (3) Å]. The greatest deviations from regular geometry are in the angles that contain atoms that are more tightly bonded (N7, N17, N35 and N57; see Table 1).

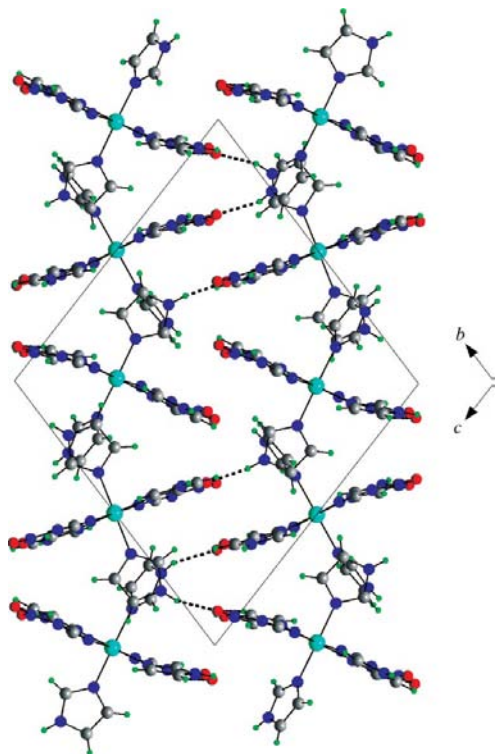


Figure 2
Packing diagram of (I), viewed along the *a* axis. Hydrogen-bond interactions are indicated by dashed lines.

For chromophore CuN₆, the CSD contains 45 crystal structures with monodentate nitrogen ligands and with no restrictions for centrosymmetry. However, only five of these structures have a non-centrosymmetric molecule [refcodes LAXTEJ (Otieno *et al.*, 1993), LITVEP (Lipkowski *et al.*, 1999), LOYROG (Dalai *et al.*, 2002), MOGMUQ (Fedin *et al.*, 2002) and SOFCEV (Kožíšek *et al.*, 1991)]. No crystal structure containing both centrosymmetric and non-centrosymmetric moieties was found. The greatest difference between the axial distances is in SOFCEV (2.372 and 2.500 Å).

The crystal structure of (I) is stabilized by a three-dimensional network of hydrogen bonds and van der Waals interactions (Fig. 2 and Table 2). The closest intermolecular contacts [N9···O49 = 2.819 (4) Å, N59···O33 = 2.832 (4) Å and N19···O67 = 2.848 (4) Å] do not indicate significant π – π interaction.

Experimental

A solution of Cu(NO₃)₂ (2.0 mmol) in water (3 ml) was mixed with a solution of KNO₂NCN (4.0 mmol) in water (10 ml) and a solution of imidazole (4.0 mmol) in methanol (10 ml). This system was left to stand for a few days and blue crystals of [Cu(NCNO₂)₂(iz)₄] were isolated. The mid-IR vibrational spectrum was compared with those of NaNO₂NCN and free imidazole. The comparison revealed that many vibration bands of the *N*-nitrocyanoamide ligand (*e.g.* 2196 and 2189 cm^{−1} for the NCN asymmetric stretching vibration, 1171 and 1162 cm^{−1} for the NCN symmetric vibration, 1298 and 1284 cm^{−1} for the NO₂ symmetric stretching vibration, 968 and 962 cm^{−1} for the N–N stretching vibration, 551 and 540 cm^{−1} for the C–N torsion, and 511 and 506 cm^{−1} for the NCN bending vibration) are split by only a few wavenumbers. Similar small splittings can also be seen on some imidazole ligand bands. These features may indicate the presence of more than one crystallographically independent molecule in the lattice.

Crystal data

[Cu(CN ₃ O ₂) ₂ (C ₃ H ₄ N ₂) ₄]	<i>Z</i> = 4
<i>M_r</i> = 507.95	<i>D_x</i> = 1.551 Mg m ^{−3}
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 9.841 (2) Å	Cell parameters from 1076 reflections
<i>b</i> = 15.249 (3) Å	<i>θ</i> = 2.4–19.0°
<i>c</i> = 15.234 (3) Å	<i>μ</i> = 1.06 mm ^{−1}
<i>α</i> = 104.17 (2)°	<i>T</i> = 304 (2) K
<i>β</i> = 96.65 (2)°	Block, blue
<i>γ</i> = 96.86 (2)°	0.36 × 0.34 × 0.11 mm
<i>V</i> = 2175.6 (8) Å ³	

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	8693 independent reflections
<i>ω</i> scans	7962 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: analytical face-indexed (<i>CrysAlis RED</i> ; Oxford Diffraction, 2003)	<i>R</i> _{int} = 0.030
<i>T</i> _{min} = 0.704, <i>T</i> _{max} = 0.893	<i>θ</i> _{max} = 26.4°
14 665 measured reflections	<i>h</i> = −11 → 12
	<i>k</i> = −18 → 19
	<i>l</i> = −19 → 17

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.036 <i>P</i>) ² + 2.2497 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.088	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.05	Δρ _{max} = 0.65 e Å ^{−3}
8693 reflections	Δρ _{min} = −0.42 e Å ^{−3}
599 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	2.022 (3)	Cu34—N45	2.548 (4)
Cu1—N7	1.998 (3)	Cu51—N52	2.020 (3)
Cu1—N12	2.026 (3)	Cu51—N57	2.005 (3)
Cu1—N17	2.002 (3)	Cu51—N62	2.549 (3)
Cu1—N22	2.570 (3)	N22—C23	1.151 (4)
Cu1—N28	2.509 (3)	N28—C29	1.161 (5)
Cu34—N35	2.015 (3)	N45—C46	1.144 (5)
Cu34—N40	2.021 (3)	N62—C63	1.152 (5)
N2—Cu1—N12	179.6 (1)	N22—Cu1—N28	177.0 (1)
N7—Cu1—N17	177.7 (1)	N35—Cu34—N40	91.9 (1)
N7—Cu1—N22	92.9 (1)	N57—Cu51—N62	87.0 (1)
N17—Cu1—N28	87.6 (1)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N19—H19A...O67 ⁱ	0.86	2.00	2.848 (4)	171
N59—H59A...O33 ⁱⁱ	0.86	2.03	2.832 (4)	155
N4—H4A...O27 ⁱⁱⁱ	0.86	2.06	2.910 (4)	172
N14—H14A...O33 ^{iv}	0.86	2.06	2.886 (5)	161
N9—H9A...O49 ^v	0.86	2.06	2.819 (4)	146
N54—H54A...O66 ⁱⁱⁱ	0.86	2.09	2.918 (4)	163

 Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z$; (iii) $x - 1, y, z$; (iv) $x + 1, y, z$; (v) $-x + 2, -y, -z$.

Table 3

 Comparison of bond distances (Å) for compounds of the type $[M(NL)_4(NO_2NCN)_2]$.

<i>M</i>	Co—N _{NL}	Co—N _{nca}	CSD refcode
Co	2.098–2.151	2.136–2.167	DOQZIS ^a , TUSLOI ^b
Ni	2.067–2.093	2.076–2.110	DOQZEO ^a , OFILEU ^c
Cu	2.000–2.024	2.600–2.683	BEFBET ^d , BEFCUK ^d

 Notes: (a) Hvastijová *et al.* (2000); (b) Hvastijová *et al.* (2003); (c) Hvastijová *et al.* (2001); (d) Kohout *et al.* (1999).

H atoms were positioned geometrically and treated as riding atoms (C—H = 0.93 Å and N—H = 0.86 Å), with $U_{iso}(H)$ set at $1.2U_{eq}$ of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

The authors thank the Grant Agency of the Slovak Republic (grant Nos. VEGA 1/2449/05 and COSNET 545.03-P).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1193). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Dalai, S., Mukherjee, P. S., Mallah, T., Drew, M. G. B. & Chaudhuri, N. R. (2002). *Inorg. Chem. Commun.* **5**, 472–474.
- Díaz, J. G., Kožíšek, J. & Langer, V. (2003). *Acta Cryst.* **E59**, m241–m243.
- Fedin, V. P., Kalinina, I. V., Gerasimenko, A. & Virovets, A. V. (2002). *Inorg. Chim. Acta*, **331**, 48–51.
- Hvastijová, M., Boča, R., Kohout, J., Jäger, L., Císařová, I. & Kožíšek, J. (2003). *Inorg. Chim. Acta*, **343**, 217–223.
- Hvastijová, M., Kohout, J., Buchler, J. W., Boča, R., Kožíšek, J. & Jäger, L. (1998). *Coord. Chem. Rev.* **175**, 17–42.
- Hvastijová, M., Kohout, J., Díaz, G. J., Kožíšek, J. & Buchler, J. W. (2001). *Transition Met. Chem.* **26**, 430–434.
- Hvastijová, M., Kohout, J., Kožíšek, J., Jäger, L. & Díaz, G. J. (2000). *Polyhedron*, **19**, 1021–1027.
- Jäger, L., Tretner, C., Hartung, H. & Biedermann, M. (1997). *Z. Anorg. Allg. Chem.* **623**, 1299–1562.
- Kohout, J., Hvastijová, M., Kožíšek, J., Díaz, G. J., Valko, M., Jäger, L. & Svoboda, I. (1999). *Inorg. Chim. Acta*, **287**, 186–192.
- Kohout, J., Jäger, L., Hvastijová, M. & Kožíšek, J. (2000). *J. Coord. Chem.* **51**, 169–218.
- Kožíšek, J., Hansen, N. K. & Fuess, H. (2002). *Acta Cryst.* **B58**, 463–470.
- Kožíšek, J., Hvastijová, M., Kohout, J., Mrozinski, J. & Köhler, H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1773–1778.
- Lipkowski, J., Kislykh, N. V., Dyadin, Y. A. & Sheludiyakova, L. A. (1999). *J. Struct. Chem.* **5**, 772–780.
- Otieno, T., Rettig, S. J., Thompson, R. C. & Trotter, J. (1993). *Inorg. Chem.* **32**, 4384–4390.
- Oxford Diffraction (2001). *CrysAlis CCD*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Oxford Diffraction (2003). *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Potočňák, I., Burčák, M., Massa, W. & Jäger, L. (2002). *Acta Cryst.* **C58**, m523–m528.
- Potočňák, I., Dunaj-Jurčo, M., Mikloš, D. & Jäger, L. (2001). *Monatsh. Chem.* **132**, 315–327.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.