



# A Water Sensitive Hydrate: The Bis-Catena Complex Salt $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \times 2\text{H}_2\text{O}$

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**A Water Sensitive Hydrate: The Bis-Catena Complex Salt  
[Mn(H<sub>2</sub>O)<sub>6</sub>][BiI<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O**

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## ARTICLE

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A Water Sensitive Hydrate: The Bis-Catena Complex Salt  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$ 

Manuela Erbe, Daniel Köhler, and Michael Ruck\*

**Keywords:** Bismuth; Coordination polymer; Hydrogen bonds; Kinetic control; Manganese

Bright red crystals of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$  are obtained from a solution of  $\text{MnI}_2$ ,  $\text{BiI}_3$ , and  $\text{I}_2$  in absolute ethanol, which is exposed to humid air. Reversible dehydration sets in at about 50 °C. Added water decomposes the hydrate by irreversible precipitation of  $\text{BiOI}$ . The optical band gap is about 1.9(1) eV. X-ray diffraction

on a single-crystal revealed a monoclinic lattice (space group  $P2_1/c$ ) with  $a = 760.39(4)$  pm,  $b = 1315.6(1)$  pm,  $c = 1398.37(7)$  pm, and  $\beta = 97.438(4)^\circ$ . In the crystal structure zigzag chains of edge-sharing  $[\text{BiI}_{2/1}\text{I}_{4/2}]^-$  octahedra and linear strings of  $\text{H}_2\text{O}$ -bridged  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  octahedra run parallel [100].

## Introduction

For the successful synthesis of various inorganic solids control of the partial pressure of at least one of their constituents is necessary [1]. Less often the pathway is essential for the formation (and the decomposition) of a compound. Here we report on the perplexing case of a hydrate that crystallizes only in a water-free solvent and decomposes in water irreversibly, though reversibly in dry atmosphere.

## Experimental Section

**Synthesis:** The starting materials were handled in dry Ar atmosphere. 500 mg of a 2:3:1 mixture of water-free  $\text{MnI}_2$  (Sigma Aldrich, 99.99 %; highly hygroscopic),  $\text{BiI}_3$  (Sigma Aldrich, 99 %, sublimated three times), and  $\text{I}_2$  (Merck, two times sublimated over  $\text{BaO}_2$ ) were solved in 20 ml absolute ethanol (Berkel, 99.9 %, treated with Na and distilled) by stirring at room temperature for several hours. The dark red solution was transferred into a Petri dish open to air. The next day, bright red crystals of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$  had formed in high yield.

**Spectroscopy:** The analysis by energy dispersive X-ray spectroscopy using a scanning electron microscope (CamScan CS 44) revealed the ratio of the heavier elements Mn : Bi : I = 10 : 17 : 73 (calc. 9.1 : 18.2 : 72.7). The UV/Vis spectrum between 200 and 900 nm was recorded at room temperature on a Varian Cary 4000.

**Thermal Analysis:** 4.17 mg of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$  in an  $\text{Al}_2\text{O}_3$  crucible were heated to 370 °C (rate 2 K/min) inside a thermobalance (Netzsch STA 409 PC Luxx). The atmosphere was a stream (100 ml/min) of Ar (99.999 %; purified with Oxisorb, Messer). The gas-phase was analyzed using a mass spectrometer up to 210 °C with a heated capillary inlet system (Netzsch QMS 403 C Aeolos).

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**X-ray crystallography:** Intensity data of a single-crystal were collected at 293(2) K on an imaging plate diffraction system IPDS-II (Stoe) using graphite-monochromated  $\text{Mo-K}\alpha$  radiation. The raw data were corrected for background, polarization and Lorentz factor. The microscopic description of the crystal shape, which was later used in the numerical absorption corrections ( $\mu(\text{MoK}\alpha) = 22.0 \text{ mm}^{-1}$ ) [2], was optimized using sets of reflections that are equivalent in the monoclinic Laue class  $2/m$  [3]. The structure was solved with direct methods [4] and subsequent difference Fourier syntheses in the space group  $P2_1/c$  (no. 14). The hydrogen atoms could not be localized. Anisotropic displacement parameters were refined for all atoms. Positional and displacement parameters are listed in Table 1, selected interatomic distances in Table 2. Data in brief: 9528 reflections measured, 2919 unique;  $-9 \leq h \leq 9$ ,  $-16 \leq k \leq 16$ ,  $-17 \leq l \leq 17$ ,  $2\theta_{\text{max}} = 53.6^\circ$ ;  $R_{\text{int}} = 0.056$ ,  $R_\sigma = 0.047$ ,  $R_1 = 0.030$  for 2190  $F_o > 4\sigma(F_o)$ ,  $R_1 = 0.048$  for all  $F_o$ ,  $wR_2 = 0.041$ ; residual electron density 1.3 to  $-1.0 \text{ e}/(10^6 \text{ pm}^3)$ . The experimental powder diffractogram, which was measured with a Stadi-P powder diffractometer (Stoe) using  $\text{Cu-K}\alpha_1$  radiation, nicely matches the calculated pattern. Further data, in the form of a CIF, have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (E-mail address: crysdata@fiz-karlsruhe.de), as supplementary material no. CSD-421459, and can be obtained by contacting the FIZ quoting the article details and the CSD number. Graphics were generated with the program Diamond [5].

Table 1. Wyckoff positions, coordinates and equivalent isotropic displacement parameters of the atoms in  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$  at 293(2) K.  $U_{\text{eq}}$  (in  $\text{pm}^2$ ) is defined as one third of the trace of the orthogonalized tensor  $U_{ij}$ .

Atom	W.p.	x	y	z	$U_{\text{eq}}$
Bi	4e	0.26787(3)	0.48346(2)	0.08697(2)	471.5(9)
I1	4e	0.06066(6)	0.38003(4)	-0.10200(4)	568(1)
I2	4e	0.59435(6)	0.35611(4)	0.06691(4)	627(2)
I3	4e	0.13326(6)	0.32043(4)	0.20038(4)	631(2)
I4	4e	0.45036(7)	0.59863(5)	0.25345(4)	735(2)
Mn	2a	0	0	0	630(5)
O1	4e	0.0988(9)	-0.0122(6)	0.1534(5)	1120(30)
O2	4e	0.2044(8)	-0.1039(6)	-0.0302(5)	1090(20)
O3	4e	0.1920(9)	0.1238(5)	-0.0025(5)	1090(20)
O4	4e	0.4948(9)	0.1437(6)	-0.1003(5)	1230(30)

Table 2. Selected interatomic distances (in pm) for  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$ . Symmetry operators: (i):  $x, y, z$ ; (ii):  $-x, 1-y, -z$ ; (iii):  $1-x, 1-y, -z$ ; (iv):  $-x, -y, -z$ ; (v):  $1-x, -y, -z$ .

Bi–I <sup>ii</sup>	310.58(5)	Mn–O <sup>iiv</sup>	218.5(6)
I <sup>i</sup>	319.97(6)	O <sup>iiiv</sup>	215.3(6)
I <sup>i</sup>	303.78(5)	O <sup>iiiv</sup>	219.1(6)
I <sup>iii</sup>	328.12(6)		
I <sup>3i</sup>	292.97(6)	O4...O <sup>v</sup>	278(1)
I <sup>4i</sup>	296.73(6)	O3	284(1)

## Results and Discussion

Bright-red transparent crystals of the complex salt *catena*-hexaquaamanganese(II)-*catena*-bis(tetraiodido-bismuthate(III))-dihydrate,  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$ , can be crystallized from a dark red solution of  $\text{MnI}_2$ ,  $\text{BiI}_3$ , and  $\text{I}_2$  in absolute ethanol, which is exposed to humid air. The use of ethanol that contains significant traces of water results in the immediate precipitation of  $\text{BiOI}$ . The same happens when the crystals get in contact with liquid water.

No other aqua-complex of a transition metal with a halogenidobismuthate anion has been reported so far. With antimony, however, compounds like  $\text{Mn}(\text{SbF}_4)_2 \cdot 2\text{H}_2\text{O}$  [6],  $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2][\text{SbCl}_6] \cdot 4\text{H}_2\text{O}$  [7], or  $\text{Ni}(\text{H}_2\text{O})_6(\text{SbF}_4)_2$  [8] exist.

In the monoclinic crystal structure (space group  $P2_1/c$ ;  $a = 760.39(4)$  pm,  $b = 1315.6(1)$  pm,  $c = 1398.37(7)$  pm,  $\beta = 97.438(4)^\circ$ ,  $V = 1387.1(2) \cdot 10^6$  pm<sup>3</sup>,  $Z = 2$ ) zigzag chains of edge-sharing  $[\text{BiI}_{2/1}\text{I}_{4/2}]^-$  octahedra and linear strings of  $\text{H}_2\text{O}$ -bridged  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  octahedra run parallel to the  $a$  axis (Figure 1). Tetraiodidobismuthate(III) chains have been found previously, e.g. in  $(\text{BEDT-TTF})\text{BiI}_4$  [9],  $\text{Bi}_{13}\text{Pt}_3\text{I}_7$  [10], or  $\text{L-cystineH}_2(\text{BiI}_4)_2$  [11]. Consistent with literature, the Bi–I distances range from 292.97(6) pm in the case of a terminal ligand to 328.12(6) pm for a bridging ligand.

The  $\text{Mn}^{2+}$  cation, on an inversion center, is coordinated octahedrally by six water molecules in an average distance of 218 pm. In the picrate  $[\text{Mn}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$  the mean  $\text{Mn}^{\text{II}}\text{--O}$  distance is 215 pm [12]. Oxidation of  $\text{Mn}^{\text{II}}$  to  $\text{Mn}^{\text{III}}$  can be excluded, since Mn–O distances in the  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  complex should be about 9 % shorter [13].

The two molecules of crystal water per formula unit link the hexaquaamanganese complexes to a one-dimensional supramolecular coordination polymer (Figure 2). Although the H atoms could not be localized by X-ray diffraction, the position of the O(4) atom, which represents the crystal water, allows some speculations about hydrogen bonds. The distance to the O atoms of the coordinating water are  $282 \pm 2$  pm, and thus in the typical range found in ice. The angle  $\angle(\text{O2--O4--O3}) = 108.4(4)^\circ$  suggests linear hydrogen bonds. Further hydrogen bonds could exist between the coordinating water molecules.

As interatomic distances  $d(\text{O} \cdots \text{I}) > 360$  pm indicate, the cationic and anionic chains are not linked by hydrogen bonds. On the other hand, in view of distances  $d(\text{Mn} \cdots \text{I}) > 500$  pm and the dielectric water shell around the  $\text{Mn}^{2+}$  cation

the electrostatic interaction between them should be rather weak. This may rationalize the sensitivity of the compound to hydrolysis as well as the ease with which water is lost. In a dynamic TG-MS heating experiment,  $\text{H}_2\text{O}$  was rapidly evolved above  $50^\circ\text{C}$  (Figure 3). At  $100^\circ\text{C}$ , about 9.5 % of the initial mass was lost, which corresponds to the total amount of water in the compound (8.8 wt.-%). Even the ambient conditions of a warm and dry summer day initiate the decay. However, no  $\text{BiOI}$  is formed and by solving the decomposition product in absolute ethanol the hydrate can be recrystallized.

Since the  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  complex is known to be almost colorless, the intense red color can be attributed to the *catena*-anion  $[\text{BiI}_4]^-$ . The UV/Vis spectrum shows an absorption edge that starts at about 780 nm and reaches its maximum at about 600 nm (Figure 4). The onset point, determined by the intersection of tangents to the flat and the steep part of the edge, lies at 700 nm, the inflection point at 610 nm. This corresponds to an optical band gap of 1.8 eV or 2.0 eV, respectively.

## Conclusions

Kinetic effects seem to be the key to the understanding of the very special boundary conditions during the crystallization of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$  and its very different behavior towards gaseous and liquid water. Apparently, the ligand exchange at  $\text{Mn}^{2+}$  is fast in solution and leads into a local energetic minimum (kinetic control), while the hydrolysis of iodidobismuthate complexes is considerably slower but results in a thermodynamically very stable product (global minimum). Thus, the concentration of free water molecules must be kept low throughout the synthesis. The same holds for the dehydratization, where the water vapor has to be removed in order to prevent the formation of  $\text{BiOI}$ .

## Acknowledgement

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Figure 1. Crystal structure of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$ . Polyhedra emphasize the coordination of the cations. Ellipsoids represent 50 % probability.

Figure 2. Zigzag chain of edge-sharing  $[\text{BiI}_{2/1}\text{I}_{4/2}]^-$  octahedra and linear string of  $\text{H}_2\text{O}$ -bridged  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  octahedra running parallel [100]. Hydrogen positions were not determined, but possible hydrogen bridges are indicated by dotted lines. Distances are given in pm.

Figure 3. Thermogravimetry of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$  and mass spectrum of  $\text{H}_2\text{O}^+$  in a flow of Ar.

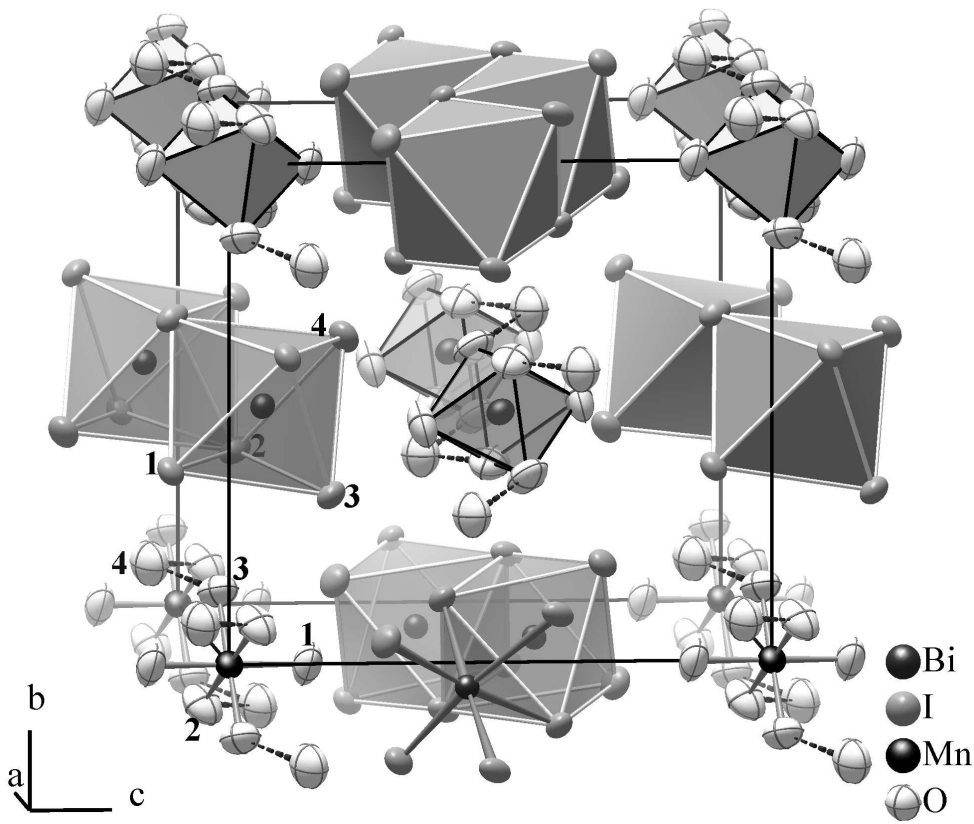
Figure 4. UV/Vis spectrum of  $[\text{Mn}(\text{H}_2\text{O})_6][\text{BiI}_4]_2 \cdot 2\text{H}_2\text{O}$ .

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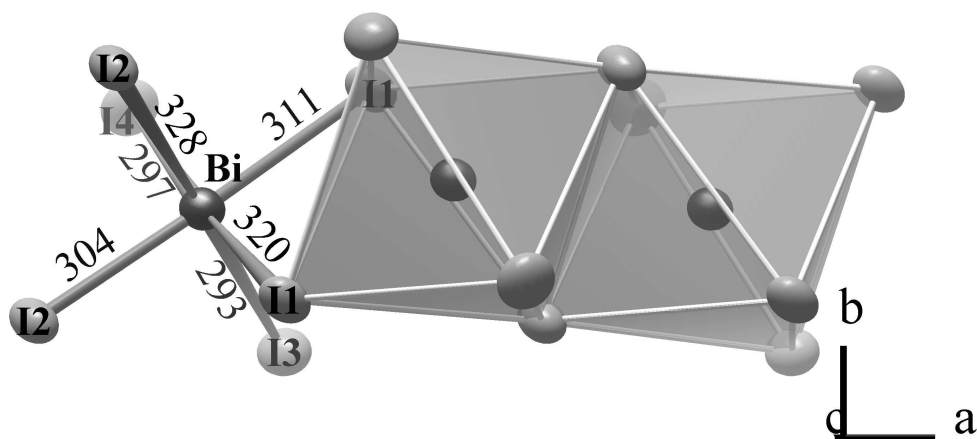
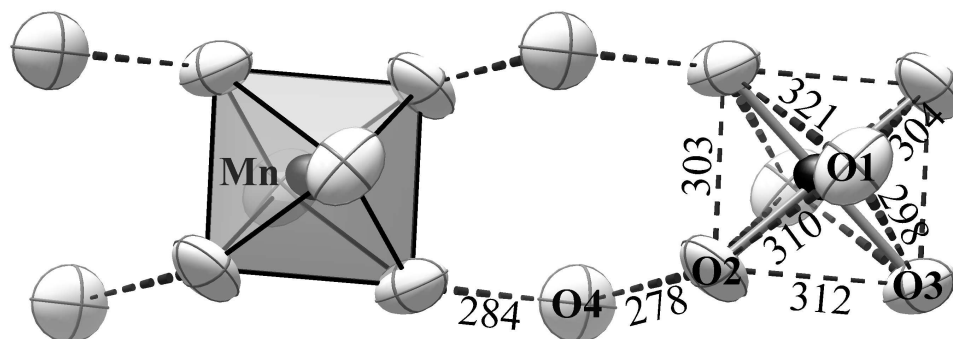
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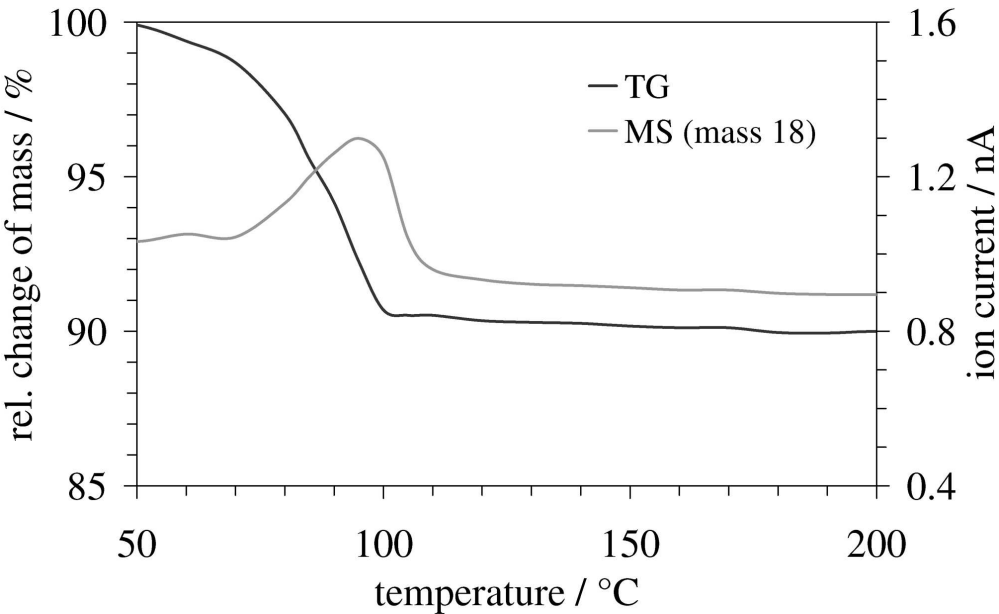


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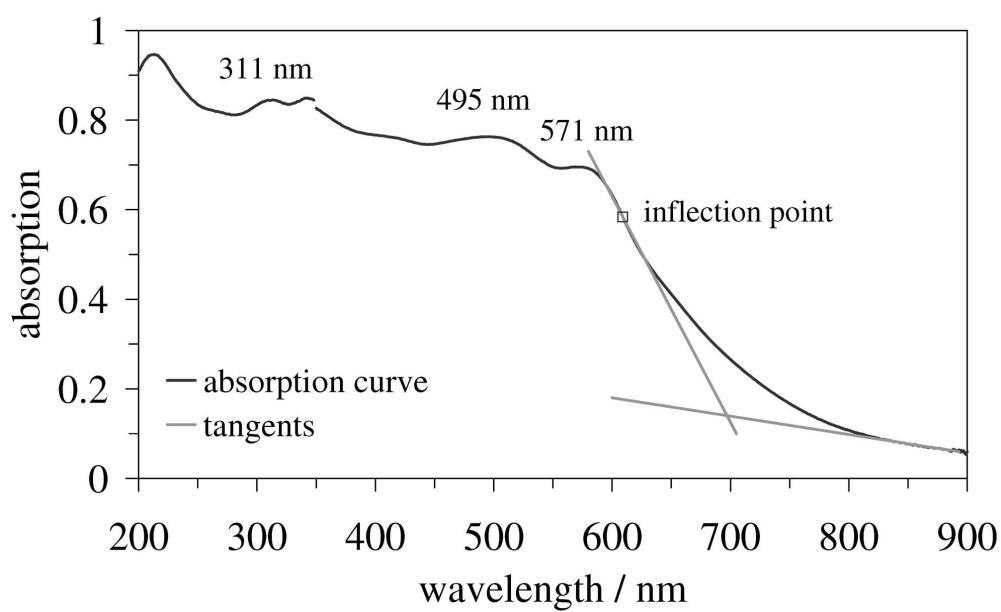


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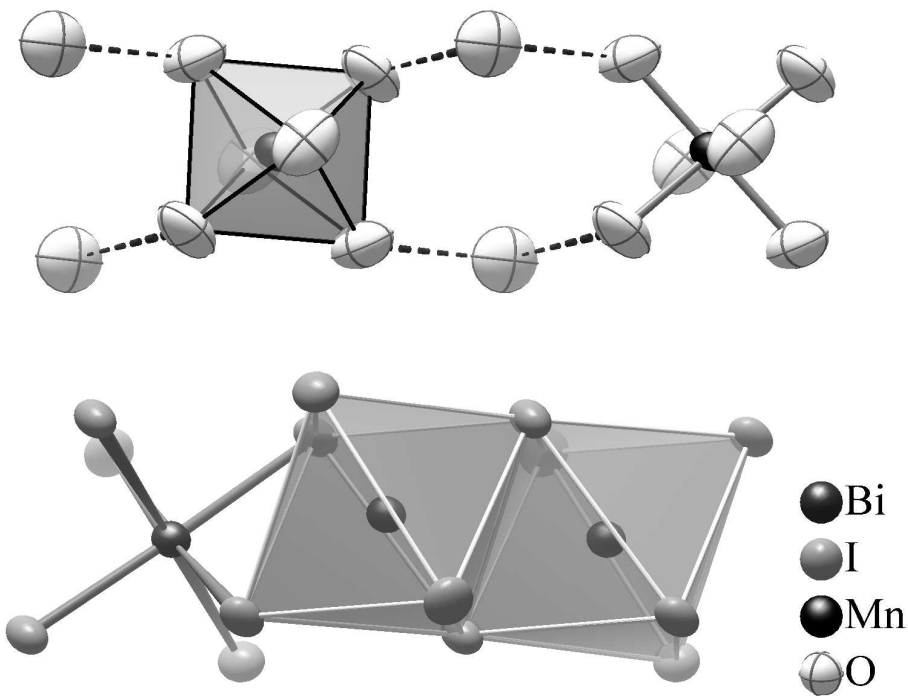




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