

STRUCTURE DETERMINATION OF SINGLE-COMPONENT MOLECULAR METALS BY X-RAY POWDER DIFFRACTION

The realization of a molecular metal based on single-component molecules had been one of the important targets in the field of molecular conductors. The difficulty in designing a single-component molecular metal is naturally related to the facts that the highest occupied molecular orbital (HOMO) is doubly occupied. However, we have noticed that even in electronic bands constructed from single-component molecules, the bottom energy level of the lowest unoccupied molecular orbital (LUMO) band can be lower than the top energy level of the HOMO band and the free carriers might be generated by the electron transfer between HOMO and LUMO bands when the molecule has sufficiently large intermolecular interactions and an unprecedented small HOMO-LUMO gap. By adopting metal complexes with extended tetrathiafulvalene (TTF) dithiolate ligands, we have realized the first example of the single-component molecular metal, $[\text{Ni}(\text{tmdt})_2]$ (tmdt = trimethylenetetrathiafulvalenedithiolate) [1,2]. Recently, direct experimental evidence of the existence of three-dimensional electron and hole Fermi surfaces was obtained by the observation of de Haas-van Alphen effect [2,3].

The neutral bis(dithiolato)gold complex has an odd number of total electrons, which makes the electromagnetic properties very attractive [2]. $[\text{Au}(\text{tmdt})_2]$ was obtained electrochemically on a platinum electrode as microcrystals. High-resolution synchrotron X-ray powder diffraction data were collected using an imaging plate detector and a Large Debye-Scherrer camera at beamline **BL02B2**. The X-ray powder pattern showed that the crystal structure of $[\text{Au}(\text{tmdt})_2]$ to be isostructural to that of $[\text{Ni}(\text{tmdt})_2]$. The lattice constants of $[\text{Au}(\text{tmdt})_2]$ were determined as $a = 6.4129(1)$, $b = 7.5514(2)$, $c = 12.1543(3)$ Å, $\alpha = 90.473(3)$, $\beta = 96.698(2)$, $\gamma = 103.008(3)^\circ$, $V = 569.21(2)$ Å³. Structure analysis was performed by the MEM/Rietveld method [4], resulting that the final R factors for 3751 points (2θ range for analysis is $2.5 - 40.0^\circ$) were $R_{\text{wp}} = 0.028$ and $R_1 = 0.073$. **Figure 1** shows the unit cell and MEM electron density of $[\text{Au}(\text{tmdt})_2]$. The molecule has an almost planar structure. The gold atom has a square planar coordination with an average Au-S distance of $2.296(2)$ Å and a S-Au-S angle of $89.9(1)^\circ$. A comparison of electron densities around the central metal atoms of $[\text{M}(\text{tmdt})_2]$ ($M = \text{Ni}, \text{Au}$) revealed a

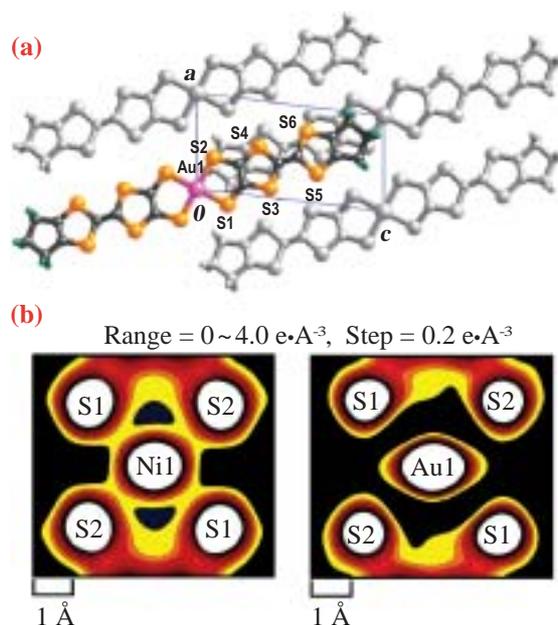


Fig. 1. (a) Simple structure of $[\text{Au}(\text{tmdt})_2]$. (b) Comparison of electron densities around central metal atoms of $[\text{M}(\text{tmdt})_2]$ ($M = \text{Ni}, \text{Au}$).

relatively small bonding electron density on Au-S bonds, which depends on the difference in the distribution of *d* electrons of the central metal atoms.

Figure 2 indicates the physical properties of [Au(tmdt)₂]. The spin susceptibilities χ_{spin} increased gradually down to ca. 130 K and decreased abruptly at ca. 110 K. For a magnetic field above 40 kOe and below 5 kOe, the static magnetic susceptibilities χ_{SQUID} were nearly constant above 50 K. These results suggest that the anomaly at ca. 110 K is an antiferromagnetic transition with the critical magnetic field of spin flipping transition between 10 and 30 kOe. The first-principle band structure calculation suggested the possibility of the nesting of warped Fermi surfaces of [Au(tmdt)₂] [5]. At the same time, the expected imperfect nesting seems to be consistent with the highly conducting properties

below 110 K. ¹H NMR studies of [Au(tmdt)₂] by Kanoda *et al.* also suggested the antiferromagnetic transition at ca. 110 K. To the best of our knowledge, [Au(tmdt)₂] is the first molecular conductor exhibiting magnetic transition above liquid nitrogen temperature without loss of its high conductivity.

We have recently succeeded in the preparation of the first “single-component alloy” [Ni_{1-x}Au_x(tmdt)₂]. The diffraction peaks of [Ni_{1-x}Au_x(tmdt)₂] shifted systematically to the lower angle with an increase in Au content (*x*), and no extra peak attributable to other phases was observed, showing that the alloys [Ni_{1-x}Au_x(tmdt)₂] with arbitrary mixing ratio could be synthesized. Single-component molecular conducting systems will provide various new materials with unprecedented electronic properties.

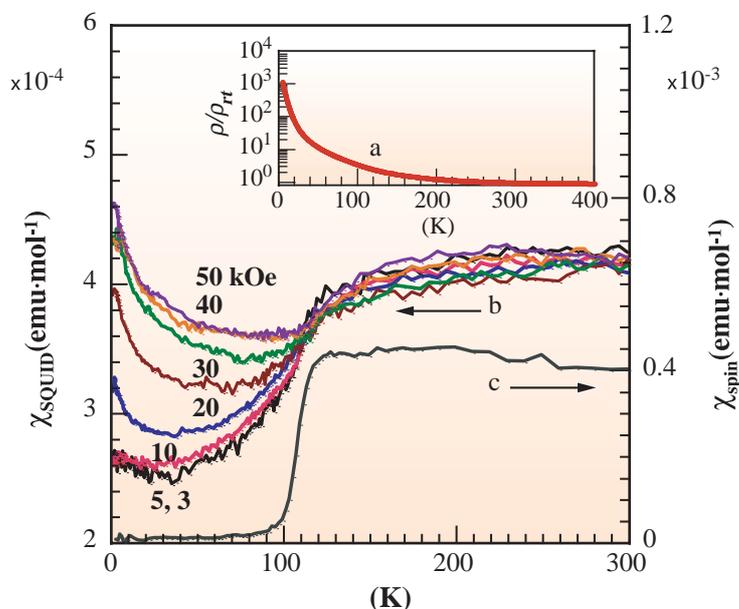


Fig. 2. Resistivities and susceptibilities of [Au(tmdt)₂]: (a) Resistivity of a compaction pellet ($\rho_{rt} = 0.02 \Omega \cdot \text{cm}$) (b) Magnetic susceptibilities by SQUID at 3, 5, 10, 20, 30, 40 and 50 kOe. (c) Spin susceptibility by ESR of polycrystalline sample ($\chi_{\text{spin rt}} = 3.8 (10^{-4} \text{ emu} \cdot \text{mol}^{-1})$).

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