

A Methylviologen Lead(II) Iodide: Novel $[\text{PbI}_3^-]_\infty$ Chains with Mixed Octahedral and Trigonal Prismatic Coordination

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Construction of low-dimensional organic–inorganic supramolecular arrays with novel properties represents new directions in solid-state chemistry.^{1,2} Due to limitations presented by differences in synthesis conditions, self-assembly of molecular and ionic components offers a viable route for preparing designed crystalline hybrid compounds.³ More importantly, self-assembly techniques which take advantage of weak intermolecular interactions to create more complex crystal structures preserve the unique characteristics of the individual components. Our current research is focused on the synthesis of low-dimensional crystalline organic–inorganic metal iodides with the possibility of incorporating unique properties associated with functional inorganic and organic moieties. The organic moieties may exhibit unique molecular properties such as hyperpolarizability, photochromicity, and polymerizability. Other examples of novel organic systems include viologens that exhibit novel redox and electrochromic properties. Our aim is to establish important structure–property relationships and to understand important organic–inorganic intermolecular interactions related to the self-assembly of crystalline hybrid materials.

Lead(II) iodide and its low-dimensional compounds are of particular interest due to their significant excitonic, third-order nonlinear optical, ferroelectric, and ferroelastic properties.^{4–6} Although there is significant interest in the physical properties of low-dimensional lead(II) iodide compounds, relevant information regarding their structure–bonding–property relationships is still lacking. Aside from the layered perovskites, other low-dimensional lead(II) iodide complexes include chains of face-sharing ideal PbI_6 octahedra and chains of corner-sharing PbI_6 octahedra.^{7,8} New lead(II) iodides which feature different chain structures of

PbI_6 octahedra have also been reported, some of which may be described as chain derivatives of the layered PbI_2 structure.^{9,10} A Pb(II) iodide complex that features an unusual $[\text{Pb}_{18}\text{I}_{44}]^{8-}$ anion cluster has also been reported.¹¹ In complex low-dimensional Pb(II) iodides, the nature of the organic cation significantly affects the overall organic–inorganic heterostructure and, to a lesser extent, the lead(II) iodide inorganic substructure. However, except for deviations from ideal symmetry, due to packing effects and stereochemical activity of the Pb ($6s^2$) lone pairs, it is generally observed that the organic counterions have no direct effect on the common octahedral $\text{Pb}^{\text{II}}\text{I}_6$ inorganic building block. In this communication, we describe the synthesis and crystal structure of $(\text{C}_{12}\text{H}_{14}\text{N}_2)\text{Pb}_2\text{I}_6$ wherein noncovalent interactions between organic and inorganic moieties significantly alter the normal coordination around Pb(II) from octahedral to an unexpected trigonal prismatic.

The title compound $(\text{C}_{12}\text{H}_{14}\text{N}_2)\text{Pb}_2\text{I}_6$ (**1**) was prepared by reacting PbI_2 and 1,1'-dimethyl-4,4'-bipyridinium dichloride hydrate, $(\text{MV}^{2+})\text{Cl}_2 \cdot x\text{H}_2\text{O}$, in solution. Separate 5 mL acetone solutions of the inorganic halides, lead(II) iodide (0.1 mmol) and NaI (0.15 mmol), and the organic methylviologen dichloride hydrate (0.12 mmol) were prepared. The addition of NaI increases the solubility of PbI_2 in polar organic solvents. The two solutions were mixed at room temperature, and the resulting red precipitate was subsequently filtered, dried, and redissolved in DMSO. The resulting solution was heated to 150 °C and slowly cooled to room temperature at a rate of 12.5 °/h. Formation of red prismatic crystals was observed after two weeks. The red air stable crystals were found to be of compound **1** and incongruently melt at 356 °C. As a general precaution, all reactions were carried out under nitrogen atmosphere and all solvents were degassed before use. The infrared spectrum of **1** recorded in KBr, in the range 400–4000 cm^{-1} , contains the characteristic IR bands (C–N and C–H) associated with the MV^{2+} cation. Measurement of the UV absorption spectra of a spin-coated thin film of **1**, in the range of 300–800 nm at 30 °C, shows a sharp absorption maxima at 370 nm.

Compound **1** crystallizes in the rhombohedral space group $R\bar{3}$.¹² The unit cell consists of six PbI_3^- units (part of a polymeric face-shared octahedral/trigonal-prismatic chain) and three MV^{2+} . The rhombohedral crystal structure, as shown in Figure 1, contains chains of face-shared PbI_6 octahedra (*O*) and trigonal prisms (*TP*) linked along the rhombohedral $\langle 111 \rangle$ axis in the manner [*O-O-TP-O-TP-O*] as the repeat unit. The MV^{2+} ions lie between the closed-packed arrangement of $[\text{PbI}_3^-]_\infty$ chains adjacent to the *T* sections, with their molecular planes parallel with the lateral faces

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(12) Single-crystal X-ray analysis, using a Siemens SMART (CCD) diffractometer, was carried out on a crystal with dimensions of $0.2 \times 0.18 \times 0.12$ mm mounted in a stream of dry nitrogen gas at -50 °C. Monochromatized Mo $K\alpha$ radiation was used to collect a hemisphere of data. Corrections on *I* for instrument and crystal stability were $<1\%$. The data were integrated and intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variations in the path lengths. Empirical absorption correction was applied and reflections were averaged. The final cell constants were refined by using 8192 reflections having $I > 10\sigma(I)$. These are $a = b = c = 12.3729$ –(4) Å, $\alpha = \beta = \gamma = 79.96(1)^\circ$, $V = 1816.20(1)$ Å³. Other relevant crystallographic data are $\text{FW} = 1362.03$; $Z = 3$; $\rho = 3.736$ g/cm^{−3}; $\mu = 21.534$ mm^{−1}; $\lambda = 0.71073$ Å; $2\theta_{\text{max}} = 46.62^\circ$; total data collected, 20695; reflections observed, 1597 ($I > 4\sigma_F$); total variables, 118; final *R* indices, $[I > 4\sigma(I)]$, $R1 = 0.0371$, $wR2 = 0.0951$; [all data], $R1 = 0.0426$, $wR2 = 0.0988$. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The thermal parameters of all non-hydrogen atoms were well-behaved and treated anisotropically. Hydrogen atoms were treated with a riding model ($d\text{C–H} = 0.96$ Å, $U_{\text{iso}} = 0.050$). All calculations were made with use of the Siemens SHELXTL package.

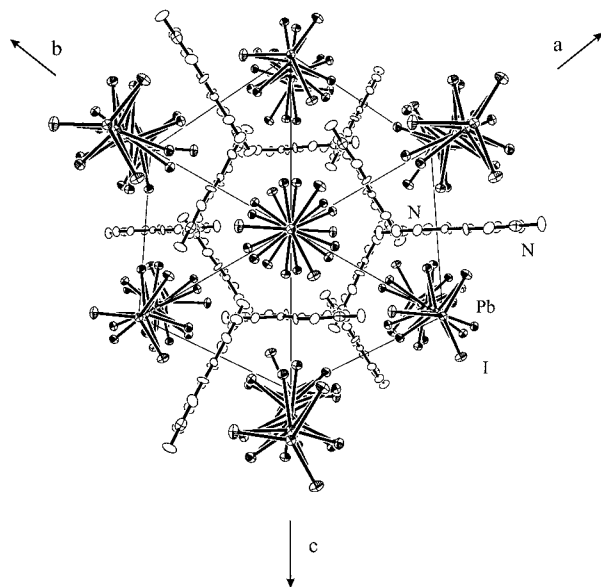


Figure 1. ORTEP representation of the unit cell of the crystal structure of **1** viewed along the rhombohedral $\langle 111 \rangle$ axis. Non-carbon atoms are represented as crosshatched ellipsoids. Hydrogen atoms are omitted and ellipsoids are drawn at 50% probability.

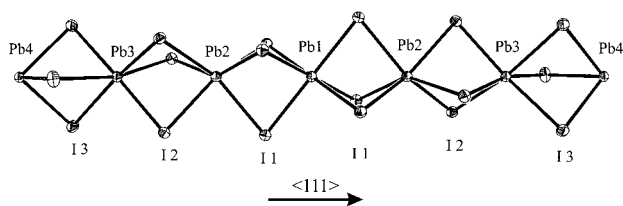


Figure 2. ORTEP representation of the repeating unit of the $[\text{PbI}_3]_\infty$ chain. Ellipsoids are drawn at 50% probability.

of the trigonal prisms, forming a “honeycomblike” arrangement around each chain.

The mixed *octahedral-trigonal prismatic* Pb(II) iodide chain is shown in Figure 2. There are three coordination types involving PbI_6 units in **1**: Pb(1) and Pb(4) have nearly ideal octahedral symmetry; Pb(3) has a distorted octahedral coordination that represents a transition between octahedral and trigonal prismatic geometry; and Pb(2) exhibits trigonal prismatic coordination.

The equidistant Pb–I distances around Pb(1) and Pb(4) are 3.214(1) and 3.249(1) Å, respectively, and the I–Pb–I angles around Pb(1) and Pb(4) are essentially 90° and 180°. The Pb–I distances around Pb(3) are 3.173(1) Å (3×) and 3.346(1) Å (3×). The corresponding I–Pb–I bond angles around Pb(3) deviate from ideal values (82.5°, 89.5°, and 166.65°) and represent an angular transition between octahedral and trigonal prismatic. The Pb–I distances within the *TP* geometry around Pb(2) are 3.238(1) (3×) and 3.263(1) Å (3×). A slight bond length inequality may be attributed to the displacement of Pb(2) atoms toward the

shared trigonal face with Pb(1). However, the angular deviation from ideal trigonal prismatic symmetry around Pb(2) is less than 3° and the trigonal (–3) symmetry is preserved. Hence, the coordination around Pb(2) is essentially trigonal prismatic. The observed trigonal prismatic geometry around Pb(2) in the $[\text{PbI}_3]_\infty$ chains is unique in lead(II) halides. Lead(II) halides with severely distorted $\text{Pb}^{\text{II}}\text{X}_6$ octahedra have been reported for chlorides and bromides. However, these chlorides and bromides exhibit asymmetric (6 + 1) geometries and low-symmetry crystal structures which strongly indicate a stereochemically active lone pair.¹³ In **1**, the rhombohedral symmetry of the inorganic chains and the regular 3-fold arrangement of MV^{2+} ions around the *TP* sites indicate that all Pb(II) lone pairs are stereochemically inactive.

The remarkable mixed *O-TP* inorganic chains in **1** are reminiscent of the metal oxide chains observed in novel transition metal oxides that crystallize in the Sr_4PtO_6 , $\text{Ba}_5\text{Ru}_2\text{O}_{10}$, and related structure types.¹⁴ However, the manner in which face-shared octahedra and trigonal prisms are arranged in **1** is unprecedented. Furthermore, in similar metal oxide chains different metal atoms or mixed-valent metal atoms occupy the *O* and *TP* sites in an ordered manner. The $[\text{PbI}_3]_\infty$ chains in **1** feature a unique case of having Pb(II) in both *O* and *TP* sites.

Close inspection of the organic–inorganic heterostructure reveals important characteristics. The molecular axes of the nearest neighbor viologens lie along the three diagonal planes of the lateral faces of the trigonal prisms. The *TP* sections of neighboring $[\text{PbI}_3]_\infty$ chains also act as “cavities” wherein organic cations lie sandwiched between two adjacent chains. The unexpected arrangement maximizes the number of nearest neighbor iodides (CN = 10) around MV^{2+} but increases the interligand repulsion between iodines. The tendency to maximize the number of nearest neighboring iodines around MV^{2+} also provides a rationale for the observed distorted octahedral coordination of Pb(3). The cooperative organic–inorganic structure suggests that strong noncovalent interactions exist between the trigonal prismatic sections of the very polarizable inorganic chain and the redox-active MV^{2+} cations. Careful comparison of the IR/Raman spectra of **1** with that of methylviologen dichloride hydrate and methylviologen gold(I) iodide¹⁵ show downshifts (8–15 cm^{-1}) of the C–N and C–H stretching frequencies in **1** which may indicate possible charge-transfer interactions between methylviologen and the inorganic $[\text{PbI}_3]_\infty$ chain. Complete vibrational, electronic, and theoretical studies are in progress to elucidate the electronic structure and the nature of the organic–inorganic interactions in this novel compound.

The synthesis of **1** demonstrates the unusual structural chemistry exhibited by low-dimensional polarizable organic–inorganic compounds that may provide materials with unique electronic properties. The complex heterostructure also affirms the importance of cooperative noncovalent bonding between organic and inorganic components, and the presence of unusual noncovalent interactions in viologen-based hybrid materials.

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Supporting Information Available: Complete list of crystallographic data, atomic parameters, and relevant bond distances and angles for $(\text{C}_{12}\text{H}_{14}\text{N}_2)\text{Pb}_2\text{I}_6$ (PDF). See any current masthead page for Web access instructions.

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