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A New Honeycomb Assemblage of a Trisdithiolene Vanadium(IV) Complex, $(PPh_4)_2[V(dbddto)_3](C_6H_4Cl_2)(hexane)_{0.5}$

Takashi Okubo,*[2] Ryoko Maeda,[3] Mitsuru Kondo,[4] Tadaoki Mitani,[2] and Susumu Kitagawa[1]
[1]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-851*
[2]*School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292*
[3]*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-1397*
[4]*Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422-8529*

(Received September 16, 2005; CL-051183; E-mail: okubo-t@jaist.ac.jp)

A new trisdithiolene vanadium(IV) complex has been synthesized and characterized. The enantiomeric anion units, $[V(dbddto)_3]^{2-}$, are packed so closely that the sulfur-rich planar ligands stack to form a honeycomb sheet structure, resulting in the creation of large cavities (12 × 5.5 Å) for guests. The magnetic susceptibilities show an existence of antiferromagnetic interaction in spite of the large interatomic separation of the vanadium ions (V···V distance = 11.069 Å (av.)), associated with the interaction between the stacking ligand pathway in the honeycomb sheet.

Molecular self-assemblies by noncovalent bonds, such as π–π interaction, S···S contact, and hydrogen bonding,[1] have emerged as an attractive approach in crystal engineering for functional materials. Especially assemblages of metal complexes with dithiolene ligands have received considerable attention as new conductive[2] and magnetic materials,[3] in which most assemblies of the dithiolene complexes have been associated with the planarity of the whole molecules, having an advantage to form the column structures to give the conductive paths. This structural requirement limits the metal cations to late transition-metal ones such as Ni, Pd, Pt, and Au, while early transition-metal dithiolene complexes have been excluded excepting some metal–dithiolene materials[4] because of the propensity to form a nonplanar octahedral geometry. Our synthetic strategy for a new assemblage is to utilize a self-assembly of complexes with an octahedral center through the π–π stacking and/or S···S contacts of the ligand parts. For the purpose, we selected a dithiolene ligand, $dbddto^{2-}$ (2,5-dithioxobenzo[1,2-*d*:3,4-*d*′]bis[1,3]dithiolene-7.8-dithiolate),[5] which has a sulfur-rich large planar structure and successfully synthesized a new porous assemblage consisting of a 2-D infinite honeycomb structure. In this paper, we describe the assembled structure constructed by the π–π stacking and magnetic properties through the stacking of the ligand parts.

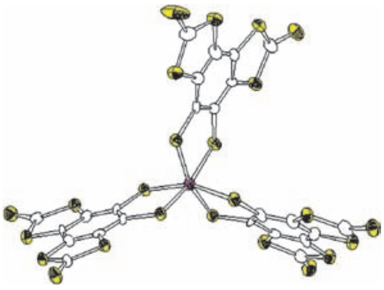

Figure 1. ORTEP drawing of an anionic moiety, $[V(dbddto)_3]^{2-}$, of **1**: V, pink; S, yellow; C, white.

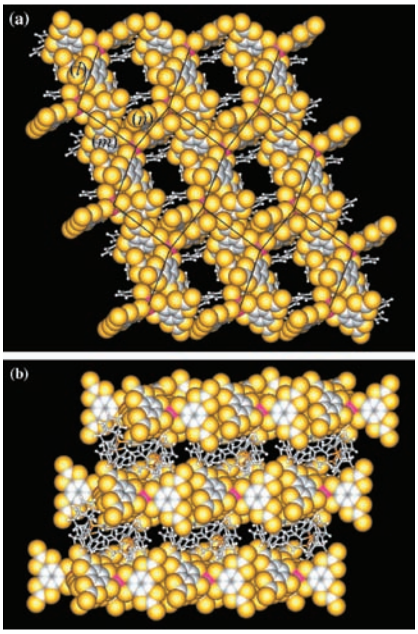

Figure 2. Extended honeycomb sheet structure of **1** represented with space-filling spheres of the anionic moieties, $[V(dbddto)_3]^{2-}$, and with cylinders of cationic moieties, PPh_4^+, along *a* axis (a) and *c* axis (b). Crystal solvents, *o*-dichlorobenzene and hexane, are omitted for clearly.

The complex, $(PPh_4)_2[V(dbddto)_3](C_6H_4Cl_2)(hexane)_{0.5}$ (**1**), was synthesized by a reaction of $H_2dbdedto$[6] with bis(acetylacetonato)oxovanadium (IV) in the presence of PPh_4Cl in an acetone solution. The mixture was refluxed for one hour, and the precipitate obtained was collected by filtration. The single crystal suitable for a single crystal X-ray crystallography[7] was grown by diffusion of *n*-hexane into a *o*-dichlorobenzene solution of **1** in a glass tube. Figure 1 shows an ORTEP drawing of an anionic part of **1**. The coordination geometry around the central V(IV) ion is approximately octahedron with six sulfur atoms of three bidentate $dbddto^{2-}$ ligands, all of which form a five-membered chelate ring. The average V–S bond distance is 2.37 Å, which is close to those of the reported $V(dithiolene)_3{}^{2-}$ complexes[8] (2.378(4) Å for $V(dmit)_3{}^{2-}$, 2.375(3) for $V(dmt)_3{}^{2-}$, and 2.36(1) Å for $V(mnt)_3{}^{2-}$), and longer than those of $V(dddt)_3{}^{-}$ (2.340(4) Å) and $V(S_2C_2Ph_2)_3$ (2.337(6) Å).[9] In addition, it is well known that the coordination geometry of the trisdithiolene metal complexes is classified to an octahedron, a trigonal prism, or the intermediate between the two geometries.

The geometry can be characterized by trans S–M–S bond angle and the trigonal twist angle.[8] The average values of the trans S–M–S angles and the twist angles of **1** are 158.0° and ca. 39°, respectively. These values mean that the V center of **1** is based on the distorted octahedron rather than the trigonal-prism.

The two enantiomeric units of Λ- and Δ-$[V(dbddto)_3]^{2-}$ interact with the intermolecular π–π stacking of the $dbddto^{2-}$ ligands. The separations between the stacking dbddto ligands are (*l*) 3.472, (*m*) 3.638, and (*n*) 3.392 Å, which are comparable to those of common organic conductive materials such as TTF (tetrathiafulvalene) derivatives (ca. 3.6 Å). The 2-D layer with a honeycomb pattern is formed in the *bc* plane as shown in Figure 2a. The sheet is constructed by the alternation of the enantiomeric units, and the V ions are located in the lattice points of the honeycomb sheet. The V···V separations between the neighbor enantiomeric $[V(dbddto)_3]^{2-}$ anions in the same layer are (*l*) 10.731(2), (*m*) 12.137(3), and (*n*) 10.341(2) Å. While, the interlayer nearest-neighbor V···V separation is 15.206 Å, and there are no direct S···S contacts between the anionic layers (Figure 2b). In addition, the assemblies of the honeycomb sheets create large cavities (12 × 5.5 Å) as shown in Figure 2a, which are occupied by the *o*-dichlorobenzene and hexane molecules. On the other hand, counter cations, PPh_4^+, are located between the honeycomb sheets (Figure 2b), preventing the interactions between the 2-D honeycomb layers, in which it is noteworthy that the counter cations are not bunging the channels as shown in Figure 2a.

To study interactions between paramagnetic d^1 centers of vanadium(IV) ions, magnetic susceptibility of **1** was measured from 300 to 2.0 K. Figure 3 shows a plot of the molar magnetic susceptibilities χ_M vs. temperature. The χ_M value increases with decreasing temperature, reaching a maximum of 0.044 emu·mol^{-1} at 3.0 K, and then rapidly decreases. The decrease of the χ_M value below 3 K apparently indicates the existence of an antiferromagnetic interaction in this complex. The data follow the Curie–Weiss law above 10 K yielding the Weiss constant $\theta = -3.5$ K. As shown in Figure 2, this complex has a 2-D honeycomb lattice. On each lattice point of the honeycomb is located at the vanadium(IV) center. The experimental data in the range of 10–300 K have been fitted with an equation of a 2-D extended honeycomb lattice based on the spin Hamiltonian $H = -2J\Sigma S_i S_{i+1}$,[10] where it is assumed that all the vanadium–vanadium magnetic interactions are identical. The *g* value of 1.97 obtained by the EPR measurement in solid state at 77 K was used as the fitting parameter. The best-fit parameters obtained from **1** by minimizing the *R* factor $\Sigma(\chi_M{}^{obs} - \chi_M{}^{calc})^2/\Sigma(\chi_M{}^{obs})^2$ were $J = -0.89\,cm^{-1}$ and $R = 8.42 \times 10^{-6}$. In addition, the magnetic behavior was also analyzed by fitting the experimental susceptibility to Weng's equation for an infinite spin linear chain,[11] since one vanadium–vanadium separation (12.137(3) Å) in this honeycomb lattice is remarkably larger than the other two separations (10.341(2) Å and 10.731(2) Å). This model resulted in a good fit to the data; the best-fit parameter is $J = -2.24\,cm^{-1}$ ($R = 4.61 \times 10^{-6}$).

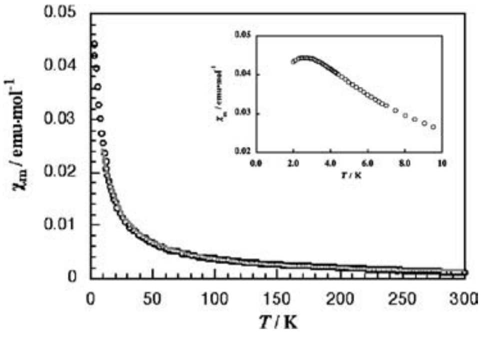

Figure 3. Temperature dependence of molar magnetic susceptibility χ_M for **1**. Line is the fit result of the honeycomb equation for the data.

All the obtained *J* values apparently indicate the existence of the weak antiferromagnetic interaction within the honeycomb layer. Consequently, the analysis shows that **1** undergoes the appreciable intermolecular antiferromagnetic interactions in spite of the large interatomic separation of the V ions. The interaction would be generated through the pathway via the π–π stacking of the dbddto ligands.

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7 Crystal data: $M_r = 1977.53$, triclinic, $P\bar{1}$ (#2), $a = 15.206(2)$, $b = 16.308(3)$, $c = 18.4972(8)$ Å, $\alpha = 107.9751(13)$, $\beta = 95.8669(14)$, $\gamma = 106.1170(10)^\circ$, $V = 4101.9(10)$ Å^3, $Z = 2$, μ(Mo Kα) = 0.71069 Å, $T = -40\,^\circ C$, $R_1 = 0.0874$, ${}_wR_2 = 0.2307$ for 7874 reflections with $I > 2\sigma$ and 967 parameters. Data collection was performed on Rigaku –CCD Mercury system. The structure was solved by direct method using SIR-92. CCDC 283717.

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