

[N-(1-Azanidyl-2,2,2-trichloroethylidene)-2,2,2-trichloroethanimidamide]-copper(II)

Namig G. Shikhaliyev,^{a*} Abel M. Maharramov,^a Vasily M. Muzalevskiy,^b Valentine G. Nenajdenko^b and Victor N. Khrustalev^c

^aBaku State University, Z. Khalilov St 23, Baku AZ-1148, Azerbaijan, ^bChemistry Department, M.V. Lomonosov Moscow State University, Leninskie gory 1/3, Moscow 119991, Russian Federation, and ^cX-Ray Structural Centre, A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St B-334, Moscow 119991, Russian Federation
Correspondence e-mail: namiq155@yahoo.com

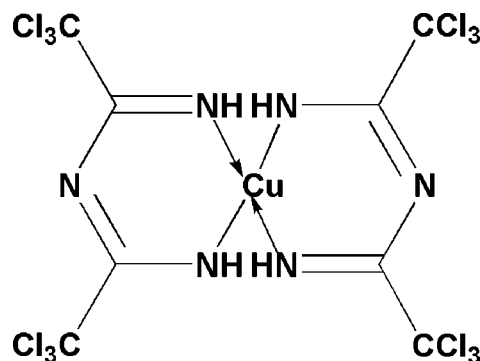
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.047; wR factor = 0.133; data-to-parameter ratio = 19.5.

The title compound, $[\text{Cu}(\text{C}_4\text{H}_2\text{Cl}_6\text{N}_3)_2]$, was obtained by the reaction of CCl_3CN with ammonia in presence of CuCl . The Cu^{II} atom is located about an inversion centre. The molecule consists of three planar units (one central square CuN_4 and two C_2N_3 fragments), adopting a staircase-like structure. The six-membered metalocycles have a sofa conformation with the Cu atom out of the plane of the 1,3,5-triazapentadienyl ligands by 0.246 (5) Å. The *ipso*-C atoms of the CCl_3 substituents are slightly out of the 1,3,5-triazapentadienyl planes by 0.149 (6) and -0.106 (6) Å. The CCl_3 groups of each 1,3,5-triazapentadienyl ligand are practically in the energetically favourable mutually eclipsed conformation. In the crystal, the molecules are packed in stacks along the a axis. The molecules in the stacks are held together by two additional axial $\text{Cu} \cdots \text{Cl}$ interactions of 3.354 (2) Å. Taking the axial $\text{Cu} \cdots \text{Cl}$ interactions into account, the Cu^{II} atom exhibits a distorted $[4 + 2]$ -octahedral coordination environment. The stacks are bound to each other by weak intermolecular attractive $\text{Cl} \cdots \text{Cl}$ [3.505 (2)–3.592 (3) Å] interactions.

Related literature

For a catalytic olefination reaction, see: Shastin *et al.* (2001); Korotchenko *et al.* (2001); Nenajdenko *et al.* (2003, 2004*a,b,c*, 2005, 2007). For related compounds, see: Boča *et al.* (1996); Kajiwara *et al.* (2002); Zhang *et al.* (2005); Igashira-Kamiyama *et al.* (2006); Zheng *et al.* (2007); Figiel *et al.* (2010).



Experimental

Crystal data

$[\text{Cu}(\text{C}_4\text{H}_2\text{Cl}_6\text{N}_3)_2]$	$\gamma = 103.662$ (5)°
$M_r = 673.11$	$V = 552.1$ (3) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.9317$ (17) Å	Mo $K\alpha$ radiation
$b = 9.078$ (3) Å	$\mu = 2.45$ mm ⁻¹
$c = 10.831$ (3) Å	$T = 296$ K
$\alpha = 98.475$ (5)°	$0.33 \times 0.24 \times 0.06$ mm
$\beta = 97.525$ (5)°	

Data collection

Bruker APEXII CCD diffractometer	5662 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2414 independent reflections
$T_{\min} = 0.499$, $T_{\max} = 0.867$	2108 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	124 parameters
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 1.18$ e Å ⁻³
2414 reflections	$\Delta\rho_{\text{min}} = -0.85$ e Å ⁻³

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2069).

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supplementary materials

Acta Cryst. (2012). E68, m1220–m1221 [doi:10.1107/S1600536812036124]

[*N*-(1-Azanidyl)-2,2,2-trichloroethylidene)-2,2,2-trichloroethanimidamide]-copper(II)

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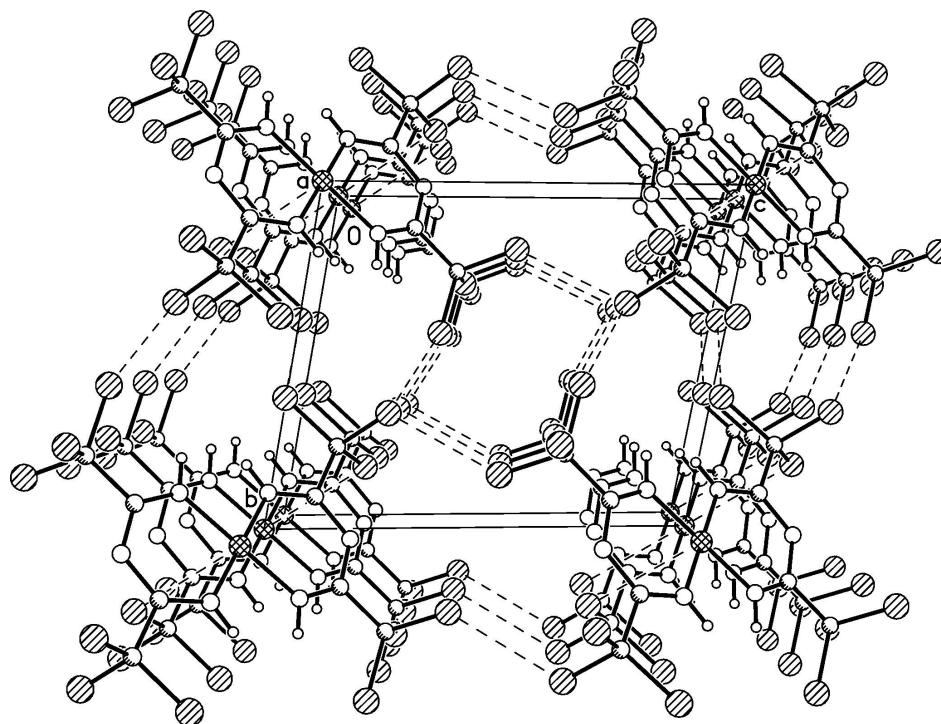
Comment

Recently we have discovered a new catalytic olefination reaction as a general method for the preparation of alkenes from polyhalogenated compounds and hydrazones (Fig. 1) (Shastin *et al.*, 2001; Korotchenko *et al.*, 2001; Nenajdenko *et al.*, 2003, 2004*a*, 2004*b*, 2005, 2007).

During our study of the catalytic olefination reaction we have found that the reaction with trichloroacetonitrile demand the use of ethylenediamine as a base because in the case of ammonia no target alkene is formed (Nenajdenko *et al.*, 2004*c*). We decided to study the reaction of CCl₃CN with ammonia in presence of CuCl more thoroughly and found that the formation of the title copper (II) chelate complex takes place (Fig. 2). The formation of this complex can be explained by high electrophilicity of trichloroacetonitrile (Fig. 3). At the first stage, ammonia reacts with CN bond to form amidine **A** as an intermediate. The subsequent reaction of **A** with second molecule of trichloroacetonitrile gives **B**. And finally, **B** reacts with CuCl₂ resulting in the copper(II) complex **I** in a high yield. We believe that Cu²⁺ is formed by oxidation of Cu¹⁺ with CCl₃CN as it was confirmed previously for catalytic olefination reaction.

The structure of the title compound **I**, C₈H₄N₆Cl₁₂Cu, was unambiguously established by X-ray diffraction study (Fig. 4). The compound **I** crystallizes in the triclinic space group *P*-1 and there is a crystallographically imposed inversion centre at the Cu atom of each molecule. The Cu atom has a square-planar coordination. The 1,3,5-triazapentadienyl ligands are also planar (r.m.s. deviation is 0.021 Å). However, the six-membered metallocycles deviate significantly from the planarity and have a *sofa* conformation with the Cu atom out of the plane of the 1,3,5-triazapentadienyl ligands by 0.246 (5) Å. Thus, the molecule of **I** consists of the three planar units adopting the *staircase*-like structure. The similar molecular conformation has been previously observed in the related compounds (Zhang *et al.*, 2005; Igashira-Kamiyama *et al.*, 2006; Figiel *et al.*, 2010). Nevertheless, it is important to note that the analogous complexes can adopt the planar conformation also (Boča *et al.*, 1996; Kajiwara *et al.*, 2002; Zheng *et al.*, 2007). The *ipso*-C atoms of the CCl₃-substituents are slightly out of the 1,3,5-triazapentadienyl planes by 0.149 (6) and -0.106 (6) Å. The CCl₃-groups of each 1,3,5-triazapentadienyl ligand are practically in the energetically favorable eclipsed mutual conformation.

In the crystal, the molecules are packed in stacks along the *a* axis (Fig. 5). The molecules in the stacks are held together by the two additional axial Cu⋯Cl [Cu1⋯Cl1ⁱ and Cu1⋯Cl1ⁱⁱ] interactions of 3.354 (2) Å. Taking the axial Cu⋯Cl interactions into account, the Cu atom attains the distorted [4 + 2]-octahedral coordination environment. The different stacks are bound to each other by weak intermolecular attractive interactions [Cu2⋯Cl2ⁱⁱⁱ 3.505 (2), Cu2⋯Cl2^{iv} 3.592 (3), Cu3⋯Cl4^v 3.516 (2) and Cu3⋯Cl6^{vi} 3.564 (2) Å]. Symmetry codes: (i) *-x, -y + 2, -z + 2*; (ii) *x - 1, y, z*; (iii) *-x + 2, -y + 3, -z + 2*; (iv) *-x + 1, -y + 3, -z + 2*; (v) *x + 1, y + 1, z*; (vi) *-x, -y + 2, -z + 1*.

**Figure 5**

The crystal packing of **I** along the *a* axis. Dashed lines indicate the intermolecular axial Cu...Cl and attractive Cl...Cl interactions.

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Crystal data

[Cu(C₄H₂Cl₆N₃)₂]

M_r = 673.11

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 5.9317 (17) Å

b = 9.078 (3) Å

c = 10.831 (3) Å

α = 98.475 (5)°

β = 97.525 (5)°

γ = 103.662 (5)°

V = 552.1 (3) Å³

Z = 1

F(000) = 327

D_x = 2.024 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3874 reflections

θ = 2.4–27.7°

μ = 2.45 mm⁻¹

T = 296 K

Plate, red

0.33 × 0.24 × 0.06 mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2003)

T_{min} = 0.499, *T_{max}* = 0.867

5662 measured reflections

2414 independent reflections

2108 reflections with *I* > 2σ(*I*)

R_{int} = 0.029

θ_{\max} = 27.0°, θ_{\min} = 1.9°

h = -7→7

k = -11→11

l = -13→13

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.133$

$S = 1.00$

2414 reflections

124 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.84P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.18 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.85 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	1.0000	1.0000	0.0000	0.03611 (19)
Cl1	0.20230 (19)	0.81177 (15)	0.21612 (13)	0.0696 (3)
Cl2	0.28874 (19)	0.61212 (13)	0.01081 (11)	0.0644 (3)
Cl3	0.5633 (2)	0.65213 (14)	0.25606 (12)	0.0677 (3)
Cl4	1.0465 (2)	1.42819 (12)	0.33037 (12)	0.0730 (4)
Cl5	0.5879 (2)	1.27757 (17)	0.35949 (16)	0.0868 (5)
Cl6	0.9881 (3)	1.18805 (17)	0.47247 (11)	0.0886 (5)
N1	0.7097 (5)	0.8671 (3)	0.0275 (3)	0.0437 (7)
H1	0.6365	0.7918	-0.0331	0.052*
C2	0.6169 (5)	0.8813 (4)	0.1278 (3)	0.0358 (6)
N3	0.6704 (5)	0.9993 (3)	0.2235 (3)	0.0441 (7)
C4	0.8405 (6)	1.1234 (4)	0.2244 (3)	0.0353 (6)
N5	0.9823 (6)	1.1456 (3)	0.1452 (3)	0.0446 (7)
H5	1.0802	1.2351	0.1582	0.054*
C6	0.4243 (6)	0.7471 (4)	0.1511 (4)	0.0421 (7)
C7	0.8629 (7)	1.2489 (4)	0.3416 (3)	0.0425 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0386 (3)	0.0301 (3)	0.0377 (3)	0.0011 (2)	0.0172 (2)	0.0035 (2)
Cl1	0.0495 (6)	0.0725 (7)	0.0932 (9)	0.0109 (5)	0.0390 (6)	0.0205 (6)
Cl2	0.0505 (5)	0.0531 (6)	0.0697 (7)	-0.0144 (4)	0.0029 (5)	0.0011 (5)
Cl3	0.0586 (6)	0.0634 (7)	0.0806 (8)	0.0026 (5)	0.0025 (5)	0.0422 (6)
Cl4	0.0951 (9)	0.0370 (5)	0.0731 (7)	-0.0102 (5)	0.0382 (6)	-0.0097 (5)
Cl5	0.0568 (7)	0.0793 (8)	0.1141 (11)	0.0171 (6)	0.0303 (7)	-0.0268 (8)

C16	0.1405 (14)	0.0778 (9)	0.0422 (6)	0.0311 (9)	-0.0047 (7)	0.0076 (5)
N1	0.0425 (15)	0.0386 (15)	0.0407 (15)	-0.0039 (12)	0.0135 (12)	-0.0039 (12)
C2	0.0343 (15)	0.0320 (15)	0.0399 (16)	0.0027 (12)	0.0094 (12)	0.0099 (12)
N3	0.0496 (16)	0.0379 (15)	0.0401 (15)	-0.0022 (12)	0.0199 (13)	0.0035 (12)
C4	0.0397 (16)	0.0312 (15)	0.0346 (15)	0.0058 (12)	0.0109 (12)	0.0063 (12)
N5	0.0515 (17)	0.0300 (14)	0.0478 (16)	-0.0025 (12)	0.0241 (13)	0.0003 (12)
C6	0.0341 (16)	0.0409 (17)	0.0505 (19)	0.0028 (13)	0.0118 (14)	0.0136 (14)
C7	0.0497 (19)	0.0364 (17)	0.0394 (17)	0.0066 (14)	0.0158 (14)	0.0014 (13)

Geometric parameters (Å, °)

Cu1—N5	1.931 (3)	N1—C2	1.284 (4)
Cu1—N1	1.941 (3)	N1—H1	0.8600
C11—C6	1.749 (4)	C2—N3	1.322 (4)
C12—C6	1.767 (4)	C2—C6	1.537 (4)
C13—C6	1.759 (4)	N3—C4	1.321 (4)
C14—C7	1.762 (4)	C4—N5	1.282 (4)
C15—C7	1.742 (4)	C4—C7	1.544 (4)
C16—C7	1.736 (4)	N5—H5	0.8600
N5—Cu1—N1	87.83 (12)	Cu1—N5—H5	116.4
C2—N1—Cu1	126.0 (2)	C2—C6—C11	111.9 (2)
C2—N1—H1	117.0	C2—C6—C13	106.7 (2)
Cu1—N1—H1	117.0	C11—C6—C13	110.2 (2)
N1—C2—N3	128.5 (3)	C2—C6—C12	112.5 (2)
N1—C2—C6	120.3 (3)	C11—C6—C12	107.50 (19)
N3—C2—C6	111.2 (3)	C13—C6—C12	108.0 (2)
C4—N3—C2	120.5 (3)	C4—C7—C16	107.4 (2)
N5—C4—N3	128.3 (3)	C4—C7—C15	110.5 (2)
N5—C4—C7	120.3 (3)	C16—C7—C15	111.2 (2)
N3—C4—C7	111.4 (3)	C4—C7—C14	112.4 (2)
C4—N5—Cu1	127.1 (2)	C16—C7—C14	108.0 (2)
C4—N5—H5	116.4	C15—C7—C14	107.3 (2)
N5—Cu1—N1—C2	-14.1 (3)	N1—C2—C6—C11	-140.6 (3)
N5 ⁱ —Cu1—N1—C2	165.9 (3)	N3—C2—C6—C11	41.9 (4)
Cu1—N1—C2—N3	12.6 (6)	N1—C2—C6—C13	98.8 (3)
Cu1—N1—C2—C6	-164.4 (2)	N3—C2—C6—C13	-78.7 (3)
N1—C2—N3—C4	-0.4 (6)	N1—C2—C6—C12	-19.5 (4)
C6—C2—N3—C4	176.7 (3)	N3—C2—C6—C12	163.0 (3)
C2—N3—C4—N5	-5.2 (6)	N5—C4—C7—C16	-105.0 (3)
C2—N3—C4—C7	177.1 (3)	N3—C4—C7—C16	72.9 (3)
N3—C4—N5—Cu1	-2.2 (6)	N5—C4—C7—C15	133.5 (3)
C7—C4—N5—Cu1	175.3 (2)	N3—C4—C7—C15	-48.6 (4)
N1—Cu1—N5—C4	9.6 (3)	N5—C4—C7—C14	13.7 (4)
N1 ⁱ —Cu1—N5—C4	-170.4 (3)	N3—C4—C7—C14	-168.4 (3)

Symmetry code: (i) $-x+2, -y+2, -z$.