

Article

(C₅H₁₂N)Cu₂Br₃: A Piperidinium Copper(I) Bromide with [Cu₂Br₃][−] Ladders

Theresa Komm ¹, Daniel Biner ¹, Antonia Neels ² and Karl W. Krämer ^{1,*}

¹ Department of Chemistry and Biochemistry, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland; E-Mail: daniel.biner@iac.unibe.ch (D.B.)

² Institute of Microtechnology, CSEM, Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland; E-Mail: antonia.neels@csem.ch

* Author to whom correspondence should be addressed; E-Mail: karl.kraemer@iac.unibe.ch; Tel.: +41-31-631-4248; Fax: +41-31-631-4322.

Received: 10 August 2012; in revised form: 3 September 2012 / Accepted: 18 September 2012 /

Published: 16 October 2012

Abstract: Piperidinium copper(I) bromide, (C₅H₁₂N)Cu₂Br₃, was obtained from a solution of CuBr₂, piperidine, and HBr in ethanol. At 60 °C ethanol slowly reduces copper(II) to copper(I). Colorless plates of (C₅H₁₂N)Cu₂Br₃ crystallize in the triclinic space group P-1 with lattice parameters of $a = 6.2948(10)$ Å, $b = 8.2624(14)$ Å, $c = 10.7612(17)$ Å, $\alpha = 75.964(19)^\circ$, $\beta = 89.232(19)^\circ$, $\gamma = 84.072(19)^\circ$, and $Z = 2$ at 173 K. [CuBr₄] tetrahedra share edges and form [Cu₂Br₃][−] ladders parallel to the a -axis. (C₅H₁₂N)⁺ ions adopt a chair conformation and connect the [Cu₂Br₃][−] ladders via H-bonding. The (C₅H₁₂N)Cu₂Br₃ structure is related to the mineral rasvumite, KFe₂S₃, space group Cmc₂m, which is isostructural to several alkali copper(I) halides.

Keywords: halides; copper; bromine; solid state structure; X-ray diffraction

1. Introduction

Piperidinium copper(I) bromide, (C₅H₁₂N)Cu₂Br₃, abbreviated as (HPip)Cu₂Br₃, has an interesting structure composed of [Cu₂Br₃][−] ladders and (C₅H₁₂N)⁺ cations. The structural motif of ladders built from edge-sharing tetrahedra is known from alkali copper and silver halides, e.g., CsCu₂Cl₃, CsCu₂Br₃ [1], CsCu₂I₃ [2], CsAg₂I₃ [3], also from chalcogenides, e.g., the mineral rasvumite,

KFe₂S₃ [4]. Compared to those orthorhombic compounds the symmetry of (HPip)Cu₂Br₃ is strongly reduced due to the bulky (HPip)⁺ cations.

(HPip)Cu₂Br₃ was obtained during crystal growth experiments for (HPip)₂CuBr₄. Cu(II) compounds attract a lot of interest in solid state physics as quantum magnets. In compounds like SrCu₂(BO₃)₂ [5] and TlCuCl₃ [6] Cu²⁺ ions form dimers which are further linked to layers or ladders, respectively. An antiferromagnetic intra-dimer coupling results in a vanishing magnetic susceptibility at low temperatures. The reduced lattice dimensionality and weak inter-dimer interactions prevent three-dimensional magnetic order. But an external magnetic field can induce a quantum phase transition leading to exotic states of matter, e.g., a Luttinger liquid. For (HPip)₂CuBr₄ all quantum phases of a spin ladder were experimentally accessible for the first time and were investigated by inelastic neutron scattering on single crystals [7,8]. A prerequisite for the crystal growth of (HPip)₂CuBr₄ was an investigation of the HPipBr–CuBr₂–ethanol system. (HPip)₂CuBr₄ [9] was known in literature. As the isostructural chloride [10], it contains isolated [CuX₄]^{2−} tetrahedra. Also (HPip)CuCl₃ is known with [CuCl_{4/2}Cl][−] chains [11]. To our knowledge, no further structural data on piperidinium copper halides are published. Here we report on the synthesis and crystal structure of the new copper(I) halide (HPip)Cu₂Br₃.

2. Results and Discussion

(HPip)Cu₂Br₃ was synthesized from a solution of CuBr₂ and HPipBr in ethanol. The slow reduction of Cu(II) to Cu(I) by ethanol at 60 °C offers a convenient method to obtain crystals of the rather insoluble (HPip)Cu₂Br₃. A direct synthesis from HPipBr and CuBr appears less facile. The low solubility of CuBr in ethanol hampers the reaction and prohibits the formation of sizeable crystals.

The crystal structure of (HPip)Cu₂Br₃ was determined by single crystal X-ray diffraction. The lattice parameters and experimental conditions are summarized in Table 1. The atomic positions are shown in Table 2 and selected distances and angles in Table 3. The structure has two Cu sites which are both tetrahedrally coordinated by Br[−] ions, see Figure 1. The Cu⁺ ions form a ladder centered at [*x*, 0.5, 0] with Cu–Cu distances of 2.889(2) Å and 2.903(2) Å along the rungs and longer distances of 3.015(2) Å and 3.283(2) Å along the legs. Br1 coordinates four Cu(I) ions alternatively in front and behind the ladder with longer Cu–Br distances between 2.53 Å and 2.58 Å. Br2 and Br3 are located at the side of the ladder. They coordinate only two Cu(I) ions at shorter distances around 2.41 Å. Accordingly, the Br2–Cu–Br3 angles of 124.8° are significantly wider than the other angles within the [CuBr₄] tetrahedra. The [Cu₂Br₃][−] ladder of (HPip)Cu₂Br₃, which also may be seen as a double chain of edge-sharing tetrahedra, is comparable to that of CsCu₂Br₃ [1]. The Cs compound crystallizes in space group Cmc₂m and is therefore less distorted than the HPip one. The sequence of the Cu–Cu rung and leg distances of 3.094 Å and 2.909 Å, respectively, is inverted for CsCu₂Br₃. The Cu–Br distances of 2.425 Å and 2.587 Å are very similar, given that the structure of the Cs compound was determined at 298 K *vs.* that of the HPip one at 173 K. The widest Br–Cu–Br tetrahedral angle of 116.9° is significantly smaller than the respective Br2–Cu–Br3 angle of 124.8°.

Table 1. Crystal data, data collection, and refinement details at 173 K.

Compound	(C ₅ H ₁₂ N)Cu ₂ Br ₃
Formula weight	452.97 g/mol
Space group, <i>Z</i>	P-1 (no. 2), 2
Lattice parameters	<i>a</i> = 6.2948(10) Å <i>b</i> = 8.2624(14) Å <i>c</i> = 10.7612(17) Å <i>α</i> = 75.964(19)° <i>β</i> = 89.232(19)° <i>γ</i> = 84.072(19)°
<i>V</i>	540.04(15) Å ³
<i>ρ</i> _{xray}	2.786 g/cm ³
Crystal size	0.45 × 0.15 × 0.1 mm ³
MoK α radiation, <i>λ</i>	0.71073 Å
Absorption coefficient	14.978 mm ^{−1}
Angle range	1.95° < <i>θ</i> < 25.96°
Index ranges	−7 ≤ <i>h</i> ≤ 7 −10 ≤ <i>k</i> ≤ 10 −13 ≤ <i>l</i> ≤ 13
Reflections measured	4244
Independent reflections, <i>R</i> _{int}	1967, 0.0687
No. of parameters	101
Transmission, max., min.	0.566, 0.102
<i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0534
<i>wR</i> ₂	0.1298
e-density, min., max.	−1.679, 1.552 e/Å ³
Extinction coefficient	0.0042(13)
Deposition no.	CCDC 873300

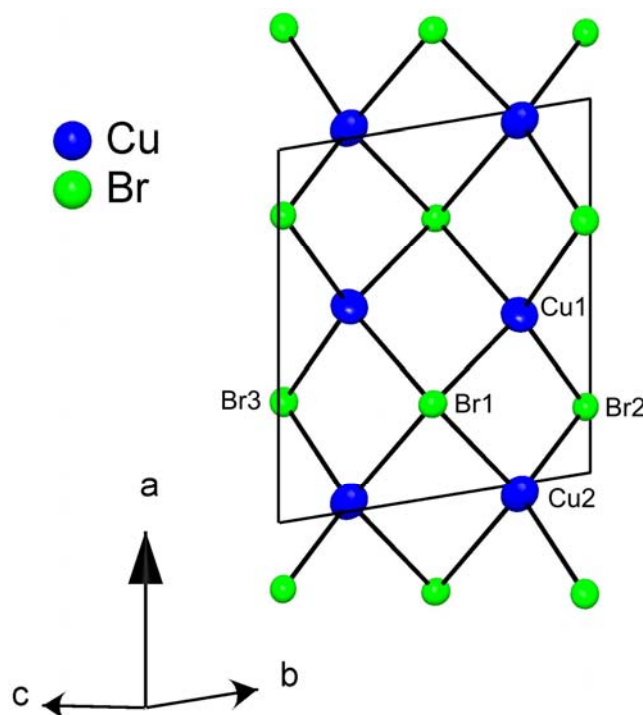
Table 2. Atomic coordinates and displacement factors *U*_{eq}/pm².

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
C1	0.0365(14)	0.7447(10)	0.3342(8)	28(2)
C2	0.1470(17)	0.7054(11)	0.4614(8)	36(2)
C3	0.2956(17)	0.8373(11)	0.4685(9)	36(2)
C4	0.4548(17)	0.8549(11)	0.3595(10)	42(2)
C5	0.3429(16)	0.8929(10)	0.2324(9)	30(2)
N1	0.1945(13)	0.7657(8)	0.2271(6)	27(2)
Cu1	0.4716(2)	0.6475(1)	0.8950(1)	41(1)
Cu2	0.9939(2)	0.6409(1)	0.8887(1)	42(1)
Br1	0.2684(1)	0.3883(1)	0.9108(1)	24(1)
Br2	0.1961(1)	0.8693(1)	0.9030(1)	24(1)
Br3	0.7283(1)	0.6547(1)	0.7256(1)	25(1)

^a The anisotropic *U*_{*ij*} are available from [12].

Table 3. Atomic distances/Å and angles/° at 173 K.

Atoms		Atoms	
Cu1–Cu1 (rung)	2.889(2)	Cu2–Cu2 (rung)	2.903(2)
Cu1–Cu2 (leg)	3.015(2)	Cu1–Cu2 (leg)	3.283(2)
Cu1–Br2	2.4065(14)	Cu2–Br3	2.4147(16)
Cu1–Br3	2.4134(15)	Cu2–Br2	2.4184(14)
Cu1–Br1	2.5755(15)	Cu2–Br1	2.5343(16)
Cu1–Br1'	2.6126(17)	Cu2–Br1'	2.6781(17)
Br1–Cu1–Br1'	112.34(5)	Br1–Cu2–Br1'	112.39(5)
Br1–Cu1–Br2	104.25(6)	Br1–Cu2–Br2	105.16(6)
Br1–Cu1–Br3	107.66(5)	Br1–Cu2–Br3	112.23(5)
Br1'–Cu1–Br2	108.18(5)	Br1'–Cu2–Br2	103.99(5)
Br1'–Cu1–Br3	99.62(6)	Br1'–Cu2–Br3	97.80(5)
Br2–Cu1–Br3	124.86(6)	Br2–Cu2–Br3	124.72(6)
C1–C2	1.492(12)	C4–C5	1.495(13)
C2–C3	1.524(14)	C5–N1	1.488(10)
C3–C4	1.522(14)	N1–C1	1.502(10)

Figure 1. View onto a $[\text{Cu}_2\text{Br}_3]^-$ ladder of $(\text{HPip})\text{Cu}_2\text{Br}_3$ centered at $[x, 0.5, 0]$. The atoms are labeled according to Table 2.

The piperidinium ions in $(\text{HPip})\text{Cu}_2\text{Br}_3$ have a chair conformation, see Figure 2. Their geometry is close to that in $(\text{HPip})_2\text{CuBr}_4$ [9] and the respective chlorides [10,11]. They connect the ladders via H-bonding, see Figure 3. The shortest distances of 3.384(6) Å and 3.370(7) Å are observed between N1 and Br2 and Br3, respectively, followed by C–Br distances in the range of 3.67 Å to 4 Å. Each $[\text{Cu}_2\text{Br}_3]^-$ ladder is surrounded by six stacks of HPip^+ ions. Compared to CsCu_2Br_3 , the bulky HPip^+ ions widen the structure and reduce the symmetry from Cmcm to P-1 .

Figure 2. View onto a piperidinium ion of (HPip) Cu_2Br_3 in chair conformation. The atoms are labeled according to Table 2.

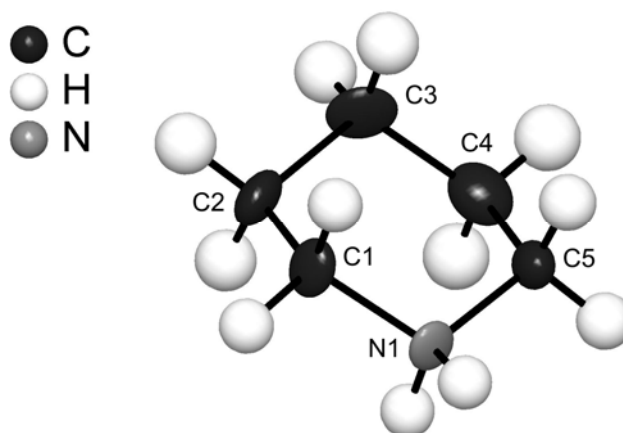
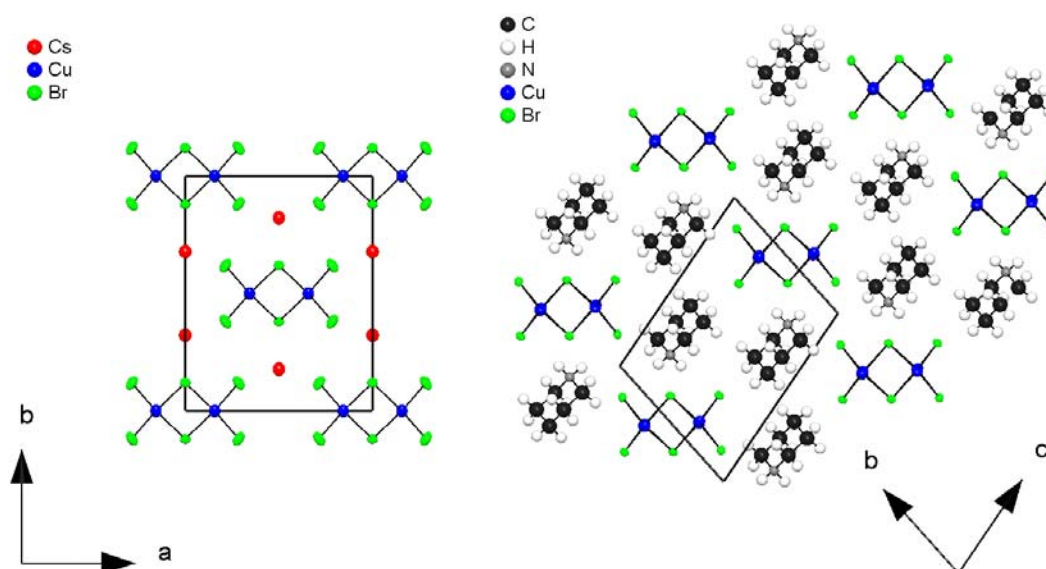


Figure 3. View along the $[\text{Cu}_2\text{Br}_3]^-$ ladders of CsCu_2Br_3 (left) and $(\text{HPip})\text{Cu}_2\text{Br}_3$ (right).



3. Experimental Section

$(\text{HPip})\text{Cu}_2\text{Br}_3$ was obtained from a solution of CuBr_2 and HPipBr in absolute ethanol. CuBr_2 (99,999%, Aldrich) is very soluble in ethanol with a deep violet color. The HPipBr solution was prepared by adding a slight excess of aqueous HBr (47%, suprapur, Merck) to a solution of piperidine ($\geq 99\%$ p.a., Sigma-Aldrich) in ethanol. The concentrated solutions with a HPip to Cu ratio of 2:1 were sealed in a flask under argon and heated to 50–60 °C. The slow reduction of Cu(II) to Cu(I) by ethanol resulted after several days in the growth of big, colorless, plate-like crystals of $(\text{HPip})\text{Cu}_2\text{Br}_3$. They were separated from the solution and dried in vacuum. $(\text{HPip})\text{Cu}_2\text{Br}_3$ is rather insoluble in ethanol. Under dry conditions $(\text{HPip})\text{Cu}_2\text{Br}_3$ crystals are stable. In contact with ethanol or water the crystals are oxidized by air.

A suitable single crystal of $(\text{HPip})\text{Cu}_2\text{Br}_3$ was selected for X-ray structure determination and mounted in a 0.3 mm capillary. Data were collected on a STOE IPDS diffractometer [13] at 173 K using graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct

methods using the program SHELXS-97 [14] and refined by full matrix least squares on F^2 with SHELXL-97 [15]. All hydrogen atoms were included at calculated positions ($d(\text{C-H}) = 97$ pm) and treated as riding atoms using SHELXL-97 default parameters. An empirical absorption correction was applied using DELREFABS (PLATON [16]). The results of the structure determination as well as selected atomic distances and angles are summarized in Tables 1–3. Further details may be obtained from the Cambridge structure database under reference CCDC 873300 [12].

4. Conclusions

The reduction of Cu(II) halides by ethanol provides a convenient way for the synthesis of the respective Cu(I) compounds. The structure of (HPip)Cu₂Br₃ resembles those of the alkali homologues AM₂X₃, but its symmetry is lower due to the bulky HPip⁺ ions. The [Cu₂Br₃][−] ladders, which also may be seen as double chains of edge-sharing tetrahedra, occur as a remarkably stable structural feature.

Acknowledgments

The financial support by the Swiss National Science Foundation is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

1. Meyer, G. Synproportionierung am metallischen Substrat: CsCu₂Cl₃ und CsCu₂Br₃. *Z. Anorg. Allg. Chem.* **1984**, *515*, 127–132.
2. Jouini, N.; Guen, L.; Tournoux, M. Structure cristalline de CsCu₂I₃. *Rev. Chim. Mineral.* **1980**, *17*, 486–491.
3. Hull, S.; Berastegui, P. Crystal structures and ionic conductivities of ternary derivatives of the silver and copper monohalides—II: Ordered phases within the (AgX)_x – (MX)_{1-x} and (CuX)_x – (MX)_{1-x} (M = K, Rb and Cs; X = Cl, Br and I) systems. *J. Solid State Chem.* **2004**, *177*, 3156–3173.
4. Clark, J.R.; Brown, G.E. Crystal structure of rasvumite, KFe₂S₃. *Am. Mineral.* **1980**, *65*, 477–482.
5. Kageyama, H.; Nishi, M.; Aso, N.; Onizuka, K.; Yosihama, T.; Nukui, K.; Kodama, K.; Kakurai, K.; Ueda, Y. Direct evidence for the localized single-triplet excitations and the dispersive multitriplet excitations in SrCu₂(BO₃)₂. *Phys. Rev. Lett.* **2000**, *84*, 5876–5879.
6. Rüegg, C.; Cavadini, N.; Furrer, A.; Güdel, H.U.; Krämer, K.W.; Mutka, H.; Wildes, A.; Habicht, K.; Vorderwisch, P. Bose-Einstein condensation of the triplet states in the magnetic insulator TlCuCl₃. *Nature* **2003**, *423*, 62–65.
7. Rüegg, C.; Kiefer, K.; Thielemann, B.; McMorro, D.F.; Zapf, V.; Normand, B.; Zvonarev, M.B.; Bouillot, P.; Kollath, C.; Giamarchi, T.; *et al.* Thermodynamics of the spin luttinger liquid in a model ladder material. *Phys. Rev. Lett.* **2008**, *101*, doi: 10.1103/PhysRevLett.101.247202.

8. Thielemann, B.; Rüegg, C.; Rønnow, H.M.; Läuchli, A.M.; Caux, S.; Normand, B.; Biner, D.; Krämer, K.W.; Güdel, H.U.; Stahn, J.; *et al.* Direct observation of magnon fractionalization in the quantum spin ladder. *Phys. Rev. Lett.* **2009**, *102*, doi: 10.1103/PhysRevLett.102.107204.
9. Patyal, B.R.; Scott, B.L.; Willett, R.D. Crystal-Structure, magnetic-susceptibility, and EPR studies of bis(piperidinium)tetrabromocuprate(II): A novel monomer system showing spin diffusion. *Phys. Rev. B* **1990**, *41*, 1657–1663.
10. Fernandez, V.; Moran, M.; Gutierrez-Rios, M.T.; Foces-Foces, C.; Cano, F.H. EPR and X-ray structural study of some tetrahalocuprates CuX_4^{2-} ($X = \text{Cl}, \text{Br}$) of protonated amines with thermochromic properties. *Inorg. Chim. Acta* **1987**, *128*, 239–243.
11. Battaglia, L.P.; Corradi, A.B.; Geiser, U.; Willett, R.D.; Motori, A.; Sandrolini, F.; Antolini, L.; Manfredini, T.; Menabue, L.; Pellacani, G.C. The crystal structures, magnetic and electrical properties of two polymeric chlorocuprate(II) compounds. *J. Chem. Soc. Dalton Trans.* **1988**, 265–271.
12. A .cif file with the crystallographic data of $(\text{C}_5\text{H}_{12}\text{N})\text{Cu}_2\text{Br}_3$ can be obtained from the Cambridge structure database at <http://www.ccdc.cam.ac.uk/> under reference number CCDC 873300.
13. Stoe & Cie. *X-Area V1.17 & X-RED32 V1.04 Software*; Stoe & Cie GmbH: Darmstadt, Germany, 2002.
14. Sheldrick, G.M. Phase annealing in *SHELX-90*: Direct methods for larger structures. *Acta Cryst. A* **1990**, *46*, 467–473.
15. Sheldrick, G.M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
16. Spek, A.L. Single-Crystal structure validation with the program PLATON. *J. Appl. Cryst.* **2003**, *36*, 7–13.

© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).