European Journal of Chemistry

Crystal structure and spectroscopic study of *bis*-tetrapropylammonium hexachlorodicuprate(II), [N(C₃H₇)₄]₂Cu₂Cl₆

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ARTICLE INFORMATION

ABSTRACT

Single crystals of the *bis*-tetrapropylammonium hexachlorodicuprate(II), [N(C₃H₇)₄]₂Cu₂Cl₆, were grown by slow evaporation solution technique at room temperature. The compound was characterized by Raman, IR and single crystal X-ray diffraction studies. Crystal data for C₁₂H₂₈Cl₃CuN (M = 356.24 g/mol): triclinic, space group P-1 (no. 2), a = 9.3851(2) Å, b = 9.3844(2) Å, c = 11.8837(3) Å, α = 106.3330(11)°, β = 100.0280(12)°, γ = 113.2830(12)°, V = 872.95(3) Å³, Z = 2, T = 293(2) K, μ(MoKα) = 1.693 mm⁻¹, D_{calc} = 1.355 g/mm³, 8056 reflections measured (6.64 ≤ 2Θ ≤ 62.02), 5526 unique (R_{int} = 0.0303) which were used in all calculations. The final R_1 was 0.0427 (>2σ(I)) and wR_2 was 0.1312 (all data). The atomic arrangement can be described by alternating organic and inorganic layers parallel to the (101) plan, made up of tetrapropylammonium groups and Cu₂Cl₆ dimers, respectively. In crystal structure, the inorganic layers, built up by Cu₂Cl₆ dimers, are connected to the organic ones through hydrogen bonding C-H...Cl and Van der Waals interaction in order to build cation-anion-cation cohesion. These interactions cause to the formation of a three-dimensional supramolecular architecture.

1. Introduction

The combination of organic molecules and inorganic materials was the starting point for the development of new hybrid compounds, with expected physical and chemical properties. These compounds have attracted great attention because of their unique opportunity to combine the remarkable features of organic compounds with those of inorganic materials. Their applications have been explored and reported in various fields, such as magnetism, conductive, luminescence and optical properties [1-5]. The materials based upon substituted complex ammoniums with halogenated metals such as Hg, Cd, Zn, Mn and Cu etc. present very interesting physical properties [6-12].

The large structural variability of copper(II) due to the presence of an active Jahn-Teller effect in the d^9 electronic system and the relative flatness of the potential surfaces make the thermochromism in chlorocuprates of continual interest. These compounds and their properties are of interest not only in inorganic chemistry but also in fields ranging from solid-state physics to bioinorganic chemistry. Among solid-state physicists and chemists, there is a great interest in the copper(II) halides owing to the plasticity of the metal coordination sphere which leads to a great variety of crystalline architectures with different coordination numbers, geometries and nuclearities, and makes copper systems as excellent candidates for analysing correlations between structural parameters and magnetic properties [13-17].

On the other hand, compounds crystallized with aliphatic tetra-ammonium cations with general formula (CₙH₂ₙ₊₁)₄N⁺, such as (CH₃)₄N⁺, (C₂H₅)₄N⁺, (C₃H₇)₄N⁺, undergo many structural phase transitions governed by the reorientational dynamics of the tetra-alkyl-ammonium groups [10,12,18]. In fact, a variety of compounds are formed by the reaction of mixed tetra-alkyl-ammonium with halogenated metals where n ≤ 2. Furthermore, the crystalline structure of these derivate can be described as a sequence of alternating layers of MX₄ tetrahedra; the organic chains are inserted between these sheets.

The Cu₂Cl₆²⁻ polyhedra can be described as two distorted tetrahedrons composed of two groups of CuCl₄ tetrahedra sharing two chlorines with a symmetry center in between. It accounts for the synthesis, the structural characterization by X-ray diffraction, IR and Raman spectroscopy of the *bis*-tetrapropylammonuim hexachlorodicuprate(II), [N(C₃H₇)₄]₂Cu₂Cl₆.

2. Experimental

2.1. Synthesis

The title compound was prepared by mixing (CH₃CH₂CH₂)₄NOH (1 mmol), CuCl₂.2H₂O (2 mmol), concentrated HCl (1 mL) and water (10 mL). The mixture was then allowed to stand and evaporate slowly at room temperature. After 3 days, brown crystals appeared and they were studied by single crystal X-ray diffraction. The analysis of the obtained phase confirms the formation of [(CH₃CH₂CH₂)₄N]₂Cu₂Cl₆.

2.2. Characterizations

The infrared spectrum was recorded in the range 700-4000 cm⁻¹ with a "Perkin Elmer FTIR-1000" spectrophotometer using a sample dispersed in a KBr pellet.
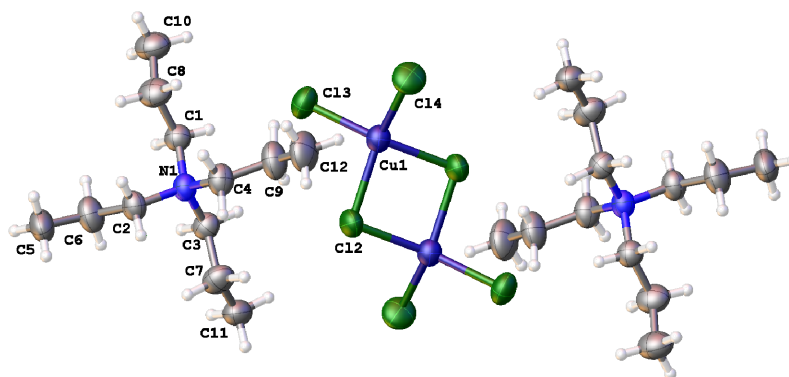
Figure 1. The asymmetric unit of [(CH₃CH₂CH₂)₄N]₂Cu₂Cl₆.

Back scattering Raman spectra were obtained under microscope with a T-64000 Raman spectrometer (ISA, Jobin Yvon) in the 50-4050 cm⁻¹ range.

2.3. X-ray single crystal structure determination

Single crystal X-ray diffraction data of the title compound were collected at room temperature on a Nonius Kappa-CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) through the program COLLECT [19]. Correction for Lorentz-polarisation effect, peak integration and background determination were carried out with the program DENZO [20]. Frame scaling and unit cell parameters refinement were performed with the program SCALEPACK [20].

Pertinent details of the crystal structure of [(CH₃CH₂CH₂)₄N]₂Cu₂Cl₆ are listed in Table 1. The crystal structure has been solved and refined in the triclinic symmetry, space group *P*-1, using the WINGX environment [21] and based on SHELXS97 [22] and SHELXL97 [23]. All the hydrogen positions of the diprotonated cation were placed geometrically and held in the riding mode. The C-H bonds were fixed and affined at 0.76 and 1.05 Å. Bond distances and angles calculated from the final atomic coordinates, as well as probable hydrogen bonds, are given in Table 2 and 3, respectively.

Table 1. Crystal data and structure refinement of [(CH₃CH₂CH₂)₄N]₂Cu₂Cl₆.

Empirical formula	C₁₂H₂₈Cl₃CuN
Formula weight, g/mol	356.24
Color	Brown
Temperature, K	293(2)
Crystal system	Triclinic
Space group	P-1
a, Å	9.3851(2)
b, Å	9.3844(2)
c, Å	11.8837(3)
α, °	106.3330(11)
β, °	100.0280(12)
γ, °	113.2830(12)
Volume, Å³	872.95(3)
Z	2
ρ_{calc}, mg/mm³	1.355
μ, mm⁻¹	1.693
F(000)	374.0
Diffractometer/scan	KAPPA CCD. Enraf-Nonius
Radiation, graphite monochromater	Mo Kα (λ = 0.71073 Å)
Crystal size, mm³	0.2 × 0.2 × 0.12
2θ range for data collection	6.64 to 62.02°
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	8056
Independent reflections	5526 [R(int) = 0.0303]
Data/restraints/parameters	5526/0/194
Goodness-of-fit on F²	1.046
Final R indexes [I>=2σ (I)]	R₁ = 0.0427, wR₂ = 0.1208
Final R indexes [all data]	R₁ = 0.0589, wR₂ = 0.1312
Largest diff. peak/hole, e Å⁻³	0.76/-0.63

3. Results and discussion

3.1. Structural analysis

The asymmetric unit is composed of half [Cu₂Cl₆]²⁻ anion and one [(CH₃CH₂CH₂)₄N]⁺ cation (Figure 1). The Cu-Cl distances are about similar (Table 2). The Cu-Cl bond distances are in the range of 2.2046(6)-2.3231(6) Å for the Cu₂Cl₆²⁻ anion. These bond distances fall in the range reported previously for compounds containing Cu-Cl bonds [24-28]. The Cl-Cu-Cl angles are present in two distinguished sets. The first contains four angles of 96.31(2) and 147.66(3) ° which are much lower than the other set which contains two angles of 97.20(3) and 146.13(3) °. These distortions are typically measured by the value of the mean *trans* and *cis*-Cl-Cu-Cl angle, which is 146.895 ° and 97.366 °, respectively. Accordingly the geometry of Cu₂Cl₆²⁻ anion is highly distorted around the Cu(II) ion, which in fact, is always distorted. The coordination about each copper is intermediate between a planar and a tetrahedral arrangement of four chlorine ligands, Cu(1)-Cl(2) (2.3152(6) Å) [29]. The principal feature of the crystal structure is the existence of essentially isolated [Cu₂Cl₆]²⁻ dimmers with a copper-chlorine-copper angle of 94.45(2)°. By space group symmetry requirements, the dimers have only a centre of symmetry connects the respective equivalent pairs of Cu(1), Cl(2), Cl(3) and Cl(4). The copper-copper separation in the dimer is in the value of 3.405 Å. The structural arrangement of [N(C₃H₇)₄]₂Cu₂Cl₆ can be described as an alternation of organic [N(C₃H₇)₄]⁺ groups and inorganic Cu₂Cl₆ dimers (Figure 2).

The lengths of the N-C bonds are in the range between 1.518(2) and 1.526(3) Å. The C-N-C angles range from 105.15(15) to 111.77(16) °. The C-C bonds lengths are in the region between 1.495(4) and 1.521(3) Å. In these layers each [Cu₂Cl₆]²⁻ anion is interacting with ten surrounding cations via five C-H...Cl. Each organic cation engages its hydrogen atoms bonded to C atoms in C-H...Cl hydrogen bonds. Accordingly, it is connected to anions and participates in the structure cohesion. The intermolecular distances C...Cl vary from 3.712(3) to 3.858(2) Å and the C-H...Cl angles range between 128(3) and 167(2) °.

3.2. Spectroscopic studies

The FT-IR and FT-Raman spectra of the title compound were measured for the powder sample at room temperature. Vibrational spectra are shown in Figures S1 and S2.

The frequencies observed in the infrared spectra at 2997 and 2987 cm⁻¹ are assigned respectively to the ν_{as} and ν_s of CH₂, CH₃ groups. The different modes of asymmetric (δ_{as}) and symmetric (δ_s) deformation of the methyl groups are found at

1385 and 1354 cm^{-1}, respectively. A weak band which appeared at 1371 cm^{-1} is related to the C-C and C-N vibration [30,31]. Besides, sharp bands observed in IR at 1111, 1139 and in Raman at 1059, 1035 cm^{-1} are associated to CH$_3$ and CH$_2$ rocking vibration modes respectively. The band observed at 970 cm^{-1} in IR and 957 cm^{-1} in Raman were assigned to ν_1(NC$_4$) stretching modes [32-34]. The deformation mode ν_2(NC$_4$) appears at 765 and 753 cm^{-1} in IR and Raman spectrum, respectively. The splitting ν(C-C-C-N) bending mode at 772 cm^{-1} may correspond to different conformers of the organic chains. The band observed at 478 cm^{-1} in Raman spectrum arises from the deformation vibration ν_4(NC$_4$) of the TPCu entity.

Table 2. Selected bond lengths and bond angles of [(CH$_3$CH$_2$CH$_2$)$_4$N]$_2$Cu$_2$Cl$_6$.

Bond length, Å		Bond length, Å	
Cu1-Cl2	2.3152(6)	C1-C8	1.505(3)
Cu1-Cl2^1	2.3231(6)	C2-C6	1.512(3)
Cu1-Cl3	2.2046(6)	C3-C7	1.521(3)
Cu1-Cl4	2.2130(6)	C4-C9	1.513(4)
Cl2-Cu1^1	2.3231(6)	C5-C6	1.495(4)
N1-C1	1.521(3)	C11-C7	1.512(4)
N1-C2	1.525(3)	C8-C10	1.516(4)
N1-C3	1.518(2)	C9-C12	1.520(4)
N1-C4	1.526(3)		
Bond angle, °		**Bond angle, °**	
Cl2-Cu1-Cl2^1	85.55(2)	C3-N1-C2	111.34(16)
Cl3-Cu1-Cl2^1	146.13(3)	C3-N1-C4	111.77(16)
Cl3-Cu1-Cl2	96.31(2)	C8-C1-N1	116.40(18)
Cl3-Cu1-Cl4	98.80(3)	C6-C2-N1	116.30(19)
Cl4-Cu1-Cl2^1	97.20(3)	N1-C3-C7	116.19(17)
Cl4-Cu1-Cl2	147.66(3)	C9-C4-N1	116.07(19)
Cu1-Cl2-Cu1^1	94.45(2)	C5-C6-C2	110.3(2)
C1-N1-C2	111.36(17)	C11-C7-C3	108.6(2)
C1-N1-C4	111.46(16)	C1-C8-C10	109.5(2)
C2-N1-C4	105.89(15)	C4-C9-C12	109.5(3)
C3-N1-C1	105.15(15)		
Torsion angle, °		**Torsion angle, °**	
Cl2^1-Cu1-Cl2-Cu1^1	0.0	C2-N1-C1-C8	57.3(3)
Cl3-Cu1-Cl2-Cu1^1	146.03(3)	C2-N1-C3-C7	-60.8(2)
Cl4-Cu1-Cl2-Cu1^1	-96.44(5)	C2-N1-C4-C9	-179.4(2)
N1-C1-C8-C10	177.9(2)	C3-N1-C1-C8	178.0(2)
N1-C2-C6-C5	-172.1(2)	C3-N1-C2-C6	-60.5(3)
N1-C3-C7-C11	178.41(19)	C3-N1-C4-C9	59.2(3)
N1-C4-C9-C12	176.4(2)	C4-N1-C1-C8	-60.7(3)
C1-N1-C2-C6	56.5(3)	C4-N1-C2-C6	177.9(2)
C1-N1-C3-C7	178.5(2)	C4-N1-C3-C7	57.4(3)
C1-N1-C4-C9	-58.1(3)		

^{1} Symmetry code: 1-x, 1-y, 1-z

Table 3. Hydrogen bonds for the title compound.

D-H...A *	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	∠ D-H...A (°)
C5-H5C...Cl3^j	0.96	2.97	3.816(3)	147.9
C11-H11A...Cl2^{ii}	0.96	2.95	3.821(3)	151.5
C6-H7...Cl2^{iii}	1.05(4)	2.97(5)	3.712(3)	128(3)
C11-H11B...Cl2	0.96	2.92	3.832(3)	158.6
C1-H16...Cl3	0.88(3)	3.00(3)	3.858(2)	167(2)

* Symmetry codes: *i*: x+1, y, z; *ii*: -x+2, -y+1, -z+1; *iii*: -x+2, -y+2, -z+1.
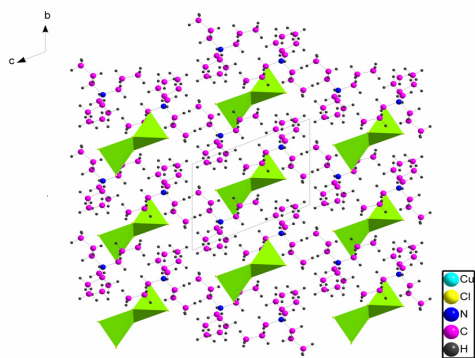
Figure 2. Projection along the a axis of the atomic arrangement of [(CH$_3$CH$_2$CH$_2$)$_4$N]$_2$Cu$_2$Cl$_6$.

The Raman and IR active bands involving mainly the Cu$_2$Cl$_6$ vibration can be proposed by comparison with Ga$_2$Cl$_6$ [35]. The isolated inorganic entities exhibit D$_{2h}$ symmetry with 18 normal modes. In this framework, among the 10 Cu$_2$Cl$_6$ Raman active modes, the 455, 311, 189, 98, 246 and 128 cm^{-1} lines can be assigned to the 4Ag (ν_1-ν_4) and 2B$_{1g}$ (ν_6, ν_7), respectively. In the end, the 2B$_{2g}$ (ν_{11}, ν_{12}) modes occur at 611 cm^{-1} of ν_{11} and 118 cm^{-1} of ν_{12}. The bands observed at 197 and 373 cm^{-1} are assigned to the B$_{3g}$ (ν_{15}) and B$_{2g}$ (ν_{18}) modes, respectively. The B$_{1u}$ (ν_8), 2B$_{2u}$ (ν_{13}, ν_{14}) and 2 B$_{3u}$ (ν_{16}, ν_{17}) modes are active in the IR spectra. Like in Ga$_2$Cl$_6$, only one (ν_8) over the 3 B$_{1u}$ is observed. In the reported study only ν_8 is observed. The ν_1, ν_8, ν_{11} and ν_{16} vibrations due to the CuCl$_2$ stretching motions and their frequencies are higher than those of ν_2, ν_6, ν_{13} and ν_{17} that witch are mainly due to the vibrations of the bridging Cu$_2$Cl$_6$ groups.

4. Conclusion

Bis-tetrapropylammonium hexachlorodicuprate(II), [N(C$_3$H$_7$)$_4$]$_2$Cu$_2$Cl$_6$, has been prepared and studied by single crystal X-ray diffraction and IR spectroscopy. The crystal packing of the salt [N(C$_3$H$_7$)$_4$]$_2$Cu$_2$Cl$_6$ is based on inorganic Cu$_2$Cl$_6$ units surrounded by organic N(C$_3$H$_7$)$_4$ entities into a triclinic crystal lattice symmetry.

Supplementary material

CCDC-857623 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

References

[1]. Braga, D.; Desiraju, G. R.; Miller, J. S.; Orpen, A. G.; Price, S. L. *Cryst. Eng. Commun.* **2002**, *4*, 500-509.
[2]. Desiraju, G. R. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311-2327.
[3]. Desiraju, G. R. *J. Mol. Struct.* **2003**, *656*, 5-15.
[4]. Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1-12.
[5]. Lacroix, P. G.; Clement, R.; Nakatani, K.; Delaire, J. A.; Zyss, J.; Ledoux, I. *Science* **1994**, *263*, 658-660.
[6]. De Zea Bermudez, V.; Carlos, L. D.; Duarte, M. C.; Silva, M. M.; Silva, C. J.; Smith, M. J.; Assunc, M.; Alcacer, L. *J. Alloys Compd.* **1998**, *21*, 275-277.
[7]. Carlos, L. D.; Sa Ferreira, R. A.; De Zea Bermudez, V.; Ribeiro, S. J. L. *Adv. Funct. Mater.* **2001**, *11*, 2111-115.
[8]. Kato, Y.; Ichii, D.; Ohashi, K.; Kunugita, H.; Ema, K.; Tanaka, K.; Takahashi, T.; Kondo, T. *Solid State Commun.* **2003**, *128*, 15-18.
[9]. El-Korashy, A.; Brik, M. G. *Solid State Commun.* **2005**, *135*, 298-303.
[10]. Ben Rhaiem, A.; Hlel, F.; Guidara, K.; Gargouri, M. *J. Alloys Compd.* **2008**, *463*, 440-445.
[11]. Cavellec, M. R.; Albinet, C.; Greneche, J. M.; Ferey, G. *J. Mater. Chem.* **2001**, *11*, 3166-3171.
[12]. Lach, G.; Laskowski, L.; Kityk, I. V.; Kapustianyk, V.; Rudyk, V.; Shchur, Y.; Tkaczyk, S.; Swiatek, J.; Piasecki, M. *J. Non-Crystalline Solid.* **2007**, *353*, 4353-4356.
[13]. Roman, P.; Sertucha, J.; Luque, A.; Lezama, L.; Rojo, T. *Polyhedron* **1996**, *15*, 1253-1262.
[14]. Angeloni, A.; Orpen, A. G. *Chem. Commun.* **2001**, *26*, 343-344
[15]. Guckian, K. M .; Schweitzer, B. A.; Ren, R. X. F.; Sheils, C. J.; Tahmassebi, D. C.; Kool, E. T. *J. Am. Chem. Soc.* **2000**, *122*, 2213-2222.
[16]. Janiak, C. *J. Chem. Soc. Dalton Trans.* **2000**, *7*, 3885-3896
[17]. Muller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143-167.
[18]. Hiroyuki, H.; Mashiyama, H.; Koshiji, N. *Acta Cryst. B.* **1989**, *45*, 467-473.
[19]. Muller, E. A.; Cannon, R. J.; Sarjeant, A. N.; Ok, K. M.; Halasyamani, P. S.; Norquist, A. J. *Cryst. Growth Des.* **2005**, *5*, 1913-1917.
[20]. Nonius, Kappa CCD Program Software, Nonius BV, Delft, The Netherlands, 1998.

[21]. Farrugia, L. J. *J. Appl. Cystallogr*. **1999**, *32*, 837-838.
[22]. Sheldrick, G. M. *SHELXS-97 Programs for Crystal Solution*. University of Gottingen, Germany, 1997.
[23]. Sheldrick, G. M. *SHELXL-97 Programs for Crystal Structure Refinement*. University of Gottingen, Germany, 1997.
[24]. Herringer, S. N.; Turnbull, M. M.; Landee, C. P.; Wikaira, J. L. *J. Coord. Chem*. **2009**, *62*, 863-875.
[25]. Luque, A.; Sertucha, J.; Castillo, O.; Roman, P. *New. J. Chem*. **2001**, *25*, 1208-1214.
[26]. Luque, A.; Sertucha, J.; Lezama, L.; Rojo, T.; Roman, P. *J. Chem. Soc. Dalton Trans*. **1997**, *5*, 847-854.
[27]. Al-Far, A. R. H.; Haddad, S. F. *Acta Cryst. E* **2008**, *64*, 689-690.
[28]. Haddad, S. F.; AlDamen, M. A.; Willett, R. D. *Inorg. Chim. Acta*. **2006**, *359*, 424-432.
[29]. Hafiz, A. A. *Iran J. Chem. Soc.* **2008**, *5*, 106-114.
[30]. Gosniowska, M.; Ciunik, Z.; Bator, G.; Jakubas, R.; Baran, J. *J. Mol. Struct*. **2000**, *555*, 243-255.
[31]. Karbowiak, M.; Hanuza, J.; Janczak, J.; Drozdzynski, J. *J. Alloys Compd*. **1995**, *225*, 338-343.
[32]. Hedderich, H. G.; Blom, C. E. *J. Chem. Phys*. **1989**, *90*, 4660-4663.
[33]. Hedderich, H. G.; Blom, C. E. *J. Mol. Spectrosc*. **1990**, *140*, 103-106.
[34]. Kirkwood, A. D.; Bier, K. D.; Thompson, J. K.; Haslett, T. L.; Hubber, A. S.; Moskovits, M. *J. Phys. Chem*. **1991**, *95*, 2644-2652.
[35]. Bellamy, L. J. The Infrared Spectra of Complex Molecules*, 3rd ed., Vol. I and II, Chapman and Hall, London, 1975, 1980.