The Crystal Structure of (BEDT-TTF)$_4$[Ni(CN)$_4$]

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Synopsis. The crystal of (BEDT-TTF)$_4$[Ni(CN)$_4$] (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) belongs to the triclinic $P\bar{1}$ with the lattice constants of a=10.994(2), b=16.443(2), c=9.703(1) Å, α=97.85(1), β=115.15(1), γ=95.94(1)°. In the crystal, there exists the face to face overlap of the BEDT-TTF molecules along the [201] direction. The intermolecular interaction by the short S···S contact is also observed along the [$\bar{2}$01] direction.

Recently Saito et al. have found the superconductivity of (BEDT-TTF)$_2$[Cu(NCS)$_2$] at an ambient pressure.[1] The charge-transfer complexes between BEDT-TTF and metal complexes have many interesting properties such as the magnetic property in addition to the electrical conductivity, because such metal ion can have the incompletely occupied electron shell. From this point of view, we investigated the magnetic and electronic properties and the crystal structures of several complexes.[2-4] In the present paper, we report the crystal structure of (BEDT-TTF)$_4$[Ni(CN)$_4$].

Table 1. Positional Parameters (×10^4) and Equivalent Isotropic Thermal Parameters (Å×10^2) with e.s.d's in Parentheses

Atom	x	y	z	B_{eq}[a]
S(1)	6982(2)	3210(1)	11779(2)	428(5)
S(2)	8571(2)	3401(1)	10025(2)	459(5)
S(3)	6248(2)	1389(1)	10876(2)	586(6)
S(4)	8086(2)	1596(1)	8720(2)	438(5)
S(5)	9547(2)	5380(1)	11662(2)	492(5)
S(6)	8027(2)	5125(1)	13483(2)	503(6)
S(7)	10730(2)	7130(1)	13153(2)	525(6)
S(8)	8964(2)	6828(1)	15350(2)	752(8)
C(9)	8067(5)	3868(3)	11372(6)	352(2)
C(10)	7076(5)	2300(3)	10692(7)	335(2)
C(11)	7781(5)	2383(3)	9871(6)	330(15)
C(12)	6651(10)	589(4)	9793(10)	879(37)
C(13)	7528(13)	707(4)	9261(15)	1629(72)
C(14)	8494(6)	4696(3)	12077(6)	367(16)
C(15)	9699(5)	6227(3)	13053(6)	358(16)
C(16)	9016(6)	6108(3)	13898(6)	417(17)
C(17)	10613(11)	7871(4)	14598(11)	1021(42)
C(18)	9622(11)	7757(4)	15057(12)	1138(47)
S(19)	2675(2)	4136(1)	2898(2)	448(5)
S(20)	4084(2)	4330(1)	954(2)	457(5)
S(21)	1677(2)	2329(1)	1741(2)	429(5)
S(22)	3359(2)	2569(1)	−596(2)	472(5)
S(23)	5052(2)	6316(1)	2528(2)	437(5)
S(24)	3673(2)	6068(1)	4483(2)	438(5)
S(25)	5891(2)	8137(1)	3626(2)	441(5)
S(26)	4317(2)	7817(1)	6048(2)	484(5)
C(27)	3675(5)	4794(3)	2377(6)	369(16)
C(28)	2594(5)	3235(3)	1664(6)	326(15)
C(29)	3234(5)	3326(3)	757(6)	352(15)
C(30)	1760(10)	1573(4)	297(10)	970(39)
C(31)	2426(15)	1673(5)	−452(15)	1712(72)
C(32)	4094(5)	5626(3)	3048(6)	356(16)
C(33)	5084(5)	7205(3)	3762(6)	344(15)
C(34)	4464(5)	7084(3)	4677(6)	344(15)
C(35)	5975(7)	8848(3)	5277(7)	534(2)
C(36)	4686(7)	8766(4)	5468(7)	517(21)
Ni(37)	10000	10000	5000	307(5)
C(38)	9613(5)	9862(3)	6665(6)	379(16)
C(39)	8128(6)	9951(3)	3776(6)	386(17)
N(40)	9358(6)	9761(4)	7665(6)	602(20)
N(41)	6978(5)	9918(3)	3054(6)	492(2)

a) $B_{eq}=\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}d_i^*d_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Experimental

Black hexagonal plate-like crystals (0.25×0.30×0.05 mm) were grown by electrochemical crystallization of BEDT-TTF in 1,1,2-trichloroethane by using K_2[Ni(CN)$_4$] as a supporting electrolyte. D_m (1.80 g dm^{-3}) was measured by flotation and D_c is 1.89 g cm^{-3} for $C_{44}H_{32}N_4S_{32}Ni$. Reflection data# were measured by Rigaku automated four-circle diffractometer AFC-5R. Crystal data: triclinic, space group $P\bar{1}$, a=10.994(2), b=16.443(2), c=9.703(1) Å, α=97.85(1), β=115.15(1), γ=95.94(1)°, and Z=1. 5473 measured reflections, $2\theta_{max}$=126°, $-13\leqslant h\leqslant 13$, $-19\leqslant k\leqslant 19$, $0\leqslant l\leqslant 11$, and R_{int}=0.03. The crystal structure was determined by the Monte-Carlo direct method with the aids of MULTAN78 program system,[5] and refined by the full matrix least squares by using 4268 non-zero unique reflections (Cu $K\alpha$, $|F_o|>3\sigma(F_o)$). Intensities were corrected for the absorption effect by the analytical method, linear absorption coefficient μ=105.45 cm^{-1} and transmission factor in the range 0.043 to 0.59. The final R value was 0.062, S=2.34, $w=1/\sigma^2(F^2)$, $(\Delta/\sigma)_{max}$=0.40 for B_{31} of C(39) atom, and $\Delta\rho_{max}$=0.7 eÅ^{-3}. The atomic parameters were given in Table 1.

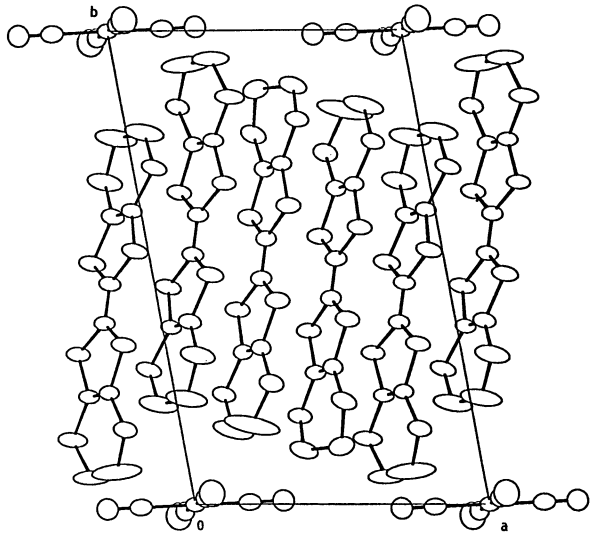


Fig. 1. Crystal structure of (BEDT-TTF)$_4$[Ni(CN)$_4$] projected on the c axis.

The complete F_o-F_c data are deposited as Document No. 8962 at the Office of the Editor of Bull. Chem. Soc. Jpn.

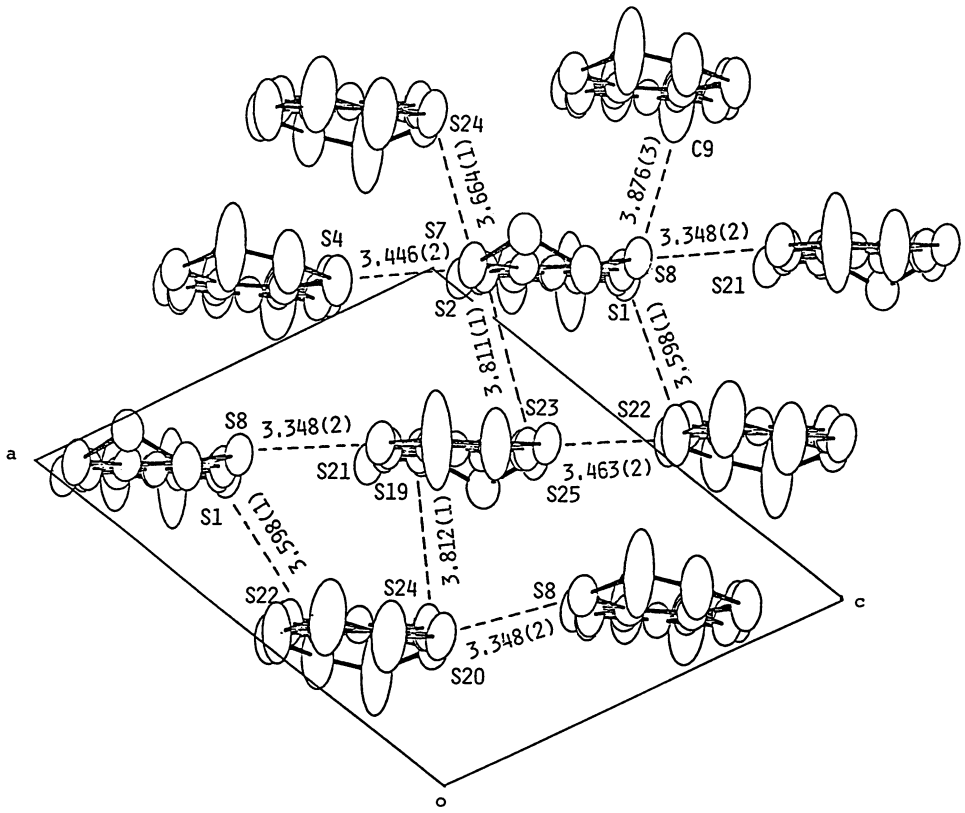


Fig. 2. Intermolecular overlaps in the BEDT-TTF sheet viewed along the molecular long axis.

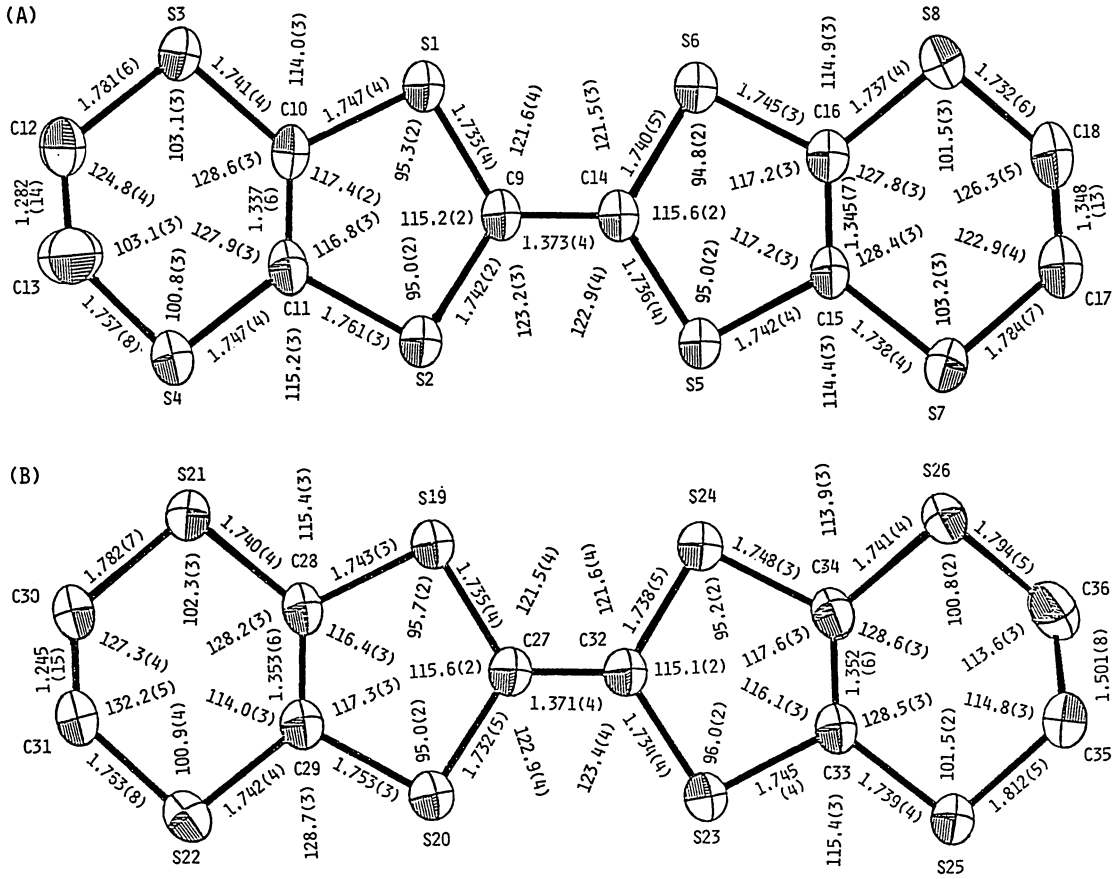


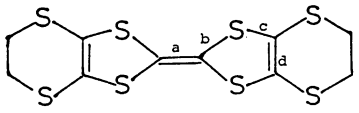
Fig. 3. Molecular dimensions for BEDT-TTF in (BEDT-TTF)$_4$[Ni(CN)$_4$].

Results and Discussion

Figure 1 shows the crystal structure viewed along the *a* axis. There are two independent BEDT-TTF molecules in an asymmetric unit and the Ni atom of $[Ni(CN)_4]^{2-}$ ion is located on the inversion center. The BEDT-TTF molecules are stacked along the [201] direction. This crystal is isostructural to the crystal of $(BEDT\text{-}TTF)_4[Pt(CN)_4]$.[6] Figure 2 shows the arrangement on the (010) plane viewed nearly along the long molecular axis. The interstacking contacts are longer than the sum of the Pauling's van der Waals radii of two sulfur atoms (3.70 Å). Several S–S contacts shorter than 3.70 Å were observed along the [$\bar{2}$01] direction. The $[Ni(CN)_4]^{2-}$ anion has the square planar structure with the average Ni–C and C–N distances of 1.874(5) and 1.146(6) Å and the C–Ni–C angle of 88.3(3)°. The geometries of two crystallographycally independent BEDT-TTF molecules are shown in Fig. 3 and no significant difference could be found between them. One ethylene group of the BEDT-TTF molecule is out of the molecular plane and two carbons in the ethylene plane are located at the opposite side of the molecular plane, while another ethylene groups are in the molecular plane. In Table 2, the bond lengths of the TTF moiety in two BEDT-TTF molecules are compared with those in other BEDT-TTF salts. The average values in $(BEDT\text{-}TTF)_4[Ni(CN)_4]$ are similar to those in half-ionized BEDT-TTF and its charge can be regarded as $\rho=1/2$.

Table 2. Comparison of Averaged Bond Length (Å) of BEDT-TTF ($\rho=0$, 1/2, and 1)[7] (The bond lengths b, c, and d are averaged values)

	Molecule A	Molecule B	$\rho=0$	$\rho=1/2$	$\rho=1$
a	1.373(4)	1.371(4)	1.312(12)	1.365(4)	1.38(3)
b	1.74(1)	1.73(1)	1.757(7)	1.740(2)	1.72(1)
c	1.75(1)	1.75(1)	1.754(8)	1.750(2)	1.73(1)
d	1.34(1)	1.35(1)	1.332(7)	1.345(3)	1.37(2)



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