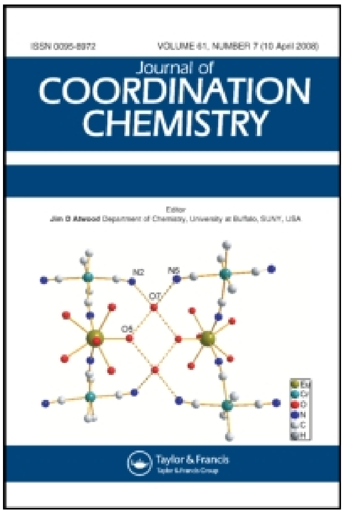

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Crystal and band structure of a layered bismuth oxalate: $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}]\cdot H_2O$

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Crystal and band structure of a layered bismuth oxalate: $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}] \cdot H_2O$

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A 2-D oxalate-containing bismuth(III) compound of formula $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}] \cdot H_2O$ has been hydrothermally synthesized and characterized by single crystal X-ray diffraction. The Bi atoms and oxalate units form a 2-D layered structure with a 12-membered aperture. The crystal band structure, calculated by the DFT method, shows that the title compound is an insulator with a band gap of 3.19 eV, a value consistent with the experimental value of 3.29 eV.

Keywords: Bismuth; Oxalate ligand; Crystal structure; Band structure

1. Introduction

Considerable efforts have been devoted to the design of open-framework inorganic materials other than silicates or phosphates, such as oxalates. The oxalate ligand can act as a linker between metal centres to yield various structures with dimensionalities ranging from zero to three. Coordination modes of oxalate ligand can be mono- and bidentate, and also tricoordinate. Metal oxalates with novel structures have been widely synthesized and investigated; bismuth oxalates are less reported [1, 2]. With highly variable coordination numbers and irregular coordination geometry, bismuth can form a range of coordination polymers with interesting structural features [3]. Compounds containing bismuth have applications in medical treatment, catalysts, luminescence, etc. [4–7] bringing interest to the coordination chemistry and synthesis of bismuth compounds.

We have made some attempts to synthesize bismuth oxalates in the presence of organic amines in the past few years [8–10]. In the present work, we introduce another new Bi oxalate compound: $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}] \cdot H_2O$ which has a 2-D layered structure with the Bi^{III} centers displaying distorted dodecahedral geometry. The energy band of the title compound is calculated to understand the structure of Bi oxalate.

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2. Experimental

2.1. *Materials and methods*

All chemicals were of analytical regent grade and commercially purchased, and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental analyzer. The IR spectrum was recorded in the 4000–400 cm^{-1} region on a Perkin–Elmer Spectrum 2000 spectrometer using a KBr pellet. The UV–Vis DRIS (Ultraviolet–Visible Diffuse Reflection Integral Spectrum) was measured by a Perkin–Elmer Lambda 900 UV–Vis spectrometer. The TGA was performed on a Delta Series TGA7 instrument in N_2 with heating rate of 10°C min^{-1} from 25 to 800°C.

2.2. *Synthesis*

A mixture of $Bi(NO_3)_3 \cdot 5H_2O$ (0.25 g, 0.52 mmol), $H_2C_2O_4 \cdot 2H_2O$ (0.63 g, 5.00 mmol), 1,2-DAP (0.30 mL) (1,2-DAP = 1,2-diamino propane) and distilled water (3.50 mL) was stirred to homogeneity for 10 min in air. The mixture was loaded into a 15 mL Teflon-lined steel autoclave and heated at 100°C for 2 days, and then cooled to room temperature. The colourless block crystals were collected. The product is stable in air and insoluble in water. Yield: 0.15 g (ca 56% based on bismuth). Anal. Found: C, 18.37; H, 2.70; N, 5.35. Calcd C, 18.25; H, 2.42; N, 5.48%. IR (KBr pellet, cm^{-1}): υ(O–H) 3396(w), υ(C–H) 3168 (w), υ(C=O) 1619 (s), 1298 (w), δ(CH2)1439 (m), δ(C–O) 789 (w), υ(Bi–O, O–C–O) 476 (w).

2.3. *X-ray measurements*

A single crystal, $0.10 \times 0.10 \times 0.05\ mm^3$, was mounted on a glass fibre. The reflection intensities were collected on a Rigaku Weissenbery IP diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Lp correction and a Ψ empirical absorption correction were made for the intensity data. A total of 13,185 reflections (independent 3103, $R_{int} = 0.0597$) with 1850 unique reflections $I > 2\sigma(I)$ were measured. The structure was solved by direct methods using the SHELXS-97 [11] and refined by full-matrix least-squares based on F^2 using SHELXL-97 program [12]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms of C and N atoms were generated geometrically, and of water molecules were located from different Fourier maps. A summary of crystal data and structure refinement for the title compound is provided in table 1. Selected bond lengths and angles are listed in table 2.

2.4. *Computational descriptions*

The crystallographic data of the title compound were used to calculate electronic band structure of this compound in the solid state. The calculations were made within the density functional theory (DFT) using one of the three nonlocal gradient-corrected

Table 1. Summary of crystal data and refinement results of the title compound.

Empirical formula	$BiC_8N_2O_{11}H_{14}$
Formula weight ($g\,mol^{-1}$)	523.19
Crystal system	Monoclinic
Space group	$P2/c$
a (Å)	9.0254(18)
b (Å)	7.703(4)
c (Å)	8.4972(17)
β (°)	92.22(3)
V (Å^3)	1356.6(5)
Z	4
D_{Calcd} ($g\,cm^{-3}$)	2.562
μ (mm^{-1})	13.061
Temperature (K)	293(2)
Final R factors ($I > 2\sigma(I)$)[a]	$R_1 = 0.0280^a$, $wR_2 = 0.0722^b$
Final R factors (all data)	$R_1 = 0.0308$, $wR_2 = 0.0741$
Largest diff. map peak and hole (e Å^{-3})	2.329 and −1.500

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. $wR_2^b = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}$ $w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 4.0218P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. The selected bond lengths (Å) and angles (°) for the title compound.

Bi(1)–O(1)#1	2.318(4)	Bi(1)–O(2)#1	2.359(4)
Bi(1)–O(6)	2.373(4)	Bi(1)–O(8)	2.463(4)
Bi(1)–O(5)#2	2.495(3)	Bi(1)–O(3)	2.508(4)
Bi(1)–O(7)	2.512(5)	Bi(1)–O(4)	2.578(4)
O(1)–C(2)	1.263(6)	O(4)–C(1)	1.247(6)
O(2)–C(1)	1.265(6)	C(6)–C(7)	1.507(9)
O(3)–C(2)	1.259(6)	C(6)–N(2)	1.518(7)
O(5)–C(3)	1.243(7)	O(7)–C(3)	1.252(6)
O(6)–C(4)	1.246(7)	O(9)–C(4)	1.212(8)
O(8)–C(5)	1.264(8)	C(1)–C(2)	1.523(7)
O(10)–C(5)	1.232(9)	C(4)–C(5)	1.555(8)
O(2)#1–Bi(1)–O(6)	78.53(16)	O(1)#1–Bi(1)–O(6)	75.05(15)
O(2)#1–Bi(1)–O(8)	78.16(15)	O(1)#1–Bi(1)–O(8)	134.79(15)
O(6)–Bi(1)–O(5)#2	69.77(14)	O(6)–Bi(1)–O(8)	66.91(14)
O(1)#1–Bi(1)–O(3)	72.35(14)	O(8)–Bi(1)–O(5)#2	113.65(14)
O(6)–Bi(1)–O(3)	142.33(15)	O(2)#1–Bi(1)–O(3)	73.43(17)
O(5)#2–Bi(1)–O(3)	116.36(13)	O(8)–Bi(1)–O(3)	128.83(13)
O(2)#1–Bi(1)–O(7)	144.00(16)	O(1)#1–Bi(1)–O(7)	100.13(17)
O(8)–Bi(1)–O(7)	123.75(18)	O(6)–Bi(1)–O(7)	134.29(14)
O(3)–Bi(1)–O(7)	70.66(15)	O(5)#2–Bi(1)–O(7)	65.62(14)
O(2)#1–Bi(1)–O(4)	80.40(14)	O(1)#1–Bi(1)–O(4)	133.46(13)
O(8)–Bi(1)–O(4)	69.37(14)	O(6)–Bi(1)–O(4)	134.35(13)
O(3)–Bi(1)–O(4)	64.59(12)	O(5)#2–Bi(1)–O(4)	143.06(13)
C(3)–O(5)–Bi(1)#2	119.7(4)	O(7)–Bi(1)–O(4)	82.04(15)
C(3)–O(7)–Bi(1)	119.0(4)	C(4)–O(6)–Bi(1)	121.5(4)

Symmetry transformations used to generate equivalent atoms: #1x, $-y+1/2$, $z-1/2$; #2 $-x+1$, $-y$, $-z+1$.

exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code [13, 14] which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential [15] for the core states. Pseudo atomic calculations were performed for Bi-$6s^26p^2$, C-$2s^22p^2$, N-$2s^22p^3$ and O-$2s^22p^4$. The number of plane waves included in the basis was determined by cutoff energy $Ec = 300\,eV$: the calculating parameters and convergence criteria were set by the default values of CASTEP cod.

3. Results and discussion

3.1. *Structure description*

The crystal structure of the title compound consists of $[Bi(C_2O_4)_{2.5}]^{2-}$ anions, protonated 1,2-DAP cations and water. There is just one crystallographically unique Bi centre in the asymmetric unit (figure 1). The Bi centre displays a distorted dodecahedral geometry, which is completed by six oxygen atoms from three bridging bisbidentate oxalate ligands with Bi–O bond lengths of 2.321(3)–2.586(4) Å and two oxygen atoms from bisdentate oxalates with Bi–O bond lengths of 2.373(4)–2.460(4) Å. The O–Bi–O angles range from 64.47(11) to 143.88(14)°. The Bi centres are interconnected by the bridging oxalate ligands to form a 2-D layered network along the *a*-axis with 12-membered aperture as shown in figure 2. Water and protonated 1, 2-DAP molecules are in layers and interact with the adjacent layers through $N\text{–}H\cdots O$ and $OW\text{–}H\cdots O$ hydrogen bonding ($N\cdots O$ distances and $OW\cdots O$ distances are in the range 2.788–3.080 Å and 2.765–3.124 Å, respectively; $N\cdots H\cdots O$ and $OW\cdots H\cdots O$ angles are in the range of 146.82–174.91° and 146.72–162.29°, respectively). Waved layers along the *c*-axis are linked by hydrogen bonds to form a 3-D super-molecule as shown in figure 3.

3.2. *Thermal analysis*

The TG curve of the title compound can be divided into a two-step mass loss stage. The first weight loss of 4.0% (Calcd 3.4%) observed from 127 to 184°C corresponds to the release of water molecules. The second of 53.2% (Calcd 52.0%) observed from 209 to 318°C arises from the decomposition of imidazole and oxalate molecules.

3.3. *Band structure, density of states*

The calculated band structure of $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}]\cdot H_2O$ at the Brillouin zone is plotted in figure 4. Both the valence bands and the conduction bands are flat. The compound $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}]\cdot H_2O$ is an insulator with direct band gap of 3.19 eV.

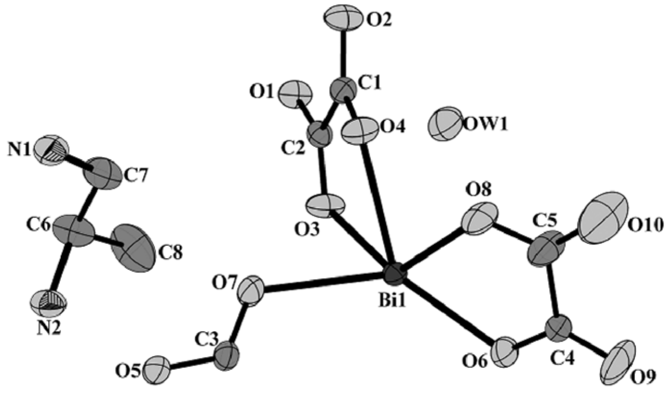

Figure 1. Thermal ellipsoid plot and atomic labeling scheme of the asymmetric unit. The hydrogen atoms are omitted for clarity.

The bands can be assigned according to the total and partial densities of states (DOS), as plotted in figure 5. The valence bands lying about between −22.5 and −20.0 eV are contributions from the C-2s, N-2s and O-2s states. The O-2s and C-2p states have significant contributions to the valence bands lying between −20.0 and −17.5 eV. The valence bands localized at −15.3 and −13.0 eV are mainly contributions from the C-2s state. The C-2p, N-2p and Bi-6s states have significant contributions to the valence bands ranging from −11.7 to −8.5 eV. The valence bands lying between −8.5 eV and the Fermi level (0.0 eV), are largely formed by mixings O-2p, C-2p, N-2p, Bi-6s and Bi-6p states. The band of the nearest Fermi level mostly originates from the O-2p states. The conduction bands between 2.5 and 5.1 eV are mainly due to antibonding states between C-2p, O-2p, and Bi-6p states. Accordingly, the absorption edge of UV–Vis DRIS spectrum observed at 380 nm (3.29 eV) is assigned as the electron transitions from the bonding to antibonding states between the Bi-6p, C-2p and O-2p states. The calculated band gap (3.19 eV, not including shift energy) is comparable with the experimental value of 3.29 eV.

4. Conclusions

In summary, a new Bi oxalate compound, $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}]\cdot H_2O$ has been synthesized by hydrothermal techniques. In the title compound, the Bi atoms

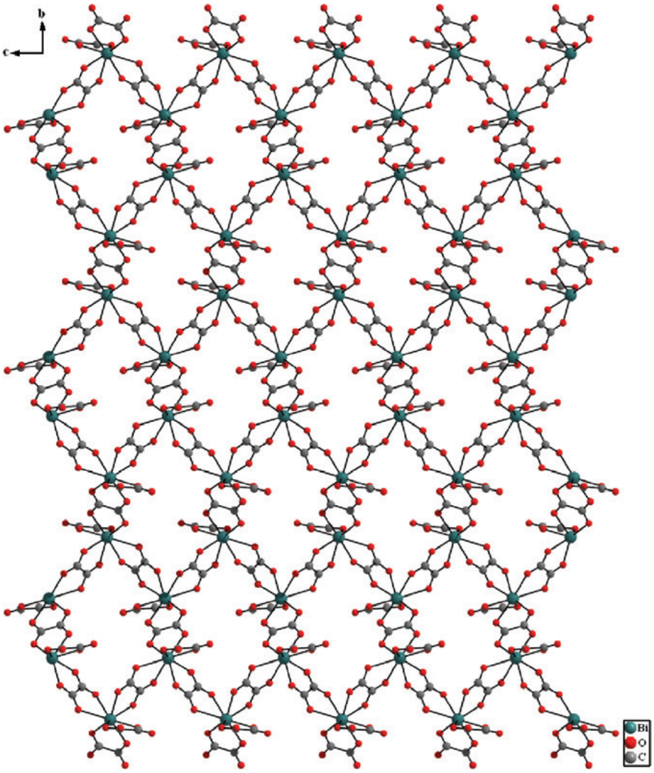

Figure 2. View of the 2-D layer structure with 12-membered aperture along the *a*-axis.

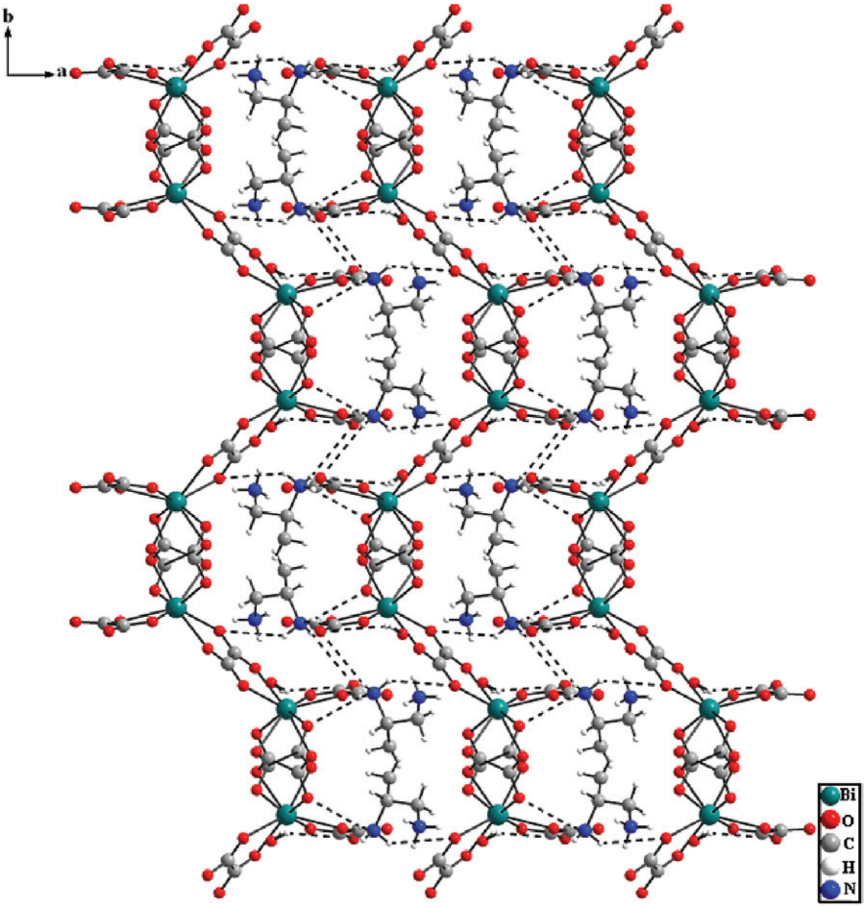

Figure 3. Hydrogen-bonded 3-D structure viewed along the *c*-axis (broken lines are hydrogen bonding).

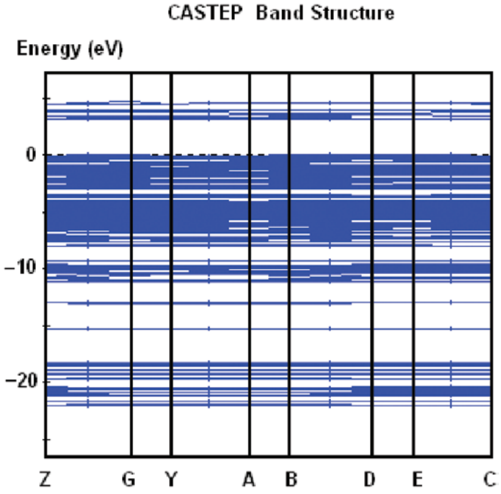

Figure 4. The calculated band structure of $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}]\cdot H_2O$.

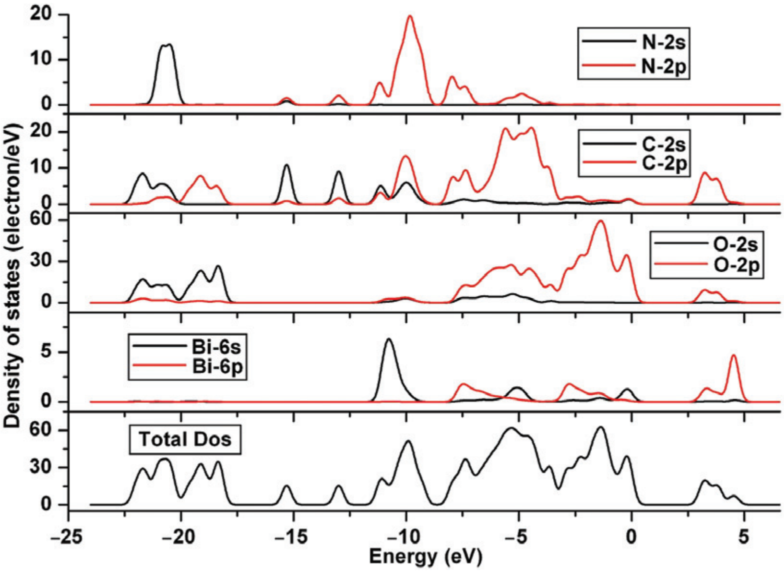

Figure 5. The calculated total and partial of states of $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}] \cdot H_2O$.

were linked to the oxygens atoms of oxalate ligands to form a 2-D layered structure with 12-membered aperture. The calculated band structure shows that the solid state of $(C_3N_2H_{12})[Bi(C_2O_4)_{2.5}] \cdot H_2O$ is an insulator with direct band gap of 3.19 eV. The absorption edge of UV–Vis DRIS spectrum at 380 nm (3.29 eV), is assigned as the electron transitions from the bonding to antibonding states between the Bi-6p, C-2p and O-2p states. The calculated band gap, 3.19 eV is consistent with the experiment value of 3.29 eV.

Supplementry material

CCDC-295892 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk].

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