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Thermochromic behavior and phase transition of new octanuclear polyiodobismuth(III)ate

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ABSTRACT

A new isomer of octanuclear polyiodobismuth(III)ate, $(Bu_4N)_4[Bi_8I_{28}]$ (**1**) was obtained and characterized. The compound is characterized by a thermal anomaly at 237 K which can be related to thermochromism. The nature of the anomaly was investigated by a combination of X-ray diffractometry at different temperatures, differential scanning calorimetry and the Bader's topological analysis of the electron density and interpreted as a phase transition. The role of intramolecular I…I contacts in the phase transition is discussed.

1. Introduction

Polynuclear iodide complexes of bismuth (polyiodobismuth(III)ates, or PIBs) represent a very attractive field of inorganic chemistry [1], demonstrating a high variety of structural types (mono- to octanuclear discrete anions, different coordination polymers, etc. [2–11]. The interest in this area is caused by both applied and fundamental aspects: for example, these compounds are considered as composition-tunable precursors for BiOI-based photocatalytic materials which are being extensively studied over the last years [12–17]. Besides, these compounds often display promising optical properties [18]; very recently, thermochromic properties of hybrid phases based on trinuclear $\{Bi_3I_{11}\}$ clusters and 1,10-phenanthroline complexes of d-elements were reported [19]. This emergent feature seems to be especially interesting, as thermochromism belongs to fundamentally and practically important properties studied over many years in terms of different branches of chemistry [20].

Only very recently zur Loye and co-workers reported pioneering studies of thermochromic behavior of six di- and trinuclear PIB complexes; in all cases the counterions were of general formula $[M(LL)_3]^{n+}$ or $[M(LLL)_2]^{n+}$ (M = transition metal, LL and LLL are bi- and tridentate ligands, respectively) [19]. To explain the nature of the thermochromism, X-ray structure determination at different temperatures was undertaken. Based on the analysis of thermoinduced changes in the molecular structure, authors conclude: “changes in Bi–I or Bi…Bi distances are more likely to be major contributors to the observed thermochromism. It is possible that future electronic structure calculations may help explain these experimental observations”.

Herein, we present the synthesis of a new octanuclear polyiodobismuth(III)ate complex which displays thermochromism, $(Bu_4N)_4[\beta\text{-}Bi_8I_{28}]$. To understand the nature of this effect, a complex of complementary techniques has been used: (1) to monitor structural changes, variation temperature (VT) X-ray structure determinations were undertaken; (2) thermodynamic parameters have been evaluated by DSC; (3) using QTAIM Bi–I and I…I contacts within $[Bi_8I_{28}]^{4-}$ were analyzed in the temperature region close to the thermochromic changes.

2. Experimental

All reagents were obtained from commercial sources and used as purchased. Acetone and toluene were additionally purified by standard procedures. Elemental analysis was performed on Euro NA 3000 Elemental Analyzer (EuroVector). IR spectra were recorded on Scimitar FTS 2000 and Bruker Vertex 80 spectrometers.

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2.1. Synthesis of $(Bu_4N)_4[\beta\text{-}Bi_8I_{28}]$ (**1**)

0.25 g (0.42 mmol) of BiI_3 was placed into a flask together with 25 ml of dry acetone. 78 mg (0.21 mmol) of Bu_4NI was added under vigorous stirring to produce a deep-orange solution. After 40–50 min, the whole amount of BiI_3 dissolved. Then 26 mg (0.21 mmol) of benzoic acid was added, followed by 20 ml of toluene; the mixture was left overnight in an open test-tube. As acetone evaporates, dark rectangular cherry-red crystals of **1** grow. Yield 74%. IR (cm^{-1}): 2956 s, 2926 s, 2868 s, 1703 w, 1603 w, 1462 s, 1377 s, 1346 m, 1279 w, 1163 m, 1062 m, 1027 m, 924 m, 880 m, 795 m, 734 m, 153 s, 144 s, 132 s, 123 s, 111 s. *Anal.* Calc. (%): C, 12.41; H, 2.34; N, 0.90. Found: C, 12.37; H, 2.39; N, 0.95%.

2.2. X-ray diffractometry

Crystallographic data and refinement details are given in Table 1. The diffraction data were collected on a Bruker Apex Duo diffractometer (at 150 and 200 K) with Mo Kα radiation ($\lambda = 0.71073$ Å) by doing φ and ω scans of narrow (0.5°) frames. Structure of **1** was solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELXTL programs set [21]. Absorption corrections were applied empirically with SADABS program [22]. All non-hydrogen atoms of main structural units were refined anisotropically. The hydrogen atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. The high difference peak of 2.07 e in the structure of **1** at 200 K is an artifact arising from truncation of Fourier series which is typical for the structures with a large number of heavy atoms. Attempts to minimize the crystal size in this particular case lead to loss of the data completeness. X-ray diffraction experiment at 298 K was done on a Bruker X8Apex CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) by doing φ and ω scans of narrow (0.5°) frames. $a = 12.1828(4)$ Å, $b = 16.2495(7)$ Å, $c = 19.1417(9)$ Å, $\alpha = 77.958(1)°$, $\beta = 81.831(1)°$, $\gamma = 71.475(1)°$, $V = 3502.2(4)$ Å^3, $Z = 1$, space group $P\bar{1}$. No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections: 26030, 15294, 7275.

Table 1
Crystal data and structure refinement for **1**.

Chemical formula	$C_{64}H_{144}Bi_8I_{28}N_4$	$C_{64}H_{144}Bi_8I_{28}N_4$
M_r	6194.87	6194.87
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
Temperature (K)	150	200
a, b, c (Å)	11.8383(4), 15.8924(6), 19.3270(8)	11.9138(4), 15.9755(6), 19.2465(8)
α, β, γ (°)	77.680(1), 81.999(1), 73.208(1)	78.056(1), 82.228(1), 73.093(1)
V (Å^3)	3389.2(2)	3417.9(2)
Z	1	1
Radiation type	Mo Kα	Mo Kα
μ (mm^{-1})	16.75	16.75
Diffractometer	Bruker Apex DUO	Bruker Apex DUO
T_{min}, T_{max}	0.260, 0.554	0.165, 0.436
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	29842, 15511, 11344	29039, 15656, 9446
R_{int}	0.024	0.028
θ values (°)	$\theta_{max} = 27.6$, $\theta_{min} = 1.6$	$\theta_{max} = 27.6$, $\theta_{min} = 1.8$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.062, 1.00	0.046, 0.125, 1.02
No. of reflections, parameters, restraints	15511, 469, 0	15656, 469, 6
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.37, −1.23	2.07, −2.30

2.3. Differential scanning calorimetry

In order to study the thermodynamic properties differential scanning calorimeter NETZSCH DSC 204 F1 Phoenix was used. DSC measurements were performed by heat flow measurement method at heating rates of 9, 12, 15, 18 K/min in open aluminum crucibles in 25 ml/min rate Ar or He flux. The baseline signal obtained by heating two empty crucibles was subtracted from the experimental results. The sensitivity calibration of the sample carrier sensors and temperature scale graduation included melting peak area measurement of six standard samples from calibration set 6.239.2–91.3 supplied by Netzsch. To increase the accuracy DSC peak area ΔH and transition temperature T values were determined by summing up the results of five experiments and averaging using Netzsch Proteus Analysis software.

3. Theoretical calculations

To study interatomic interactions in $[\beta\text{-}Bi_8I_{28}]^{4-}$, topological method of quantum chemistry QTAIM (quantum theory of atoms in molecules) has been used [23]. The structure of a many-electron system is completely determined by the set of critical points of electron density $\rho(r, R)$ (r and R are the coordinates of electrons and nuclei), hereinafter ρ, at which the electron density gradient $\nabla\rho$ is zero. Only four types of the critical points are possible: *ncp* is the local maximum that corresponds to the positions of nuclei; *bcp* is the saddle bonding critical point; *rcp* is the saddle ring critical point; and *ccp* is cage critical point or the local minimum of ρ. The types of interatomic interactions (covalence, ionicity, etc.) are determined by the following properties calculated in the critical points: electron density ρ; the Laplacian of the electron density $\nabla^2\rho$; the densities G and U of kinetic and potential energies, respectively; the total energy $E = U + G$, and the ratio E/ρ. The Laplacian of electron density $\nabla^2\rho$ is a measure of local charge concentration and, consequently, covalency of interatomic bonding for $\nabla^2\rho < 0$ in the corresponding *bcp* point but for transition metals the Laplacian can also be positive [24,25]. The ratio E/ρ, which gives full local energy per one electron, is another important property to classify the type of bonding. Larger $|E/\rho|$ values indicate more covalency, E being negative. The calculation of G, U, and the total energy E were carried out according to [26].

Calculations of ρ for $[\beta\text{-}Bi_8I_{28}]^{4-}$ with C_i symmetry were carried out on the basis of spin-restricted ZORA method with all relativistic effects (spin–orbit coupling and scalar effects) [27] implemented in the code ADF2012 [28]. We used the local density approximation within the Vosko–Wilk–Nusair parametrization for local exchange correlations (LDA) [29] and generalized gradient approximation (GGA) functional BP86 [30,31]. The standard Slater-type orbital basis sets with triple-ξ quality plus one polarization function were employed for all atoms (TZP) [32]. The full geometry optimizations of the ground states were performed with the quasi-Newtonian method [33]. Vibrational spectra calculated for optimized structure of anion $[\beta\text{-}Bi_8I_{28}]^{4-}$ contain no imaginary frequencies (See Supplementary, Fig. S1). In addition, we investigated the electron density of $[Bi_8I_{28}]^{4-}$ with the structure as found by X-ray diffractometry at $T = 150$, 200 and 298 K.

4. Results

4.1. Synthesis, structure and spectroscopy of $(Bu_4N)_4[\beta\text{-}Bi_8I_{28}]$

As several another PIBs [3,9], $(TBA)_4[\beta\text{-}Bi_8I_{28}]$ was synthesized by reaction of BiI_3 and Bu_4NI (2:1 molar ratio) in acetone. Surprisingly we found that the yield of this compound appreciably increases when benzoic acid is added to the reaction mixture