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Crystal structure of $[(C_2H_5)_2NH_2]_2[Cd_3Br_8(CdBr_2)] \cdot H_2O$: An augmented ribbon structure

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Abstract

The crystal structure of $[(C_2H_5)_2NH_2]_2[Cd_3Br_8(CdBr_2)] \cdot H_2O$ contains decorated $[Cd_3Br_8]_n^{2n-}$ ribbons. The ribbons can be visualized as triple chains of edge-shared $CdBr_6$ octahedra excised from the parent hexagonal $CdBr_2$ lattice by the action of the diethylammonium 'molecular scissors'. Each ribbon is augmented by $CdBr_2$ groups that bind to pairs of terminal Br^- ions on the edges of the ribbons to create a fringe of distorted tetrahedral $CdBr_4$ species. N–H···Br and O–H···Br hydrogen bonds stabilize the resultant networks.

Keywords: Crystal structure; Cadmium bromide salt; Hybrid organic–inorganic salt; Extended halometallate lattice

1. Introduction

The analysis of extended metal halide frameworks in organoammonium halometallate(II) salts in our laboratory has used a process that we have termed ''retro-crystal engineering'' to describe the resultant structures [1]. Due to our success in the application of this concept to the Jahn-Teller distorted Cu(II) halide systems [2], we are seeking to extend these ideas to other metal(II) halide systems, in particular, those systems where octahedral coordination is preferred [1,3]. In this approach, an attempt is made to describe the observed structures in terms of known structure types. Typically, this process starts with a dimensional reduction analysis that relates part or all of the observed metal halide network to a high symmetry parent lattice [4]. In many cases, this dimensional reduction process yields the observed network, as in the case of the $(Cd_4Cl_{12})_n^{4n-}$ ribbons (Fig. 1a) that are found in the structures of $(CH_3NH_2C_2H_4NH_3)_2Cd_4Cl_{12} \cdot 2H_2O$ [1] and $(C_2H_5NH_2C_2H_4NH_3)_2Cd_4Cl_{12} \cdot H_2O$ [5]. In other cases, the segments obtained in this process are recombined to obtain the more complex final networks, such as the perforated layer network in $(CH_3NH_2C_2H_4NH_3)Cd_3Br_8 \cdot xH_2O$, shown in Fig. 1b [1].

In this paper, we describe a novel extended network obtained in our study of the reaction of dialkylammonium salts with halocadmate(II) salts [6]. The compound, $(DEA)_2[Cd_3Br_8(CdBr_2)] \cdot H_2O$, (where DEA^+ is the diethylammonium cation), contains triple chains of edge-shared $CdBr_6$ octahedra decorated with auxiliary Cd atoms in tetrahedral sites.

2. Experimental

2.1. Synthesis

All solvents and reagents were used as received. Diethylammonium bromide, (DPA)Br, was prepared by dissolving 3 mL of diethylamine in 3 mL of deionized water in a small, chilled beaker. The solution was then acidified with concentrated hydrobromic acid and allowed to evaporate at room temperature (23 °C). Crystalline bis(diethylammonium)decabromotetracadmate(II)hydrate, $(DEA)_2[Cd_3Br_8$-

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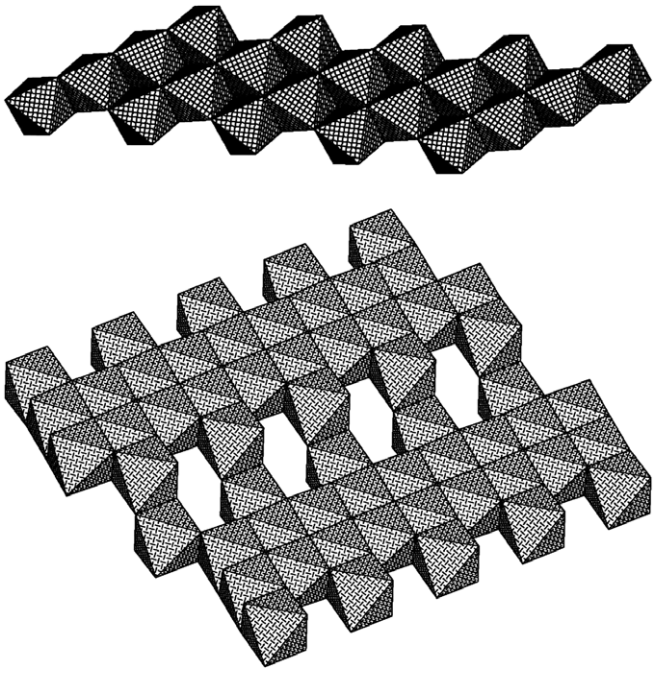

Fig. 1. Top: the $(Cd_4Cl_{12})_n^{4n-}$ ribbon in $(CH_3NH_2C_2H_4NH_3)_2Cd_4Cl_{12} \cdot 2H_2O$. Bottom: the fused serrated $(Cd_3Br_9)_n^{3n-}$ ribbons in $(CH_3NH_2C_2H_4NH_3)Cd_3Br_8 \cdot xH_2O$.

$(CdBr_2)] \cdot H_2O$, was prepared by mixing [DEA]Br (0.171 g, 1 mmol) and $CdBr_2$ (0.819 g, 3 mmol) in a solution of deionized water (10 mL) and methanol (3 mL). Short, clear, colorless needles formed after one week.

2.2. X-ray structure analysis

Crystals were removed from solution and immediately placed in hydrocarbon oil to prevent the crystalline material from possible deterioration due to solvent loss. A suitable crystal was selected, attached to a glass fiber, and placed immediately in the low-temperature nitrogen stream [7]. Data was collected at ca. 86(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame, and a full sphere of data was collected. The first 50 frames were recollected at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART [8] software and refined using SAINTPLUS [9] on all observed reflections. Data reduction and correction for Lp and decay was performed using the SAINTPLUS [9] software. Absorption corrections were applied using SADABS [10]. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL program package [11]. No decomposition was observed during data collection. The pendant $CdBr_2$ group was disordered with occupancies of 95% for Cd5, Br9, and Br10 and 5% for Cd6, Br11, and Br12. The major moiety was refined anisotropically. It was not possible to resolve the disorder in the organic groups, so

Table 1
Data collection and refinement parameters for $[DEA]_2[Cd_3Br_8(CdBr_2)] \cdot H_2O$

Empirical formula	$C_8H_{26}Br_{10}Cd_4N_2O$
Formula weight	1415.01
Temperature (K)	86(2)
Description	colorless needle
Size (mm^3)	$0.39 \times 0.07 \times 0.06$
System	triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	7.9884(8)
b (Å)	12.6197(13)
c (Å)	15.3982(16)
α (°)	80.031(2)
β (°)	84.339(2)
γ (°)	76.587(2)
V ($Å^3$)	1484.4(3)
Exposure (s)	5
D_{calc} ($Mg\ m^{-3}$)	3.166
Reflections used	5301
Goodness-of-fit	1.027
R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0465$
	$wR_2 = 0.1012$
R indices (all data)	$R_1 = 0.0696$
	$wR_2 = 0.1094$

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|^2$; $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum[w(F_c^2)^2]\}^{1/2}$.

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the structure of $[DEA]_2[Cd_3Br_8(CdBr_2)] \cdot H_2O$

	x	y	z	U_{eq}
Cd(1)	10000	10000	10000	9(1)
Cd(2)	5000	10000	10000	9(1)
Cd(3)	8299(1)	8824(1)	8019(1)	9(1)
Cd(4)	13277(1)	8779(1)	8071(1)	9(1)
Cd(5)[a]	12085(1)	5670(1)	7351(1)	8(1)
Cd(6)[b]	6944(1)	5599(9)	7315(7)	8(1)
Br(1)	7436(1)	10779(1)	8796(1)	9(1)
Br(2)	12424(1)	10748(1)	8809(1)	9(1)
Br(3)	10756(1)	8080(1)	9298(1)	9(1)
Br(4)	5833(1)	8090(1)	9312(1)	9(1)
Br(5)	10789(1)	9511(1)	6926(1)	12(1)
Br(6)	8963(1)	6806(1)	7469(1)	15(1)
Br(7)	15683(1)	9552(1)	6934(1)	10(1)
Br(8)	14397(1)	6644(1)	7704(1)	13(1)
Br(9)[a]	12107(1)	3872(1)	8435(1)	12(1)
Br(10)[a]	12965(1)	5284(1)	5773(1)	17(1)
Br(11)[b]	7220(2)	3855(1)	8472(1)	9(1)
Br(12)[b]	8040(2)	5224(2)	5752(9)	9(1)
C(1)[a]	2251(1)	8388(9)	4650(7)	23(1)
C(2)[a]	3900(1)	8300(9)	5109(7)	23(1)
N(3)[a]	5188(9)	7305(6)	4901(5)	10(1)
C(4)[a]	6861(1)	7163(9)	5330(7)	23(1)
C(5)[a]	7813(1)	8048(9)	4930(7)	23(1)
C(6)[a]	7269(1)	4669(9)	9719(7)	23(1)
C(7)[a]	6883(1)	4014(9)	9045(7)	23(1)
N(8)[a]	7799(1)	4317(7)	8173(5)	10(1)
C(9)[a]	7544(1)	3715(9)	7462(7)	23(1)
C(10)[a]	8539(1)	4026(9)	6620(7)	23(1)
O(1)[a]	4428(1)	2336(6)	6934(5)	27(2)

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.
[a] Site occupancy factor set to 0.950.
[b] Site occupancy factor set to 0.050.