

Physical properties and electronic states of cation radical salts based on unsymmetrical type metal-dithiolene complexes

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Recently, we have succeeded in preparation and crystallization of various radical cation salts based on unsymmetrical metal-dithiolene complexes $[(\text{bpy} \text{ or } \text{ppy})\text{M}(\text{S-S})_2[\text{Q}][\text{solvent}]_n$ [bpy = 2,2'-bipyridine; ppy⁻ = C-deprotonated-2-phenylpyridine; S-S = C₈H₄S₈²⁻ and C₈H₄S₆O₂²⁻; Q = PF₆⁻, BF₄⁻, AsF₆⁻ and TaF₆⁻; solvent = PhCl and PhCN; n = 0-0.5].¹⁻³ Among them, the salt $[(\text{ppy})\text{Au}(\text{C}_8\text{H}_4\text{S}_8)]_2[\text{PF}_6]$ (**1**) (Figure 1) is the first metallic molecular conductor based on the organometallic and unsymmetrical metal-dithiolene complexes, even though pressure above 0.8 GPa is required to achieve this state. In the crystal, the columnar structure is formed by two-fold head-to-head stacking of the cation radicals. Energy band calculation based on the crystal structure indicated that the salt has a quasi-one dimensional Fermi surface. However, the salt is an insulator at ambient pressure ($\rho_{\text{r.t.}} = 2.6 \Omega \text{ cm}$; $E_a = 0.03 \text{ eV}$). A metallic behavior is observed from 300 K to 100 K under 0.8 GPa, and it is retained down to 20 K under 1.6 GPa. In this work, in order to determine the ground state of the salt exactly, magnetic susceptibility, Raman and infrared reflectance spectra were measured. The spin susceptibility of **1** gradually decreased from 300 K ($\chi = 5.1 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$) to 50 K ($\chi = 4.0 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$). Below 50 K, the susceptibility exhibited a rapid decrease ($\chi = 2.8 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ at 12 K) accompanied by anisotropic temperature dependence, which is an indication of an antiferromagnetic ordering. Raman spectra of **1** showed three peaks (1520, 1490, 1460 cm⁻¹) which are due to three C=C double bonds on the dithiolene ligand. These peaks do not shift by variation in temperature (300 K -10 K), indicating that the molecular charges do not change from 300 K to 10 K. In the infrared reflectance spectrum of **1**, electronic contribution between donors was observed around 2500 cm⁻¹ for $E \parallel a$, not shown for $E \parallel b$ and c . The spectrum along the a axis also exhibited a broad vibronic peak (1100 cm⁻¹) which is explained by the charge transfer transitions occurring in a dimeric structure. Taking the results into account, we concluded that the salt has the quasi-one dimensional electronic character and the ground state is a Mott insulating state close to the metal-insulator boundary under ambient pressure with +1 of formal charge on the dimer.

Other radical cation salts including $[(\text{ppy})\text{Au}(\text{C}_8\text{H}_4\text{S}_6\text{O}_2)]_2[\text{BF}_4]$ and $[(\text{bpy})\text{Pt}(\text{C}_8\text{H}_4\text{S}_8)][\text{BF}_4]$ (Figure 1) have similar molecular arrangements of **1**. In spite of the similarity, their conducting properties ($\rho_{\text{r.t.}} > 10^5 \Omega \text{ cm}$) and electronic states were quite different from those of **1**. We will

also discuss their conducting and other physical properties.

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3. K. Kubo *et al.*, *Inorg. Chim. Acta* **2002**, 336, 120-124.

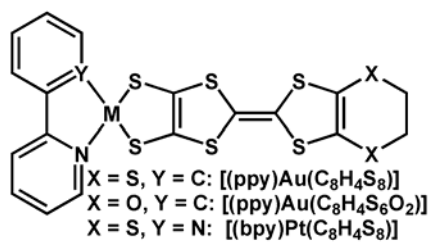


Figure 1. Schematic drawing of unsymmetrical donor molecules.