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Note

Crystal structure of a supramolecular cation salt (adamantylammonium$^+$)$_2$(benzo[18]crown-6)$_2$[Pd(dmit)$_2$]$^{2-}$(acetone)$_2$

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ABSTRACT

Single crystal of supramolecuar cation salt (adamantylammonium$^+$)$_2$(benzo[18]crown-6)$_2$[Pd(dmit)$_2$]$^{2-}$(-acetone)$_2$ were synthesized by an electrochemical crystallization. In the crystal, two supramolecular cations and two acetones and one [Pd(dmit)$_2$]$^{2-}$ dianion were crystallographically asymmetric. Molecular rotation of adamantyl groups was suggested from anisotropic thermal factors in the X-ray analysis at 173 K.

1. Introduction

A large number of the artificial molecular machines, involving molecules such as unidirectional molecular motor and molecular gyroscope, have been studied [1–7]. We have reported a solid state supramolecular rotator (*m*-FAni$^+$)(DB[18]crown-6)[Ni(dmit)$_2$] (*m*-FAni$^+$ = *m*-fluoroanilinium$^+$, DB[18]crown-6 = dibenzo[18]crwon-6, dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate) which exhibited a ferroelectric transition at 346 K due to the flip-flop motion of the *m*-FAni$^+$ cation causing an inversion of the dipole moment [8]. Next targets should be to (i) reduce the potential energy barrier for the molecular rotation and (ii) explore the multifunctional materials based on the molecular rotation. Supramolecular rotators formed by adamantylammonium$^+$ (AD–NH$_3^+$) cation and bulky stators such as DB[18]crown-6 and dicyclohexano[18]crown-6 preserved enough space for rotation of the cation in the solid state, and exhibited smaller energy barrier for the rotation than that of the flip-flop motion of the anilinium$^+$ cation with C_2 rotation axis, due to the higher symmetry of the AD–NH$_3^+$ [9,10]. Magnetically and electronically active [M(dmit)$_2$]$^{n-}$ (M = Ni, Pd, Pt; $0 < n \leqslant 2$) anion can coexist with the supramolecular rotators. We reported various supramolecular cation salts with the [Ni(dmit)$_2$]$^-$ anion exhibiting various magnetic properties such as ferromagnetic [11–13], antiferromagnetic [14–16], spin ladder behavior [17,18]. Furthermore, salts of partially oxidized [M(dmit)$_2$]$^{n-}$ molecules provided various superconductors and metals such as (TTF)[Ni(dimt)$_2$]$_2$ (TTF = tetrathiafulvalene) [19,20]. Such hybrid solids between the molecular rotators and magnetic spin or conduction electrons of the [Ni(dmit)$_2$]$^-$ anion has a potential to show peculiar electronic functions coupled with the molecular motion [21,22]. Generally, [Pd(dmit)$_2$]$^{n-}$ anion can form different electronic structures from that of [Ni(dmit)$_2$]$^{n-}$ anion [20], and is expected to provide new functional materials based on the electronic structures correlating with molecular rotations. In this report, we present a novel single crystal of a supramolecular cation with the [Pd(dmit)$_2$]$^{2-}$ anion, (AD–NH$_3^+$)$_2$(benzo[18]crown-6)$_2$-[Pd(dmit)$_2$]$^{2-}$(acetone)$_2$ (**1**).

2. Experimental

2.1. Materials

All chemicals were of reagent grade, purchased from Wako Pure Chemical Industries, Ltd. and used without further purifition. (adamantylammonium$^+$)(BF$_4^-$) and (Bu$_4$N)[Pd(dmit)$_2$] was prepared as reported in the literatures [9,23].

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2.2. Preparation of (AD–NH_3^+)$_2$(benzo[18]crown-6)$_2$[Pd(dmit)$_2$]$^{2-}$(acetone)$_2$ (**1**)

Black needle single crystals of (adamantylammonium$^+$)$_2$(benzo[18]crown-6)$_2$[Pd(dmit)$_2$]$^{2-}$(acetone)$_2$ (**1**) were prepared by the electrocrystallization of acetone (15 ml) solution of (Bu_4-N)[Pd(dmit)$_2$] (5.5 mg, 5.6 mmol), benzo[18]crwon-6 (26 mg, 107 mmol), and (adamantylammonium$^+$)(BF_4) (17 mg, 110 mmol) at a constant current of 1 μA for one month under nitrogen atmosphere at 30 °C. The composition of **1** was confirmed by the X-ray crystallographic analysis.

2.3. Crystal structure determination

Crystallographic data of the single crystal **1** was collected using a Rigaku R-AXIS RAPID diffractometer with Mo Kα radiation (λ = 0.71075 Å) from a graphite monochromator at 173 K. The structure was solved by the direct method (SIR 2004) and expanded using Fourier techniques and refined on F^2 by the full-matrix least-squares method (SHELXL97) compiled into Yadokari-XG [24–26]. The parameters were refined using anisotropic temperature factors, except for the hydrogen atoms, which were refined using the riding model with a fixed C–H bond distance of 0.95 Å. The crystallographic data of salt **1** at 173 K are summarized in Table 1.

3. Result and discussion

Fig. 1 shows a packing motif of crystal **1** at 173 K. In this crystal, two AD–NH_3^+ cations, two benzo[18]crwon-6, one [Pd(dmit)$_2$]$^{2-}$, and two acetones were crystallographically asymmetric. Two crystallographically independent benzo[18]crown-6 and AD–NH_3^+ cation molecules were arranged parallel to the $(a + b) - c$ plane (Fig. 2(a)). The [Pd(dmit)$_2$]$^{2-}$ molecules filled the crystalline spaces between the supramolecular cations (Fig. 2(b)), and were isolated each other by the benzo[18]crown-6 and AD–NH_3^+ cation molecules. Two acetone molecules positioned near the AD–NH_3^+ cation.

Table 1
Crystallographic data for **1**.

	1
Chemical formula	$C_{64}H_{96}N_2O_{14}PdS_{10}$
Formula weight	1544.43
T (K)	173
Crystal size (mm^3)	0.40 × 0.14 × 0.10
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	22.7209(6)
b (Å)	11.2713(3)
c (Å)	28.7172(7)
β (°)	96.5229(8)
V (Å^3)	7306.7(3)
Z	4
D_{calc} (g cm^{-1})	1.404
F(000)	3248
μ (mm^{-1})	6.01
θ (°)	6.04–54.96
No. of reflections collected	69513
Independent reflections	16698
Observed reflections with $I > 2.00\ s(I)$	11970
R_{int}	0.0527
$R[I > 2\sigma(I)]$[a]	0.0525
$_wR$ (all data)[b]	0.1415
Goodness-of-fit (GOF) on F^2	1.047

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $R_w^2 = \Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2) - (0.0679P)^2 - 4.8480P$, where $P = (F_o^2 - 2F_c^2)/3$.

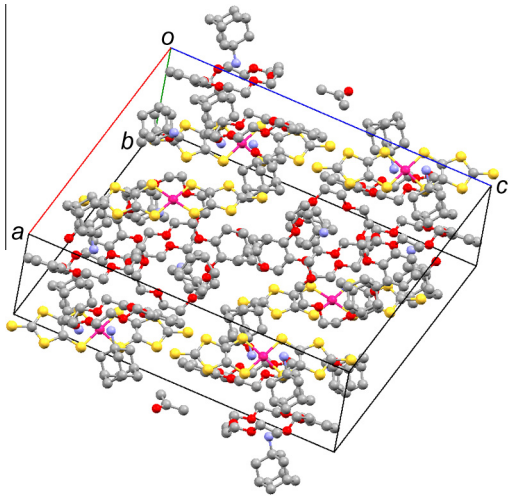

Fig. 1. Packing diagram in crystal **1**. Hydrogen atoms were omitted for clarity. Pd, pink; S, yellow, O, red; C, grey; N, blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

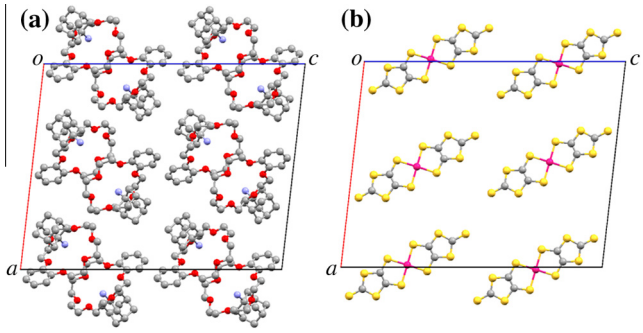

Fig. 2. Molecular arrangements of (a) the supramolecular cations and (b) [Pd(dmit)$_2$]$^{2-}$ molecules parallel to the *ac* plane.

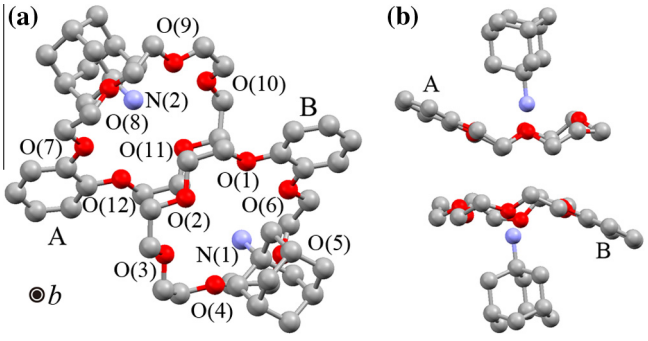

Fig. 3. Molecular arrangements of adamantylammonium$^+$ cations and benzo[18]crwon-6 molecules. (a) Viewed along the *b* axis. (b) Side view in the asymmetric unit. Hydrogen atoms were omitted for clarity.

Fig. 3 shows the arrangement of AD–NH_3^+ cations and benzo[18]crown-6 molecules, A and B, in the asymmetric unit. Two benzo[18]crwon-6 molecules formed a dimer structure. Each phenyl ring arranged opposite position. Face-to-face π–π interactions between the phenyl rings were observed neither within nor between the dimers. Distances between the ammonium moieties of the AD–NH_3^+ cations and the six oxygen atoms of the benzo[18]-crown-6 molecules are summarized in Table 2. Shortest distances between N–$H^+\cdots$O atoms were observed at N(1)–$H^+\cdots$O(2)