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Supramolecular cation of an acyclic polyether: potassium(pentaethylene glycol) in a molecular conducting nickel dithiolate salt

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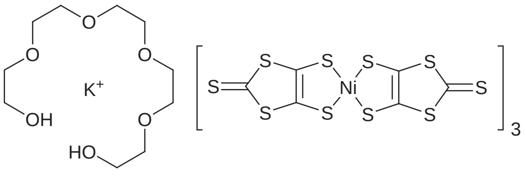
The X-ray structural analysis of the title compound revealed the formation of segregated [Ni(dmit)$_2$] (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) columns and dimeric K$^+_2$[PEG]$_2$ (PEG = pentaethylene glycol) supramolecular cations in the crystal; the interaction between K$^+$ and acyclic PEG was found to be weaker that that between K$^+$ and cyclic polyether 18-crown-6.

Composite organic polymer electrolytes are promising candidates for applications in high energy density electrochemical batteries.[1] Polyethylene oxide (PEO) derivatives especially have been extensively examined as non-crystalline polymeric ion-conducting materials. The crystal structure of a uniaxially oriented PEO–NaI ionic conductor has been reported previously.[2] The structure of a single crystal of PEO as an ion-transport environment has not been reported. The classification of the nature of the coordination in PEO–ion moieties will assist in the construction of organic crystalline ionic conductors.

Organic π-molecular systems have a tendency to form a one-dimensional columnar stack structure, in which electrons can move along the stack through overlap of the π-systems.[3] We have been attempting to construct electron–ion hybrid conducting systems based on crystalline molecular conductors, and have reported the formation of supramolecular cation (SC$^+$) structures within organic conductors.[4] For example, a typical cation complex of a cyclic polyether, K$^+$(18-crown-6), can be incorporated into a highly conducting [Ni(dmit)$_2$] (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) salt as K$^+$(18-crown-6)[Ni(dmit)$_2$]$_3$ with a room temperature conductivity (σ_{RT}) of 0.08 S cm^{-1}.[5] We report here the incorporation of a cation complex of an acyclic polyether as a new SC$^+$ unit in a [Ni(dmit)$_2$] organic conductor, in which the potassium cation is included within the cyclic pentaethylene glycol (PEG) (Scheme 1).

Single crystals of K$^+$(PEG)[Ni(dmit)$_2$]$_3$ were prepared by the electrocrystallization method.† The unit cell contains three crystallographically independent [Ni(dmit)$_2$] units **A–C** and one K$^+$(PEG) unit. A segregated non-uniform [Ni(dmit)$_2$] column is observed with the stacking order of **A–C–B** along the *c*-axis; the molecular planes of [Ni(dmit)$_2$] are nearly parallel to the *ab*-plane (Fig. 1). Each [Ni(dmit)$_2$] molecule is connected by side-by-side S···S interactions, forming a layer structure within the *ac*-plane, and the K$^+$(PEG) units exist in the interlayer space. The plane of K$^+$(PEG) is inclined at 45° to the *b*-axis. A weak interatomic contact is found between the terminal sulfur of [Ni(dmit)$_2$] **C** and K$^+$(PEG), K$^+$···S(30) = 3.282(7) Å. This distance is *ca*. 0.15 Å longer than the sum of the van der Waals radius of S and the ionic radius of K$^+$.[6]

The mean interplanar distances of [Ni(dmit)$_2$] within a column are 3.50 (**A–B**), 3.65 (**A–C**), and 3.45 Å (**B–C**) with overlap modes of slipped metal–ring (**A–B**), metal–metal (**A–C**), and metal–ring (**B–C**) types, respectively [Fig. 1(b)]. A



K$^+$(PEG)[Ni(dmit)$_2$]$_3$

Scheme 1

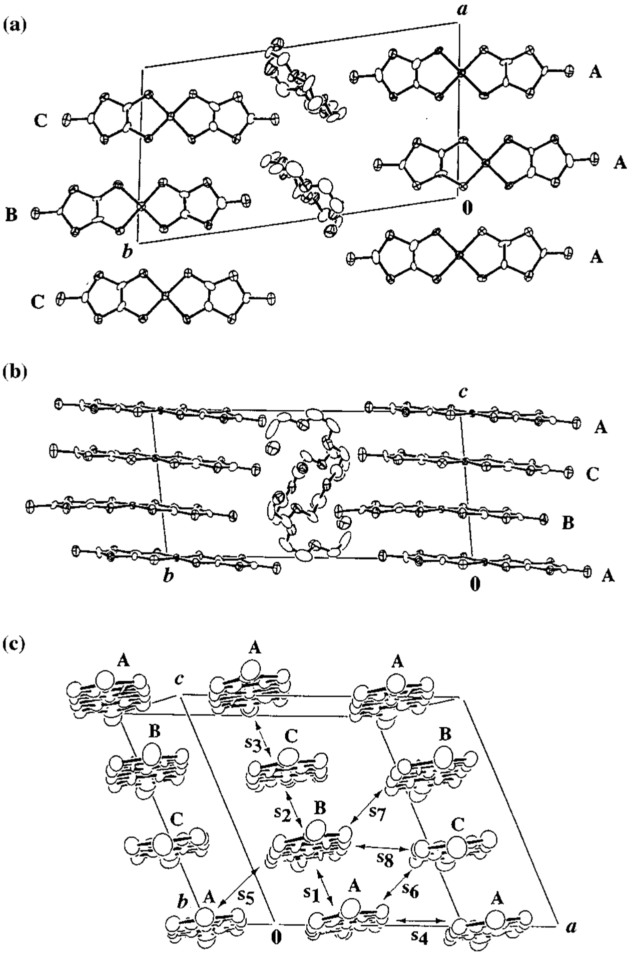


Fig. 1 Crystal structure of K$^+$(PEG)[Ni(dmit)$_2$]$_3$, (a) viewed along the *c*-axis, (b) along the *a*-axis. (c) [Ni(dmit)$_2$] layer viewed along the long axis of [Ni(dmit)$_2$] together with the numbering scheme of overlap integrals (s$_1$–s$_8$).

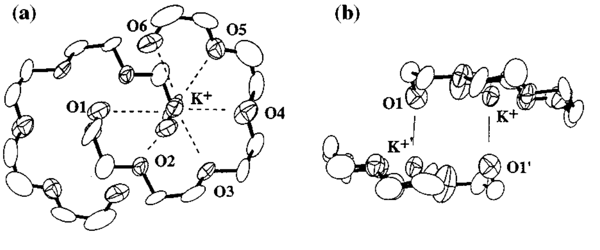


Fig. 2 Supramolecular cation (SC^+) unit of $K^+_2(PEG)_2$, (a) viewed along the perpendicular direction to the K^+(PEG) plane, (b) side view of K^+(PEG) dimer with the oxygen atom numbering scheme. Primes indicate atoms generated by passing through the inversion center. Dashed and solid lines indicate the $K^+\cdots O$ interactions.

similar trimer structure was also observed in K^+(18-crown-6)[Ni(dmit)$_2$]$_3$ with an **A–B–A** stacking arrangement. Fig. 1(c) shows the intermolecular interactions within the [Ni(dmit)$_2$] layer viewed along the long axis of [Ni(dmit)$_2$]. The overlap integrals (s_1–$s_8 \times 10^{-3}$) were obtained by using extended Hückel molecular orbital calculatons.[7] Since the **A–B** interaction ($s_1 = 19.07$) is significantly larger than **A–C** ($s_2 = -1.05$) and **B–C** ($s_3 = 2.47$), the [Ni(dmit)$_2$] column mainly consists of **A–B** dimers and weakly interacting **C** molecules between the **A–B** dimers in the order –(**A–B**)–**C**–(**A–B**)–. In the case of K^+(18-crown-6)[Ni(dmit)$_2$]$_3$, the intratrimer s value ($s_{\text{intra}} = 15.3$) indicated the formation of tightly bounded **A–B–A** trimers within the column. By replacing the SC^+ unit of the cyclic [K^+(18-crown-6)] with the acyclic [K^+(PEG)], the stacking mode of [Ni(dmit)$_2$] within the column is changed from the trimer to the dimer.

Within the *ab*-plane, the [Ni(dmit)$_2$] molecules form a sheet-like structure of **–A–A–A–** and **–B–C–B–** arrangements along the *a*-axis [Fig. 1(a)]. Owing to the symmetry of the LUMO of [Ni(dmit)$_2$], the interstack interactions along the *a*-axis are small ($s_4 = 0.10$ and $s_8 = 0.20$), resulting in weak interactions within the sheets. The interactions along the $a + c$ direction ($s_5 = 0.50$, $s_6 = 0.86$, and $s_7 = -0.33$) also do not effectively increase the interstack interactions.

Fig. 2 shows the SC^+ unit viewed along the orthogonal [Fig. 2(a)] and parallel [Fig. 2(b)] directions to the molecular plane of K^+(PEG). The SC^+ unit has two K^+(PEG) units which are related by the inversion center, and are connected by two axial K^+ (K^+)$\cdots$O1′ (O1) interactions [solid lines in Fig. 2(b)] to form a dimerized $K^+_2(PEG)_2$ supramolecular cation. The K^+ is coordinated by six PEG oxygen atoms [dashed lines: $K^+\cdots O1 = 3.00(1)$, $K^+\cdots O2 = 2.90(1)$, $K^+\cdots O3 = 2.81(1)$, $K^+\cdots O4 = 2.86(1)$, $K^+\cdots O5 = 2.90(1)$, $K^+\cdots O6 = 2.77(2)$ Å] and an axial oxygen of another PEG unit [solid lines: $K^+\cdots O1 = 2.86(2)$ Å]. The average $K^+\cdots O$ distance within the PEG unit (2.87 Å) is in the same range as the sum of the van der Waals radius of oxygen and the ionic radius of K^+ (2.85 Å). In the case of K^+(18-crown-6), the average $K^+\cdots O$ distance (2.804 Å) is*ca.* 0.07 Å shorter than that in the acyclic K^+(PEG) system, indicating a weaker cation binding ability of the acyclic polyether relative to the corresponding cyclic one due to the *macrocyclic effect*.[8] The weaker cation binding ability (10 000×) should be more appropriate to ionic conductivity in the solid.

The K^+(PEG)[Ni(dmit)$_2$]$_3$ salt showed semiconducting behavior over the temperature range 150–300 K, which is consistent with the non-uniform dimerized stack of [Ni(dmit)$_2$]. Fig. 3 shows the log(resistivity/Ω cm) *vs.* T^{-1}/K^{-1} plots of (i) K^+(PEG)[Ni(dmit)$_2$]$_3$ and (ii) K^+(18-crown-6)[Ni(dmit)$_2$]$_3$.[5] The room temperature conductivity ($\sigma_{RT} = 0.001$ S cm^{-1}) is two orders of magnitude lower that that of K^+(18-crown-6)[Ni(dmit)$_2$]$_3$ ($\sigma_{RT} = 0.08$ S cm^{-1}). The activation energy E_a (0.17 eV) of the acyclic system is intermediate in range between the high (0.28 eV) and low (0.12 eV) temperature semiconducting phases of K^+(18-crown-6)[Ni(dmit)$_2$]$_3$.

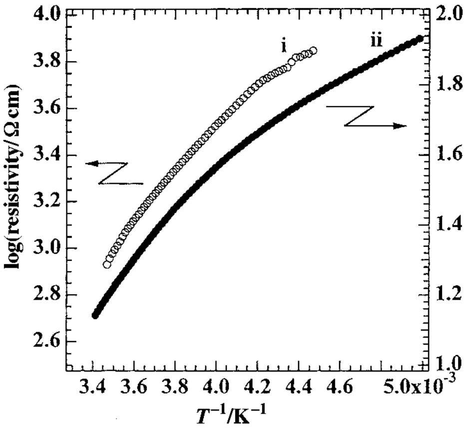


Fig. 3 Log(resistivity/Ω cm) *vs.* T^{-1}/K^{-1} plots of (i) K^+(PEG)[Ni(dmit)$_2$]$_3$ (○) and (ii) K^+(18-crown-6)[Ni(dmit)$_2$]$_3$ (●).

In conclusion, the supramolecular cation of acyclic K^+(PEG) has been incorporated into the electrically conducting [Ni(dmit)$_2$] salt. The coordination ability of PEG to K^+ is smaller that that of 18-crown-6 due to the loss of macrocyclic effect, which helps to construct the ion-conducting field within the crystalline solid. Attempts to insert shorter or longer polyethylene glycol chains into the conducting [Ni(dmit)$_2$] salts are now in progress to construct ion-conducting paths.

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Notes and references

† The constant current (1.5 μA) electrocrystallization of (n-Bu$_4$N)[Ni(dmit)$_2$] (19.6 mg), KClO$_4$ (42.3 mg), and PEG (140 mg) in acetonitrile (18 ml) gave black-plate single crystals. The crystal data are as follows: $C_{28}H_{20}O_6S_{30}Ni_3K$, $M = 1629.5$, crystal dimensions $0.75 \times 0.25 \times 0.02$ mm^3, Rigaku AFC-7R diffractometer, Mo-Kα radiation ($\lambda = 0.71069$ Å), triclinic, space group $P\bar{1}$ (no. 2), $a = 12.700(5)$, $b = 21.826(5)$, $c = 11.166(7)$ Å, $\alpha = 91.40(3)$, $\beta = 113.54(3)$, $\gamma = 99.14(3)$°, $U = 2788(2)$ Å^3, $T = 298$ K, $Z = 2$, $D_c = 1.941$ g cm^{-3}, $F(000) = 1638.0$, μ(Mo-Kα) 22.41 cm^{-1}, Lorentz polarization and absorption corrections applied, 13374 reflections measured, 12797 independent reflections, 4391 reflections with $I > 3.00\sigma(I)$ used in refinement. Calculations were performed using teXsan crystallographic software packages with refinements based on F. Weighting scheme employed: $w = 1/\sigma^2(F_o)$. Solution by direct methods: non-hydrogen atoms refined anisotropically, and no refinement of hydrogen atoms. $(\Delta\rho)_{\max} = 1.22$ e Å^{-3}, $(\Delta\rho)_{\min} = -0.97$ e Å^{-3}, $R = 0.080$, $R' = 0.083$. CCDC 182/1061.

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