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Article

$\{[P(o\text{-}tolyl)_3]Br\}_2[Cu_2Br_6](Br_2)$—An Ionic Compound Containing Molecular Bromine

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Dark green cuboid-shaped crystals of the composition $\{[P(o\text{-}tolyl)_3]Br\}_2[Cu_2Br_6](Br_2)$ are obtained by the reaction of $P(o\text{-}tolyl)_3$ and $CuBr_2$ with Br_2 in the ionic liquid $[NMeBu_3][N(Tf)_2]$. The bromocuprate crystallizes triclinic [space group $P\bar{1}$; $Z = 1$; $a = 10.667(2)$ Å; $b = 10.695(2)$ Å; $c = 11.582(2)$ Å; $\alpha = 74.42(3)°$; $\beta = 75.64(3)°$; and $\gamma = 85.68(3)°$]. The title compound is constituted of $\{[P(o\text{-}tolyl)_3]Br\}^+$ cations and $[Cu_2Br_6]^{2-}$ anions and contains molecular dibromine [$d_{Br-Br} = 2.341(1)$ Å]. The latter is verified by thermogravimetry and mass spectrometry.

Introduction

Molecular dihalides (Cl_2, Br_2, and I_2) in the solid state may occur at low temperatures in the element as well as a molecular unit in complex metal compounds. Thus, two types of crystalline compounds have been reported to contain molecular chlorine: $[C(NH_2)_3]_3[BiCl_6](Cl_2)$[1] and the clathrates $[Me_4N]_2[MCl_6](Cl_2)$ (M = Pd, Sn).[2] In contrast, several compounds containing diiodine have been described. In these solids, iodine occurs as a raw I_2 unit[3] as well as in polyiodide type building blocks, ranging from $[I_3]^{-4}$ to expanded $[I_{21}]^{3-}$ networks.[5] The limited number of compounds containing Cl_2 can be ascribed to its high volatility and reactivity. The much larger number of solid compounds containing molecular iodine is in accordance to this view.

With regard to molecular dibromine, a few complex metal compounds have been structurally characterized. In fact, three different situations have been described: first, a formation of $[Br_3]^-$ type polybromide {e.g., $[Bu_3P]_2Au(Br_3)(Br_2)$[6] or $Cs_3(AuBr_4)_2Br_3$};[7] second, a coordination of Br_2 to anionic metal bromides {e.g., $[Me_4N]_3[Sb_2Br_9](Br_2)$};[8] and finally, an incorporation of Br_2 units without any strong interaction toward close-by atoms or ions (e.g., $CsF\cdot Br_2$).[9] In the case of complex metal bromides till now, only a few compounds have been described to contain molecular bromine. These are restricted to the systems $A-M-(Br_2)$ (A = alkali metal, alkaline earth metal, or organic cation; M = Ti, Au, Pt, Sb, or Te). These compounds were prepared by applying standard crystallization methods with, for instance, dichloromethane as a solvent. With $\{[P(o\text{-}tolyl)_3]Br\}_2[Cu_2Br_6](Br_2)$, here, a first example in the system $A-Cu-(Br_2)$ is synthesized. The title compound resulted as a part of our investigations aiming at a potential benefit of ionic liquids (ILs) in inorganic synthesis.[10,11] Because of their outstanding properties (e.g., wide liquid range, negligible vapor pressure, high thermal and chemical stability, wide electrochemical window, and weakly coordinating anions), ILs have already turned out to be very interesting reaction media for various types of reactions.[12,13]

Experimental Section

All experimental and analytical studies were performed under an inert gas atmosphere (glovebox, Schlenk technique). The commercially available starting materials [$CuBr_2$: ≥98%, Merck;

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(1) Bator, G.; Zeegers-Huyskens, T.; Jakubas, R.; Zaleski, J. *J. Mol. Struct.* **2001**, *570*(1–3), 61–74.
(2) Storck, P.; Weiss, A. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*(9), 1214–1218.
(3) Nunez, R.; Farras, P.; Teixidor, F.; Vinas, C.; Sillanpaa, R.; Kivekas, R. *Angew. Chem., Int. Ed.* **2006**, *45*(8), 1270–1272.
(4) Slater, R. C. L. M. *Acta Crystallogr.* **1959**, *12*, 187–196.
(5) Pantenburg, I.; Mueller, I. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1637–1640.
(6) Schneider, D.; Schuster, O.; Schmidbaur, H. *Dalton Trans.* **2005**, *11*, 1940–1947.
(7) Lehnis, B.; Straehle, J. *Z. Naturforsch., B: Chem. Sci.* **1981**, *12*, 1504–1508.
(8) Hubbard, C. R.; Jacobson, R. A. *Inorg. Chem.* **1972**, *11*, 2247–2250.
(9) Drews, T.; Marx, R.; Seppelt, K. *Chem. Eur. J.* **1996**, *2*, 1303–1307.
(10) Okrut, A.; Feldmann, C. *Z. Anorg. Allg. Chem.* **2006**, *632*, 409–412.
(11) Okrut, A.; Feldmann, C. Z. *Anorg. Allg. Chem.* **2007**, *633*, 2144–2146.
(12) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2003.
(13) Guloy, A. M.; Ramlau, R.; Tang, Z.; Schnelle, W.; Baitinger, M.; Grin, Y. *Nature (London)* **2006**, *443*, 320–323.

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Table 1. Crystallographic Data of {[P(o-tolyl)$_3$]Br}$_2$[Cu$_2$Br$_6$](Br$_2$)

formula	$C_{42}H_{42}Br_{10}Cu_2P_2$
crystal system/space group	triclinic/$P\bar{1}$ (no. 2)
cell parameters	$a = 10.667(2)$ Å, $\alpha = 74.42(3)°$ $b = 10.695(2)$ Å, $\beta = 75.64(3)°$ $c = 11.582(2)$ Å, $\gamma = 85.68(3)°$ $V = 1232.9(6)$ Å^3
formula units per cell	$Z = 1$
calculated density	$\rho_{calc} = 2.067$ g cm^{-1}
crystal size	0.05 mm × 0.05 mm × 0.1 mm
temperature	$T = 203$ K
measurement device	imaging plate diffraction system (IPDS I, STOE)
radiation	graphite-monochromated Mo K$_\alpha$ ($\lambda = 0.71073$ Å)
measurement limits	$1.88 \le \theta \le 25.99$ $-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$
absorption correction	numerical
absorption coefficient	9.059 mm^{-1}
no. of reflections	11260 measured, 4381 independent
data averaging	$R_{int} = 0.07(1)$
structure refinement	full matrix least-squares on F_o^2; anisotropic displacement parameters for all nonhydrogen atoms
no. of parameters	256
residual electron density	1.058 to −0.990 e/Å^3
figures of merit	$R1$ (all F_o) = 0.084(1) $R1$ [3091 $F_o > 4\sigma(F_o)$] = 0.049(1) $wR2 = 0.115(1)$ $GooF = 1.038$

P(o-tolyl)$_3$: (o-tolyl) = C_7H_7, ≥97%, Merck; bromine: ≥99%, Fluka] were used as obtained; the IL [NMeBu$_3$][N(Tf)$_2$] [Tf = N(SO$_2$CF$_3$)$_2$] was synthesized as described elsewhere.[14]

To synthesize {[P(o-tolyl)$_3$]Br}$_2$[Cu$_2$Br$_6$](Br$_2$), 147 mg (0.66 mmol) of CuBr$_2$ and 200 mg (0.66 mmol) of P(o-tolyl)$_3$ were stirred in 2 mL of [NMeBu$_3$][N(Tf)$_2$] at 100 °C. Bromine was added dropwise, and immediately, a dark green solution was obtained. The addition of bromine was stopped as soon as the atmosphere above the solution had not been discolored. Finally, the solution was filtered through a glass filter. After a few days, a formation of dark green crystals was observed. To remove the solvent, the crystals were washed five times with diethyl ether and dried by evacuation. The pure title compound was obtained with about 25% yield.

Single crystal X-ray diffraction was carried out with an IPDS I diffractometer (STOE, Darmstadt) using Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). A suitable crystal was mounted into a glass capillary under argon atmosphere. Data collection was performed at −70 °C. Additional information regarding data collection, structure solution, and refinement is summarized in Table 1. Powder diffraction patterns were obtained with a STADI-P diffractometer (Stoe, Darmstadt) using germanium monochromatized Cu K$_{\alpha 1}$ radiation. The sample was filled into a glass capillary and measured at ambient temperature. Silicon was used as an external reference. Rietveld calculations were performed using the program package FULLPROF.[20]

Differential thermal analysis (DTA) was performed with a STA409C device (Netzsch). The measurements were performed in nitrogen atmosphere. The samples (typically 20–50 mg, corundum crucibles) were heated and cooled with a rate of 3 K min^{-1}. The resulting data were baseline corrected by subtraction of an analogue measurement with an empty crucible. Mass spectrometry was performed with a MAT8200 equipment (Thermo Finnigan, Bremen) using an acceleration voltage of 70 eV (source temperature, 180 °C).

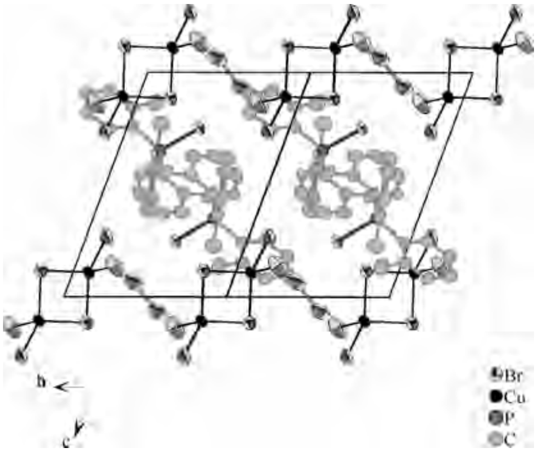

Figure 1. Unit cell of the compound {[P(o-tolyl)$_3$]Br}$_2$[Cu$_2$Br$_6$](Br$_2$).

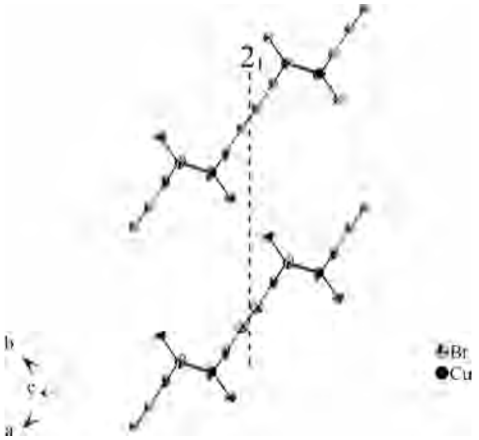

Figure 2. Part of the infinite $^\infty{}_1${[Cu$_2$Br$_6$](Br$_2$)}$^{2-}$ chain with the pseudo 2-fold screw axis along the monoclinic b'-axis. Thermal ellipsoids are drawn with 50% probability of finding.

Results and Discussion

{[P(o-tolyl)$_3$]Br}$_2$[Cu$_2$Br$_6$](Br$_2$) was prepared by reaction of P(o-tolyl)$_3$ and CuBr$_2$ with Br$_2$ in the IL [NMeBu$_3$][N(Tf)$_2$]. Its crystal structure is shown in Figure 1. The title compound can be regarded to consist of ions. First, two {[P(o-tolyl)$_3$]Br}$^+$ cations occupy the center of the unit cell. [Cu$_2$Br$_6$]$^{2-}$ as the anion is located on all corners. In addition, bromine molecules are arranged at the center of four opposite edges along the crystallographic a-axis. The [Cu$_2$Br$_6$]$^{2-}$ anion consists of two distorted edge-sharing [CuBr$_4$] tetrahedra. These are bridged by bromine molecules to form infinite $^\infty{}_1${[Cu$_2$Br$_6$](Br$_2$)} chains (Figure 2). Altogether, cations and anions are arranged like a slightly distorted two-dimensional hexagonal packing perpendicular to the (111) layer (Figure 3). These layers are stacked right on top of each other (AA type of packing) and interconnected via the bromine molecules.

The crystal structure of {[P(o-tolyl)$_3$]Br}$_2$[Cu$_2$Br$_6$](Br$_2$) obviously exhibits two pairs of very similar lattice parameters [$a = 10.667(2)$ Å, $b = 10.695(2)$ Å, $\alpha = 74.42(3)°$, and $\beta = 75.64(3)°$] and can therefore be described as a super cell

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[14] MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, N. *J. Phys. Chem. B* **1999**, *103*, 4164–4170.

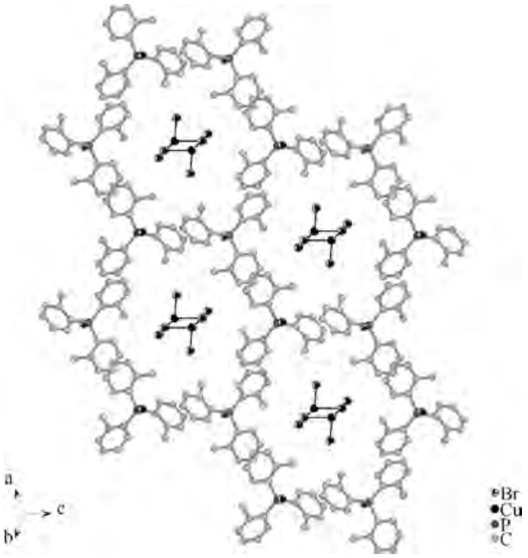

Figure 3. Three-dimensional packing of $\{[P(o\text{-tolyl})_3]Br\}^+$ and $[Cu_2Br_6]^{2-}$ perpendicular to the [111] direction.

with approximate monoclinic lattice metrics [$a' = 15.66(1)$ Å, $b' = 14.52(1)$ Å, $c' = 11.58(1)$ Å, $\alpha' = 90.9(1)°$, $\beta' = 110.6(1)°$, and $\gamma' = 89.1(1)°$]. The absence of both—a 2-fold screw axis along b' and a glide plane perpendicular to c'—causes the choice of the triclinic crystal system. Locally, the decrease in symmetry is a consequence of the reduction of the point symmetry of the isolated $[Cu_2Br_6]^{2-}$ anion (D_{2h}) to inversion only in the lattice. This finding is directly related to the linkage of the $[Cu_2Br_6]^{2-}$ anions via bromine molecules and results in $[Cu_2Br_6]^{2-}$ anions that are tilted out of the $a'c'$ plane and a 2-fold screw axis along the b'-axis that is omitted (Figure 2).

The bond length $d(Br_{mol}-Br_{mol})$ of the bromine molecule in $\{[P(o\text{-tolyl})_3]Br\}_2[Cu_2Br_6](Br_2)$ averages to 2.341(2) Å. In comparison to solid elemental dibromine, the distance is slightly enlengthened [2.267(1) Å].[15] This finding indicates a somewhat weaker $Br_{mol}-Br_{mol}$ bonding, which is in accordance with an additional $Br_{mol}-Br_{anion}$ interaction between the Br_2 molecules and the $[Cu_2Br_6]^{2-}$ anion. With regard to the anion, the general composition $[Cu_xX_y]^{(y-2x)-}$ (X = Cl, Br, I) has been observed with a wide adaptability of bond length and angles. In fact, the coordination of copper has been found to depend strongly on the relevant counterion.[16] Hence, the binary $CuBr_2$ exhibits a square planar coordination of copper. In contrast, a distorted octahedral coordination was observed for $CsCuBr_3$.[17] In the case of $\{[P(o\text{-tolyl})_3]Br\}_2[Cu_2Br_6](Br_2)$, Cu^{2+} occurs with a distorted tetrahedral coordination. As expected, the distance $d(Cu-Br_{anion})$ between Cu^{2+} and a Br atom, which is close to the Br_2 unit, is slightly longer [2.346(2) Å] than the distance $d(Cu-Br_{anion})$ to a bromine atom without any contact to molecular bromine [2.321(2) Å]. This again confirms a weak interaction between $[Cu_2Br_6]^{2-}$ and molecular bromine. Finally, all C–C, C–P, and P–Br distances of the $\{[P(o\text{-tolyl})_3]Br\}^+$ cation are in accordance to the expected values.

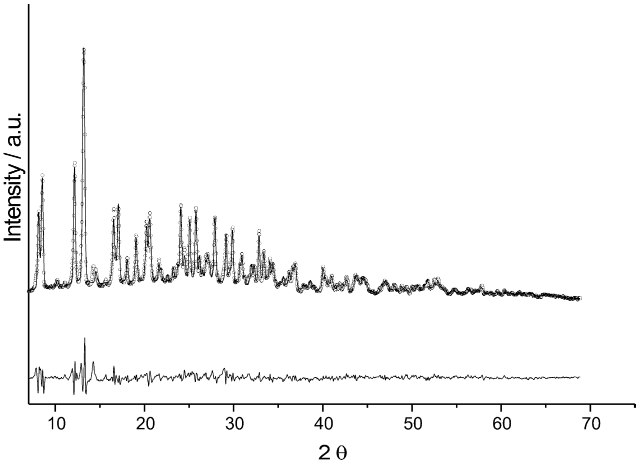

Figure 4. Rietveld plot of $\{[P(o\text{-tolyl})_3]Br\}_2[Cu_2Br_6](Br_2)$. The difference between observed (dots) and calculated (line) powder pattern based on single crystal structure analysis is shown as a difference line ($R_{bragg} = 6.56\%$; $R_f = 3.86\%$).

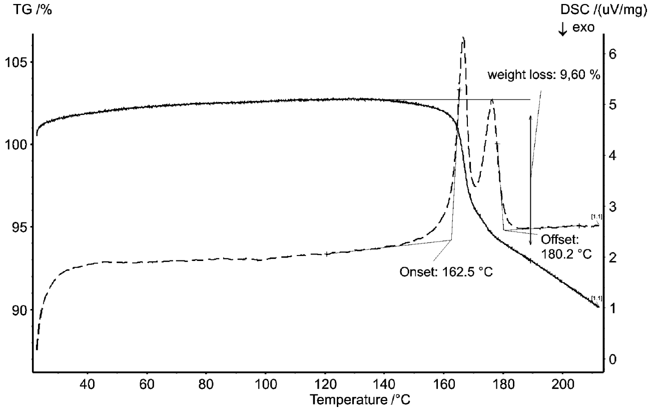

Figure 5. Thermal behaviour of $\{[P(o\text{-tolyl})_3]Br\}_2[Cu_2Br_6](Br_2)$.

To characterize the material properties and to prove the presence of molecular bromine independent from crystal structure analysis, an access to larger quantities of the pure title compound is mandatory. To this concern, separation of the as-prepared compound from the IL turned out to be complicated since both exhibit a quite similar polarity and, therefore, solubility in conventional solvents. In fact, both the title compound and the IL show a similar solubility in nonpolar solvents (e.g., hexane or toluene) and are well-soluble in polar solvents (e.g., acetone, dichloromethane, or ethanol). Detailed considerations resulted in filtration and washing with small portions of diethyl ether as a successful attempt to yield $\{[P(o\text{-tolyl})_3]Br\}_2[Cu_2Br_6](Br_2)$ as a single-phase compound with all ILs removed. On the basis of this procedure, the purity of the product is proven by X-ray powder diffraction patterns, which also confirm the crystallographic data (Figure 4).

To verify the presence of molecular bromine, the thermal behavior of the title compound was investigated via DTA and thermogravimetry (Figure 5). An endothermic decomposition is observed above a temperature of about 150 °C. The steep weight loss (observed, 9.6%) up to 180 °C corresponds well with the expected evaporation of molecular

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(15) Vonnegut, B.; Warren, B. E. *J. Am. Chem. Soc.* **1936**, *58*, 2459–2461.

(16) Bloomquist, D. R.; Willett, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 2615–2619.

(17) Li, T. I.; Stucky, G. D. *Inorg. Chem.* **1973**, *12*, 441–445.

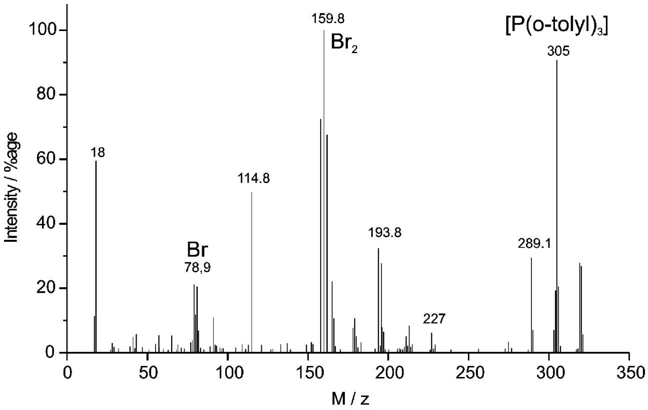

Figure 6. Mass spectrum of {[P(o-tolyl)$_3$]Br}$_2$[Cu$_2$Br$_6$](Br$_2$) (source temperature, 180 °C).

bromine (calculated, 10.4%). The continuous weight loss at even higher temperatures can be ascribed to a proceeding decomposition of the {[P(o-tolyl)$_3$]Br}$^+$ cation. For further quantification, the decomposition process and the composition of the gaseous products were validated via mass spectrometry (Figure 6). Again, the presence of Br$_2$ molecules is clearly evidenced. Further fragments can be attributed to bromine atoms, [P(o-tolyl)$_3$], as well as to secondary decomposition products of the organic cation.[18]

Mechanistically the preparation of {[P(o-tolyl)$_3$]Br}$_2$ [Cu$_2$Br$_6$](Br$_2$) can be understood as a bromination of P(o-tolyl)$_3$ with Br$_2$. Such a type of reaction is well-known indeed in the case of phosphanes PR_3 (R = aromatic substituent) and typically yields products with a composition [(PR_3)Br]$^+$Br$^-$ or [(PR_3)Br]$^+$(Br$_3$)$^-$.[19] The formation of the {[P(o-tolyl)$_3$]Br}$^+$ cation is furthermore accompanied by the generation of Br$^-$, which is complexed thereafter by CuBr$_2$ to gain the [Cu$_2$Br$_6$]$^{2-}$ anion. Finally, an excess of bromine is used to interlink the [Cu$_2$Br$_6$]$^{2-}$ anions to infinite chains. ILs obviously support this type of reaction and the formation of the title compound (e.g., due to their stability against oxidation and the sufficient solubility of all starting materials). Attempts to crystallize the bromocuprate applying standard solvents (e.g., acetonitrile, acetone, dichloromethane, and ethanol) have so far failed.

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(18) SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 10.04.2007).

(19) Godfrey, S. M.; McAuliffe, C. A.; Mushtaq, I.; Pritchard, R. G.; Sheffield, J. M. *Dalton Trans.* **1998**, *22*, 3815–3818.

(20) Rodríguez-Carvajal, J. *Physica B* **1993**, *192*, 55–69.