CHEMISTRY LETTERS, pp. 1161-1164, 1986.

Synthesis and Crystal Structure of a Highly Conducting (Phthalocyaninato)nickel Hexafluoroantimonate, $(NiPc)_2SbF_6$

Kyuya YAKUSHI,* Makoto SAKUDA, Haruo KURODA, Atsushi KAWAMOTO,† and Jiro TANAKA†

Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Tokyo 113
† Department of Chemistry, Faculty of Science, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464

Sigle crystals of a metallic (phthalocyaninato)nickel hexafluoro antimonate, $(NiPc)_2SbF_6$, were newly prepared by the use of an electrochemical technique. NiPc is stacked one-dimensionally in a slight zigzag way, which quite resembles the structure of highly conducting NiPcI.

Studies on highly conducting quasi-one-dimensional solids of metallo-macrocylic compounds have been extensively conducted by the group of Northwestern University.1-6) They prepared many halogen complexes by changing the porphine skeleton and the central metal. A non-halogenated (phthalocyaninato)nickel salt with metallic behavior, $NiPc(BF_4)_{0.33}$, was recently prepared.7) In all these materials, one third of the macrocyles are oxidized by counter anions. Depending on the combination of the central metal and the porphine skeleton, either the central metal or the porphine moiety is oxidized in these salts. We prepared a new highly conducting single crystal of (phthalocyaninato)nickel hexafluoro-anitmonate, $(NiPc)_2SbF_6$, which is the first metallophthalocyanine salt with the 2:1 chemical composition. A preliminary ESR experiment suggested that a partial oxidation is taking place both on the central metal and the phthalocyanine moiety in this salt.

Single crystals of $(NiPc)_2SbF_6$ were prepared by electrochemically oxidizing NiPc in the 1-chloronaphthalene solution, $(n\text{-}Bu)_4NSbF_6$ being used as the supporting electrolyte. NiPc, solvent, and electrolyte were extensively purified. The electrochemical oxidation were performed in the galvanostatic mode (1-5 μA) at 120 °C in the argon atmosphere. The dimension of a typical single crystal was 0.07 mm × 0.05 mm × 5 mm. The X-ray oscillation photograph along the needle axis indicated the existence of two kinds of crystal modification, the periodic units of which were 6.4 Å and 9.6 Å, respectively. The modification with 9.6 Å periodic unit was the minor component and almost all these crystals were twinned. Since the two modifications were difficult to be distinguished by visual observation, we selected out the crystals with 6.4 Å periodic unit by examining X-ray diffraction.

The atomic ratio between Ni and Sb in this salt was determined to be 0.48 0.04 by means of ICP atomic emission spectrometry.[8] The electrical conductivity measured by a standard four probe technique was about 50 $\Omega^{-1}cm^{-1}$ at room temperature and exhibited a metallic behavior down to about 200 K, below which crystals often cracked.

Table 1. Fractional atomic coordinates and equivalent temperature factors (Å^2)

	x($\times10^4$)	y($\times10^4$)	z($\times10^4$)	B_{eq} a)		x($\times10^4$)	y($\times10^4$)	z($\times10^4$)	B_{eq} a)
Ni	4874.7(6)	2456.5(2)	5110(13)	1.9	C1c	3359(4)	1753(2)	5215(43)	2.4
N1a	5428(4)	3057(2)	5122(37)	2.4	C2c	3221(4)	1248(2)	5105(45)	3.0
N2a	7105(4)	2864(2)	5207(36)	2.7	C3c	2399(5)	978(3)	5187(53)	4.0
C1a	6390(4)	3161(2)	5156(43)	2.5	C4c	2517(7)	495(3)	5031(51)	4.7
C2a	6529(5)	3663(2)	5158(45)	2.8	C5c	3419(7)	303(3)	5144(64)	4.9
C3a	7352(6)	3935(2)	5104(45)	3.8	C6c	4235(6)	571(3)	5168(60)	4.0
C4a	7218(7)	4411(3)	5310(63)	4.9	C7c	4105(5)	1050(2)	5116(39)	3.0
C5a	6321(7)	4611(3)	5062(65)	4.8	C8c	4784(5)	1432(2)	5166(49)	2.6
C6a	5497(6)	4342(3)	5245(55)	3.9	N1d	6091(4)	2181(2)	5168(32)	2.5
C7a	5633(5)	3862(2)	5107(43)	2.8	N2d	5704(4)	1360(2)	5026(39)	2.8
C8a	4956(5)	3479(3)	5231(42)	2.3	C1d	6300(5)	1717(3)	5162(31)	2.7
N1b	3653(4)	2730(2)	5050(34)	2.3	C2d	7321(5)	1642(2)	5134(45)	2.9
N2b	4040(4)	3554(2)	5084(37)	2.6	C3d	7863(6)	1236(3)	5124(50)	3.9
C1b	3438(5)	3196(2)	5193(39)	2.4	C4d	8839(6)	1289(4)	5283(60)	4.5
C2b	1864(6)	3270(2)	5214(47)	2.6	C5d	9246(6)	1730(4)	4923(56)	4.3
C3b	897(6)	3674(3)	5049(49)	3.4	C6d	8713(6)	2135(3)	5017(56)	4.1
C4b	897(6)	3609(3)	5222(54)	4.6	C7d	7731(5)	2078(3)	5149(39)	2.8
C5b	489(6)	3168(3)	5005(60)	4.3	C8d	6958(4)	2415(2)	5101(41)	2.6
C6b	1039(5)	2767(3)	5158(54)	3.7	Sb	0	5000	5000	7.8
C7b	2014(4)	2832(2)	5121(46)	2.6	F1	-1128(6)	5263(3)	5790(43)	14.9
C8b	2799(5)	2499(2)	5118(44)	2.6	F2	503(9)	5475(4)	6629(38)	15.2
N1c	4308(4)	1856(2)	5182(35)	2.3	F3	228(23)	5328(9)	3059(33)	25.9
N2c	2640(4)	2046(2)	5157(37)	2.7					

a)$B_{eq} = (4/3)\Sigma_{ij}\Sigma_{ij}(a_i \cdot a_j)$.

The intensities of X-ray diffraction were collected with a Rigaku automated diffractometer using a CuKα radiation monochromated with a graphite plate. We obtained 2211 independent reflections which have intensities larger than the statistical counting error and used all of them for the analysis. The crystal belongs to the orthorhombic system with a space group, Pnc2, the lattice parameters being a=14.113(1), b=28.710(2), c=6.441(2) Å, Z=2. The calculated density, 1.754 g cm^{-3}, agreed with the observed density, 1.75 g cm^{-3}. The structure was solved by the direct method, and was refined by the full-matrix least-squares method after applying the absorption corrections. We made an analysis by assuming the space group, Pncm, but we could not determine the positions of F atoms in this space group. The refinement including all hydrogen atoms reduced the R value to 0.064. The final atomic parameters except hydrogen atoms were listed in Table 1.

Figure 1 shows the arrangement of molecules projected onto the (001) plane. The column structure of NiPc and the positions of the counter anions are quite similar to those of NiPcI, although the crystal structure is not isomorphous. The staggered angle and the intermolecular spacing between the adjacent molecules are respectively 41.0°and 3.22 Å, which are nearly equal to the corresponding values of NiPcI, 39.5°and 3.24 Å. The different point in the structural characteristics of this material from NiPcI is in the slight zigzag stacking in the NiPc column, which is probably introduced by the large ion size (3.12 Å)[9] of SbF_6^-, as shown in Fig.2. The deviation of Ni atom from the glide planes are 0.12 Å and 0.18 Å in

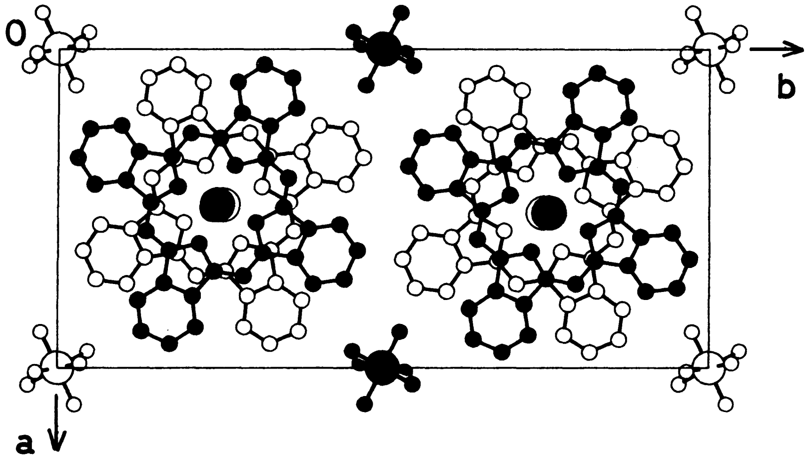


Fig. 1. Projection of the molecular arrangement of $(NiPc)_2SbF_6$ onto the (001) plane. The molecules illustrated by open and solid circles are located at z ≃ 0.5 and z ≃ 1.0, respectively.

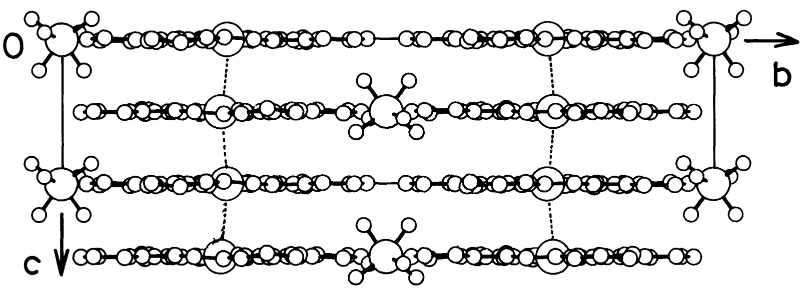


Fig. 2. Side view of the molecular columns of $(NiPc)_2SbF_6$ along the a-axis. This figure shows that the zigzag stack is introduced by the large anion, SbF_6^-.

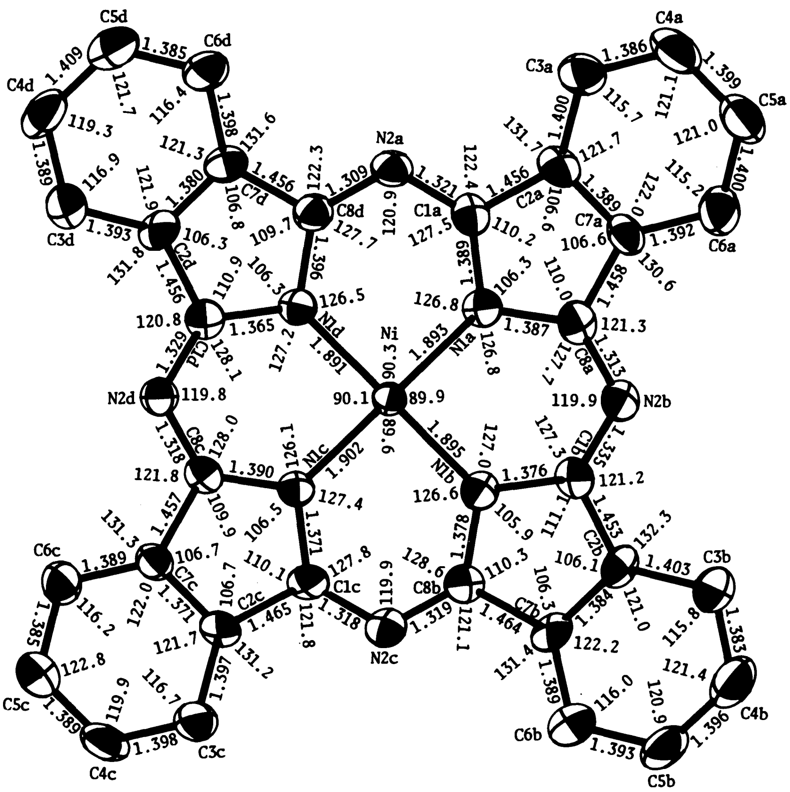


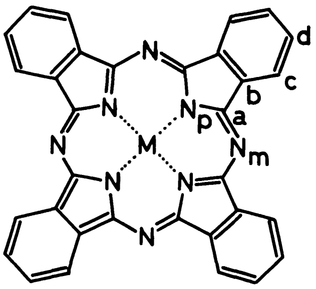
Fig. 3. Bond lengths and bond angles of NiPc. The estimated standard deviations (esd) of bond lengths are 0.005 Å for Ni-N, 0.008-0.009 Å for N-N, 0.009-0.01 Å for C-C in the pyrrole rings, and 0.011-0.017 Å for C-C in the peripheral benzene rings. The esd's of bond angles are 0.2° for N-Ni-N, 0.8-1.2° for the $C-C_{4a-4d}-C$ and $C-C_{5a-5d}-C$, and 0.6-0.8° for the rest.

the directions of b- and a-axes, respectively. Therefore, the distance between the successive nickel atoms is 3.230 Å. Another noteworthy aspect of the structure is the absence of the positional disorder of SbF_6^-, which is a strong contrast to the positional disorder of I_3^- along the stacking direction of NiPc in NiPcI, although this anion have extraordinally large temperature factors as shown in Table 1. The molecular geometry of NiPc is drawn in Fig.3. The lengths of the chemically equivalent bond were averaged and the results were compared in Table 2 with those of NiPcI and the average values for metal phthalocyanine. Any systematic difference due to the partial oxidation could not be found. The geometry of SbF_6^- is not reliable because of the large temperature factors, being heavily distorted from an octahedron.

Table 2. Average bond lengths (Å) of NiPc

	$(NiPc)_2SbF_6$	NiPcI[a)]	MPc[a)]
$Ni-N_p$	1.895(6)	1.900(5)	---
N_p-C_a	1.382(9)	1.379(12)	1.376(10)
N_m-C_a	1.320(9)	1.320(9)	1.328(7)
C_a-C_b	1.458(10)	1.456(7)	1.453(3)
C_b-C_b	1.381(10)	1.392(10)	1.395(4)
C_d-C_d	1.398(14)	1.394(11)	1.394(2)
C_b-C_c	1.395(11)	1.387(7)	1.394(2)
C_c-C_d	1.390(13)	1.388(6)	1.385(7)

a)Ref. 1.



We acknowledge Professor H. Haraguchi and Dr. T. Akagi in the Chemistry Department of the University of Tokyo for assistance with the quantitative analysis of Ni and Sb. We thank Professor M. Kinoshita and Dr. T. Sugano in the Institute for Solid State Physics for their assistance in the ESR measurement. This work was supported by the Grant-in-Aid for the Special Project Research on "The Properties of Molecular Assemblies"(No. 60104001) from the Ministry of Education, Science and Culture.

References

1) C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers, and T. J. Marks, J. Am. Chem. Soc., 102, 6702 (1980).
2) T. E. Phillips, R. P. Scaringe, B. M. Hoffman, and J. A. Ibers, J. Am. Chem. Soc., 102, 3435 (1980).
3) J. Martinsen, L. J. Pace, T. E. Phillips, B. M. Hoffman, and J. A. Ibers, J. Am. Chem. Soc., 104, 83 (1982).
4) J. Martinsen, S. M. Palmer, J. Tanaka, R. C. Greene, and B. M. Hoffman, Phys. Rev. B, 30, 6269 (1984).
5) S. M. Palmer, J. L. Stanton, N. K. Jaggi, B. M. Hoffman, J. A. Ibers, and L. H. Schwartz, Inorg. Chem. 24, 2040 (1985).
6) J. Martinsen, J. L. Stanton, R. L. Greene, J. Tanaka, B. M. Hoffman, and J. A. Ibers, J. Am. Chem. Soc., 107, 6915 (1985).
7) T. Inabe, S. Nakamura, W. B. Liang, T. J. Marks, R. L. Burton, C. R. Kannewurf, and K. Imaeda, J. Am. Chem. Soc., 107, 7224 (1985).
8) Inductively Coupled Plasma Atomic Emission Spectrometry.
9) R. D. Schannon, Acta Crystallogr., Sect.A, 32, 75 (1976).

(Received April 12, 1986)