metal-organic compounds

Di-μ-chlorido-bis[(2-aminobenzamide-κ²N²,O)chloridocopper(II)]

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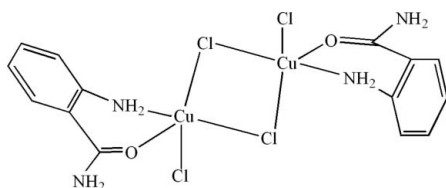Correspondence e-mail: bouacida_sofiane@yahoo.fr

The title compound, $[Cu_2Cl_4(C_7H_8N_2O)_2]$, crystallizes as discrete $[CuLCl_2]_2$ (L = 2-aminobenzamide) dimers with inversion symmetry. Each Cu^{II} ion is five-coordinated and is bound to two bridging chloride ligands, a terminal chloride ligand and a bidentate 2-aminobenzamide ligand. The crystal structure exhibits alternating layers parallel to (010) along the b-axis direction. In the crystal, the components are linked via N—H⋯Cl hydrogen bonds, forming a three-dimensional network. These interactions link the molecules within the layers and also link the layers together and reinforce the cohesion of the structure.

Related literature

For general background to 2-aminobenzamide derivatives, see: Nagaoka *et al.* (2006); Butsch *et al.* (2011); Kapoor *et al.* (2010). For related structures, see: Yang *et al.* (2012); Lah *et al.* (2006). For standard bond lengths, see: Allen (2002)

Experimental

Crystal data

$[Cu_2Cl_4(C_7H_8N_2O)_2]$	a = 8.1888 (5) Å
M_r = 541.21	b = 13.8545 (6) Å
Monoclinic, $P2_1/c$	c = 8.1592 (4) Å

β = 98.771 (5)°	μ = 2.93 mm^{-1}
V = 914.85 (8) Å^3	T = 180 K
Z = 2	0.15 × 0.13 × 0.12 mm
Mo $K\alpha$ radiation	

Data collection

Agilent Xcalibur (Sapphire1) diffractometer	5578 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011) T_{min} = 0.699, T_{max} = 1	2058 independent reflections 1897 reflections with $I > 2\sigma(I)$ R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022	118 parameters
$wR(F^2)$ = 0.058	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.41 e Å^{-3}
2058 reflections	$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯Cl2^i	0.9200	2.4100	3.3113 (16)	166.00
N2—H2A⋯Cl1^{ii}	0.8800	2.7800	3.6439 (16)	169.00
N2—H2B⋯Cl2^{iii}	0.8800	2.5400	3.3493 (17)	153.00

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y, z+1$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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supporting information

Di-*µ*-chlorido-bis[(2-aminobenzamide-*κ²N²,O*)chloridocopper(II)]

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S1. Comment

2-aminobenzamide derivatives are well known compounds as anticancer agents (Nagaoka *et al.*, 2006). In addition, it was reported that some 2-aminobenzamide derivatives possessed biological activities, such as Anti-herpes simplex virus activity (Yang *et al.*, 2012). As part of our ongoing studies of complexes based on copper and derivates we report here synthesis and the crystal structure of the title compound, obtained by the reaction of 2-aminobenzamide ligand with copper(II) chloride. The molecular structure of (I), and the atomic numbering used, is illustrated in Fig. 1. The asymmetric unit of (I) consists of one-half of the molecule, with the other half generated by a crystallographic inversion center. All bond distances and angles are within the ranges of accepted values(CSD, Allen, 2002) The complex contain five-coordinate Cu atoms (Fig. 1) with may be described either as square pyramidal with C11 apically bound to a pseudoplanar Cu1—O1—C12—Cl1a—N1 (a:-*x*, -*y*,1 - *z*) fragment or as trigonal bipyramidal with N1 and Cl1a apical (Butsch *et al.*, 2011; Kapoor *et al.*, 2010). The Cu atoms are linked by double Cl atoms bridges, resulting in the formation of dimer. The two Cu atoms, separated by 3.430 (1) Å, are doubly bridged by two chlorido ligands. The bridge is far from symmetrical with Cu—Cl1 and Cu—Cl1a (with a: -*x*, -*y*,1 - *z*) distances of 2.3983 (5) and 2.2990 (6) Å, respectively, and a Cu—Cl1-Cua bridging angle of 93.77 (2)°. The 2-aminobenzamide ligand binds to a single Cu metal ion within the dimer in a chelating manner [Cu—N1: 1.9923 (15) Å and Cu–O1: 2.0988 (13) Å]. The fifth coordination site is occupied by a terminal chlorido ligand at a distance of 2.3043 (6) Å (Lah *et al.*, 2006).

   The crystal structure exhibit alternating layers parallel to (010) plane along the *b* axis (Fig. 2). In the crystal, the components of the structure are linked *via* intermolecular N—H⋯Cl hydrogen bonds to form a three-dimensional network (Table1 and Fig.2) These interaction bonds link the molecules within the layers and also link the layers together and reinforcing the cohesion of the structure.

S2. Experimental

An aqueous acidic solution of copper(II) chloride was added to an aqueous solution of the 2-aminobenzamide ligand (*L*) (1:l mol ratio). The mixture was then stirred for several hours during which time darkish green crystals of [CuLCl₂]₂ were deposited. This crystalline product was collected and washed with ether and was carefully isolated under polarizing microscope for analysis by X-ray diffraction.

S3. Refinement

All non-H atoms were refined with anisotropic atomic displacement parameters. The remaining H atoms were localized on Fourier maps but introduced in calculated positions and treated as riding on their parent atoms (C and N) with C—H=0.95 Å and N—H=0.88 or 0.92 Å and U_{iso}(H)=1.2U_{eq}(C or N).
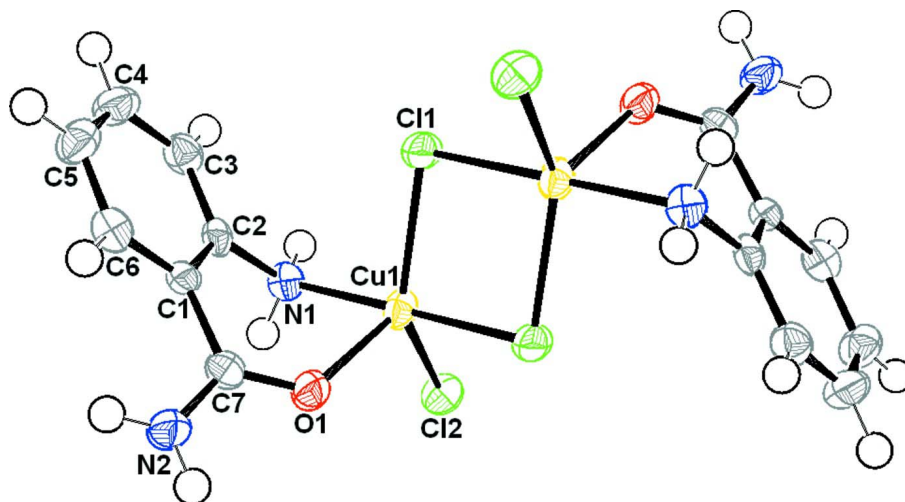
Figure 1

(Farrugia, 2012) The molecule structure of the title dimer with the atomic labelling scheme·Displacement are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radius. Only the contents of the asymmetric unit are numbered.
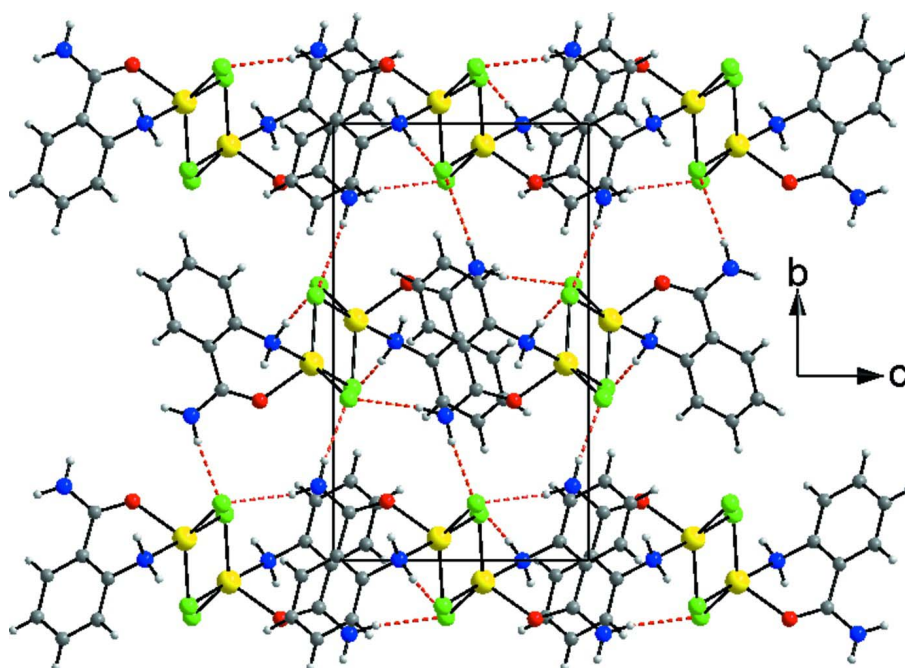
Figure 2

(Brandenburg & Berndt, 2001) A diagram of the layered crystal packing in (I), viewed down the *b* axis, showing layers parallel to (010) and hydrogen bond connections as dashed line.

Di-µ-chlorido-bis[(2-aminobenzamide-*κ²N²*,*O*)chloridocopper(II)]

Crystal data

[Cu$_2$Cl$_4$(C$_7$H$_8$N$_2$O)$_2$]	Monoclinic, *P*2$_1$/*c*
M_r = 541.21	Hall symbol: -P 2ybc

$a = 8.1888\ (5)$ Å
$b = 13.8545\ (6)$ Å
$c = 8.1592\ (4)$ Å
$\beta = 98.771\ (5)°$
$V = 914.85\ (8)$ Å^3
$Z = 2$
$F(000) = 540$
$D_x = 1.965$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3363 reflections
$\theta = 2.9–28.2°$
$\mu = 2.93$ mm^{-1}
$T = 180$ K
Cube, green
$0.15 \times 0.13 \times 0.12$ mm

Data collection

Agilent Xcalibur (Sapphire1)
   diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.2632 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
   (*CrysAlis PRO*; Agilent, 2011)
$T_{min} = 0.699$, $T_{max} = 1$

5578 measured reflections
2058 independent reflections
1897 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.9°$
$h = -9 \rightarrow 10$
$k = -17 \rightarrow 18$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.058$
$S = 1.04$
2058 reflections
118 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
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.3739P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Experimental. Absorption correction: empirical using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm CrysAlis PRO (Agilent, 2011).

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cu1	0.18491 (3)	−0.04957 (2)	0.58700 (3)	0.0126 (1)
Cl1	0.05270 (6)	0.10533 (3)	0.57135 (6)	0.0161 (1)
Cl2	0.36324 (6)	−0.12970 (3)	0.44121 (6)	0.0162 (1)
O1	0.15024 (17)	−0.13480 (9)	0.79155 (16)	0.0156 (4)
N1	0.37924 (19)	−0.00155 (11)	0.74251 (18)	0.0126 (4)
N2	0.1556 (2)	−0.16908 (11)	1.0607 (2)	0.0180 (5)
C1	0.2398 (2)	−0.00937 (12)	0.9884 (2)	0.0107 (5)

C2	0.3341 (2)	0.04226 (12)	0.8882 (2)	0.0111 (5)
C3	0.3819 (2)	0.13689 (13)	0.9288 (2)	0.0147 (5)
C4	0.3337 (3)	0.18053 (13)	1.0665 (2)	0.0181 (5)
C5	0.2408 (3)	0.13070 (13)	1.1664 (2)	0.0171 (5)
C6	0.1958 (2)	0.03556 (13)	1.1275 (2)	0.0140 (5)
C7	0.1801 (2)	−0.10930 (12)	0.9406 (2)	0.0122 (5)
H1A	0.43529	0.04286	0.68835	0.0152*
H1B	0.44964	−0.05231	0.77350	0.0152*
H2A	0.11781	−0.22765	1.03652	0.0216*
H2B	0.17697	−0.15031	1.16476	0.0216*
H3	0.44744	0.17143	0.86209	0.0176*
H4	0.36477	0.24546	1.09246	0.0217*
H5	0.20810	0.16101	1.26070	0.0206*
H6	0.13389	0.00073	1.19728	0.0168*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0105 (1)	0.0152 (1)	0.0119 (1)	0.0003 (1)	0.0005 (1)	−0.0027 (1)
Cl1	0.0141 (2)	0.0125 (2)	0.0198 (2)	0.0006 (2)	−0.0036 (2)	−0.0023 (2)
Cl2	0.0160 (2)	0.0175 (2)	0.0162 (2)	0.0013 (2)	0.0059 (2)	−0.0026 (2)
O1	0.0214 (7)	0.0129 (6)	0.0121 (6)	−0.0036 (5)	0.0016 (5)	−0.0002 (5)
N1	0.0118 (7)	0.0148 (7)	0.0119 (7)	−0.0002 (6)	0.0038 (6)	0.0005 (6)
N2	0.0280 (10)	0.0118 (7)	0.0140 (8)	−0.0036 (7)	0.0026 (7)	−0.0001 (6)
C1	0.0100 (8)	0.0100 (8)	0.0113 (8)	0.0013 (7)	−0.0007 (7)	0.0004 (7)
C2	0.0084 (8)	0.0147 (8)	0.0094 (8)	0.0021 (7)	−0.0011 (7)	0.0005 (7)
C3	0.0141 (9)	0.0149 (8)	0.0146 (9)	−0.0020 (7)	0.0009 (7)	0.0026 (7)
C4	0.0193 (10)	0.0124 (8)	0.0217 (10)	−0.0016 (7)	0.0004 (8)	−0.0032 (7)
C5	0.0177 (10)	0.0176 (9)	0.0162 (9)	0.0016 (8)	0.0030 (8)	−0.0049 (7)
C6	0.0118 (9)	0.0167 (9)	0.0135 (9)	0.0006 (7)	0.0022 (7)	0.0026 (7)
C7	0.0103 (9)	0.0127 (8)	0.0135 (9)	0.0016 (7)	0.0018 (7)	0.0014 (7)

Geometric parameters (Å, º)

Cu1—Cl1	2.3983 (5)	C1—C2	1.403 (2)
Cu1—Cl2	2.3043 (6)	C1—C6	1.389 (2)
Cu1—O1	2.0988 (13)	C1—C7	1.500 (2)
Cu1—N1	1.9923 (15)	C2—C3	1.394 (2)
Cu1—Cl1[i]	2.2990 (6)	C3—C4	1.385 (2)
O1—C7	1.254 (2)	C4—C5	1.382 (3)
N1—C2	1.433 (2)	C5—C6	1.392 (3)
N2—C7	1.322 (2)	C3—H3	0.9500
N1—H1A	0.9200	C4—H4	0.9500
N1—H1B	0.9200	C5—H5	0.9500
N2—H2A	0.8800	C6—H6	0.9500
N2—H2B	0.8800		
Cl1—Cu1—Cl2	136.06 (2)	C2—C1—C6	118.81 (15)

Cl1—Cu1—O1	115.54 (4)	C2—C1—C7	120.37 (14)
Cl1—Cu1—N1	92.60 (5)	C6—C1—C7	120.74 (15)
Cl1—Cu1—Cl1ⁱ	86.23 (2)	N1—C2—C1	120.14 (15)
Cl2—Cu1—O1	108.22 (4)	N1—C2—C3	119.81 (15)
Cl2—Cu1—N1	88.98 (5)	C1—C2—C3	120.04 (15)
Cl1ⁱ—Cu1—Cl2	95.55 (2)	C2—C3—C4	119.93 (16)
O1—Cu1—N1	82.72 (6)	C3—C4—C5	120.73 (17)
Cl1ⁱ—Cu1—O1	93.00 (4)	C4—C5—C6	119.28 (16)
Cl1ⁱ—Cu1—N1	174.57 (5)	C1—C6—C5	121.19 (16)
Cu1—Cl1—Cu1ⁱ	93.77 (2)	O1—C7—C1	121.32 (15)
Cu1—O1—C7	125.63 (11)	N2—C7—C1	117.78 (15)
Cu1—N1—C2	112.82 (11)	O1—C7—N2	120.88 (16)
C2—N1—H1A	109.00	C2—C3—H3	120.00
C2—N1—H1B	109.00	C4—C3—H3	120.00
H1A—N1—H1B	108.00	C3—C4—H4	120.00
Cu1—N1—H1A	109.00	C5—C4—H4	120.00
Cu1—N1—H1B	109.00	C4—C5—H5	120.00
H2A—N2—H2B	120.00	C6—C5—H5	120.00
C7—N2—H2A	120.00	C1—C6—H6	119.00
C7—N2—H2B	120.00	C5—C6—H6	119.00
Cl2—Cu1—Cl1—Cu1ⁱ	94.09 (3)	Cu1—N1—C2—C1	55.55 (18)
O1—Cu1—Cl1—Cu1ⁱ	−91.53 (5)	C6—C1—C2—N1	−179.03 (15)
N1—Cu1—Cl1—Cu1ⁱ	−174.69 (5)	C7—C1—C6—C5	−175.43 (17)
Cl1ⁱ—Cu1—Cl1—Cu1ⁱ	0.00 (4)	C2—C1—C7—O1	−29.6 (2)
Cl1—Cu1—Cl1ⁱ—Cu1ⁱ	0.00 (4)	C6—C1—C2—C3	0.0 (2)
Cl2—Cu1—Cl1ⁱ—Cu1ⁱ	−135.94 (2)	C6—C1—C7—O1	147.06 (17)
O1—Cu1—Cl1ⁱ—Cu1ⁱ	115.41 (4)	C6—C1—C7—N2	−31.2 (2)
Cl1—Cu1—O1—C7	−53.92 (15)	C2—C1—C7—N2	152.19 (16)
Cl2—Cu1—O1—C7	121.99 (14)	C2—C1—C6—C5	1.3 (3)
N1—Cu1—O1—C7	35.49 (15)	C7—C1—C2—C3	176.68 (15)
Cl1ⁱ—Cu1—O1—C7	−141.17 (14)	C7—C1—C2—N1	−2.3 (2)
Cl1—Cu1—N1—C2	55.31 (11)	C1—C2—C3—C4	−1.2 (3)
Cl2—Cu1—N1—C2	−168.63 (11)	N1—C2—C3—C4	177.83 (17)
O1—Cu1—N1—C2	−60.11 (11)	C2—C3—C4—C5	1.2 (3)
Cu1—O1—C7—C1	2.6 (2)	C3—C4—C5—C6	0.1 (3)
Cu1—O1—C7—N2	−179.23 (12)	C4—C5—C6—C1	−1.3 (3)
Cu1—N1—C2—C3	−123.45 (14)		

Symmetry code: (i) −x, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2ⁱⁱ	0.9200	2.4100	3.3113 (16)	166.00
N2—H2A···Cl1ⁱⁱⁱ	0.8800	2.7800	3.6439 (16)	169.00
N2—H2B···Cl2ⁱᵛ	0.8800	2.5400	3.3493 (17)	153.00

Symmetry codes: (ii) −x+1, −y, −z+1; (iii) −x, y−1/2, −z+3/2; (iv) x, y, z+1.