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High-Pressure (up to 10.7 GPa) Crystal Structure of Single-Component Molecular Metal [Au(tmdt)$_2$]

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Abstract: The crystal structure of the single-component molecular metal [Au(tmdt)$_2$] was examined at pressures up to 10.7 GPa in order to examine whether the high-pressure structure reflects the crystal's metallic nature. Crystal structure analyses were performed at 0.2, 0.8, 1.3, 3.0, 5.5, and 10.7 GPa on the basis of the powder X-ray diffraction data obtained by using the synchrotron radiation source SPring-8. The unit cell volume at 10.7 GPa was ~75% of the initial volume, indicating that [Au(tmdt)$_2$] is a 'soft material' like a typical molecular crystal in spite of its metallic nature. The pressure dependences of the bond lengths of the Au(tmdt)$_2$ molecule were found to be ~1 order of magnitude smaller than those of the intermolecular atomic distances. These results seem to justify the commonly accepted conjecture that the molecule usually behaves almost like a rigid body up to a fairly high pressure. It was found that the anisotropy of the lattice compression of the insulating I$_2$ crystal below 20 GPa can be essentially interpreted on the basis of a very simple '*interatomic repulsion model*', which assumes that the molecules in the crystal are packed such that as far as possible, an increase in the interatomic repulsions between neighboring molecules is avoided. However, the maximum decrease in the intermolecular distance in [Au(tmdt)$_2$] was observed along the *a* direction although there were many intermolecular S···S contacts shorter than the van der Waals distance (3.70 Å) along this direction. The shortest intermolecular S···S distance was 2.73 Å at 10.7 GPa, which is ~1 Å shorter than the S···S van der Waals distance (3.70 Å). The crystal lattice of [Au(tmdt)$_2$] is considered to be stabilized by the enhancement of the intermolecular overlapping of the conduction molecular orbitals having large amplitudes on peripheral S atoms. Although the crystal is composed of '*isolated molecules*' like a typical insulating molecular crystal, its compressibility behavior seems to reflect its metallic nature.

Introduction

Under very high pressure, molecular crystals such as hexaiodobenzene (C_6I_6) and iodine are converted into metals and superconductors.[1,2] In order to eliminate the energy gap of conduction bands of molecular crystals by applying pressure, it may be roughly said that intermolecular interactions must be enhanced to be comparable to intramolecular interactions.[3] However, under such extreme conditions, the initial molecular structure can be broken. In fact, I$_2$ crystals undergo molecular dissociation at around 20 GPa and the resultant monatomic I crystal exhibits both metallic and superconducting behavior.[1,4,5] Compared with the metallization of I$_2$, the metallization of crystals of planar molecules with π frontier electrons is considerably difficult. The C_6I_6 molecule has a distorted planar structure at atmospheric pressure under the influence of a large repulsive force between the intramolecular iodine atoms; the crystal undergoes an insulator-to-metal transition at 35 GPa.[2,6] We have recently attempted to examine the possibility of pressure-induced metallization of a crystal of *peri*-ditellurium-bridged π molecules, tetramethyltetratelluronaphthalene (2,3,6,7-tetramethylnaphto[1,8-*cd*:4,5-*c′d′*]bis[1,2]ditellurole) at pressures up to 30 GPa.[3] However, the metallic temperature dependence of resistivity could not be observed at temperatures above 100

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(1) Shimizu, K.; Yamauchi, T.; Tamitani, N.; Takeshita, N.; Ishizuka, M.; Amaya, K.; Endo, S. *J. Supercond.* **1994**, *7*, 921.
(2) Iwasaki, E.; Shimizu, K.; Amaya, K.; Nakayama, A.; Aoki, K.; Carlón, R. P. *Synth. Met.* **2001**, *120*, 1003.
(3) Cui, H.; Okano, Y.; Zhou, B.; Kobayashi, A.; Kobayashi, H. *J. Am. Chem. Soc.* **2008**, *130*, 3738.
(4) Takemura, K.; Minomura, S.; Shimomura, O.; Fujii, Y. *Phys. Rev. Lett.* **1980**, *45*, 1881.
(5) Takemura, K.; Minomura, S.; Shimomura, O.; Fujii, Y.; Axe, J. D. *Phys. Rev. B* **1982**, *26*, 998.
(6) Nakayama, A.; Fujihisa, H.; Aoki, K.; Carlón, R. P. *Phys. Rev. B* **2000**, *62*, 8759.

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K. In contrast, we have succeeded in preparing a metallic crystal consisting of a single type of molecules (single-component molecular metal) [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate) by chemical synthesis, where Ni(tmdt)$_2$ is a planar molecule with π frontier orbitals.[7,8] The existence of three-dimensional Fermi surfaces in [Ni(tmdt)$_2$] was confirmed by the observation of de Haas−van Alphen (dHvA) oscillations at very high magnetic fields and very low temperatures.[9] An isostructural [Au(tmdt)$_2$] exhibits electronic properties that are considerably different from those of the conventional molecular metals. [Au(tmdt)$_2$] is transformed into an antiferromagnetic metal at 110 K (T_N).[10−12] This temperature is comparable to the transition temperature of a typical inorganic antiferromagnetic metal, Mn ($T_N \approx 100$ K), and is extremely high as compared to the magnetic transition temperatures of representative magnetic organic conductors such as the first ferromagnetic organic metal, (BEDT-TTF)$_3$[MCr(C$_2$O$_4$)$_3$](CH$_2$Cl$_2$) (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; $T_c = 5.5$ K (M = Mn), 9.2 K (M = Co))[13,14] and the first antiferromagnetic organic superconductor, κ-BETS$_2$FeBr$_4$ (BETS = bis(ethylendithio)tetraselenafulvalene; $T_N = 2.5$ K and $T_c = 1.1$ K).[15,16] In contrast to conventional molecular metals, in which the charge carriers are generated by a charge transfer between the molecules forming the conduction band and the other chemical species, the conduction electrons in single-component molecular metals are automatically generated by the self-assembling of the single type of molecules. This carrier generation is similar to that in the case of typical inorganic metals that consist of metal elements such as Cu and Au. Thus, the single-component molecular metal is a material that does not conform to the traditional concept of a molecular crystal. In contrast, from the structural viewpoint, crystals of single-component molecular metals can be regarded as molecular crystals because they are composed of ‘independent molecules’. In general, molecules in the crystal are packed such that as far as possible, the appearance of intermolecular atomic contacts shorter than the corresponding van der Waals distances is avoided. That is, the molecular crystal tends to be compressed by pressure along the direction with loose intermolecular contacts. However, the shortening of intermolecular contacts is not always disadvantageous for the metallic crystal because the metallic state is stabilized by the enhancement of the intermolecular transfer integrals of the frontier molecular orbitals that form conduction bands (conduction molecular orbitals). Since the single-component molecular metal simultaneously possesses both the nature of a metallic crystal and the nature of a molecular crystal, the examination of the effect of high pressure on the crystal structure of [Au(tmdt)$_2$] is of special interest.

Recently, remarkable progress has been made in the analysis of high-pressure crystal structures by utilizing diamond anvil cells (DACs), synchrotron X-ray sources, and new methodologies for powder X-ray structure determination. However, structure analyses of molecular crystals at pressure levels of around 10 GPa have been limited. To the best of our knowledge, it appears that X-ray crystal structure analyses of molecular crystals containing more than 15 crystallographically independent non-hydrogen atoms have not yet been performed. In this study, we have examined the structure of [Au(tmdt)$_2$] (AuS$_{12}$C$_{18}$H$_{12}$) at 0.2, 0.8, 1.3, 3.0, 5.5, and 10.7 GPa.

Experimental Section

The crystals of [Au(tmdt)$_2$] were prepared electrochemically under an argon atmosphere using standard H-type glass cells with Pt electrodes. The starting material, (^{n}Bu$_4$N)[Au(tmdt)$_2$] was prepared according to the procedure given in the literature.[8] Microcrystals with the dimensions of ~20 μm, which are highly suitable for X-ray powder diffraction experiments, were grown on a Pt electrode within ~4 weeks.

High pressures of up to 10.7 GPa were applied using a DAC with a culet size of 600 μm. A fluorinert was used as the pressure medium. The pressure was determined by using a ruby fluorescence method. X-ray experiments were carried out by using a synchrotron radiation source on the beamline BL10XU station at SPring-8. The wavelength was tuned with a Si (111) double-crystal monochromator to 0.4977 Å, and an X-ray collimator with a diameter of 55 μm was also used. Powder diffraction patterns were obtained by using an angle dispersive method with an imaging plate (IP) detector. The powder patterns were measured at 0.2, 0.8, 1.3, 3.0, 5.5, and 10.7 GPa. The structure was solved by using a self-consistent iterative analysis of a combination of the maximum entropy method (MEM) and Rietveld analysis. The *R*-factors were 0.039 (0.2 GPa), 0.042 (0.8 GPa), 0.040 (1.3 GPa), 0.027 (3.0 GPa), 0.030 (5.5 GPa), and 0.035 (10.7 GPa).

Results and Discussion

The relationships between pressure and the lattice constants of [Au(tmdt)$_2$] are shown in Figure 1 and the molecular arrangement at 10.7 GPa is shown in Figure 2. All the lattice constants decrease smoothly with an increase in pressure, indicating no phase transition up to 10.7 GPa. Between 0.2 and 10.7 GPa, the lattice spacings are varied by $\Delta a = 0.634$ Å, $\Delta b = 0.935$ Å, and $\Delta c = 0.548$ Å. The unit cell volume (V) of [Au(tmdt)$_2$] at 10 GPa is 74% of the cell volume at ambient pressure (V_o). This pressure dependence of V/V_o is approximately equal to those of anthracene and C$_6$I$_6$, whose crystal structures have been obtained at pressures above 9.5 GPa: $V/V_o = 0.71$ (anthracene),[6] 0.74 (C$_6$I$_6$).[17] These results show that [Au(tmdt)$_2$] is a ‘soft material’ like typical molecular crystal in spite of its metallic nature.

It has been believed that the bond length remains almost constant up to very high pressure because of the stiffness of the covalent bond. However, thus far, for pressures above 10 GPa, there have not been reports on the bond lengths of the molecules composed of more than 30 non-hydrogen atoms. In the crystal of [Au(tmdt)$_2$], all the molecules are on the lattice points, and half of the molecule is crystallographically independent (Figure 2). The obtained average bond lengths are 2.280(6) (Au−S), 1.742(12) (S−C), 1.320(16) (C=C), and 1.49(2) Å (C−C) at 10.7 GPa and 2.331(8) (Au−S), 1.748(15)

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(7) Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kobayashi, A. *Science* **2001**, *291*, 285.

(8) Kobayashi, A.; Fujiwara, E.; Kobayashi, H. *Chem. Rev.* **2004**, *104*, 5243.

(9) Tanaka, H.; Tokumoto, M.; Ishibashi, S.; Graf, D.; Choi, E. S.; Brooks, J. S.; Yasuzuka, S.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **2004**, *126*, 10518.

(10) Suzuki, W.; Fujiwara, E.; Kobayashi, A.; Fujishiro, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Fujiwara, H.; Kobayashi, H. *J. Am. Chem. Soc.* **2003**, *125*, 1486.

(11) Zhou, B.; Shimamura, M.; Fujiwara, E.; Kobayashi, A.; Higashi, T.; Nishibori, E.; Sakata, M.; Cui, H.; Takahashi, K.; Kobayashi, H. *J. Am. Chem. Soc.* **2006**, *128*, 3872.

(12) Hara, Y.; Miyagawa, K.; Kanoda, K.; Shimamura, M.; Zhou, B.; Kobayashi, A.; Kobayashi, H. *J. Phys. Soc. Jpn.* **2008**, *77*, 053706.

(13) Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447.

(14) Coronado, E.; Day, P. *Chem. Rev.* **2004**, *104*, 5419.

(15) Ojima, E.; Fujiwara, H.; Kato, K.; Kobayashi, H.; Tanaka, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc.* **1999**, *121*, 5581.

(16) Kobayashi, H.; Cui, H.; Kobayashi, A. *Chem. Rev.* **2004**, *104*, 5265.

(17) Oehzelt, M.; Resel, R.; Nakayama, A. *Phys. Rev. B* **2002**, *66*, 174104.

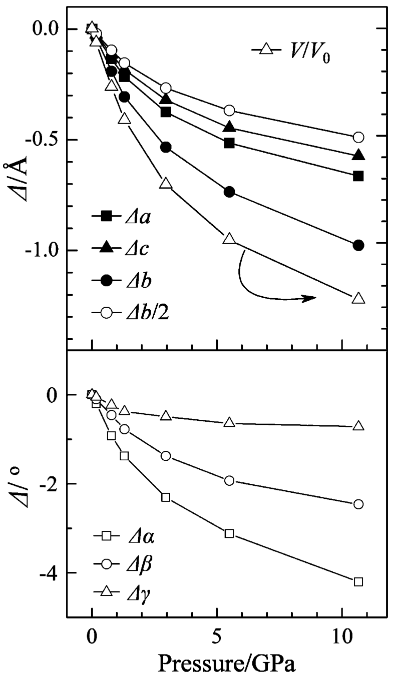

Figure 1. Magnitudes of the changes in the lattice constants (Δa, Δb, Δc, $\Delta\alpha$, $\Delta\beta$, and $\Delta\gamma$) of [Au(tmdt)$_2$] at a high pressure, where $\Delta b/2$ is also presented (see text). The lattice constants are a = 6.3985(5) Å, b = 7.5006(5) Å, c = 12.1931(9) Å, α = 90.320(7)°, β = 96.714(6)°, and γ = 103.080(9)° at 0.2 GPa; and a = 5.765 (1) Å, b = 6.566(1) Å, c = 11.591(2) Å, α = 86.32(1)°, β = 94.35(2)°, and γ = 102.41(3)° at 10.7 GPa. The open triangles in the upper figure show the pressure dependence of the unit cell volume (V), where V_0 is the unit cell volume at ambient pressure.

(S−C), 1.361(16) (C=C), 1.46(2) Å (C−C) at 0.2 GPa. All bond lengths except the C−C bond length of the terminal trimethylene group with a large standard deviation are shortened. However, the magnitudes of the variations in the bond lengths at pressures between 0.2 and 10.7 GPa (<0.06 Å) are ∼1 order of magnitude smaller than Δa (=0.63 Å), Δb (=0.94 Å), and Δc (=0.55 Å), which implies that most of the lattice compression is due to the compression of the intermolecular distances. Consequently, the result of the high-pressure analyses of [Au(tmdt)$_2$] is considered to justify the commonly accepted conjecture that the molecule behaves almost like a rigid body up to a fairly high pressure.

As shown in Figure 1, the maximum change in the lattice constant is observed along the b axis. However, along this direction, there are two intermolecular contacts within one period (b) (see Figure 2c). Because the molecule behaves almost like a rigid body, the intermolecular distances are diminished by ∼0.63, 0.47 (=$\Delta b/2$), and 0.55 Å at 10.7 GPa along the a, b, and c directions, respectively. That is, the intermolecular distance exhibits the largest variation along the a direction. In contrast, as shown in Figure 2a, the molecules exhibit the closest packing along the a direction. All the intermolecular S···S contacts are shorter than the van der Waals distance (r_{vdW}(S···S) = 3.70 Å) even at 0.2 GPa. Nevertheless, the shortest intermolecular S···S distance (B: S1(x, y, z)···S2(1 + x, y, z) along the a direction decreases by ∼0.60 Å and becomes as short as 2.729 Å at 10.7 GPa, which is 0.93 Å shorter than r_{vdW}(S···S) and only 0.64 Å longer than the S−S covalent bond length (r_{c}(S−S) = 2.08 Å), where Sj(x, y, z) denotes the atomic coordinate of the jth crystallographically independent S atom of the molecule on the lattice origin (0, 0, 0) (see Figures 2 and 3). Since the intermolecular contacts along the a axis are considerably shorter than those along the b and c directions, the pressure dependences of the second and the third shortest S···S distances (A, C) are also presented in Figure 3. The shortest S···S distances along the b and c directions are 3.214 (J: S3(x, y, z)···S5(1 − x, −y, 1 − z)) and 3.321 Å (G: S2(x, y, z)···S6(−x, −y, −1 − z)) at 10.7 GPa, respectively, which are considerably longer than B (Figures 2 and 3). In the crystal, planar Au(tmdt)$_2$ molecules are packed very compactly in order to form a molecular layer parallel to (0, 2, −1) like a graphite plane (graphene) (Figures 2c and 4b). However, unlike in a graphene sheet, there is no covalent bond between the neighboring molecules. The translational vectors in the *molecular sheet* are a and l (=2a + b + 2c). The pressure dependence of l is shown in Figure 4a. In spite of the anisotropic molecular structure of Au(tmdt)$_2$, l and a exhibit almost the same pressure dependences. Two independent interplanar distances between the neighboring molecules are 3.542 (=$d_{(0,\,0,\,0)\text{-}(1,\,1,\,1)}$) and 3.682 Å (= $d_{(0,0,0)\text{-}(1,0,1)}$) at 0.2 GPa, where $d_{(0,\,0,\,0)\text{-}(1,\,n,\,1)}$ (n = 0, 1) is the interplanar distance between the molecule on the lattice origin (0, 0, 0) and the molecule on the lattice point (1, n, 1) (see Figure 2c). Since $d_{(0,\,0,\,0)\text{-}(1,\,1,\,1)}$ and $d_{(0,\,0,\,0)\text{-}(1,\,0,\,1)}$ are comparable to the interplanar distance of TTF molecules in the typical metallic TTF complexes, (TTF)X$_n$ (X = halogen ions, SCN; n ≈ 0.6−0.8) (d ≈ 3.60 Å),[18] sufficient interactions can be expected between the molecular sheets even at an ambient pressure. At 10.7 GPa, $d_{(0,\,0,\,0)\text{-}(1,\,1,\,1)}$ and $d_{(0,\,0,\,0)\text{-}(1,\,0,\,1)}$ are 3.038 and 3.056 Å, respectively. That is, the difference between $d_{(0,\,0,\,0)\text{-}(1,\,1,\,1)}$ and

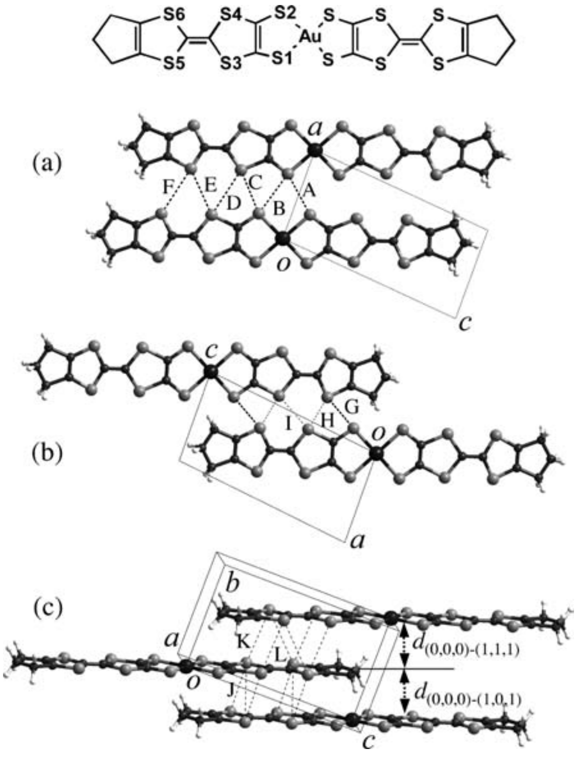

Figure 2. (a) Numbering of S atoms and molecular arrangement along the a axis at 10.7 GPa. The dotted lines (A−F) indicate the intermolecular short S···S distances: A = 2.937 Å (3.394 Å), B = 2.729 Å (3.331 Å), C = 2.937 Å (3.421 Å), D = 3.014 Å (3.633 Å), E = 3.207 Å (3.667 Å), and F = 3.003 Å (3.645 Å), where the values in parentheses indicate the S···S distances at 0.2 GPa. (b) Molecular arrangement along the c axis. The short S···S distances are G = 3.321 Å (3.634 Å), H = 3.576 Å (3.890 Å), and I = 3.457 Å (3.788 Å) at 10.7 GPa (0.2 GPa). (c) Molecular arrangement along the b direction. The short S···S distances are J = 3.214 Å (3.904 Å), K = 3.290 Å (3.768 Å), and L = 3.295 Å (3.769 Å). $d_{(0,0,0)\text{-}(1,0,1)}$ and $d_{(0,0,0)\text{-}(1,1,1)}$ are two independent distances between the molecular planes.

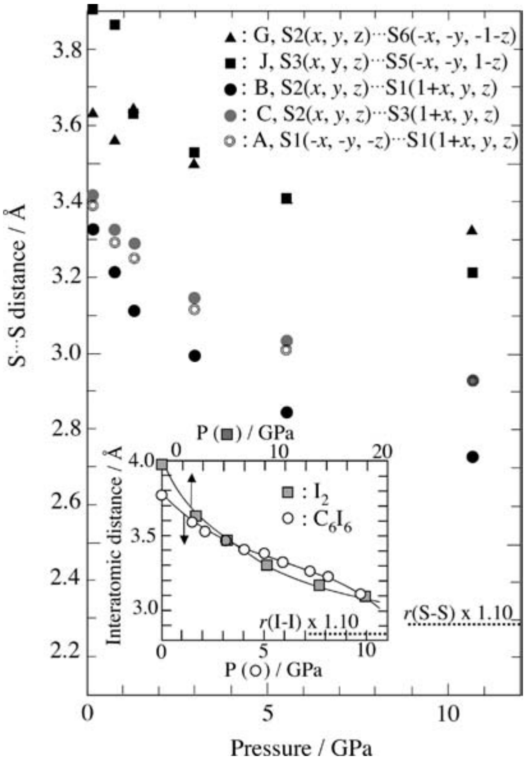

Figure 3. Pressure dependence of intermolecular short S···S distances. The closed squares indicate the shortest intermolecular S···S contact along the *b* direction (J in Figure 2c). The triangles show the shortest intermolecular S···S distances along the *c* axis (G in Figure 2b). The closed circles indicate the shortest intermolecular S···S distance along the *a* axis (B in Figure 2a). The pressure dependences of the second (A) and the third (C) shortest S···S distances are also presented (see also Figure 2a). The dotted line at 2.29 Å (=2.08 Å (=r_c(S−S)) × 1.10) shows the tentatively assumed critical S···S distance where the possible S−S bond formation begins to develop *between the molecules* (see text). The inset, which was prepared on the basis of the reported data,[5,17] shows the pressure dependences of the shortest intermolecular I···I distances in the crystals of I_2 and C_6I_6.

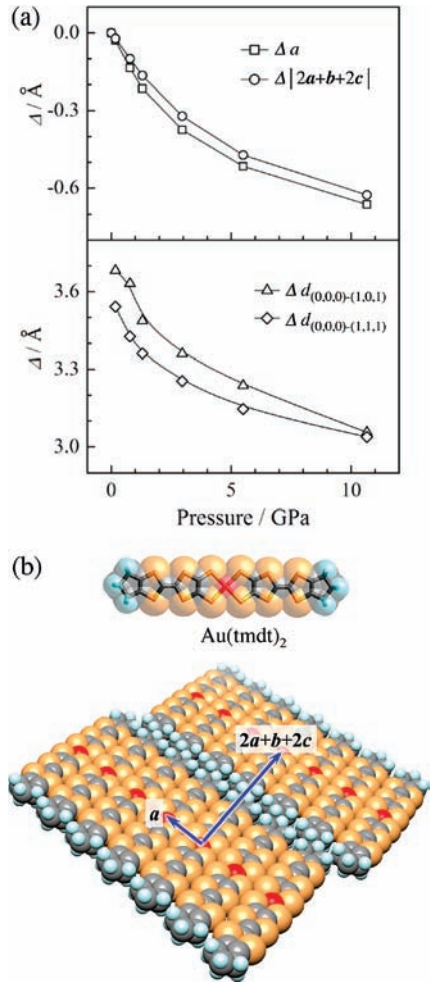

Figure 4. (a) Pressure dependence of Δ*a*, Δ|2***a*** + ***b*** + 2***c***|, $d_{(0,0,0)\text{-}(1,0,1)}$, and $d_{(0,0,0)\text{-}(1,1,1)}$ (see Figure 2c). (b) Molecular structure of Au(tmdt)$_2$ and two-dimensional molecular arrangement in the (0, 2, −1) plane (or molecular sheet).

$d_{(0,\ 0,\ 0)\text{-}(1,\ 0,\ 1)}$ decreases to only 0.018 Å, which implies that *molecular sheet* becomes almost flat at 10.7 GPa. The magnitude of the change in the average interplanar distance between 0.2 and 10.7 GPa is 0.565 Å, which is ~90% of Δ*a* (0.634 Å) and Δ*l* (0.639 Å). Considering the highly anisotropic crystal structure, it is quite surprising that the crystal exhibits a nearly isotropic compression. The three-dimensionality of [M(tmdt)$_2$] crystal has also been suggested by the dHvA and magnetoresistance experiments of [Ni(tmdt)$_2$].[9,19]The nearly isotropic compression of [Au(tmdt)$_2$] crystal will be consistent with the three-dimensional nature of the electronic structure of [M(tmdt)$_2$].[20]

Considering the role of repulsive forces between nonbonding atoms in the molecular packing, the large decrease in the shortest S···S distance (B) is a quite unexpected result. In the case of anthracene crystal, the shortest C···C distance at around 10 GPa is reported to be ~2.90 Å,[17] which is approximately twice that of the C−C covalent bond length (r_c(C−C) = 1.54 Å). The anthracene molecules are quite isolated in the crystal even at 10 GPa. It is very surprising that the shortest S···S distance (B) at 10.7 GPa (2.73 Å) is shorter than the shortest C···C distance in anthracene at 10 GPa (2.90 Å). This anomalous structural feature appears to be related to the metallic nature of [Au(tmdt)$_2$]. As mentioned before, the metallic crystal is stabilized by the enhancement of the intermolecular overlap integrals of the conduction molecular orbitals (or the enhancement of the bandwidth). Furthermore, the conduction molecular orbitals of [Au(tmdt)$_2$] have a large amplitude on the peripheral S atoms (see Figure 5c).[8,21] Consequently, the bandwidths can be significantly increased by shortening the intermolecular S···S distances. Thus, the large decrease in the short S···S distances contributes to the stabilization of the metallic state of [Au(tmdt)$_2$].

The inset in Figure 3 shows the pressure dependences of the shortest intermolecular I···I distances of the crystals of I_2 and C_6I_6.[5,6] Both graphs show distances as small as 3.10 Å at 19.8 (I_2) and 9.7 GPa (C_6I_6); the smallest distance shown in these graphs, i.e., 3.10 Å, is 0.52 Å longer than the I−I covalent bond length (r_c(I−I) = 2.58 Å) (the I−I bond length and the shortest intermolecular I···I distance in the I_2 crystal at 19.8 GPa are

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(18) LaPlaca, S. J.; Corfield, P. W. R.; Thomas, R.; Scott, B. A. *Solid State Commun.* **1975**, *17*, 635. (a) Johnson, C. K.; Watson, C. R. *J. Chem. Phys.* **1976**, *64*, 2271. (b) Kobayashi, H.; Kobayashi, K *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3127.

(19) Yasuzuka, S.; Tanaka, H.; Tokumoto, M.; Graf, D.; Choi, E. S.; Brooks, J. S.; Kobayashi, H.; Kobayashi, A. *J. Phys. Soc. Jpn.* **2008**, *77*, 034709.

(20) Seo, H.; Ishibashi, S.; Okano, Y.; Kobayashi, H.; Kobayashi, A.; Fukuyama, H.; Terakura, K. *J. Phys. Soc. Jpn.* **2008**, *77*, 023714.

(21) Ishibashi, S.; Terakura, K.; Kobayashi, A. *J. Phys. Soc. Jpn.* **2008**, *77*, 024702.

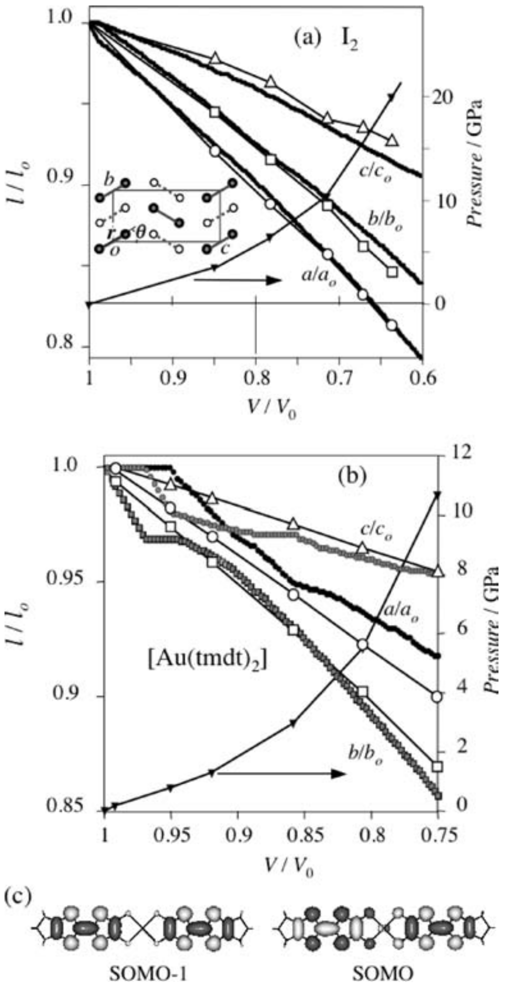

Figure 5. Relationship between the relative lattice constants (a/a_o, b/b_o, and c/c_o) vs relative cell volume, V/V_o of (a) I$_2$ crystal and (b) [Au(tmdt)$_2$] obtained by a simulation based on the simple '*interatomic repulsion model*', where a_o, b_o, c_o, and V_o represent the lattice constants and cell volume at an ambient pressure, respectively. V/V_o vs pressure curve of I$_2$ crystal was obtained using the reported data,[5] and that of [Au(tmdt)$_2$] was obtained in the present experiments. The open circles, open square, open triangles, and small solid triangles show the data points obtained from the present experiments ([Au(tmdt)$_2$]) and from the reference (I$_2$).[5] (c) Molecular orbitals that mainly contribute toward the formation of conduction bands of [Au(tmdt)$_2$].[8,21]

2.71 and 3.10 Å, respectively[5]). When the I···I distance approaches the I−I covalent (or metallic) bond length, the initial molecular structure must be changed because I atoms tend to form covalent bonds (or metal bonds) between adjacent molecules. The *critical* I···I *distance* for the possible bond formation ([I···I]$_c$) is between 2.71 and 3.10 Å. In Figure 3, the *critical distance* is tentatively assumed to be ~10% longer than the covalent bond length (2.84 Å = r_c(I−I) × 1.10) (see the dotted line in the inset of Figure 3). As mentioned earlier, the I$_2$ crystal is transformed into monatomic I metal at 20 GPa.[4,5] In comparison with the small separation between [I···I]$_c$ and the shortest I···I distances in I$_2$ and C$_6$I$_6$ crystals, the separation between the critical S···S distance (2.29 Å = r_c(S−S) × 1.10) and the shortest S···S distance (B) in [Au(tmdt)$_2$] is fairly large (see Figure 3). This suggests the molecularity of [Au(tmdt)$_2$] that has to be maintained even at very high pressures.

In general, molecules in a molecular crystal are considered to be packed in such a manner that as far as possible, an increase in the intermolecular repulsion is avoided. In order to verify the validity of this simple principle with regard to the molecular packing at a high pressure, we attempted to simulate the anisotropy of the compressibility of an I$_2$ crystal according to the '*interatomic repulsion model*', where the molecules in the crystal are assumed to be packed such that as far as possible, an increase in the repulsion energies between nonbonding atoms is avoided. Below 20 GPa, the I$_2$ crystal belongs to an orthorhombic system with the space group *Cmce* (or *Cmca*). The lattice constants are a = 7.136 Å, b = 4.686 Å, and c = 9.784 Å at 0.1 MPa (see the inset of Figure 5a).[5] There exists only one crystallographically independent atom located on the mirror plane whose atomic coordinate is given as (0, y, z). Therefore, if the I−I bond length (r) is assumed to be unchanged (rigid-body model), the atomic position can be assigned by using only one parameter, the molecular rotation angle (θ) (see the inset of Figure 5a). The simulation process is described as follows. (1) The initial lattice constants (a, b, c) are shortened by 0.1% and the parameters (r, θ) are fixed. All the intermolecular I···I distances are calculated for three lattices with the lattice constants, (0.999a, b, c), (a, 0.999b, c), and (a, b, 0.999c) in order to obtain the minimum I···I distance ([I···I]$_{\min}$) for each lattice. For example, if the [I···I]$_{\min}$ of the (0.999a, b, c) lattice is larger than the [I···I]$_{\min}$ of the other two lattices, the lattice constants are considered to vary as (a, b, c) → (0.999a, b, c) so that a tight interatomic contact is avoided. (2) The same calculations are repeated for a lattice with new starting lattice constants of (0.999a, b, c). (3) When the magnitude of the change in the cell volume becomes 1%, the angle θ is readjusted in order to maximize [I···I]$_{\min}$. Then, the simulation cycles are repeated. Through these processes, the relationships between the lattice constants, a, b, and c and the cell volume V are determined. If the reported $P-V$ curve is adopted,[5] the pressure dependences of a, b, and c can be obtained. As shown in Figure 5a, except for a slight deviation observed in c, the experimental results are almost completely reproduced. Thus, it is confirmed that the essential feature of the lattice compression of the I$_2$ crystal can be explained by using a simple '*interatomic repulsion model*'.

A similar calculation was also carried out for [Au(tmdt)$_2$]. As mentioned previously, all the molecules are situated on the lattice points but the lattice angles are varied by the pressure applied ($\Delta\alpha = 4.0°$, $\Delta\beta = 2.4°$, and $\Delta\gamma = 0.7°$ at pressures between 0.2 and 10.7 GPa (see Figure 1)). In addition, the terminal (CH$_2$)$_3$ group of the Au(tmdt)$_2$ molecule is not very rigid. However, for the sake of simplicity, in this study, the lattice angles α, β, and γ are fixed, and the molecule is assumed to be a rigid body. The calculation process is as follows. (1) As in the case of the calculation for the I$_2$ crystal, the intermolecular atomic distances (r_{ij}) of all the atom pairs (i, j) are calculated for three lattices with cell dimensions of (0.999a, b, c), (a, 0.999b, c) and (a, b, 0.999c), and the minimum value of r_{ij}/R_{ij} for each lattice ([r_{ij}/R_{ij}]$_{\min}$) is obtained, where R_{ij} denotes the van der Waals distance of the (i, j) atom pair. The adopted values of the van der Waals radii are 1.66 (Au), 1.85 (S), 1.7 (C), and 1.2 Å (H). If the value of [r_{ij}/R_{ij}]$_{\min}$ for the (a, 0.999b, c) lattice is larger than the values of [r_{ij}/R_{ij}]$_{\min}$ for the other two lattices, the lattice constant is changed as (a, b, c) → (a, 0.999b, c). (2) The same calculations are repeated for a lattice with new starting lattice constants of (a, 0.999b, c). (3) When the cell volume is varied by 1%, the orientation of the molecule is readjusted by slightly rotating the molecule around the a, b, and c axes in order to obtain the maximum possible value of [r_{ij}/R_{ij}]$_{\min}$. Then, the calculation cycles are repeated. The results are shown in

Figure 5b. Although the assumptions adopted in the calculations are oversimplified, the calculations permit a rough estimation of the anisotropy of the lattice compression when the '*interatomic repulsion*' is a dominant factor in the molecular packing. As shown in Figure 5b, the calculated b/b_o vs V/V_o and c/c_o vs V/V_o curves exhibit fairly good agreement with the experimentally obtained curves at $V/V_o < 0.95$ (>0.8 GPa) and $V/V_o < 0.86$ (>3 GPa), respectively; however, a/a_o remains fairly larger than the experimentally determined value. In particular, in the low-pressure regions ($V/V_o > 0.95$ or $P < 0.8$ GPa), the calculated results and experimental data are completely different. In the above-mentioned calculations, only the *b* axis is shortened initially. Then, the *c* axis begins to shrink; finally, the *a* axis begins to shrink. From the viewpoint of the role of interatomic repulsion, the obtained results are highly natural because the intermolecular contact is the closest along the *a* axis and the loosest along the *b* direction (see Figure 2). The large deviation observed along the *a* axis indicates that the *a* axis is shortened beyond that expected from the simple '*interatomic repulsion model*'. Because [Au(tmdt)$_2$] is metallic, its electronic state can be stabilized by increasing the bandwidth. As mentioned previously, the conduction molecular orbitals of [Au(tmdt)$_2$] have the same sign and large amplitudes on the S atoms of a tmdt ligand (see Figure 5c);[8,21] the shortening of the intermolecular distance increases the bandwidth very effectively.

Conclusion

In this study, crystal structure analyses of a single-component molecular metal [Au(tmdt)$_2$] were performed at pressures up to 10.7 GPa on the basis of the powder X-ray diffraction data collected by using a synchrotron radiation source. The pressure dependences of the bond lengths of the Au(tmdt)$_2$ molecule were ~1 order of magnitude smaller than those of the intermolecular distances. That is, the high-pressure structure analyses of [Au(tmdt)$_2$] show that the molecule can almost be regarded as a rigid body up to a fairly large pressure. In contrast to the insulating I_2 crystal whose anisotropy of the lattice compression can be essentially interpreted by using a very simple '*interatomic repulsion model*', the [Au(tmdt)$_2$] crystal exhibited maximum compressibility along the *a* direction although there were many S•••S contacts shorter than the van der Waals distance (3.70 Å) between the molecules arranged along this direction. The shortest intermolecular S•••S distance was as short as 2.73 Å at 10.7 GPa, which was ~1 Å shorter than the corresponding van der Waals distance. This large compressibility along the *a* axis suggested that the lattice was stabilized by the enhancement of the intermolecular overlapping of the conduction molecular orbitals of [Au(tmdt)$_2$]. Although like a typical usual molecular crystal, the [Au(tmdt)$_2$] crystal was composed of '*isolated molecules*', its compressibility seemed to reflect its metallic nature.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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