Crystal Structure of (ImH)[Ni(dmit)$_2$]$_2$ with Intercolumnar Interaction through an Imidazolium Counter Ion

Akira Miyazaki, Akira Izuoka, and Tadashi Sugawara*
Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
(Received February 28, 1992)

Synopsis. In the crystal of semiconductive salt, (ImH)[Ni(dmit)$_2$]$_2$ (ImH=imidazolium, H$_2$dmit=4,5-dimercapto-1,3-dithiol-2-thione), Ni(dmit)$_2$ molecules are dimerized and stacked in columns, with two types of intercolumnar interaction through an imidazolium counter cation. One is based on three-centered S···NH···S type hydrogen bonds, and the other is van der Waals contacts between imidazolium cation and dmit ligand.

Introduction of intercolumnar interaction ought to have essential effect on the structure and physical properties of low-dimensional systems. In the crystal of [Ni(*R,R*-chxn)$_2$Br]Br$_2$, for example, two neighboring Ni–Br–Ni columns are tightly connected through hydrogen bonds between amino groups of the ligands and bromide counter anion. Increase in dimensionality through these intercolumnar hydrogen bonds suppresses Peierls distortion of columns, resulting in appearance of a SDW state.[1]

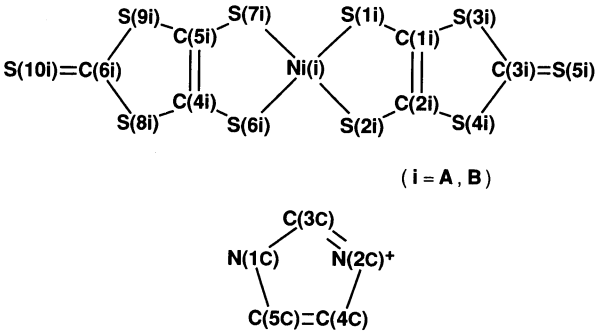
Imidazolium ion, which has two proton-donating sites (iminium groups), may connect conduction columns consisted of molecules with proton-accepting sites, such as Ni(dmit)$_2$ (accepting sites=thiocarbonyl groups). Furthermore, the imidazolium ring is isoelectronic to a cyclopentadienyl anion with the opposite formal charge. Therefore it might have some π-coordination type interaction between the imidazolium ring and thiocarbonyl groups of Ni(dmit)$_2$ in the conduction column.

From these points of view, we investigated the crystal structure and physical properties of imidazolium salt of the Ni(dmit)$_2$ complex.

Experimental

n-Bu$_4$N[Ni(dmit)$_2$] was prepared according to the literature.[2] (ImH)BPh$_4$ was obtained as white precipitates by adding aqueous solutions of NaBPh$_4$ to aqueous imidazole hydrochloride, and recrystallized from a mixture of acetone and water (1 : 1).[3] (ImH)[Ni(dmit)$_2$]$_2$ salts were grown as black plates (typically 0.6×0.1×0.03 mm) by galvanostatic (I=1 μA) oxidization of *n*-Bu$_4$N[Ni(dmit)$_2$] (30 mg) in acetonitrile (25 ml), using (ImH)BPh$_4$ (0.39 g) as a supporting electrolyte, a platinum plate (10×5×0.1 mm) as an anode.

X-Ray diffraction data were collected at room temperature by a Rigaku AFC-5 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). Crystal data: $(C_3N_2H_5)[Ni(C_3S_5)_2]_2$, M=971.80, triclinic, $P\bar{1}$, a=12.209(2), b=16.537(3), c=8.179(3) Å, α=91.64(2), β=112.43(2), γ=89.74(2)°, V=1525.7(6) Å^3, Z=2, D_c=2.115 g cm^{-3}, μ=25.8 cm^{-1}. 6021 reflections ($2\theta<55°$) were measured using ω-scan ($2\theta<40°$) and ω–2θ scan ($40\leq 2\theta<55°$) methods, and 4555 independent reflections ($|F_o|>3\sigma(F_o)$) were used for the analysis. Absorption correction was applied analytically[4] ($0.74<T<0.92$). The structure was solved by direct methods



using SHELXS 86,[5] and refined by the block-diagonalized least-squares method. All of non-H atoms were refined anisotropically, and H atoms isotropically. Final R=0.045, R_w=0.043, S=1.28, $w^{-1}=\sigma(F_o)^2+0.0002|F_o|^2$, max($\Delta/\sigma$)=0.34, max$|\Delta\rho|$=0.58 e Å^{-3}. The calculation were performed on a FACOM A-70 computer using the UNICS-III system[6] and ORTEP II.[7] The atomic parameters, selected bond lengths and angles are given in Tables 1 and 2, respectively.[8]

The DC electrical conductivity along the long axis of the crystals (c axis) was measured down to 180 K with a four-probe method. Electrical contacts were made by gold wire (25 μm) and gold paste.

Results and Discussion

The ratio of acceptor and counter ion (Ni(dmit)$_2$: ImH$^+$) was 2 : 1, and the crystals showed a semiconductive behavior (σ_{RT}=0.03 S cm^{-1}, E_A=0.2 eV). Figure 1 shows a unit cell viewed along the c axis. There are two crystallographically independent Ni(dmit)$_2$ molecules (A and B) within an asymmetric unit. Molecules A and B are approximately planar (max deviation from the least-squares plane: Molecule A: 0.047(1) [S(4A)], B: 0.081 (2) Å [S(10B)]), and no significant differences are found between their structures. Molecules A and B are stacked separately along the c axis to form column I and II (Fig. 2). The Ni(dmit)$_2$ molecules are parallel but dimerized in each column. The separations between molecules are for column I: 3.512(3), 3.675(3) Å; and for column II: 3.549(3), 3.574(3) Å. As for ImH$^+$ cation, the imidazolium ring is planar (max deviation from the least-squares plane: 0.002(5) Å [C(3C)]) and has pseudo C_{2v} symmetry within experimental errors.

There are several S···S contacts between columns (minimum: 3.499(2) Å [S(6A)···S(6B)^{i}][9]), whose distances are shorter than the twice of Bondi's van der Waals radius of sulfur atom (3.60 Å).[10] One ImH$^+$ cation is surrounded by six Ni(dmit)$_2$ molecules (Fig. 2). In the column I, a pair of Ni(dmit)$_2$ molecules are tied through a three-centered hydrogen bond between the iminium

Table 1. Positional Parameters ($\times10^4$ for Ni, S, C; $\times10^3$ for H) and Equivalent Isotropic Thermal Parameters (Å^2), with esd's in Parentheses

Atom	x	x	z	B_{eq}[a)]	Atom	x	x	z	B_{eq}[a)]
Ni(A)	−99(1)	447(1)	2895(1)	1.98(2)	S(4B)	5543(1)	3205(1)	5022(2)	2.79(4)
S(1A)	−1585(1)	1263(1)	2153(2)	2.48(4)	S(5B)	4019(1)	4405(1)	5971(2)	3.52(5)
S(2A)	1067(1)	1297(1)	4852(2)	2.38(4)	S(6B)	6314(1)	−112(1)	2416(2)	2.63(4)
S(3A)	−1848(1)	2934(1)	3535(2)	2.72(4)	S(7B)	3790(1)	−606(1)	2178(2)	2.43(4)
S(4A)	590(1)	2980(1)	6002(2)	2.96(4)	S(8B)	6522(1)	−1780(1)	972(2)	2.74(4)
S(5A)	−975(2)	4378(1)	5904(2)	4.17(5)	S(9B)	4185(1)	−2247(1)	781(2)	2.65(4)
S(6A)	1353(1)	−393(1)	3591(2)	2.46(4)	S(10B)	5628(2)	−3434(1)	−309(2)	4.03(5)
S(7A)	−1268(1)	−372(1)	905(2)	2.61(4)	C(1B)	3990(4)	1999(3)	4098(6)	2.2(1)
S(8A)	1556(1)	−2065(1)	2126(2)	2.76(4)	C(2B)	5109(4)	2213(3)	4264(6)	2.1(1)
S(9A)	−879(1)	−2034(1)	−387(2)	2.75(4)	C(3B)	4251(4)	3491(3)	5253(6)	2.5(2)
S(10A)	604(2)	−3477(1)	−314(2)	4.03(6)	C(4B)	5753(4)	−1045(3)	1658(6)	2.1(1)
C(1A)	−1011(4)	2084(3)	3524(6)	2.1(1)	C(5B)	4649(4)	−1266(3)	1583(6)	2.2(1)
C(2A)	144(4)	2095(3)	4701(6)	2.1(1)	C(6B)	5450(4)	−2533(3)	447(6)	2.5(2)
C(3A)	−755(5)	3476(3)	5176(7)	2.7(2)	N(1C)	3175(5)	5041(3)	1491(8)	5.5(2)
C(4A)	767(4)	−1193(3)	2195(6)	2.1(1)	N(2C)	1600(5)	4612(3)	−460(8)	5.4(2)
C(5A)	−395(4)	−1188(3)	989(6)	2.3(1)	C(3C)	2222(6)	4642(4)	1215(9)	4.6(2)
C(6A)	426(4)	−2574(3)	433(7)	2.5(2)	C(4C)	2170(6)	5011(4)	−1298(8)	4.7(2)
Ni(B)	4896(1)	467(1)	2959(1)	2.01(2)	C(5C)	3202(6)	5297(4)	−41(1)	5.3(3)
S(1B)	3429(1)	1050(1)	3360(2)	2.40(4)	H(N1)	410(6)	505(4)	257(9)	7.9(20)
S(2B)	6016(1)	1536(1)	3786(2)	2.59(4)	H(N2)	68(6)	443(4)	−108(9)	8.5(21)
S(3B)	3181(1)	2746(1)	4668(2)	2.80(4)					

a) $B_{eq}=(4/3)(B_{11}a\cdot a+B_{12}a\cdot b+B_{13}a\cdot c+\cdots)$.

Table 2. Selected Bond Lengths (Å) and Angles (°), with esd's in Parentheses

Ni(A)–S(1A)	2.160(2)	Ni(B)–S(1B)	2.158(2)	S(1A)–Ni(A)–S(2A)	93.2(1)	S(1B)–Ni(B)–S(2B)	93.4(1)
Ni(A)–S(2A)	2.170(2)	Ni(B)–S(2B)	2.167(2)	S(1A)–Ni(A)–S(6A)	178.4(1)	S(1B)–Ni(B)–S(6B)	177.1(1)
Ni(A)–S(6A)	2.156(2)	Ni(B)–S(6B)	2.159(2)	S(1A)–Ni(A)–S(7A)	85.9(1)	S(1B)–Ni(B)–S(7B)	86.6(1)
Ni(A)–S(7A)	2.154(2)	Ni(B)–S(7B)	2.164(2)	S(2A)–Ni(A)–S(6A)	88.4(1)	S(2B)–Ni(B)–S(6B)	87.5(1)
S(1A)–C(1A)	1.708(5)	S(1B)–C(1B)	1.714(5)	S(2A)–Ni(A)–S(7A)	178.6(1)	S(2B)–Ni(B)–S(7B)	179.1(1)
S(2A)–C(2A)	1.709(5)	S(2B)–C(2B)	1.711(5)	S(6A)–Ni(A)–S(7A)	92.6(1)	S(6B)–Ni(B)–S(7B)	92.6(1)
S(3A)–C(1A)	1.736(5)	S(3B)–C(1B)	1.741(5)	Ni(A)–S(1A)–C(1A)	102.4(2)	Ni(B)–S(1B)–C(1B)	102.0(2)
S(3A)–C(3A)	1.720(6)	S(3B)–C(3B)	1.720(6)	Ni(A)–S(2A)–C(2A)	101.8(2)	Ni(B)–S(2B)–C(2B)	102.0(2)
S(4A)–C(2A)	1.744(5)	S(4B)–C(2B)	1.747(5)	C(1A)–S(3A)–C(3A)	97.3(3)	C(1B)–S(3B)–C(3B)	97.1(3)
S(4A)–C(3A)	1.732(6)	S(4B)–C(3B)	1.722(6)	C(2A)–S(4A)–C(3A)	97.4(3)	C(2B)–S(4B)–C(3B)	97.0(3)
S(5A)–C(3A)	1.648(6)	S(5B)–C(3B)	1.667(6)	Ni(A)–S(6A)–C(4A)	103.0(2)	Ni(B)–S(6B)–C(4B)	102.9(2)
S(6A)–C(4A)	1.693(5)	S(6B)–C(4B)	1.693(5)	Ni(A)–S(7A)–C(5A)	103.2(2)	Ni(B)–S(7B)–C(5B)	102.4(2)
S(7A)–C(5A)	1.702(5)	S(7B)–C(5B)	1.695(5)	C(4A)–S(8A)–C(6A)	97.3(3)	C(4B)–S(8B)–C(6B)	97.0(3)
S(8A)–C(4A)	1.742(5)	S(8B)–C(4B)	1.740(5)	C(5A)–S(9A)–C(6A)	97.3(3)	C(5B)–S(9B)–C(6B)	97.0(3)
S(8A)–C(6A)	1.737(6)	S(8B)–C(6B)	1.733(6)	S(1A)–C(1A)–S(3A)	122.5(3)	S(1B)–C(1B)–S(3B)	122.6(3)
S(9A)–C(5A)	1.726(5)	S(9B)–C(5B)	1.746(5)	S(1A)–C(1A)–C(2A)	120.9(4)	S(1B)–C(1B)–C(2B)	121.4(4)
S(9A)–C(6A)	1.729(6)	S(9B)–C(6B)	1.730(6)	S(3A)–C(1A)–C(2A)	116.6(4)	S(3B)–C(1B)–C(2B)	116.0(4)
S(10A)–C(6A)	1.642(6)	S(10B)–C(6B)	1.641(6)	S(2A)–C(2A)–S(4A)	123.2(3)	S(2B)–C(2B)–S(4B)	123.0(3)
C(1A)–C(2A)	1.370(7)	C(1B)–C(2B)	1.367(7)	S(2A)–C(2A)–C(1A)	121.7(4)	S(2B)–C(2B)–C(1B)	121.2(4)
C(4A)–C(5A)	1.385(7)	C(4B)–C(5B)	1.377(7)	S(4A)–C(2A)–C(1A)	115.1(4)	S(4B)–C(2B)–C(1B)	115.7(4)
N(1C)–C(3C)	1.28(1)	N(2C)–C(3C)	1.29(1)	S(3A)–C(3A)–S(4A)	113.6(3)	S(3B)–C(3B)–S(4B)	114.2(3)
N(1C)–C(5C)	1.35(1)	N(2C)–C(4C)	1.34(1)	S(3A)–C(3A)–S(5A)	123.1(4)	S(3B)–C(3B)–S(5B)	121.4(3)
C(4C)–C(5C)	1.36(1)	N(2C)–H(N2)	1.08(8)	S(4A)–C(3A)–S(5A)	123.3(4)	S(4B)–C(3B)–S(5B)	124.4(3)
N(1C)–H(N1)	1.14(7)			S(6A)–C(4A)–S(8A)	123.7(3)	S(6B)–C(4B)–S(8B)	123.1(3)
				S(6A)–C(4A)–C(5A)	121.2(4)	S(6B)–C(4B)–C(5B)	120.7(4)
				S(8A)–C(4A)–C(5A)	115.1(4)	S(8B)–C(4B)–C(5B)	116.2(4)
				S(7A)–C(5A)–S(9A)	123.2(3)	S(7B)–C(5B)–S(9B)	122.8(3)
				S(7A)–C(5A)–C(4A)	120.1(4)	S(7B)–C(5B)–C(4B)	121.4(4)
				S(9A)–C(5A)–C(4A)	116.7(4)	S(9B)–C(5B)–C(4B)	115.8(4)
				S(8A)–C(6A)–S(9A)	113.6(3)	S(8B)–C(6B)–S(9B)	114.0(3)
				S(8A)–C(6A)–S(10A)	122.5(3)	S(8B)–C(6B)–S(10B)	122.5(3)
				S(9A)–C(6A)–S(10A)	124.0(3)	S(9B)–C(6B)–S(10B)	123.5(3)
				C(3C)–N(1C)–C(5C)	110.8(7)	C(3C)–N(2C)–C(4C)	109.2(7)
				N(2C)–C(4C)–C(5C)	107.1(7)	N(1C)–C(5C)–C(4C)	104.2(8)
				N(1C)–C(3C)–N(2C)	108.7(7)	C(3C)–N(2C)–H(N2)	126(4)
				C(3C)–N(1C)–H(N1)	135(4)	C(4C)–N(2C)–H(N2)	123(4)
				C(5C)–N(1C)–H(N1)	111(4)		

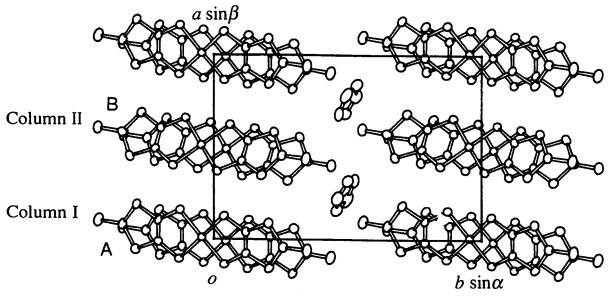


Fig. 1. Crystal structure of (ImH)[Ni(dmit)$_2$]$_2$ viewed along the *c* axis.

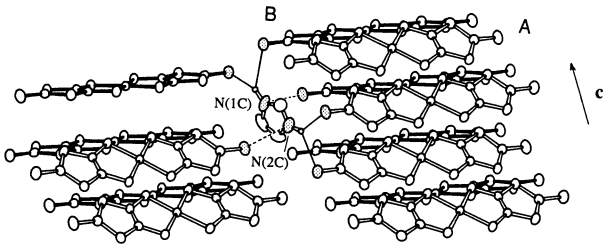


Fig. 2. Stacking of Ni(dmit)$_2$ molecules. Hydrogen bonds (solid lines) and van der Waals contacts (dashed lines) between Ni(dmit)$_2$ molecule and ImH$^+$ cation are also shown. Molecules within column II are designated by black bonds.

hydrogen [H(N2)] of this cation and thiocarbonyl groups of the ligands (solid lines in Fig. 2, N(H)···S: 3.418(7) [N(2C)···S(5A)^{iii}], 3.546(7) Å [N(2C)···S(10A)^{iv}]),[11] which may be the reason for the dimerized structure of the column I. Another three-centered hydrogen bond is also found among the Ni(dmit)$_2$ molecules (B) in each neighboring columns II (N(H)···S: 3.594(7) [N(1C)···S(5B)], 3.374(7) Å [N(1C)···S(5B)^{ii}]).[11] Two other Ni(dmit)$_2$ molecules are located perpendicular to the imidazolium ring. Close N···S contacts between the imidazolium ring and the thiocarbonyl groups are also shown in Fig. 2 (dashed lines), and their N···S distances (3.322(7) [N(1C)···S(10B)^{v}], 3.397(7) Å [N(2C)···S(10A)^{vi}]) are nearly the same as the sum of van der Waals radii of N and S atoms (1.55+1.80=3.35 Å).[12,13] Thus the neighboring columns turn out to be connected by these two types of contacts each other.

In summary, Ni(dmit)$_2$ molecules form dimeric pairs within columns, and the neighboring columns are connected, not only by van der Waals contacts between S atoms, but also by intermolecular contacts through imidazolium cation. The latter contacts are classified into two types, hydrogen bonds and van der Waals contacts as described above. The van der Waals contact through the cation is particularly interesting from a viewpoint of connecting electronic structure of neighboring columns.

This work was partly supported by a Grant-in-Aid No. 02453006 from the Ministry of Education, Science and Culture.

References

1) K. Toriumi, Y. Wada, T. Mitani, S. Bandow, M. Yamashita, and Y. Fujii, *J. Am. Chem. Soc.*, **111**, 2341 (1989).
2) G. Steimecke, H. J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus Sulfur*, **7**, 49 (1979).
3) This procedure is similar to the preparation of ammonium tetraphenylborate and other BPh_4 salts of protonated amines. See, for example: W. J. Westerhaus, O. Knop, and M. Falk, *Can. J. Chem.*, **58**, 1355 (1980).
4) W. R. Busing and H. A. Levy, *Acta Crystallorg.*, **10**, 180 (1957).
5) G. M. Sheldrick, SHELXS 86. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany (1986).
6) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1978).
7) C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976).
8) Tables of structure factors, anisotropic thermal parameters, and coordinates of calculated hydrogen atoms are deposited as Document No. 9027 at the Office of the Editor of Bull. Chem. Soc. Jpn.
9) Symmetry operations: i: $1-x,-y,1-z$, ii: $1-x, 1-y,1-z$, iii: $x, y, z-1$, iv: $-x, -y, -z$, v: $1-x, -y, -z$, vi: $x, y+1, z$.
10) A. Bondi, *J. Chem. Soc.*, **68**, 441 (1964).
11) These N···S distances are somewhat longer than the sum of the van der Waals radii of N and S atoms (3.35 Å). Nevertheless, the geometrical arrangement justifies the description of the bifurcated hydrogen bonds.
12) Considering the canonical structures of the imidazolium cation, the formal charge is localized on N(1C)–C(3C)–N(2C) site, whereas the S atoms of the thiocarbonyl groups are located above N(1C)–C(5C) and N(2C)–C(4C) bonds of the imidazolium ring. This suggests that the contribution of the Coulombic attraction between cation and thiocarbonyl group is not a dominant factor.
13) This type of contact is similar to that observed in the benzene–Cl_2 system (C···Cl: 3.53(2) Å), for example. See: O. Hassel and K. Stromme, *Acta Chem. Scand.*, **13**, 1781 (1959).