

Short Communication

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Synthesis, characterization, and thermal properties of *N,N,N',N'*-tetramethyl guanidinium tribromidocadmate(II) exhibiting an unusual coordination geometry

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Abstract: The reaction of *N,N,N',N'*-tetramethyl guanidine, $\text{NHC}(\text{CH}_3)_2$ (TMGD) and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ in ethanol led to the formation of $[\text{TMGDH}][\text{CdBr}_3]$ (**1**), which crystallizes in the monoclinic space group *Cc* with $Z=4$, $a=8.9079(7)$  , $b=18.5810(14)$  , $c=8.1637(6)$  , $\beta=107.953(3)^\circ$, and $V=1285.44(17)$  ³. In the crystal lattice, **1** is organized in one-dimensional anionic chains of CdBr_4 tetrahedra sharing two corners. To our knowledge, this is the first evidence of such a coordination geometry described for a bromocadmate derivative. The negative charges are compensated by monoprotonated *N,N,N',N'*-tetramethyl guanidinium cations (TMGDHs), which are in N-H hydrogen bonding interaction with the terminal bromide atoms of the anionic chain. The title compound was also characterized by middle and far-infrared spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The elemental analysis corroborates as well the X-ray elucidation. Multinuclear solution nuclear magnetic resonance (NMR) spectroscopic measurements (¹H, ¹³C{¹H}) were conducted in D₂O.

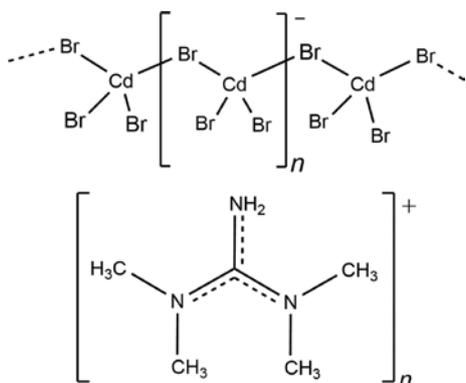
Keywords: bromocadmate(II); differential scanning calorimetry; N-H...Br interaction; organic-inorganic hybrid materials; thermogravimetric analysis; X-ray crystallography.

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Organic-inorganic hybrid materials have received much attention over the past 25 years offering extraordinary possibilities of combinations and structures, which led to various properties and applications. To date, they are involved in many fields including catalysis, optic, magnetism, nanomaterials chemistry, and often in an interdisciplinary approach (Nicole et al., 2010). In the domain of crystal engineering, the synthesis of hydrogen bond-based organic-inorganic salts also arouses a great interest, facilitating the design and control of unexpected crystal structures (Brammer et al., 2002). The association of protonated organic synthons and metallic-based moieties, such as anions (Mercier et al., 2009), complexes (Braga et al., 2003), and polyatomic clusters (Schubert, 2011), led to a remarkable diversity of assemblies. While amines are commonly selected as potential hydrogen bonding donors, metal halides are particularly considered as suitable synthons acting as strong hydrogen bond acceptors (Gillon et al., 2000). The role and contribution of halogen bonding in crystal engineering were recently reviewed by Haukka and coworkers (Ding et al., 2012). As metal halides, halocadmates are appropriate candidates leading to a large diversity of architectures (Corradi et al., 1998; Sharma et al., 2012). In addition to structural and supramolecular interests, the resulting organic-inorganic salts aroused a particular attention in semiconductor physics as they were considered as suitable models for predicting electronic configurations of impurities and their lattice locations (Bensekrane et al., 1985; Chanh et al., 1985; Mokhlisse et al., 1985). Halocadmates are also known to exhibit photoluminescent properties (Ma et al., 2006). More recently, in the domain of bio-inorganic chemistry, their interactions with biomacromolecules is generating also a growing interest in the context of cancer chemotherapy studies (Jana et al., 2016).

In the quest of new hydrogen-bond-based organic-inorganics salts, some of us recently described the crystal structure of catena-poly[*N,N,N',N'*-tetramethyl guanidinium cation [(chloridocadmate)-di- μ -chlorido]], $\{(\text{C}_5\text{H}_{14}\text{N}_3)[\text{CdCl}_3]\}_n$ as exhibiting a polyanionic zigzag chain (Ndiaye



Scheme 1: Molecular representation of **1**.

et al., 2016). Continuing to investigate the potential of *N,N,N',N'*-tetramethyl guanidinium as counter cation of halometallates, we report, herein, the synthesis and the structural characterization of a new bromocadmate(II) salt, $[C_5H_{14}N_3][CdBr_3]$ (**1**) (Scheme 1).

Colorless crystals of **1** were obtained by reacting *N,N,N',N'*-tetramethyl guanidine, $NHC(N(CH_3)_2)_2$ (TMGD), and $CdBr_2 \cdot 4H_2O$ in ethanol. The structure of **1** was then resolved by X-ray diffraction analysis from a suitable single crystal. Selected crystallographic data and refinement details are reported in the Experimental section. The asymmetric unit of **1** comprises one $[CdBr_3]^-$ anion and one *N,N,N',N'*-tetramethyl guanidinium cation. An ORTEP view with selected bond lengths and angles [\AA , $^\circ$] is shown in Figure 1. In the crystal structure, inorganic anions describe an infinite chain of $[CdBr_4]$ tetrahedra sharing two corners (Figure 2). Interestingly, a similar organization has recently been published by Ishihara and coworkers for an iodocadmate organic-inorganic salt, $[C(NH_2)_3]CdI_3$ (Gesing et al., 2016), but to our knowledge, it is unprecedented for bromocadmate derivatives. Cadmium atoms are linked to two terminal bromides [$Cd-Br1 = 2.5290(9)$ and $Cd-Br3 = 2.5531(9)$ \AA] and two bridging bromides [$Cd-Br2 = 2.6590(9)$ and $Cd-Br2^{ii} = 2.6753(9)$]. In both cases, these distances are in the range of those generally reported for such bonds (Ishihara et al., 1994, 1996, 1998). The coordination geometry around cadmium can be considered as a slightly disordered tetrahedron [$Br3-Cd-Br2^i = 107.19(3)$, $Br3-Cd-Br2 = 108.61(3)$, $Br1-Cd-Br2 = 110.29(3)$, $Br1-Cd-Br2^i = 108.77(3)^\circ$]. Halocadmates are known to result in a wide variety of structural arrangements. This is, in particular, due to the d^{10} electronic structure of the Cd^{2+} ion, which can describe various modes of coordination and geometry. In the specific case of bromocadmates, Ishihara's group have, to date, elucidated by X-ray diffraction analysis a multitude of examples, including a monomer and polymer type, in which

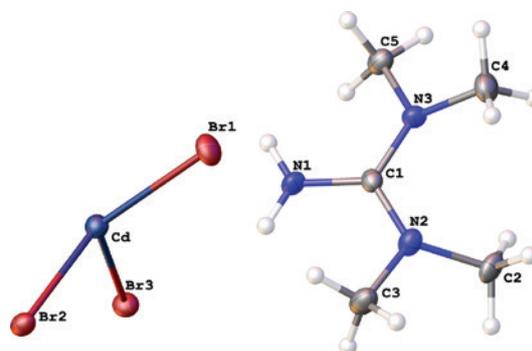


Figure 1: Molecular structure of **1** showing 40% probability ellipsoids and the crystallographic numbering scheme (ORTEP view in OLEX2) [Br (red), Cd (turquoise), N (blue), C (gray), H (white)]. Selected bond lengths and angles [\AA , $^\circ$]: $Cd-Br1 = 2.5290(9)$, $Cd-Br2 = 2.6590(9)$, $Cd-Br3 = 2.5531(9)$, $Cd-Br2^i = 2.6753(9)$, $N3-C1 = 1.335(9)$, $N3-C5 = 1.456(8)$, $N3-C4 = 1.464(10)$, $N2-C2 = 1.462(10)$, $N2-C1 = 1.353(8)$, $N2-C3 = 1.467(9)$, $N1-C1 = 1.315(9)$; $Br2-Cd-Br2^i = 99.87(3)$, $Br3-Cd-Br2^i = 107.19(3)$, $Br3-Cd-Br2 = 108.61(3)$, $Br1-Cd-Br2 = 110.29(3)$, $Br1-Cd-Br2^i = 108.77(3)$, $Br1-Cd-Br3 = 120.15(3)$, $Cd-Br2-Cd^{ii} = 106.84(3)$, $C5-N3-C4 = 115.3(6)$, $C1-N3-C5 = 120.2(6)$, $C1-N3-C4 = 123.1(6)$, $C2-N2-C3 = 115.6(6)$, $C1-N2-C2 = 121.7(6)$, $C1-N2-C3 = 119.9(6)$, $N3-C1-N2 = 119.5(6)$, $N1-C1-N3 = 120.6(6)$, $N1-C1-N2 = 119.9(6)$ [symmetry code: (i) $= +x, 1 - y, -1/2 + z$; (ii) $= +x, 1 - y, 1/2 + z$].

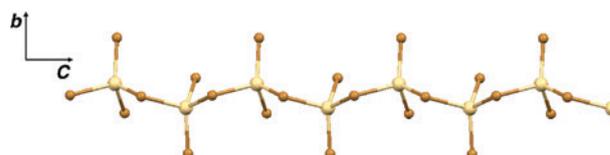
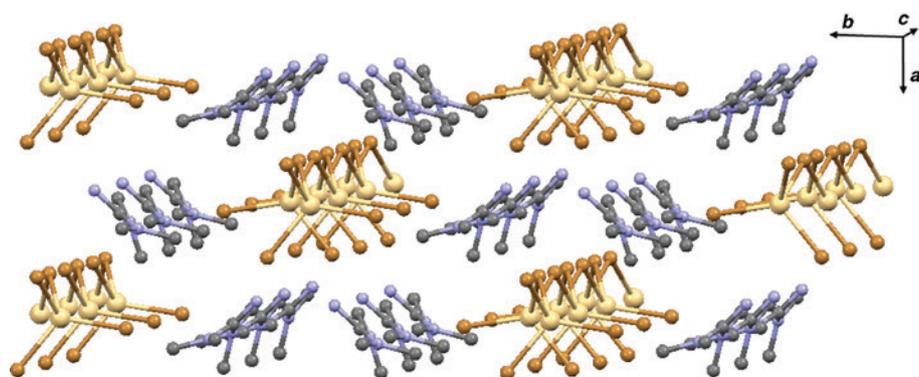


Figure 2: The infinite chain of $[CdBr_4]^-$ [Br (brown), Cd (beige)]. *N,N,N',N'*-tetramethyl guanidinium cations have been omitted.

the environment around the cadmium atom can be tetrahedral (Ishihara et al., 1998), square pyramidal (Ishihara et al., 1994), and octahedral (Ishihara et al., 1996). To our knowledge, the tetrahedral geometry of $[CdBr_4]^-$ is mainly reported for discrete anions. A few examples describe such coordination in polymeric arrangements. It is particularly interesting to cite the previous work of Reiser et al. who reported a one-dimensional chain of pentagonal-bipyramidal-coordinated Cd centers, connected by tetrahedral $CdBr_4$ units (Seitz et al., 2004). Thus, the inorganic chain observed in **1** can be considered as relatively unusual. The distance $Cd \cdots Cd$ is $4.2836(7)$ \AA , which is longer than the values usually encountered for bromide-cadmium-based chains. This can be viewed as corroborating the coordination mode described by the cadmium atom. A comparison with previous examples of structures is given in Table 1.

Table 1: Comparison of the Cd...Cd distance in polymeric chains vs. the geometry of the cadmium atom.

Compound	Cadmium atom	$d(\text{Cd}\cdots\text{Cd})$	Reference
	Coordination	(Å)	
$(\text{C}_6\text{H}_5\text{NH}_3)_4\text{Cd}_3\text{Br}_{10}$	Octahedron	3.571(1)	Ishihara et al., 1994
$[\text{N}(\text{CH}_3)_4][\text{CdBr}_3]$	Octahedron	3.483	Aguirre-Zamalloa et al., 1993
$[\text{C}(\text{NH}_2)_3]\text{Cd}_2\text{Br}_5$	Octahedron	3.945	Ishihara et al., 2000
$(4-(\text{CH}_3)_2\text{C}_5\text{H}_4\text{NH})\text{CdBr}_3$	Tetragonal pyramid	3.953	Ishihara et al., 1994
$\{(\text{C}_8\text{H}_{20}\text{NO})[\text{CdBr}_3]\}_n$	Trigonal-bipyramid	4.1612(9)	Wang et al., 2015
		4.0446(9)	
$[\text{C}_5\text{H}_{14}\text{N}_3][\text{CdBr}_3]$ (1)	Tetrahedron	4.2836(7)	This work

**Figure 3:** Packing diagram for **1** [Br (brown), Cd (beige), N (blue), C (gray)]. Hydrogen atoms are omitted for clarity.

The negative charge of $[\text{CdBr}_3]^-$ is compensated by one monoprotonated *N,N,N',N'*-tetramethyl guanidinium cation (TMGDH). As shown in Figure 3, TMGDHs are positioned along the $[\text{CdBr}_3]_{\infty}$ chain. The CN_3 fragment of each cation is planar. The N-C distances are in the range of 1.315(9) to 1.353(8) Å, which confers a partial double-bond character. The positive charge is delocalized. The three N-C-N angles are between 119.5(6) and 120.6(6)° leading to a trigonal-planar geometry. The *N,N*- and *N',N'*-dimethylammonium groups are twisted by 27.3(6)° for C4N3C5 and 29.6(5)° for C3N2C2 with respect to the C1N1N2N3 plane. Comparable structural data were recorded in previous X-ray structures involving the TMGDH cation (Bujak et al., 1999; Bujak and Zaleski, 2007; Tiritiris, 2012; Ndiaye et al., 2016). The NH_2^+ groups of the cations face the bromine atoms. This results in the presence of several N-H...Br interactions, which keep the TMGDH cations close and along the $[\text{CdBr}_3]_{\infty}$ chain. The details are given in Table 2. These values of distances and angles are in the range of those observed for such hybrid materials (Bujak and Zaleski, 2007; Rademeyer, 2007). In addition, direct and long Br...C contacts exist also between anions and cations [Br3-C4 = 3.544(8) Å, Br2-C1 = 3.547(8) Å]. All these intermolecular interactions

Table 2: Hydrogen-bonding geometry (Å, °).

D	H	A	$d(\text{D-H})$ (Å)	$d(\text{H-A})$ (Å)	$d(\text{D-A})$ (Å)	D-H-A (°)
N1-H1A	...	Br3 ⁱ	0.88	2.66	3.488 (6)	158
N1-H1B	...	Br3	0.88	2.67	3.435 (6)	147
C5-H5A	...	Br2 ⁱⁱⁱ	0.98	3.06	3.842 (7)	137
C5-H5B	...	Br1 ^{iv}	0.98	3.19	3.804 (7)	122
C2-H2C	...	Br1 ^v	0.98	3.02	3.861 (7)	144
C4-H4A	...	Br1 ^{iv}	0.98	3.19	3.941 (8)	134

Symmetry codes: (i) $x, -y+1, z-1/2$; (iii) $x+1, -y+1, z-1/2$; (iv) $x+1, y, z$; (v) $x+1/2, -y+3/2, z+1/2$.

that are displayed in Figure 4 lead to a three-dimensional organization of **1**.

Crystals of **1** were also investigated by middle and far-infrared spectroscopy [attenuated total reflectance (ATR) mode]. The middle infrared spectrum of **1** (supplementary Figure S1) reveals the characterization vibration bands of the TMGDH cation: $\nu(\text{N-H}^+)$ (3422, 3337, and 3245 cm^{-1}), $\nu(\text{C-H})$ (2967 and 2914 cm^{-1}), $\nu(\text{C=N})$ (1726), $\delta(\text{N-H})$ (1635, 1611 and 1560 cm^{-1}), $\delta(\text{C-H})$ (1477, 1445, 1421, and 1405 cm^{-1}), $\nu(\text{C-N})$ (1070 and 1037 cm^{-1}), CN_3 angle deformation (528 cm^{-1}) (Berg et al., 2010). The far-infrared spectrum (supplementary Figure S2) exhibits three major

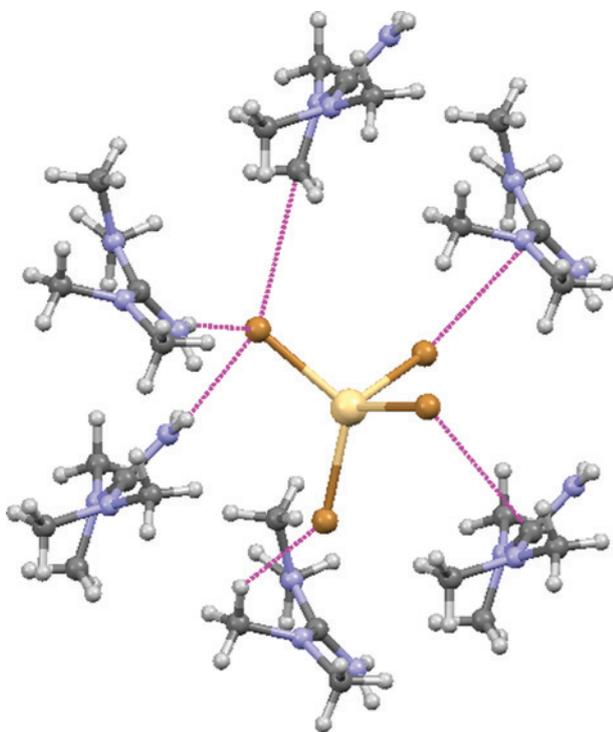


Figure 4: Intermolecular contacts involving bromide atoms in **1** [Br (brown), Cd (beige), N (blue), C (gray), H (white)]. Hydrogen atoms are omitted for clarity. Interactions are shown as pink dotted lines.

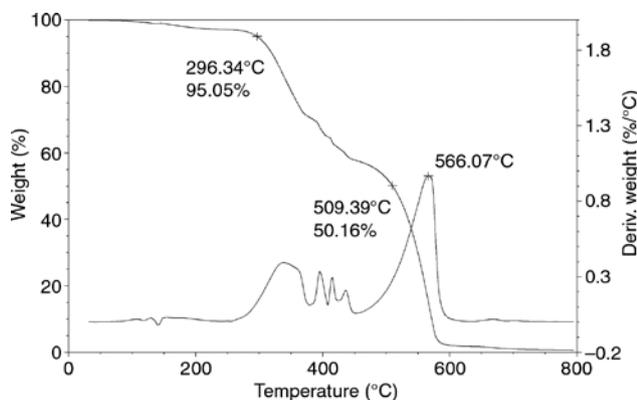


Figure 5: TG-DTG analyses of **1** at a heating rate of $20^{\circ}\text{C min}^{-1}$ under nitrogen.

bands located at 207, 186, and 130 cm^{-1} and which were assigned as resulting of the Cd-Br bonds ($\nu_{\text{asym,sym}}$ stretching and deformation vibrations), in agreement with previous spectroscopic studies (Davies and Long, 1968; Bruni et al., 1991). Furthermore, the CHN elemental analysis performed on crystals also supports the formula of **1**.

The thermal behavior of **1** was also studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 5 reports the weight loss percentage

and the first derivative of the weight loss as a function of the temperature. Degradation temperatures, recorded by TGA under nitrogen atmosphere, corresponding to 5%, 50% weight loss, and maximum degradation rate were found to be, respectively, equal to 295°C ($T_{5\%}$), 509°C ($T_{50\%}$), and 566°C (T_{max}). Interestingly, a similar TGA profile was recorded for $[(\text{HPy})_3(\text{Cd}_3\text{Cl}_9)]_{\infty}$ ($y = \text{pyridine}$) (Jian et al., 2006). However, the chlorocadmate derivative exhibits a first loss of weight at a lower temperature (214°C). Figure 6 depicts the DSC curves of **1**, heated from -10°C to 200°C and cooled from 200°C to -20°C at a heating/cooling rate of $10^{\circ}\text{C min}^{-1}$. This measurement allowed to detect the reversible phase transition behavior of **1**. A sharp endothermic peak at 119°C is detected upon heating and at 93°C upon cooling. This indicates that **1** exhibits a reversible phase transition at 119°C with a large hysteresis of about 25°C suggesting the discontinuous first-order phase transition character. A comparable behavior was recently reported for the organic-inorganic hybrid compound, $[\text{C}_3\text{H}_7\text{NH}_3]_2\text{SbI}_5$, describing also a zigzag chain (Mao et al., 2016).

In solution, crystals of **1** are well soluble in water. Multi-nuclear nuclear magnetic resonance (NMR) spectroscopic measurements were conducted in D_2O . ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show the characteristic signals of the TMGDH cation (supplementary Figures S3 and S4), exhibiting the $-\text{N}(\text{CH}_3)_2$ and N_3C^+ moieties. The hydrogen atom of the $-\text{NH}_2$ group was not observed. The ^{113}Cd NMR spectrum exhibit a unique resonance at 104 ppm [based on a 1-M $\text{Cd}(\text{NO}_3)_2$ solution in dimethyl sulfoxide (DMSO) as a reference] (Figure 7).

In summary, an unprecedented bromocadmate-based organic-inorganic hybrid salt has been isolated, using the *N,N,N',N'*-tetramethyl guanidinium as counter cation. The structural arrangement describes a chain-like structure and in where cadmium atoms exhibit an unusual coordination geometry for this class of compounds. Further work is in progress in our laboratory, in order to isolate new examples of halometalates involving *N,N,N',N'*-tetramethyl guanidinium as counter cation.

Experimental

General

N,N,N',N'-tetramethyl guanidine [TMGD, $\text{NCNC}(\text{SCH}_3)_2$, 98% purity] and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (98% purity) were purchased from Sigma-Aldrich (Steinheim am Albuch, Germany) and were used without any further purification. Middle infrared spectra ($4000\text{--}500\text{ cm}^{-1}$) of solid samples were recorded on a Bruker Vector 22 spectrometer (Wissembourg, France) equipped with a Specac Golden Gate™ ATR device (Orpington, UK). The far FT-IR measurements ($700\text{--}70\text{ cm}^{-1}$) were performed using a Bruker Vertex 70v spectrometer under vacuum

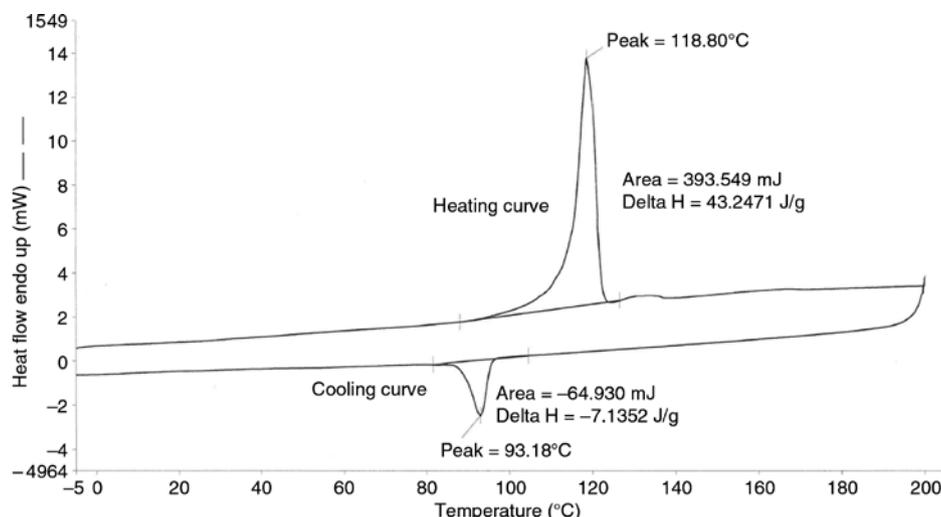


Figure 6: DSC analysis of **1** from -10°C to 200°C and cooled from 200°C to -20°C at a heating/cooling rate of $10^{\circ}\text{C min}^{-1}$.

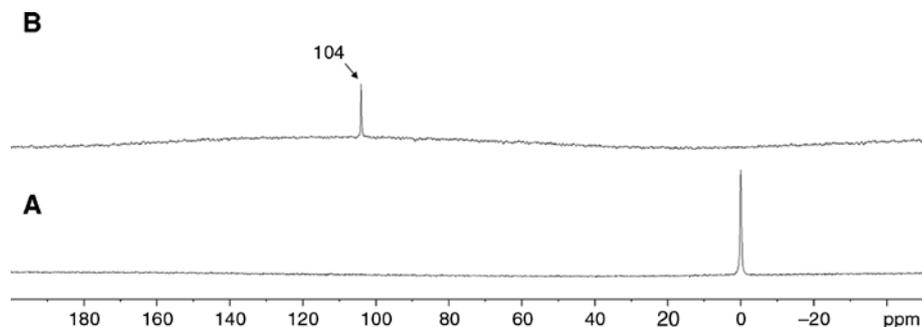


Figure 7: ^{133}Cd solution NMR spectra of (A) $\text{Cd}(\text{NO}_3)_2$ and (B) from crystals of **1**.

(Wissembourg, France), with an attenuated total reflectance (ATR) module. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{133}Cd NMR spectra were recorded on Bruker 500- and 600-MHz spectrometers in D_2O (Wissembourg, France). A DMSO- d_6 solution of 1-M $\text{Cd}(\text{NO}_3)_2$ served as a reference for the ^{133}Cd NMR experiments (Summers and Marzilli, 1984). Differential scanning calorimetry (DSC) analysis was carried out using a Perkin Elmer Pyris DSC 6 calorimeter (Waltham, USA). Experiments were performed under nitrogen with a sample mass of 9.1 mg. The sample was heated from -10°C to 200°C and cooled from 200°C to -20°C at a heating/cooling rate of $10^{\circ}\text{C min}^{-1}$. A thermogravimetric analysis (TGA) was performed on a TA Instruments TGA SDT-Q600 thermo-analyzer using alumina pans (New Castle, USA). The sample (5.3 mg) was heated from room temperature to 800°C at a rate of $20^{\circ}\text{C min}^{-1}$ under nitrogen flow. Weight loss percentages were determined using the TA Universal Analysis 2000 software accompanying the instrument. Elemental analyses were performed at the Institut de Chimie Moléculaire (Université de Bourgogne Franche-Comté, Dijon-France) using a Thermo Electron CHNS/O Flash EA 112 Series analyzer.

Preparation of $[\text{C}_5\text{H}_{14}\text{N}_3][\text{CdBr}_3]$ (**1**)

Ethanol solutions (15 mL) of 1,1,3,3-tetramethyl guanidine (0.500 g, 4.347 mmol, 99% purity) and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (2.990 g, 8.695 mmol)

were mixed together at room temperature (298 K). A white turbid solution is quickly obtained, which is then filtered off (the infrared spectrum of the material removed exhibits the cation's fingerprint, but its accurate composition is still unknown). After several weeks of slow evaporation at room temperature, colorless crystals, suitable for an X-ray crystallographic analysis, were grown from the filtrate and were finally characterized as **1** (42% yield, based on crystalline materials).

IR (ATR, cm^{-1}): 3422 (m), 3337 (s), 3245 (m), 2967 (w), 2914 (w), 1726 (m), 1635 (s), 1611 (s), 1560 (m), 1477 (w), 1445 (m), 1421 (m), 1405 (m), 1070 (m), 1037 (m), 864 (w), 528 (m), 357 (w), 207 (w), 186 (w), 130 (w). ^1H NMR (500 MHz, D_2O , 298 K): $\delta = 2.97$ [s, 12H, $-\text{N}(\text{CH}_3)_2$]. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, D_2O , 298 K): $\delta = 38.8$ [$-\text{N}(\text{CH}_3)_2$], 161.4 (N_3C^+). ^{133}Cd (133 MHz, D_2O , 300 K): $\delta = 104$. Anal. Calcd. for $\text{C}_5\text{H}_{14}\text{Br}_3\text{N}_3\text{Cd}$ (468.307 g mol^{-1}): C 12.82, H 3.01, N 8.97. Found: C 13.13; H 3.02; N 8.70.

X-ray crystallography

A single colorless prism-shaped crystal ($0.23 \text{ mm} \times 0.15 \text{ mm} \times 0.05 \text{ mm}$) was selected and mounted on a Mylar loop oil on a Bruker APEX-II CCD diffractometer operating at $T = 115 \text{ K}$. Data were measured using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The total number of runs and images was based on the strategy calculation from the program APEX2

(Bruker, 2014). Cell parameters were retrieved and refined using the SAINT software (Bruker, 2014). Data reduction was performed using the SAINT software, which corrects for Lorentz polarization. The structure was solved by direct methods using the SHELXT structure solution program (Sheldrick, 2015a) and refined by full matrix least squares on F^2 using SHELXL (Sheldrick, 2015b) with the aid of the OLEX2 program (Dolomanov et al., 2009). All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated geometrically and refined using the riding model. The programs used for the representation of the molecular and crystal structures: OLEX2 (Dolomanov et al., 2009) and Mercury (Macrae et al., 2008).

Selected crystallographic parameters of **1**: Formula $C_5H_{14}Br_3CdN_3$, $M = 468.32 \text{ g mol}^{-1}$, $a = 8.9079(7) \text{ \AA}$, $b = 18.5810(14) \text{ \AA}$, $c = 8.1637(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 107.953(3)^\circ$, $\gamma = 90^\circ$, $V = 1285.44(17) \text{ \AA}^3$, $D_{\text{calcd}} = 2.420 \text{ g cm}^{-3}$, $\mu = 10.99 \text{ mm}^{-1}$, $Z = 4$, monoclinic, space group *Cc*, 7791 reflections collected (index ranges : h : -11, 7; k : -24, 24; l : -10, 10), 2150 independent ($R_{\text{int}} = 0.0473$) and 2019 observed reflections [$I \geq 2\sigma(I)$], 114 refined parameters, two restraints, R indices for observed reflections: $R_1 = 0.0268$, $wR_2 = 0.0547$, R indices for all data: $R_1 = 0.0297$, $wR_2 = 0.0560$, goodness-of-fit = 1.011, maximum residual electron density 0.931 and $-0.822 \text{ e \AA}^{-3}$.

CCDC 1557041(1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting information

Middle, far infrared, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** are given as online-only Supplementary Information (Figures S1–S4).

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