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Crystal Structures of $M(DCNQIs)_2$ (DCNQIs=N,N'-dicyanoquinonediimines; M=Li, Na, K, NH_4, Cu, Ag)

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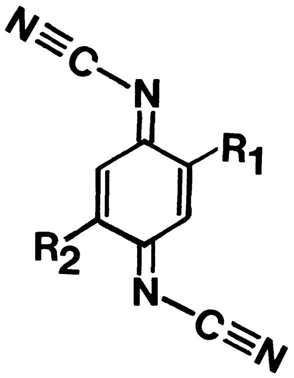
Crystal structures of highly conducting title compounds were determined. The basic structure of all compounds consists of uniform face-to-face columns of acceptor molecules. These columns are connected to each other through N-coordinated cations. The geometry of coordination depends on the counter cation.



1: $R_1=R_2=CH_3$
2: $R_1=CH_3$, $R_2=Cl$

It has been the first step toward the molecular superconductor based on π-conjugated moleucules to suppress the Peierls instability and stabilize the metallic state. We consider that typical successful examples are observed in the two-dimensional electronic structure (BEDT-TTF salts),$^{1)}$ and the "multi-Fermi surface" system with the parallel band structure (TTF[Ni(dmit)$_2$]$_2$).$^{2)}$ Recently, Cu(2,5-DM-DCNQI)$_2$ (2,5-DM-DCNQI= 2,5-dimethyl-N,N'-dicyanoquinonediimine; **1**) was reported to be extremely high conductive down to 1.3 K without metal-semiconductor transition.$^{3)}$ In the crystal of this compound, 2,5-DM-DCNQI columns are connected to each other by tetrahedrally coordinated copper atoms. Although origin of the stable metallic state of this system has been an open question, the 2,5-DM-DCNQI molecule whose N atoms in two N-cyano groups can form the coordinate bond with the copper atom has suggested possibility of a new way to the three-dimensional π-conjugated system, that is, three-dimensional contact of organic $p\pi$ molecules through metal $d\pi$ orbitals. In order to reveal two faces of DCNQIs as "acceptor" and "ligand", we first take up 2,5-substituted DCNQIs (**1** and **2**)$^{4)}$ and report here crystal structures of their anion radical salts.

Anion radical salts of **1** and **2** were electrochemically obtained as black needles. A solution containing **1** (or **2**) and appropriate electrolyte ($LiClO_4$, $NaClO_4$, KPF_6, NH_4PF_6, $[Cu(CH_3CN)_4]BF_4$, and $AgBF_4$) in acetonitrile was electrolyzed with a constant current (30-70 μA) under N_2. Crystal data of these anion radical

Table 1. Crystal data of $M(DCNQIs)_2$

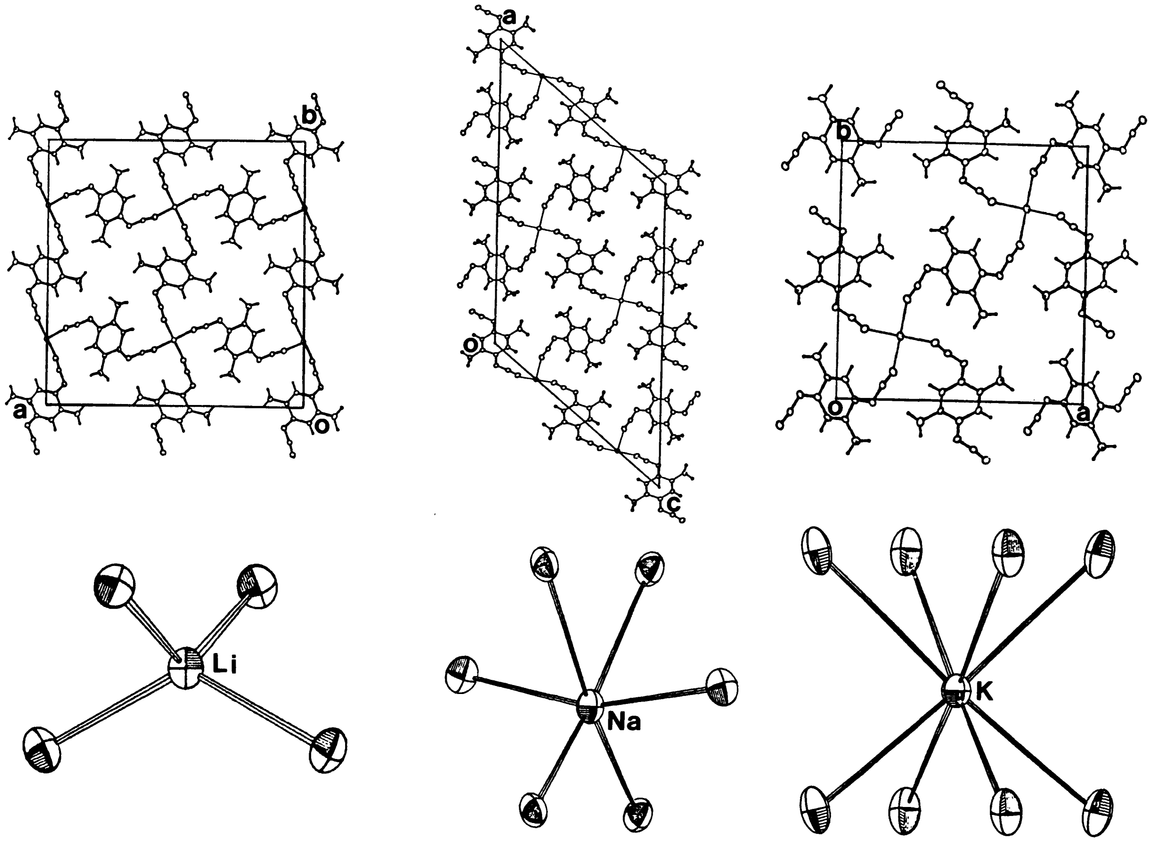
M	DCNQI	Space group[a)]	Lattice constants		Z	R value
Cu	1	$I4_1/a$	a=21.548(9),	c=3.871(2) Å	4	0.068
Cu	2	$I4_1/a$	a=21.599(8),	c=3.823(2)	4	0.069
Ag	1	$I4_1/a$	a=22.348(10),	c=3.818(1)	4	0.111
Li	1	$I4_1/a$	a=21.790(11),	c=3.834(1)	4	0.053
Li	2	$I4_1/a$	a=21.851(8),	c=3.790(1)	4	0.060
Na	1	C2/c	a=31.16(3), c=21.89(3),	b=3.788(2), β=132.19(8)°	4	0.074
K	1	P4/n	a=15.989(7),	c=3.767(2)	2	0.070
NH_4	2	P4/n	a=16.309(5),	c=3.792(1)	2	0.068

a) Origin at $\bar{1}$ for $I4_1/a$ and P4/n.

Table 2. Structural parameters of $M(DCNQIs)_2$

M	DCNQI	Interplanar distance/ Å	M•••N distance /Å	Point symmetry of M's positions[a)]	Coordination number
Cu	1	3.188	1.976	$\bar{4}$ (a)	4
Cu	2	3.150	1.969	$\bar{4}$ (a)	4
Ag	1	3.207	2.308	$\bar{4}$ (a)	4
Li	1	3.177	2.054	$\bar{4}$ (a)	4
Li	2	3.154	2.055	$\bar{4}$ (a)	4
Na	1	3.236/3.195	2.386/2.447/2.814	2 (e)	6
K	1	3.223	2.891/3.046	4 (c)	8
NH_4	2	3.268	N•••N; 2.906 N•••H; 0.96	$\bar{4}$ (a)	4

a) Wyckoff notation in parenthesis.



(a) (b) (c)

Fig. 1. Crystal structure and geometry of coordination of $M(2,5\text{-}DM\text{-}DCNQI)_2$. (a) M=Li, (b) M=Na, (c) M=K.

salts are listed in Table 1.

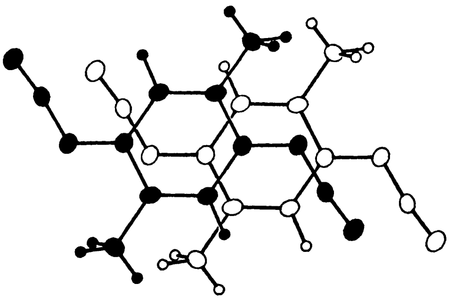


Fig. 2. Mode of overlapping. (Na salt)

The basic structure of all these compounds consists of uniform face-to-face stacks of DCNQI molecules (Fig. 1). The DCNQI molecule is almost planar. In the salts of asymmetric DCNQI **2**, which are isostructural with the corresponding salts of symmetric DCNQI **1**, we observe the anion of **2** on the inversion center superposed upon its inverted image and there is an orientational disorder. Interplanar distances in the acceptor column are in the range of 3.15-3.27 Å (Table 2), which are almost equal to that in TTF-TCNQ (3.17 Å).5) The mode of stacking is the "ring-double bond" type, which is often observed in the anion radical salts of TCNQs (Fig. 2).

These DCNQI columns in M(DCNQIs)$_2$ are connected to each other by M cations coordinated to nitrogen atoms (in the case of NH_4 salt, hydrogen-bonded NH_4^+ ion). The geometry of coordination and M•••N distances depend on the counter cation (Table 2 and Fig. 1). The repeating distance along the stacking axis (b axis for the Na salt and c axis for others; 3.77-3.87 Å) is sparingly affected by the cation radius, while those along the axes perpendicular to the stacking axis vary with the counter cation.

The type of crystal structures (space group) is considered to change with the cation radius. The Li and Ag salts are isostructural with the Cu salt and the counter cation is tetrahedrally coordinated.6) The Ag•••N distance (2.308 Å) in Ag(2,5-DM-DCNQI)$_2$ is in the range of those in [Ag(CH_3CN)$_4$]ClO_4 (2.18-2.33 Å).7) In the Na salt, symmetry of the crystal system is lowered to monoclinic. Four DCNQI columns around sodium ion are interrelated to each other by a two-fold axis and six neighboring nitrogen atoms occupy positions at the corner of a distorted octahedron. Both of the K and NH_4 salts take the same space group symmetry (P4/n). A potassium ion at the position with 4 symmetry shows eight-coordination, while tetrahedral configuration of nitrogen atoms is observed around an ammonium ion at the position with $\bar{4}$ symmetry.

The most interesting and important point in this DCNQI system is the nature of the coordination. Considering crystal structures, the conduction path is formed mainly by overlapping of pπ orbitals (LUMO; lowest unoccupied molecular orbital) of DCNQI. If the atomic orbitals of the counter cation interact with the LUMO of DCNQI, the original one-dimensional system with a pair of planar Fermi surfaces will turn into the "multi-Fermi surface" system with several (gathered) plane-like Fermi surfaces 2) or the multi-dimensional system with closed Fermi surfaces. If not, the electronic structure will be described in the quarter filled one-dimensional band picture. Even in this case, however, interchain contacts through the coordinated cation will increase an elastic constant and make the system resist the periodical lattice distortion.

In the case of M=Li, Na, K, and NH_4, the atomic orbitals of the counter cation would not mix with the LUMO of DCNQI. These salts are conductive at room temperature (Table 3). With lowering temperature, the electrical conductivity

Table 3. Electrical properties of M(DCNQIs)$_2$

M	DCNQI	$\sigma_{R.T.}$/S cm^{-1}	
Cu	1	1000-2000	metallic down to 1.5 K
Cu	2	700	metal-semiconductor transition at ca. 210 K
Ag	1	100	metal-semiconductor transition around ca. 150 K
Li	1	300	metal-semiconductor transition around ca. 200 K
Li	2	300	metal-semiconductor transition around ca. 150 K
Na	1	60-130	metal-semiconductor transition around ca. 200 K
K	1	70	metal-semiconductor transition around ca. 250 K
NH_4	2	60	metal-semiconductor transition around ca. 200 K

shows weak metallic behavior followed by the metal-semiconductor transition with broad transition temperature range.

Copper and silver have d-orbitals which can interact with the LUMO of DCNQI, and take several oxidation states. The possibility of pπ-dπ mixing depends on the valence state of M and overlap integrals. If all M ions take M^+ state, the d-orbitals are fully occupied and the energy levels of the d-orbitals lie below the Fermi energy. This means that the one-dimensional band structure near the Fermi energy would not be affected by the d-orbitals. On the other hand, if M takes a mixed valence state, the d-orbitals are partially occupied and there exist d-levels crossing the Fermi level. In this case, the tetrahedral crystal field removes the orbital degeneracy, leaving the d_{xy}, d_{yz}, and d_{xz} orbitals as the partially occupied atomic orbitals. The band structure near the Fermi energy will be approximately described by a simple tight-binding model including the LUMO of DCNQI and the d_{xy}, d_{yz}, and d_{xz} orbitals of M.

Detailed studies (X-ray crystallographic analysis at low temperature, electronic sturucture of the Cu salts, thermal expansion of M(DCNQIs)$_2$,8) and pressure-dependence of electrical conductivity of Cu(2,5-DM-DCNQI)$_2$9)) will be reported elsewhere.

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