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Further Evidence for the Tetraoxoiodate(V) Anion, IO_4^{3-}: Hydrothermal Syntheses and Structures of $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ and $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$

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The hydrothermal reaction of MoO_3 with BaH_3IO_6 at 180 °C for 3 days results in the formation of $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**). Under similar conditions, the reaction of $Ba(OH)_2\cdot 8H_2O$ with MoO_3 and $Ba(IO_4)_2\cdot 6H_2O$ yields $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**). The structure of **1**, determined by single-crystal X-ray diffraction, consists of corner- and edge-sharing distorted MoO_6 octahedra that create two-dimensional slabs. Contained within this molybdenum oxide framework are approximately C_{2v} tetraoxoiodate(V) anions, IO_4^{3-}, that are involved in bonding with five Mo(VI) centers. The two equatorial oxygen atoms of the IO_4^{3-} anion chelate a single Mo(VI) center, whereas the axial atoms are μ_3-oxo groups and complete the octahedra of four MoO_6 units. The coordination of the tetraoxoiodate(V) anion to these five highly electropositive centers is probably responsible for stabilizing the substantial anionic charge of this anion. The Ba^{2+} cations separate the layers from one another and form long ionic contacts with neighboring oxygen atoms and a water molecule. Compound **2** also contains distorted MoO_6 octahedra. However, these solely edge-share with octahedral hexaoxoiodate(VII), IO_6^{5-}, anions to form zigzagging one-dimensional, $^1_\infty[(MoO_2)(IO_6)]^{3-}$, chains that are polar. These chains are separated from one another by Ba^{2+} cations that are coordinated by additional water molecules. Bond valence sums for the iodine atoms in **1** and **2** are 5.01 and 7.03, respectively. Crystallographic data: **1**, monoclinic, space group $C2/c$, $a = 13.584(1)$ Å, $b = 7.3977(7)$ Å, $c = 20.736(2)$ Å, $\beta = 108.244(2)°$, $Z = 4$; **2**, orthorhombic, space group $Fdd2$, $a = 13.356(7)$ Å, $b = 45.54(2)$ Å, $c = 4.867(3)$ Å, $Z = 8$.

Introduction

Oxoanions of penta- and heptavalent halogens are limited to trigonal pyramidal halate, XO_3^{1-}, and tetrahedral perhalate, XO_4^{1-}, anions with chlorine and bromine. However, the increased size of iodine allows for higher coordination numbers, and up to six oxo groups can be contained within its inner sphere. Therefore, both the solution and solid-state chemistry of iodine oxides and oxoanions of iodine are quite rich and unparalleled by the lighter halogens. For example, the octahedral hexaoxoiodate(VII) anion, IO_6^{5-}, actually exists in solution as a complex series of protonated species, e.g., $H_2IO_6^{3-}$, with the tetrahedral tetraoxoiodate(VII) iodate anion, IO_4^{1-}, predominating in aqueous media at 25 °C.[1−13] In the solid state, five-coordinate I(VII) is also known in K_3IO_5, which contains the square pyramidal pentaoxoiodate(VII) anion, IO_5^{3-}.[14] We have recently reported the observation of a new oxoanion of iodine, namely, tetraoxoiodate(V), IO_4^{3-}, in $Ag_4(UO_2)_4(IO_3)_2(IO_4)_2O_2$.[15] The tetraoxoiodate(V) anion has a stereochemically active lone pair of electrons, and density functional theory (DFT) calculations demonstrate

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that its approximately C_{2v} geometry can be ascribed to a symmetry-allowed mixing of the HOMO with a low-lying excited state (LUMO), which is termed a second-order Jahn–Teller distortion.[16–22]

Both the hexaoxoiodate(VII) and iodate anions have independent histories of yielding transition metal compounds with atypical structures and properties. For instance, hexaoxoiodate(VII) has the ability to stabilize unusually high oxidation states for transition metals, for example, Ni(IV), Cu(III), and Ag(III) in $KNiIO_6$,[23,24] $Na_3K[H_3Cu(IO_6)_2]\cdot 14H_2O$,[25] and $K_5[Ag(IO_5OH)_2]\cdot 8H_2O$.[26] Alternatively, the pentavalent oxidation state of iodine in iodate provides a stereochemically active lone pair of electrons that leads to remarkable structures and properties. While it is highly unusual for iodate to bind transition metals through the iodine atoms, the lone pairs do show a tendency for aligning in the solid state to create polar structures. These polar compounds have found uses in the development of new nonlinear optical (NLO) materials.[27–34] For example, we have recently shown that the alkali metal molybdenyl iodates, $AMoO_3(IO_3)$ (A = Rb, Cs), crystallize in the polar space group $Pna2_1$ and are efficient materials for second-harmonic generation.[35] This property is also known for other anions with stereochemically active lone pairs of electrons, such as selenite and tellurite, and polar structures have been observed for $AVSeO_5$ (A = Rb, Cs),[36] $A(VO)_3(SeO_3)_2$ (A = NH_4, K, Rb, or Cs),[36,37] $A_2(MoO_3)_3SeO_3$ (A = NH_4, Rb, Cs, or Tl),[38] Te_2SeO_7,[39] and Bi_2TeO_5.[40]

Studies on the preparation of Mo(VI) iodate and hexaoxoiodate(VII) compounds have a long and rich history beginning in the 1890s with work by Blomstrand,[41] Chrétien,[42] and Liebknecht.[43] It is difficult to ascertain the nature of the compounds that they prepared based on these works, because they predate most spectroscopic methods and X-ray diffraction techniques and were, therefore, largely based on detailed elemental analyses. Modern studies have shown that Anderson-type heteropolyanions, which consist of six octahedral metals arranged hexagonally around a central octahedral heteroatom, can be prepared from Mo(VI) and hexaoxoiodate(VII) as observed in $K_5[Mo_6(IO_6)O_{18}]$.[44] The smaller heteropolyanion, $[Mo_2(IO_6)O_4]^{6-}$, has also been structural characterized.[45]

There are two key questions that remain unanswered in our previous work with the tetraoxoiodate(V) anion. First, does IO_4^{3-} have an existence independent of $Ag_4(UO_2)_4(IO_3)_2(IO_4)_2O_2$?[15] Second, what is responsible for stabilizing the substantial negative charge on this anion? In the present study, we report the hydrothermal preparation of two new Mo(VI) compounds containing oxoanions of iodine, $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**) and $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**). The former compound provides definitive evidence of the tetraoxoiodate(V) anion independent of U(VI) chemistry.

Experimental Section

Syntheses. MoO_3 (99.95%, Alfa-Aesar), H_5IO_6 (98%, Alfa-Aesar), $Ba(OH)_2\cdot 8H_2O$ (99.7%, Fisher), and $BaCO_3$ (ACS grade, Fisher) were used as received. BaH_3IO_6 and $Ba(IO_4)_2\cdot 6H_2O$ were prepared by literature methods from the aqueous reaction of $BaCO_3$ with H_5IO_6 in a 1:1 or 1:2 ratio, respectively.[46] Distilled and Millipore filtered water with a resistance of 18.2 MΩ was used in all reactions. Reactions were run in Parr 4749 23-mL autoclaves with PTFE liners for 3 days at 180 °C and cooled at a rate of 9 °C/h to 23 °C. The reactions reported produced the highest yields of the desired compounds. SEM/EDX analyses were performed using a JEOL 840/Link Isis instrument. Ba and Mo percentages were calibrated against standards. Typical results are within 4% of actual ratios. IR spectra were collected on a Nicolet 5PC FT-IR spectrometer from KBr pellets.

$Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (1). MoO_3 (86 mg, 0.599 mmol) and BaH_3IO_6 (135 mg, 0.371 mmol) were loaded in a 23-mL PTFE-lined autoclave. Water (1 mL) was then added to the solids. The product consisted of a colorless solution over clusters of colorless prisms of **1** embedded in a white pellet of unreacted MoO_3. The mother liquor was decanted from the crystals, which were then

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washed with water and methanol and allowed to dry. Yield after manual separation of **1** from unreacted MoO_3, 137 mg (35% yield based on Mo). EDX analysis for $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ provided a Ba/Mo/I ratio of 1:6:2. IR (KBr, cm^{-1}): $\nu(H_2O, Mo{=}O, Mo{-}O, \text{and } I{-}O)$ 1246 (w, br), 984 (m), 975 (m), 931 (s), 917 (s), 891 (s), 828 (s, br), 807 (s, sh), 762 (m), 732 (m), 702 (s, br), 668 (w), 649 (w, br).

$Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (2). MoO_3 (109 mg, 0.754 mmol), $Ba(IO_4)_2\cdot 6H_2O$ (392 mg, 0.624 mmol), and 1 mL of a 2.5 M $Ba(OH)_2\cdot 8H_2O$ suspension were loaded in a 23-mL PTFE-lined autoclave. The product consisted of a colorless solution over small, colorless needles of **2** embedded in a pellet of MoO_3. The mother liquor was decanted from the crystals, which were then washed with water and methanol and allowed to dry. Yield after manual separation of **2** from unreacted MoO_3, 82 mg (25% yield based on Mo). EDX analysis for $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ provided a Ba/Mo/I ratio of 3:2:2. IR (KBr, cm^{-1}): $\nu(H_2O, Mo{=}O, Mo{-}O, \text{and } I{-}O)$ 1277 (w, br), 1121 (m, br), 930 (s), 918 (w), 898 (s), 887 (s), 881 (s), 804 (m, br), 777 (s), 772 (s), 735 (s), 701 (s), 694 (s, sh), 668 (w), 636 (w, br), 615 (s).

Crystallographic Studies. Crystals of $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**) were often intergrown and have an approximately prismatic habit. The crystal of **1** chosen for this study had dimensions of 0.104 × 0.074 × 0.036 mm. Crystals of $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**) take the form of small prismatic needles, and a crystal with dimensions of 0.200 × 0.010 × 0.010 mm was selected for X-ray diffraction experiments. Crystals of **1** and **2** were mounted on glass fibers and aligned on a Bruker SMART APEX CCD X-ray diffractometer. Intensity measurements were performed using graphite monochromated Mo Kα radiation from a sealed tube with a monocapillary collimator. SMART was used for preliminary determination of the cell constants and data collection control. For all compounds, the intensities of reflections of a sphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal, and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 30 s for **1** and 60 s for **2**.

For **1** and **2**, determination of integral intensities and global cell refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. A semiempirical absorption correction was applied on the basis of the intensities of symmetry-related reflections measured at different angular settings using SADABS.[47] The ratios of minimum to maximum transmission factors for the crystals of **1** and **2** were 0.516751 and 0.605633, respectively. The program suite SHELXTL (v 5.1) was used for space group determination (XPREP), structure solution (XS), and refinement (XL).[48] Hydrogen atom positions were not located from difference maps and were not included in the final refinement. The final refinements included anisotropic displacement parameters for all atoms except hydrogen and a secondary extinction parameter.

Table 1. Crystallographic Data for $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**) and $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**)

	$Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$	$Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$
fw (amu)	1368.79	1149.73
color, habit	colorless prism	colorless needle
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c* (No. 15)	*Fdd*2 (No. 43)
a (Å)	13.584(1)	13.356(7)
b (Å)	7.3977(7)	45.54(2)
c (Å)	20.736(2)	4.867(3)
α (deg)	90	90
β (deg)	108.244(2)	90
γ (deg)	90	90
V (Å^3)	1979.0(3)	2961(3)
Z	4	8
T (°C)	−80	−80
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	4.591	5.141
μ(Mo Kα) (cm^{-1})	88.78	137.79
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0426	0.0367
$R_w(F_o^2)$ [b]	0.1206	0.0758

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4]^{1/2}$.

Is it not immediately obvious from the structure of **2** why it should crystallize in the polar space group *Fdd*2. Therefore, missed symmetry was tested for using both the ADDSYMM and NEWSYMM programs of PLATON.[49] No missing symmetry was suggested. Furthermore, examination of the structure factors shows that the extinction of the *hk*0 reflections is fully consistent with *mm2* symmetry and not *mmm*. Some crystallographic details are listed in Table 1 for **1** and **2**; additional details can be found in the Supporting Information.

Secord-Order NLO Measurements. Powder SHG measurements on ungraded polycrystalline $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**) were performed on a modified Kurtz-NLO system using a 1064 nm light source.[50] No index matching fluid was used in the measurements. A detailed description of the apparatus has been published.[39]

Results and Discussion

Syntheses. The reactions of MoO_3 with $Ba(IO_4)_2\cdot 6H_2O$ and $Ba(OH)_2\cdot 8H_2O$ or with BaH_3IO_6 have been explored through the use of compositional space diagrams[51−54] under mild hydrothermal conditions (180 °C). We have also investigated the effects of temperature, reaction duration, pH, and water content on product composition and yield. While the syntheses of both $Ba(IO_4)_2\cdot 6H_2O$ and BaH_3IO_6 have been reported from the reaction of $BaCO_3$ with H_5IO_6,[46] we have found that the white precipitates formed in these reactions are in fact product mixtures on the basis of powder XRD experiments. Furthermore, spectroscopic evidence indicates that solids with a nominal composition of $Ba(IO_4)_2\cdot 6H_2O$ actually contain protonated forms of the hexaoxoiodate(VII) anion, IO_6^{5-}.[46] We have found that the reaction of $BaCO_3$ with H_5IO_6 in a 1:1 ratio at 180 °C for 3 days yields BaH_3IO_6 with trace amounts of $Ba(IO_3)_2\cdot H_2O$.

While we anticipated that the exploration of the reactions of MoO_3 with "$Ba(IO_4)_2\cdot 6H_2O$" and BaH_3IO_6 would yield numerous products because of the variable nature of the starting materials, we instead found that product analysis was

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straightforward because only a few compounds were present. However, the preparations of **1** and **2** are impeded by either the formation of molybdenum oxide byproducts or incomplete reactions. For example, when MoO_3 is reacted with BaH_3IO_6, $Ba[(MoO_2)_6(IO_4)_2O_4]{\cdot}H_2O$ (**1**) forms, but a considerable amount of MoO_3[55] is left unreacted. The synthesis reported in the Experimental Section produced the highest yield of **1**.

When molybdenum trioxide is reacted with $Ba(IO_4)_2{\cdot}6H_2O$ and $Ba(OH)_2{\cdot}8H_2O$, $Ba_3[(MoO_2)_2(IO_6)_2]{\cdot}2H_2O$ (**2**) is isolated as small colorless needles. However, in many regions of compositional space, only $BaMo_4O_{13}{\cdot}2H_2O$[56] and unreacted MoO_3 are isolated. The production of **2** has proven to be highly sensitive to reaction duration, pH, and reaction composition. In some cases, multiple reactions had to be run under identical conditions to ensure its formation. Similar observations have been made in the preparation of $BaMo_2O_5(SeO_3)_2$ and $BaMoO_3SeO_3$, where $BaMo_4O_{13}{\cdot}2H_2O$ was also obtained in many regions of compositional space.[52] In both the syntheses of **1** and **2**, we found that there was no obvious correlation between reaction stoichiometry and product composition. These complications are probably caused by the reduction of IO_6^{5-} to IO_3^{1-} by water, which has occurred in most other reactions we have performed using I(VII) starting materials.[15,57−59] Therefore, we were actually surprised to have isolated a hexaoxoiodate(VII) compound from hydrothermal conditions, even in low yield.

Structures. $Ba[(MoO_2)_6(IO_4)_2O_4]{\cdot}H_2O$ (1). The structure of $Ba[(MoO_2)_6(IO_4)_2O_4]{\cdot}H_2O$ consists of two-dimensional ${}^{2}_{\infty}[(MoO_2)_3(IO_4)O_2]^{1-}$ slabs separated by Ba^{2+} cations and water molecules as shown in Figure 1. The slabs are constructed from corner- and edge-sharing distorted MoO_6 octahedra and approximately C_{2v}, tetraoxoiodate(V) anions. The molybdenum oxide framework can be constructed from edge-sharing $[Mo_2O_{10}]$ dimers that corner-share along (001) to form infinite columns. These columns are joined together by corner-sharing with additional MoO_6 units that are turned perpendicular to the columns. Part of a layer from **1** is shown in Figure 2. This creates slabs in the *ab* plane that have parallel channels running through them along the *b*-axis. These channels are filled by IO_4^{3-} anions that bind five Mo(VI) centers, as shown in Figure 3. The tetraoxoiodate(V) anions utilize their equatorial oxo groups to chelate one Mo(VI) ion. The remaining axial oxo groups are μ_3 atoms and bind four additional Mo atoms. Ba^{2+} cations that separate these slabs are 9-coordinate and reside in distorted tricapped trigonal prismatic environments.

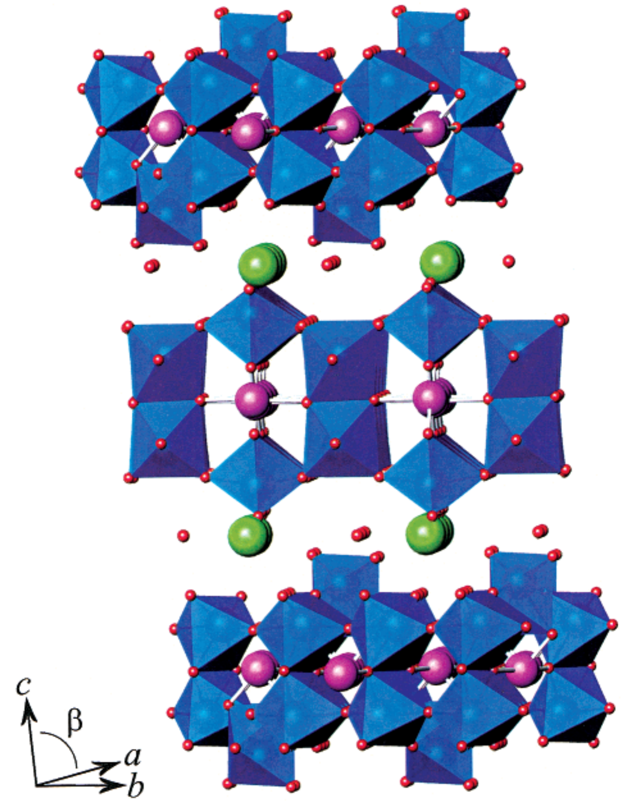

Figure 1. Part of the structure of $Ba[(MoO_2)_6(IO_4)_2O_4]{\cdot}H_2O$ (**1**) showing two-dimensional ${}^{2}_{\infty}[(MoO_2)_3(IO_4)O_2]^{1-}$ slabs separated by Ba^{2+} cations and water molecules. Ba = green, MoO_6 octahedra = blue, I = purple, O = red.

There are three crystallographically unique Mo atoms in **1**, all of which are contained within orthorhombically distorted MoO_6 octahedra. These distortions can be attributed to a second-order Jahn−Teller effect that is symmetry allowed for these d^0 metal centers.[60−62] Many other compounds containing Mo(VI) show this type of distortion, including $AMoO_3(IO_3)$ (A = K, Rb, Cs)[35] and $A_2(MoO_3)_3SeO_3$ (A = NH_4, Rb, Cs, or Tl).[38] The Mo−O bonds within each octahedra also show a commonly observed 2 + 2 + 2 bonding pattern with two long, two intermediate, and two short bonds.[63−66] The two shortest bonds, which range from 1.695(6) to 1.733(6) Å, are assigned to the molybdenyl, *cis*-MoO_2^{2+}, units. The intermediate bonds that occur from 1.841(6) to 2.026(6) Å are those involved in forming Mo−O−Mo chains. Many of the longest bonds of 2.167(6) to 2.312(6) Å are formed with the tetraoxoiodate(V) anion. These bond distances are listed in Table 2.

The geometry around I(1) in tetraoxoiodate(V) comes close to approximating an idealized C_{2v} (H−M *mm2*) geometry, although it is not crystallographically constrained in this manner. There are two long axial bond distances of 2.054-

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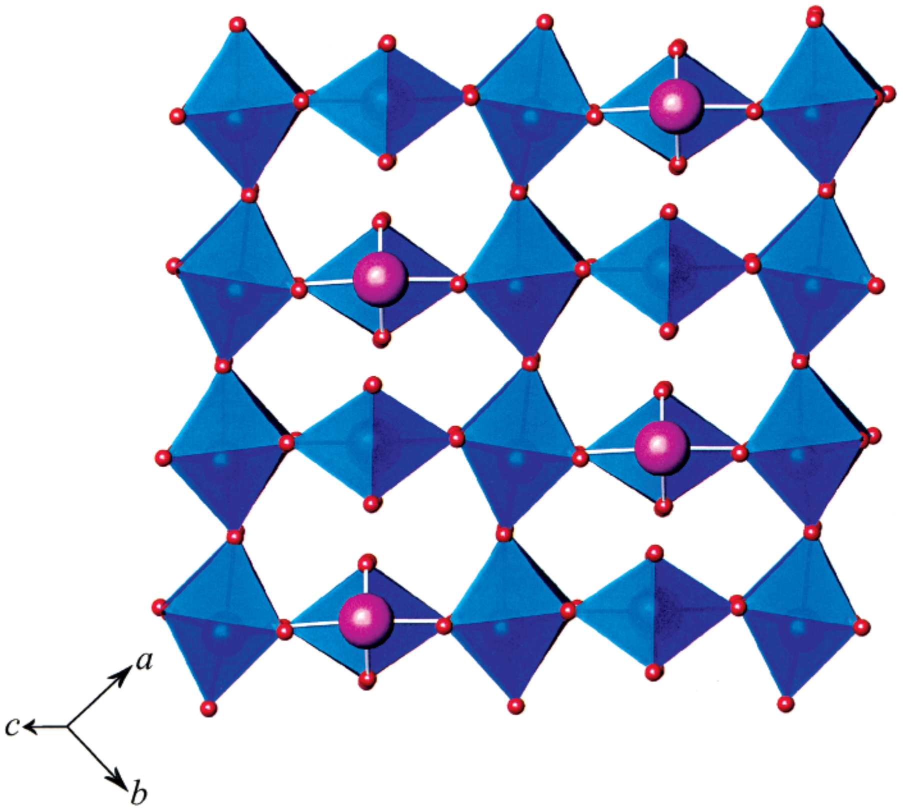

Figure 2. View down the *c*-axis showing part of a $^{2}_{\infty}[(MoO_2)_3(IO_4)O_2]^{1-}$ slab present in $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**). MoO_6 octahedra = blue, I = purple, O = red.

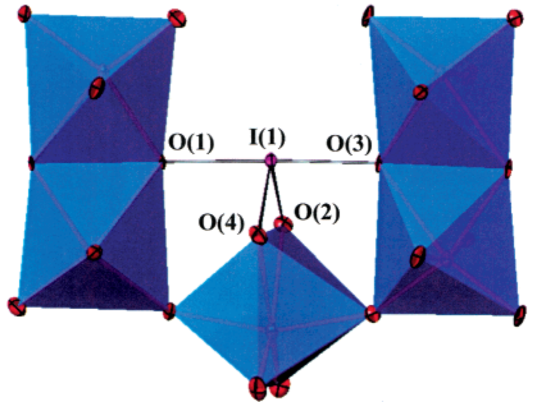

Figure 3. Local environment of the tetraoxoiodate(V) anions, IO_4^{3-}, present in $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**). 50% thermal ellipsoids are depicted. MoO_6 octahedra = blue, I = purple, O = red.

(6) and 2.030(6) Å, and two short equatorial distances of 1.818(6) and 1.828(6) Å. There are also two long I···O contacts of 2.711(6) and 2.948(6) Å that actually place I(1) within a distorted octahedral site. Iodate also commonly forms long interactions with neighboring oxygen atoms to create pseudo-octahedral environments.[67a] This is exemplified by $VO_2IO_3\cdot 2H_2O$, which has three short I−O bonds ranging from 1.799(3) to 1.856(3) Å and three long I···O interactions of 2.641(3), 2.696(3), and 2.690(4) Å.[67b] However, because the sum of covalent radii of iodine and oxygen is 2.06 Å,[68] these interactions must be weak. The bond distances for tetraoxoiodate(V) in **1** compare well with those observed in $Ag_4(UO_2)_4(IO_3)_2(IO_4)_2O_2$, which showed average long and short distances of 1.98(2) and 1.84(2) Å.[15] These distances are also in reasonable agreement with those calculated from DFT methods that showed bond lengths of 2.059 and 1.935 Å. It is important to note that these calculations do not include the effects of the highly electron withdrawing metal centers in these compounds or crystal forces.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**)

Mo(1)−O(1)	2.167(6)	Mo(2)−O(11)	1.921(6)
Mo(1)−O(1)′	2.011(6)	Mo(3)−O(3)	2.226(6)
Mo(1)−O(5)	2.203(6)	Mo(3)−O(3)′	2.026(6)
Mo(1)−O(6)	1.841(6)	Mo(3)−O(5)	1.733(6)
Mo(1)−O(7)	1.720(6)	Mo(3)−O(8)′	2.167(6)
Mo(1)−O(8)	1.721(6)	Mo(3)−O(11)	1.861(6)
Mo(2)−O(2)	2.274(6)	Mo(3)−O(12)	1.710(6)
Mo(2)−O(4)	2.312(6)	I(1)−O(1)	2.054(6)
Mo(2)−O(6)	1.963(6)	I(1)−O(2)	1.828(6)
Mo(2)−O(9)	1.695(6)	I(1)−O(3)	2.030(6)
Mo(2)−O(10)	1.706(6)	I(1)−O(4)	1.818(6)

Bond Angles (deg) for Tetraoxoiodate(V), IO_4^{3-}

O(1)−I(1)−O(2)	86.9(3)	O(2)−I(1)−O(3)	88.9(3)
O(1)−I(1)−O(3)	175.7(2)	O(2)−I(1)−O(4)	90.0(3)
O(1)−I(1)−O(4)	90.5(3)	O(3)−I(1)−O(4)	90.4(3)

In **1**, the alteration of the geometry around I(1) that results from the oxo groups coordinating five Mo(VI) centers is notable. First, the O(1)−I(1)−O(3) and O(2)−I(1)−O(4) bond angles are 175.7(2)° and 90.0(3)°, respectively. This

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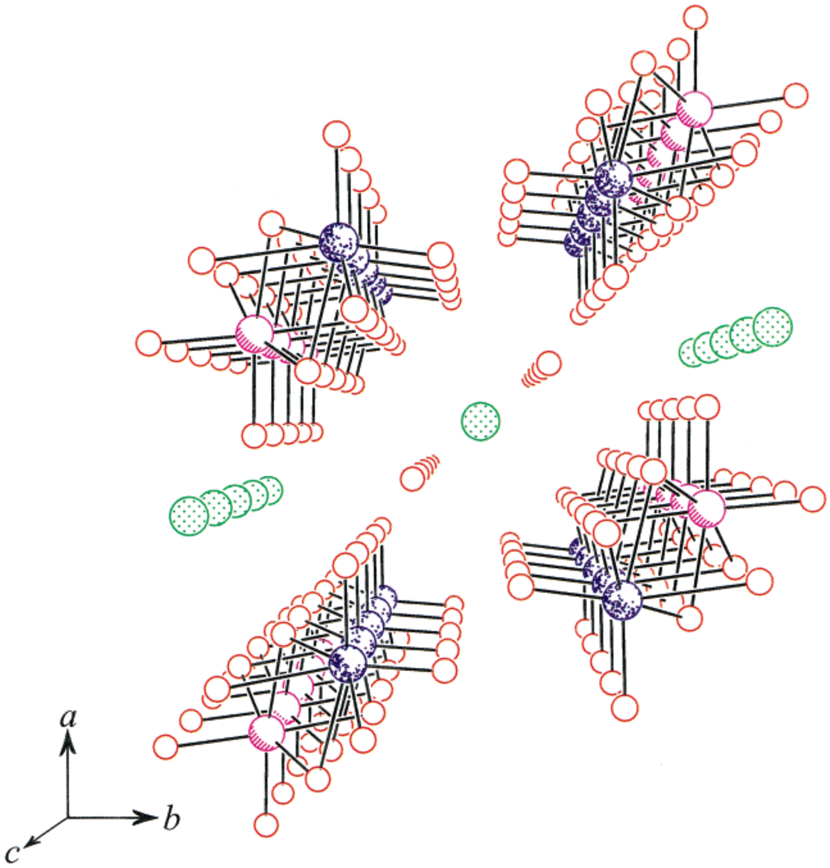

Figure 4. Part of the structure of $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**) showing one-dimensional $^{1}_{\infty}[(MoO_2)(IO_6)]^{3-}$ chains separated by Ba^{2+} cations and water molecules. Ba = green, Mo = blue, I = purple, O = red.

indicates that the stereochemically active lone pair is not compressing the O(1)−I(1)−O(3) bond angle as much as should be expected on the basis of DFT calculations that provide a value of 154.1(7)°.[15] However, the O(2)−I(1)−O(4) bond angle is more compressed than expected from these same calculations which give a value of 102.4(7)° for this angle. These observations are readily explained by the highly electron withdrawing nature of the five Mo(VI) centers that are ligated by the tetraoxoiodate(V) anion. The more linear nature of the O(1)−I(1)−O(3) angle is likely due to the removal of electron density from the iodine center by the five Mo(VI) atoms. The smaller than expected O(2)−I(1)−O(4) angle is probably the result of the involvement of these atoms in the chelation of a Mo center. On the basis of this and the data obtained from $Ag_4(UO_2)_4(IO_3)_2(IO_4)_2O_2$,[15] we proposed that the large anionic charge of this rather small anion is delocalized by the highly electropositive metals to which it binds. Therefore, it will probably be difficult to isolate IO_4^{3-} without the use of high-valent early transition metals, lanthanides, and actinides.

$Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (2). The structure of **2** is actually quite simple when compared to that of **1** and consists of one-dimensional $^{1}_{\infty}[(MoO_2)(IO_6)]^{3-}$ chains separated by Ba^{2+} cations and water molecules as shown in Figure 4. These chains are built from the edge-sharing of alternating MoO_6 and IO_6 octahedra and can be thought of as coordination polymers of molybdenyl, MoO_2^{2+}, with hexaoxoiodate(VII), IO_6^{5-}. The bond distances in **2** are typical for both Mo(VI) and I(VII). As in **1**, there is a 2 + 2 + 2 bonding pattern around Mo(1) with distances of 2.257(8), 2.277(8), 1.954(8), 1.928(8), 1.728(8), and 1.704(8) Å.[63−66] Again, an orthorhombic C_2 second-order Jahn−Teller distortion of the Mo center is observed. The hexaoxoiodate(VII) anion utilizes four of its oxo atoms to bind the molybdenyl moiety. This actually results in a geometry around I(1) which is substantially distorted from an idealized octahedron. The bond distances for I(1) range from 1.981(8) to 1.788(8) Å. The two shortest distances of 1.830(8) and 1.788(8) Å are to the terminal oxo atoms. Selected bond distances are given in Table 3.

An unusual feature of **2** is that it crystallizes in the polar space group *Fdd*2. Given the *mm*2 crystal class, **2** must have a polar *c*-axis. Examination of the crystal structure shows that this is the direction along which the one-dimensional $^{1}_{\infty}[(MoO_2)(IO_6)]^{3-}$ chains propagate, and that both the MoO_6 and IO_6 octahedra are distorted in the same direction along the chain, which is depicted in Figure 5. Therefore, the polarity of **2** can be directly attributed to the second-order Jahn−Teller distortion of the Mo(VI) centers that also leads to asymmetric bonding around the I(VII) centers. The fact that Ba^{2+} serves as the counterion for these chains also aids in obtaining a noncentrosymmetric structure because it also readily resides in highly distorted environments.[69] In this case, the two crystallographically unique Ba^{2+} cations reside

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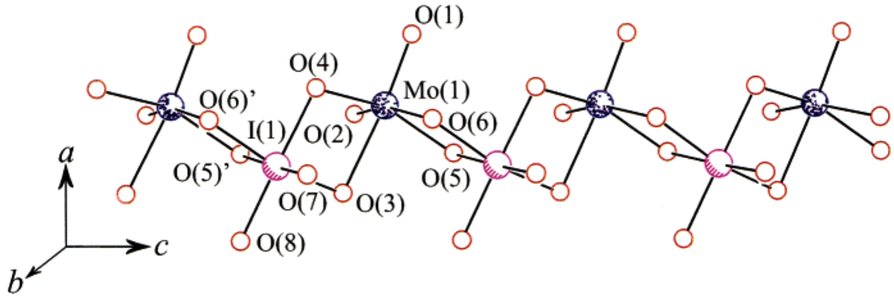

Figure 5. View of a polar, one-dimensional $^{1}_{\infty}[(MoO_2)(IO_6)]^{3-}$ chain, that propagates down the *c*-axis, in $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**). This view shows that both the MoO_6 and IO_6 octahedra are distorted in the same direction along the chain. Mo = blue, I = purple, O = red.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**)

Mo(1)−O(1)	1.728(8)	I(1)−O(3)	1.846(8)
Mo(1)−O(2)	1.704(8)	I(1)−O(4)	1.967(8)
Mo(1)−O(3)	2.257(8)	I(1)−O(5)′	1.981(8)
Mo(1)−O(4)	1.954(8)	I(1)−O(6)′	1.857(8)
Mo(1)−O(5)	1.928(8)	I(1)−O(7)	1.788(8)
Mo(1)−O(6)	2.277(8)	I(1)−O(8)	1.830(8)
O−Mo−O Bond Angles			
O(1)−Mo(1)−O(2)	103.8(4)	O(2)−Mo(1)−O(6)	165.1(3)
O(1)−Mo(1)−O(3)	165.1(3)	O(3)−Mo(1)−O(4)	72.1(3)
O(1)−Mo(1)−O(4)	95.7(4)	O(3)−Mo(1)−O(5)	83.9(3)
O(1)−Mo(1)−O(5)	103.7(4)	O(3)−Mo(1)−O(6)	81.2(3)
O(1)−Mo(1)−O(6)	88.7(4)	O(4)−Mo(1)−O(5)	147.4(3)
O(2)−Mo(1)−O(3)	87.6(4)	O(4)−Mo(1)−O(6)	81.7(3)
O(2)−Mo(1)−O(4)	103.3(4)	O(5)−Mo(1)−O(6)	72.9(3)
O(2)−Mo(1)−O(5)	97.2(4)		
O−I−O Bond Angles			
O(3)−I(1)−O(4)	81.4(3)	O(4)−I(1)−O(8)	172.2(3)
O(3)−I(1)−O(5)	86.8(3)	O(5)−I(1)−O(6)	81.7(3)
O(3)−I(1)−O(6)	163.3(4)	O(5)−I(1)−O(7)	176.3(4)
O(3)−I(1)−O(7)	96.8(4)	O(5)−I(1)−O(8)	87.7(3)
O(3)−I(1)−O(8)	93.5(4)	O(6)−I(1)−O(7)	94.5(4)
O(4)−I(1)−O(5)	86.0(3)	O(6)−I(1)−O(8)	98.2(4)
O(4)−I(1)−O(6)	85.6(4)	O(7)−I(1)−O(8)	93.1(4)
O(4)−I(1)−O(7)	93.5(4)		

in 10-coordinate environments. The polarity of **2** was confirmed by irradiating a sample with a 1064 nm laser; the compound revealed a distinct green light (532 nm) consistent with second-harmonic generation.

Bond Valence Sums. The bond valence sums[70,71] for the Mo and I atoms in **1** and **2** provide further verification that the formulas have been correctly assigned, and, more importantly, that **1** and **2** actually contain I(V) and I(VII), respectively. For compound **1**, the three crystallographically unique Mo centers have bond valence sums (BVSs) of 6.20, 6.02, and 6.07. Using BVS parameters for I(V), I(1) has a BVS of 5.01 for the four covalently bound oxygen atoms and 5.23 if the two long I···O contacts are included. The latter value is actually closer to that obtained for tetraoxoiodate(V) in $Ag_4(UO_2)_4(IO_3)_2(IO_4)_2O_2$, which lacks long I···O contacts.[15] Bond valence sums for **2** also clearly indicate hexavalent molybdenum with a value of 5.93. Furthermore, using BVS parameters for I(VII), the iodine center in **2** has a BVS of 7.03. Therefore, these straightforward calculations are strongly in support of our assignment of **1** and **2** containing penta- and heptavalent iodine, respectively.

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Supporting Information Available: X-ray crystallographic files for $Ba[(MoO_2)_6(IO_4)_2O_4]\cdot H_2O$ (**1**) and $Ba_3[(MoO_2)_2(IO_6)_2]\cdot 2H_2O$ (**2**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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