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Square-Planar Noble Metal Iodate $[M(IO_3)_4]^{n-}$ (M = Pd^{II}, Au^{III}; *n* = 2, 1) Anions and Their Ability to Form Polar and Centrosymmetric Architectures

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K^+ salts of the square-planar noble metal iodate $[M(IO_3)_4]^{n-}$ (M = Pd^{II}, Au^{III}; *n* = 2, 1) anions have been prepared under mild hydrothermal conditions, and the structures elucidated to demonstrate that while both are highly polar anions, polar and centrosymmetric extended architectures can form using these building units.

Introduction

Iodate compounds have been the subject of intense interest because of their propensity for adopting noncentrosymmetric structures that are often polar,[1–8] a feature that is aptly illustrated by $A[MoO_3(IO_3)]$ (A = Rb, Cs),[9] $A[(VO)_2(IO_3)_3O_2]$ (A = NH_4, Rb, Cs),[10] and $NaYI_4O_{12}$.[11] This structural attribute can be exploited in the development of new nonlinear optical, pyroelectric, piezoelectric, and ferroelectric materials, with the first property being the most heavily investigated. Structure–property relationships in early d-block and f-block iodates are becoming well-developed.[1–11] However, noble metal iodates are virtually unknown.[12]

Renewed interest in noble metal oxoanion compounds has led to the discovery of a plethora of remarkable solids including $AuSO_4$, which contains a Au^{II}–Au^{II} dimer,[13] and polar $Au_2(SeO_3)_2(SeO_4)$, which is constructed from square-planar Au^{III} and both selenite and selenate anions.[14] Despite repeated attempts over the past eight years, gold iodates have remained elusive for several reasons. First, common anions employed in gold reactions such as chloride and nitrate can interfere with the formation of these compounds. Second, iodate and periodate do not react appreciably with elemental gold, even under acidic compounds. Finally, as with many iodates, gold iodates are quite insoluble under normal conditions precluding simple crystallization techniques.

Results and Discussion

The solution to the synthesis of a gold iodate proved to be the use of a strongly oxidizing mixed-anion system. In this case the reaction of elemental gold with concentrated selenic acid and KIO_4 under mild hydrothermal conditions results in the formation of $K[Au(IO_3)_4]$. As is shown in Figure 1, single crystals of $K[Au(IO_3)_4]$ grow directly off of the surface of the gold metal and ultimately passivate the surface. We speculate that selenic acid dissolves small quantities of the gold metal to yield a halo of Au^{III} that rapidly reacts with iodate to yield $K[Au(IO_3)_4]$ crystals. The in situ generation of iodate by the reduction of periodate by water is a critical feature of this reaction, because it allows for the slow introduction of the key reactant that controls solubility.[9,10,15]

Figure 1. A photograph showing yellow crystals of $K[Au(IO_3)_4]$ that have grown directly on the surface of elemental gold under hydrothermal conditions. Crystals typically have maximum dimensions of several millimeters.

The structure of $K[Au(IO_3)_4]$ is quite unusual in that it crystallizes in the lowest symmetry space group *P*1. The origin of the asymmetry becomes obvious by viewing the $[Au(IO_3)_4]^{1-}$ anion shown in Figure 2, and the packing of these anions in Figure 3. The $[Au(IO_3)_4]^{1-}$ anions contain square-planar Au^{III} bound by four monodentate iodate

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anions. As can be viewed in Figure 2, all of the iodate anions in the $[Au(IO_3)_4]^{1-}$ anions are aligned on one side of the AuO_4 square plane. Hence, these anions are highly polar, and pack in the lattice with identical orientation yielding a polar structure consistent with the space group. The Au–O bond lengths range from 1.981(9) Å to 1.987(9) Å, and are normal.[16] We have surveyed 28 high-resolution iodate crystal structures to arrive at a value of 1.792(5) Å for terminal I–O bonds. The terminal I–O bonds in the $[Au(IO_3)_4]^{1-}$ anions are normal in this respect. In contrast, I–O bond lengths for bridging or μ_2-O bonds from 32 different structures, show an average distance 1.831(5) Å. The bridging I–O bond lengths strain the normal limits and average 1.882(9) Å. The bridging I–O bond lengths are of a length expected for protonated moieties, suggesting polarization in the Au–O–I bonds. There are several other Au^{III} compounds with monodentate oxoanions that share features in common with the bonding found in $K[Au(IO_3)_4]$; these compounds include $K[Au(NO_3)_4]$,[17] $(H_5O_2)[Au(NO_3)_4]\cdot H_2O$,[18] and $(ClO_2)[Au(ClO_4)_4]$.[19] In all three examples significant lengthening of the bridging E–O (E = N, Cl) bonds is observed.

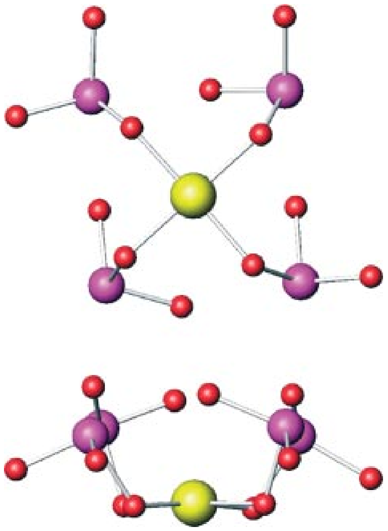

Figure 2. Two views of the $[Au(IO_3)_4]^{1-}$ anion in the structure of $K[Au(IO_3)_4]$. Gold is shown in yellow, iodine in magenta, and oxygen in red.

Short contacts on the order of 2.5 to 2.8 Å between the oxygen atom from one iodate anion and the iodine atom of a neighboring iodate play a critical role in the structures of iodate compounds and minerals.[20] The importance of iodate···iodate interactions in the structure of $K[Au(IO_3)_4]$ can not be underestimated. We have previously shown that these interactions can lead to alignment of the lone pair of electrons on the iodate anions in $Na_2[UO_2(IO_3)_4(H_2O)]$.[21] This also occurs in the structure of $K[Au(IO_3)_4]$ where there are numerous intermolecular iodate···iodate interactions. These interactions stitch what appears to be a molecular structure into a complex polar network.

The IR vibrational spectrum of $K[Au(IO_3)_4]$ shows four weak bands at 519, 514, 503 and 499 cm^{-1} that are attributed to vibrations within the $[AuO_4]$ unit.[22,23] Iodate stretching vibrations (ν_1 and ν_3) are found at 822, 803, 778, 765, 741, and 664 cm^{-1}.[24–26] The Raman spectrum shows a broad peak centered at 508 cm^{-1} that coincides well with the IR features. In addition, there is a broad envelope for the various iodate modes with discernible vibrational modes at 860, 821, 773, and 741 cm^{-1}.

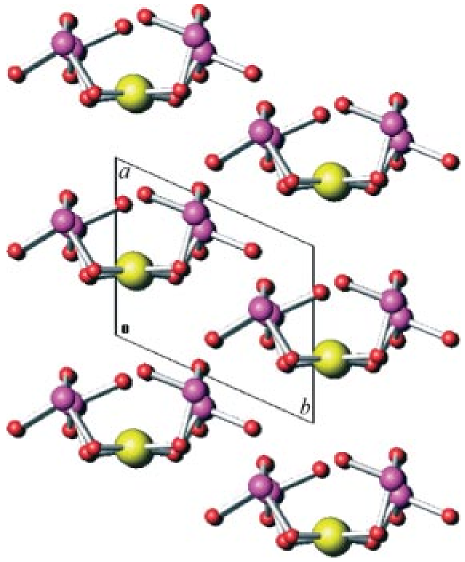

Figure 3. A view down the *c* axis of the structure of $KAu(IO_3)_4$ showing the polar stacking of the $[Au(IO_3)_4]^{1-}$ anions. K^+ cations have been omitted for clarity. Gold is shown in yellow, iodine in magenta, and oxygen in red.

The thermal behavior of $K[Au(IO_3)_4]$ was addressed using differential scanning calorimetry (DSC), and shows that it is stable to 375 °C. Two sharp endotherms are then observed at 387 and 518 °C, which are ascribed to the decomposition of $K[Au(IO_3)_4]$ to elemental gold and thermal disproportionation of iodate, respectively. The first endotherm is immediately followed by an exothermic event, again consistent with the formation of elemental gold, which can be visually observed in the sample containers at the end of the thermal analysis.

In contrast to the difficulties in synthesizing $K[Au(IO_3)_4]$, the synthesis of its Pd^{II} analog, $K_{2.5}[Pd(IO_3)_4]\cdot H_{0.5}IO_3$, proved to be quite straightforward as it can be prepared from the reaction of $Pd(NO_3)_2\cdot 2H_2O$ with KIO_4 under mild hydrothermal conditions. Again the in situ reduction of IO_4^- to IO_3^- is utilized. The complexation of Pd^{II} by four iodate anions yields $[Pd(IO_3)_4]^{2-}$ anions. Unlike the $[Au(IO_3)_4]^{1-}$ anion, in which the bridging I–O bonds are slightly polarized with an average bond length of 1.882(9) Å, all I–O bond lengths in the $[Pd(IO_3)_4]^{2-}$ anions are within the range of 1.790(4) to 1.865(5) Å, and no excessive lengthening of the bridging I–O bonds are observed. The $[Pd(IO_3)_4]^{2-}$ anions are similar to $[Au(IO_3)_4]^{1-}$ in that all of the four iodate anions in the $[Pd(IO_3)_4]^{2-}$ anions are aligned on one side of the PdO_4 square plane, as is shown in Figure 4. However, individual anions are related through inversion centers, and it crystallizes in the centrosymmetric space group *C*2/*m* (Figure 5).

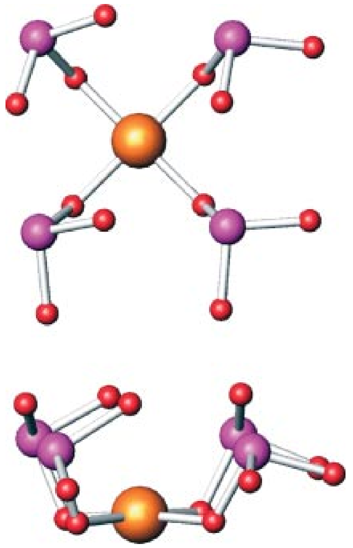

Figure 4. Two depictions of the $[Pd(IO_3)_4]^{2-}$ anion in the structure of $K_{2.5}Pd(IO_3)_4{\cdot}H_{0.5}IO_3$. Palladium is shown in orange, iodine in magenta, and oxygen in red.

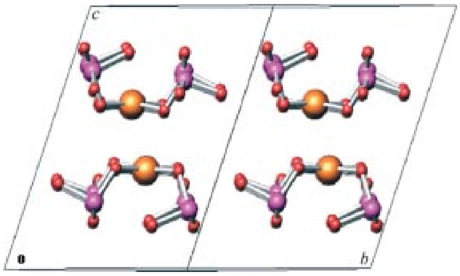

Figure 5. An illustration of the centrosymmetric packing of the $[Pd(IO_3)_4]^{2-}$ anions in $K_{2.5}Pd(IO_3)_4{\cdot}H_{0.5}IO_3$. K^+ cations and iodate/iodic acid units have been omitted for clarity. Palladium is shown in orange, iodine in magenta, and oxygen in red.

The critical feature of the vibrational spectrum of $K_{2.5}[Pd(IO_3)_4]{\cdot}H_{0.5}IO_3$ is the presence of a I–OH stretch at 1180 cm^{-1}, confirming the protonation of the co-crystallized iodate moiety.[27] In addition, a low frequency band at 495 cm^{-1} is observed that might be attributable to a stretch mode of Pd–O. A set of weak bands centered at 560 cm^{-1} can potentially be assigned to distortions of the $[PdO_4]$ square plane.[28,29] Iodate stretching vibrations (ν_1 and ν_3) are found at 797, 782, 728, 696, 673 and 659 cm^{-1}.

Conclusions

In conclusion, we have demonstrated that two new noble metal iodates can be prepared under mild hydrothermal conditions by using in situ reduction of periodate to iodate. These compounds are the first members a new family of noble metal iodate compounds containing square-planar metal ions. The importance of these compounds lies in their ability to form polar structures that will allow for the development of new nonlinear optical, pyroelectric, piezoelectric, and ferroelectric materials.

Experimental Section

$K[Au(IO_3)_4]$: Prepared by loading gold (70 mg, 0.355 mmol), KIO_4 (300 mg, 1.304 mmol), 0.2 mL concentrated H_2SeO_4 solution, and 0.05 mL of distilled and filtered water (Millipore) in 23 mL PTFE-lined autoclave. The autoclave was heated at 200 °C for 4 d, and slowly cooled to 9 °C/h to 22 °C. The product consisted of yellow crystals of $K[Au(IO_3)_4]$ that had grown on the surface of unreacted gold metal, and a bright yellow solution, that was converted into a yellow precipitate of $Au_2(SeO_3)_3$ when water was added. Yield for $K[Au(IO_3)_4]$: 50 mg (15% based on Au). EDX analysis provided a K/Au/I ratio of 1:1:4.

$K_{2.5}[Pd(IO_3)_4]{\cdot}H_{0.5}IO_3$: Prepared by loading $Pd(NO_3)_2{\cdot}2H_2O$ (105.8 mg, 0.397 mmol), KIO_4 (284.2 mg, 1.236 mmol), and 0.5 mL distilled and filtered water (Millipore) in 23 mL PTFE-lined autoclave. The autoclave was heated at 200 °C for 3 d, and slowly cooled to 9 °C/h to 22 °C. The product consisted of dark orange plates of $K_{2.5}[Pd(IO_3)_4]{\cdot}H_{0.5}IO_3$ and unreacted $Pd(NO_3)_2{\cdot}2H_2O$. Yield for $K_{2.5}[Pd(IO_3)_4]{\cdot}H_{0.5}IO_3$: 54 mg (12% based on Pd). EDX analysis provided a K/Pd/I ratio of 2.3:1:5.1.

X-ray Structural Analyses

$K[Au(IO_3)_4]$ (1): Yellow block, crystal dimensions $0.084 \times 0.048 \times 0.046$ mm, triclinic, $P1$, $Z = 1$, $a = 5.6484(5)$, $b = 7.1935(7)$, $c = 8.1377(8)$ Å, $\alpha = 105.264(2)°$, $\beta = 93.585(2)°$, $\gamma = 111.840(2)°$, $V = 291.30(5)$ Å^3 ($T = 193$ K), $\mu = 236.39$ cm^{-1}, $R_1 = 0.0289$, $wR_2 = 0.0762$.

$K_{2.5}[Pd(IO_3)_4]{\cdot}H_{0.5}IO_3$ (2): Dark orange plate, crystal dimensions $0.055 \times 0.020 \times 0.012$ mm, monoclinic, $C2/m$, $Z = 4$, $a = 11.3270(13)$, $b = 11.8246(14)$, $c = 12.9665(15)$ Å, $\beta = 114.417(2)°$ $V = 1581.4(3)$ Å^3 ($T = 193$ K), $\mu = 116.67$ cm^{-1}, $R_1 = 0.0277$, $wR_2 = 0.0635$. Bruker APEX CCD diffractometer: $\theta_{max} = 56.58°$ (for **1**) and 56.62° (for **2**), Mo-K_α, $\lambda = 0.71073$ Å, 0.3° ω scans, 2796 (for **1**) and 7413 (for **2**) reflections measured, 2440 (**1**) and 2007 (**2**) independent reflections all of which were included in the refinement. The data were corrected for Lorentz polarization effects and for absorption (numerical and SADABS), solutions were solved by direct methods, anisotropic refinement on all heavy atoms of F^2 by full-matrix least-squares, 164 (**1**) and 125 (**2**) parameters. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [Fax: (+49)-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de] on quoting depository numbers CSD-417267 and -417268. G. M. Sheldrick, SHELXTL PC, Version 5.0, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

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