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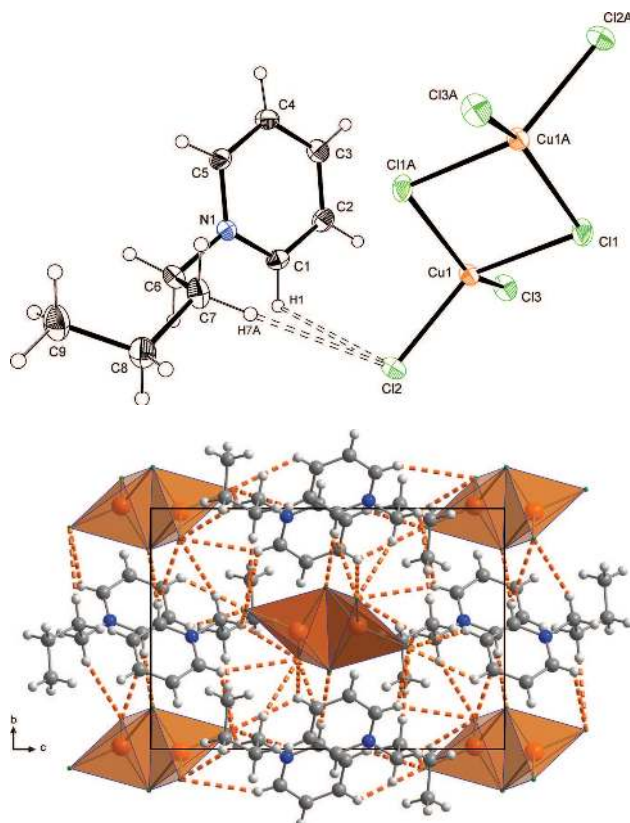
The crystal structure of *N*-butylpyridinium bis(μ_2 -dichlorido)- tetrachloridodicopper(II), $C_{18}H_{28}N_2Cu_2Cl_6$

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The crystal structure of *N*-butylpyridinium bis(μ_2 -dichlorido)-tetrachloridodicopper(II), $C_{18}H_{28}N_2Cu_2Cl_6$

**Table 1:** Data collection and handling.

Crystal:	Red block
Size:	1.00 × 0.45 × 0.33 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.36 mm ⁻¹
Diffractometer, scan mode:	STOE IPDS 2, ω -scan, $\Delta\omega = 1.0$ deg
θ_{\max} , completeness:	25°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	15411, 2186, 0.049
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2121
$N(\text{param})_{\text{refined}}$:	184
Programs:	SHELX [1], WinGX and ORTEP [2], DIAMOND [3], PLATON [4]

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The title compound has been prepared according to Refs. [5–8]. To a solution of *N*-butylpyridinium chloride (0.342 g, 2 mmol) in dry acetonitrile (6 mL) copper(II) chloride (0.34 g, 2 mmol) was added. This mixture was stirred to reflux for 3 h. The solvent was evaporated with a rotary evaporator at 60 °C under reduced pressure and the product was dried in vacuo. Yield: 0.59 g (98.3%). MS positive mode: $m/z = 136.1126$ [$C_9H_{14}N$]⁺, and MS negative mode: $m/z = 169.8$ [$CuCl_3$]⁻. Elemental analysis for $C_{18}H_{28}Cl_6Cu_2N_2$ calculated (found) C, 35.31% (35.34%); H, 4.61% (4.43%); N, 4.58% (4.59%). Red crystals (Mp. 94–96 °C) suitable for single crystal X-ray diffraction were grown by diffusion of methyl *tert*-butyl ether vapor into ethanolic solution of the compound.

Experimental details

Coordinates of hydrogen atoms were refined without any constraints or restraints.

Elemental analysis (CHN) was carried out on an Elementar vario EL III analyser with a limit of detection of 0.3%. Mass spectroscopy (MS) was performed on a Micromass QTOF (Quadrupol – Time of flight) with an electrospray ionization

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Abstract

$C_9H_{14}Cl_3CuN$, monoclinic, $P2_1/n$ (no. 14), $a = 9.6625(6)$ Å, $b = 9.3486(3)$ Å, $c = 14.1168(8)$ Å, $\beta = 102.288(5)^\circ$, $V = 1245.97(11)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0182$, $wR_{\text{ref}}(F^2) = 0.0499$, $T = 210(2)$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Cl1	0.50633(4)	0.82761(4)	−0.00540(3)	0.03410(12)
Cl2	0.44379(4)	1.07973(4)	0.22997(2)	0.03259(12)
Cl3	0.20539(4)	0.87418(4)	0.08240(3)	0.03547(12)
Cu1	0.40485(2)	0.98814(2)	0.08398(2)	0.02442(10)
N1	0.28674(13)	1.46735(14)	0.11596(9)	0.0242(3)
C1	0.21892(16)	1.34958(18)	0.13482(12)	0.0297(3)
H1	0.2378(19)	1.322(2)	0.1974(15)	0.039(5)*
C2	0.12862(17)	1.27846(19)	0.06119(12)	0.0343(4)
H2	0.089(2)	1.191(2)	0.0757(15)	0.051(6)*
C3	0.10826(16)	1.33051(19)	−0.03214(12)	0.0331(4)
H3	0.0436(19)	1.288(2)	−0.0842(13)	0.035(5)*
C4	0.17871(17)	1.45291(19)	−0.04981(12)	0.0329(4)
H4	0.163(2)	1.4933(19)	−0.1093(16)	0.038(6)*
C5	0.26794(18)	1.51946(18)	0.02547(12)	0.0297(3)
H5	0.311(2)	1.601(2)	0.0194(14)	0.037(5)*
C6	0.38816(16)	1.53919(19)	0.19600(11)	0.0289(3)
H6A	0.384(2)	1.635(2)	0.1834(14)	0.038(5)*
H6B	0.352(2)	1.5181(19)	0.2543(15)	0.035(5)*
C7	0.53618(18)	1.48169(19)	0.20422(15)	0.0350(4)
H7A	0.533(2)	1.378(2)	0.2114(14)	0.045(5)*
H7B	0.562(2)	1.501(2)	0.1446(17)	0.042(6)*
C8	0.64016(19)	1.5454(2)	0.29048(14)	0.0395(4)
H8A	0.725(3)	1.495(2)	0.2967(16)	0.043(6)*
H8B	0.607(2)	1.525(2)	0.3482(17)	0.044(6)*
C9	0.6639(2)	1.7040(2)	0.28281(17)	0.0471(5)
H9A	0.584(2)	1.757(2)	0.2827(14)	0.042(5)*
H9B	0.739(2)	1.741(2)	0.3342(16)	0.059(6)*
H9C	0.695(3)	1.726(3)	0.2235(19)	0.071(7)*

(ESI) source operating in positive and negative ionization modes, with a range of *m/z* 50–800. Samples were injected as dilute solutions in methanol. Melting points were measured with a Melting Point Meter KSP1N.

Comment

Copper (II) complexes exhibit very rich and diverse coordination geometries due to the presence of the Jahn-Teller distortions in the *d*⁹ electronic system [9]. Among those, chloridocuprate(II) salts have attracted considerable interest due to their magnetic [10, 11], thermochromic [9], phase transition [12], and non-linear optical behavior [13]. For example, Willett and co-workers [14, 15] demonstrated that the hydrogen bonding plays an important role in the thermochromism that these compounds are known for; these authors also associated the color change with a change in ligand geometry.

Quite some of the tetrachloridocuprates are ionic liquids (ILs). ILs, low-temperature molten salts of a highly diverse chemical composition, have received tremendous attention for their (projected) high potential in many fields [16]. A number of these applications are driven by the specific physical

and chemical properties of ILs, such as very low vapor pressure or low melting points but high ionicity [17–21]. As ILs are composed entirely of ions, their properties can be tuned by an judicious choice of the cation and the anion [22].

Of particular interest to the current study, metal-containing ILs (MILs) have been studied for a variety of properties such as their structural flexibility [23, 24], electrochemical behavior [25], and the exploitation of their unique redox behavior, for example in applications for mercury removal from natural gas, etc. [26–29]. Besides their intrinsic properties and application, MILs have also been used as ionic liquid precursors (ILPs) for inorganic nanomaterials, where the ILP acts as the solvent, the template, and the precursor for the inorganic material at the same time [19, 30, 31]. For example, ILPs have been used to synthesize CuCl, Au, Ag, metal oxide, Fe₃C, and CuS nanomaterials [8, 30, 32–37].

One of the key challenges in the ILP approach is the fact that for successful and efficient inorganic nanomaterials synthesis the fraction of the metal (which will be transformed to e.g. a metal sulfide in the course of the reaction) needs to be fairly high. Strategies to increase the metal content in the ILPs are thus of a very direct interest for improved yields from the synthetic procedure. In the quest for higher metal contents in the ILPs, we have therefore expanded the ILP platform to multinuclear ILs that can also serve as ILPs. The title compound is the first example of such a binuclear ILP. The article current focuses on the structure of the title compound. The transformation of the ILP to a series of inorganic materials will be described elsewhere.

The asymmetric unit of the title compound contains one cation and a half anion upper part of the figure. The second half is generated by symmetry because the [Cu₂Cl₆]^{2−} unit is centrosymmetric. The CuCl₃ subunits are doubly-bridged over the inversion centre. The average Cu–Cl bond lengths are 2.1936(4) Å (terminal) and 2.3100(4) Å (bridging) with a bridging Cu–Cl–Cu angle of 91.27(2)°, giving a distance between both copper atoms of 3.3027(4) Å. The coordination environment of the Cu atoms can be better described by a flattened tetrahedron rather than square-planar arrangement. The corresponding angles are 88.73(2)° [Cl(bridging)–Cu–Cl(bridging)], 100.01(2)° [Cl(terminal)–Cu–Cl(terminal)] and 98.79(2)° to 140.43(2)° [Cl(terminal)–Cu–Cl(bridging)]. The plane formed by the Cu atom and both terminal Cl atoms is twisted by an angle of 55.12° with respect to the plane defined by both Cu atoms and the bridging Cl atoms. The Cambridge Database contains 64 structures with isolated bibridged [Cu₂Cl₆]^{2−} dimers, for example in [P(C₆H₅)₄]₂[Cu₂Cl₆] [38]. In contrast to the synthesis described here, where a 1:1 ratio of copper(II) chloride and *N*-butylpyridinium chloride was used yielding the dinuclear species, mononuclear

isolated tetrachloridocopper(II) [CuCl₄]²⁻ was formed when *N*-butylpyridinium and copper(II) chloride in a ratio of 2:1 are used. In contrast, infinite zig-zag chains where the [Cu₂Cl₆]²⁻ moieties are linked by weak interactions are observed when piperazinium rather than *N*-butylpyridinium cation is employed [39].

The packing of the title compound is stabilized by non-classical C—H···Cl hydrogen bonds between the [Cu₂Cl₆]²⁻ anions and the pyridinium cations lower part of the figure. There are no interactions between neighboring [Cu₂Cl₆]²⁻ groups.

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