

Crystal Structure and Vibrational Spectra of a New Viologen Gold(I) Iodide

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The synthesis of low-dimensional organic–inorganic hybrid materials with novel physical properties is motivated by the notion that complex solid-state systems consisting of organic and inorganic components have great potential for the creation of functional materials.^{1,2} Due to the limitations presented by differences in the synthesis conditions, for organic and inorganic materials, formation of crystalline hybrid compounds by self-assembly of molecular and ionic components provides new challenges in chemical synthesis.³ Our interest in the synthesis of low-dimensional crystalline organic–inorganic metal halides lies with the possibility of modulating useful properties associated with the organic and inorganic components. Examples of novel organic systems include viologens, which exhibit novel redox and electron-emitting properties. The synthetic approach to these materials is essentially via self-assembly of the organic and inorganic moieties into crystalline hybrid compounds. Self-assembly techniques take advantage of weak intermolecular interactions to create more complex crystal structures while preserving the unique characteristics of the individual components. Hence, the synthesis, crystal structure, and properties of low-dimensional organic–inorganic compounds should provide a wealth of valuable information for the synthesis of artificial and self-assembled hybrid multilayers and multicomposites.

Much research interest has been focused on Au(I) halides due to their unique properties.⁴ Fundamental and systematic investigations have rationalized the novel luminescent properties of gold(I) compounds in terms of Au aggregation.^{5–7} Studies also show that strong closed-shell Au(I)–Au(I) interactions collectively known as “aurophilic” interactions are mainly due to correlation and relativistic effects.⁵ These weak aurophilic interactions have important effects on structure and properties and, thus, have significant consequences on the supramolecular chemistry of gold(I) compounds. Herein we report the synthesis, crystal structure, and vibrational spectra of a new methyl viologen gold(I) iodide.

The title compound, (C₁₂H₁₄N₂)Au₂I₄ (**1**), crystallizes in a tetragonal space group *P*4₂/*mnm*.⁸ The crystal structure of **1**, as shown in the synopsis, is described as a 4₂ stacking, along the

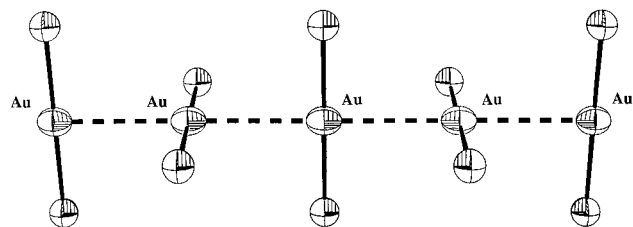


Figure 1. Portion of a single 1D chain of Au₂[−] ions in **1**. The dashed lines represent Au(I)–Au(I) aurophilic interactions (Au–Au = 3.3767(3) Å). (Ellipsoids are drawn at 50% probability.)

c-axis, of layers consisting of methyl viologen (MV²⁺) and [Au₂][−] ions. In Figure 1, the stacking results in chains of “crossed-sticks” Au₂[−] ions with equidistant gold atoms parallel to the *c*-axis. The Au–Au distance of 3.3767(3) Å is a reasonable “aurophilic” distance.⁵ The Au–I distance in the Au₂[−] units is 2.5560(7) Å (2×), comparable to those found in similar gold(I) iodides.⁹ The structure also features staggered orientation of MV²⁺ dications, resulting in interplanar distances of 6.7534(3) Å between parallel viologens. The absence of significant hydrogen bonding leads us to conclude that electrostatic and “aurophilic” interactions are the dominant intermolecular forces within the crystal. However, the unique structure of the anionic [Au₂][−]∞ chains is essentially dictated by aurophilicity.

Raman scattering spectra of single crystals of **1** were measured in the backscattering geometry at 300 K on a triple Jobin Yvon spectrometer equipped with a microscope and liquid nitrogen cooled CCD detector. The spectral resolution was less than 2.5 cm^{−1}, using an Ar⁺ laser line λ = 514.5 nm for the excitation. A typical spectrum taken for the parallel polarization of the incident and scattered light is shown in Figure 2a. The inset shows the low-frequency part of the spectrum where one expects the vibrations of heavy gold and iodine atoms to occur.¹⁰

Group theoretical analyses according to the site symmetries of Au and I atoms of C_{2h}^z and C_s^h, respectively, result in the following sets of long-wavelength vibrations of the atoms in *P*4₂/*mnm*:¹¹

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- (8) Single-crystal X-ray analysis, using a Siemens SMART diffractometer equipped with a CCD area detector, was carried out on a crystal with dimensions of 0.12 × 0.10 × 0.04 mm mounted in a stream of dry nitrogen gas at −50 °C. Monochromatic Mo Kα radiation was used to collect a full sphere of data with the narrow-frame method. The data were integrated, and intensities were corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path lengths. Empirical absorption correction was applied and redundant reflections were averaged. Final cell constants were refined using 3935 reflections having *I* > 10σ(*I*). The tetragonal cell constants are *a* = 12.6167(7) Å, *c* = 6.7534(6) Å, *V* = 1075.01(13) Å³; *Z* = 2; 2θ_{max} = 56°; final *R* indices [*I* > 2σ(*I*)], *R*₁ = 0.0244, *wR*₂ = 0.0596; *R* indices (all data), *R*₁ = 0.0263, *wR*₂ = 0.0589. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The thermal motion of all atoms was treated anisotropically. No attempts were made to locate hydrogen atoms. All calculations were made using the Siemens SHELXTL crystallographic package.
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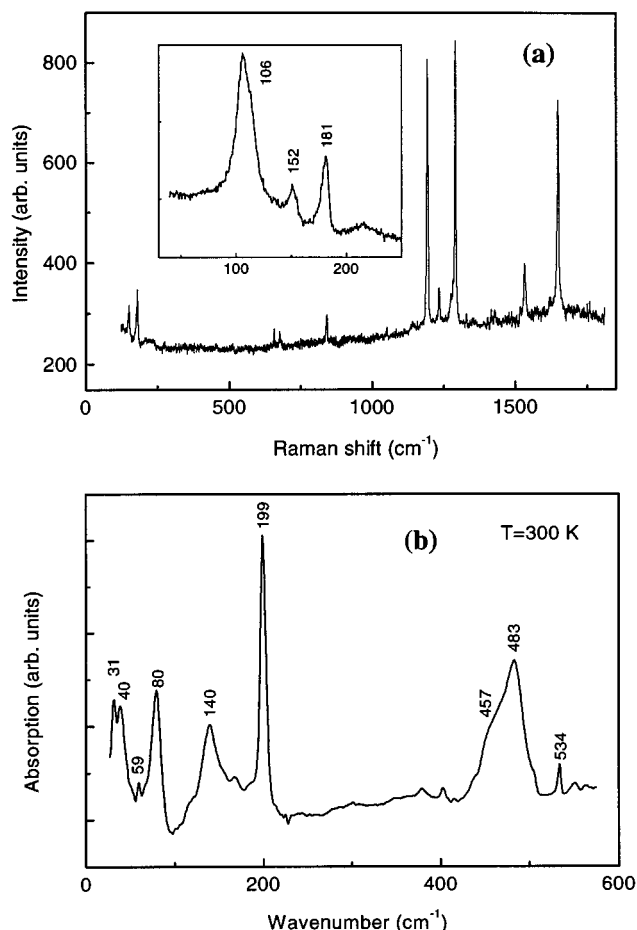


Figure 2. (zz)-polarized Raman scattering spectrum of **1** at $T = 300$ K and $\lambda_{\text{exc}} = 514.5$ nm. The inset shows the spectrum of **1** in the range 30–250 cm^{-1} . (b) Infrared absorption spectrum of **1** at $T = 300$ K.

$$\Gamma_{\text{Au}} = A_{1u} + A_{2u}(z) + B_{1u} + 4E_u(x,y)$$

$$\Gamma_{\text{I}} = 2A_{1g}(xx + yy, zz) + A_{1u} + 2A_{2g} + A_{2u}(z) + 2B_{1g}(xx - yy) + B_{1u} + 2B_{2g}(xy) + B_{2u} + 4E_g(xz, yz) + 4E_u(x,y)$$

The symbols in parentheses denote the selection rules (i.e., Raman or IR activity of a given mode). Analyses of the Au phonon modes show that their vibrational modes are Raman-inactive and only contribute to the IR-active A_{2u} and $4E_u$ and silent (A_{1u} and B_{1u}) modes. The analyses also show that iodine atoms contribute 10 Raman-active vibrations, namely, of A_{1g} , B_{1g} , B_{2g} and E_g symmetry. This is different from results of previous work on a low-symmetry compound $\text{Au}_2(\text{tmb})\text{Cl}_2$, where all atoms lie at C_1 sites¹² and hence contribute to both Raman and infrared spectra. This fact has been explored in evaluating Au(I)–Au(I) interactions, which are believed to be governed by an empirical linear relationship between bond lengths and force constants.¹⁰ On the basis of the Au–Au distances in **1** the frequency of the Raman-active Au–Au mode is expected to lie between 35 and 50 cm^{-1} .¹⁰ The absence of Raman lines in the range 35–100 cm^{-1} confirms the restrictions of the space group symmetry on Au vibrations. Two iodine A_{1g} modes, active in (zz) scattering geometry, are expected to be the strongest and correspond to the in- and out-of-phase stretching motion of the iodine atoms perpendicular to the gold chain axis. The intense lines at 181 and 106 cm^{-1} are

assigned to these vibrations. Their “average” frequency lies close to the reported stretching mode of the AuI_2^- ion at 156 cm^{-1} .¹³

The low-frequency IR absorption spectrum was measured on thin disks of **1** at 300 K with a Bomem DA8 FT interferometer in the range 30–600 cm^{-1} . The spectra, as shown in Figure 2b, are dominated by the absorption line at 199 cm^{-1} . Both the high intensity and the position of the line agree with results of earlier studies on $[\text{AuI}_2]^-$ ions and correspond to the antisymmetric stretch (ν_3) of the linear ion.¹³ The lines at 59 and 80 cm^{-1} are assigned to the bending vibration (ν_2) of $[\text{AuI}_2]^-$, which splits into a doublet. The absorption lines at lower frequencies (31 and 40 cm^{-1}) lie within the frequency range expected for lattice phonon modes, which involve contributions from Au–Au stretching. The expected absorption line for the Au–Au stretch, as predicted by the empirical relationship,¹⁰ was not observed in the IR scattering spectra, and investigations are currently in progress to further assess the model.

The “crossed-sticks” orientation of the AuI_2 units in the gold iodide chain is reminiscent of the gold(I) linear ion tetramers in $[(\text{Me}_2\text{PhP})_2\text{Au}]^+[\text{Au}(\text{GeCl}_3)_2]^-$ and in the strings of gold atoms in $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NC})_2\text{Au}]^+[\text{Au}(\text{GeCl}_3)_2]^-$.^{14,15} Recent quantum mechanical calculations have shown that net electrostatic effects in these structures are very small.¹⁶ Compound **1** represents a simple anionic system wherein electrostatic and aurophilic contributions have opposing effects on the overall gold interactions. The dominant interactions within the purely inorganic and anionic gold(I) chain of “crossed-sticks” AuI_2^- ions are largely due to aurophilicity. Although chemical systems with extensive Au(I)–Au(I) interactions are known to exhibit luminescent properties, preliminary experiments, using a hand-held UV lamp, indicate **1** is not luminescent. This may be attributed to the quenching of luminescence by methyl viologens.

Experimental Procedure. All reactions were carried out under nitrogen atmosphere, and all solvents were degassed before use. Hydrogen tetrachloroaurate, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, was prepared by dissolving Au (99.9999%) in aqua regia and evaporating to dryness. Methyl viologen dichloride dihydrate (65 mg) was dissolved in 5 mL of 0.33 M HI solution under an ultrasonic bath at 3–4 °C. Dropwise addition of 5 mL of 0.05 M HAuCl_4 to the methyl viologen/HI solution resulted in the immediate formation of a black precipitate, which was centrifuged, filtered, and redissolved in a 1:1 acetone/toluene solution. The resulting red solution was allowed to slowly evaporate at room temperature. Formation of orange parallelepiped and red platelike crystals was observed after several days. The red platelike crystals were found to be methyl viologen tetraiodide, $[\text{MV}^{2+}]_2\text{I}_4$. The air-stable orange crystals were found to be of compound **1** and melt at 220 °C. Qualitative chemical analyses by SEM/microprobe of **1** show that gold and iodine are the only heavy elements present.

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Supporting Information Available: Complete list of crystallographic data, atomic coordinates and anisotropic thermal parameters, and relevant bond distances and angles (4 pages). A file containing crystallographic data collection and refinement data, atomic coordinates, thermal parameters, bond distances, and bond angles, in CIF format, is also available on the Internet only. Ordering and access information is given on any current masthead page.

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