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The Structure of Bis(μ-thiocyanato)-bis[tris(benzylamine)(thiocyanato)nickel(II)], $[Ni(SCN)_2(C_6H_5CH_2NH_2)_3]_2$

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Synopsis. The crystal and molecular structure of the title complex was determined by means of a single-crystal X-ray diffraction method. A crystal of $Ni_2C_{46}H_{54}N_{10}S_4$, F. W. 992.67, is triclinic with a space group $P\bar{1}$, a=13.259(4), b=15.627(5), c=6.5150(16) Å, α=90.60(3), β=93.64(2), γ=112.601(19)°, U=1242.9(6) Å^3, Z=1, D_m=1.32(3), D_x=1.33 Mg m^{-3}, and μ(Mo $K\alpha$)=9.60 cm^{-1}. The central metal atom is hexa-coordinated, being ligated with three benzylamine and two thiocyanato (SCN) nitrogen atoms as well as one SCN sulfur atom. Two metal atoms are bridged by two SCN ions; however, the Ni-S bond length is 2.639(3) Å, which is a little longer than the sum of the Shannon's ionic radii. The distance Ni···Ni is 5.717(3) Å and the dimeric complexes are discrete in a crystal.

It has already been found that in Lewis-base adducts of thiocyanate (SCN) complexes, where the central metal is relatively soft (such as mercury, cadmium, or silver), the SCN ion bridges the metal atoms forming linear, planar, or three-dimensional networks.[1–7] On the other hand, in cases of the adducts of nickel(II) thiocyanate, many of them are monomeric and the metal atom is in an octahedral geometry.[8–10] However, Lipkowski has reported that in the case of 4-methylpyridine (pic) adduct, $[Ni(SCN)_2(pic)_3]_2$ (**2**), the adduct takes a dimer structure where two metal atoms are bridged by two SCN ions.[11] Since such types of nickel(II) complexes which include SCN bridges are not common, we started to find another example and obtained the title complex. Its structure was determined by an X-ray diffraction method using its single crystal.

Experimental

Synthesis of Bis(μ-thiocyanato)-bis[tris(benzylamine)(thiocyanato)nickel(II)] (1). Anhydrous nickel(II) thiocyanate (0.87 g, 5.0 mmol) and benzylamine (bza) (1.59 g, 15 mmol) are dissolved into warm methanol (20 cm^3), and the solution was left standing at ambient temperature. Pale-blue needle-like crystals were deposited, filtered off, washed with methanol and dried over a silica-gel desiccator. Yield: 1.9 g, 75%. Anal. ($Ni_2C_{46}H_{54}N_{10}S_4$), Ni, C, H, N.

Single-Crystal X-Ray Analysis. The crystal used for the structure determination was about 0.3×0.25×0.2 mm^3 in size, and was used without shaping. The reflections in the range of $3° < 2\theta < 60°$ were collected on a Rigaku AFC-6A automated 4-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation, by means of ω—2θ scan technique (scan speed, 4° min^{-1}: scan width 1.40+0.5 tanθ°(θ)). The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. Of 7285 independent reflections collected, 3110 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. All the calculations were carried out on a HITAC M-280H computer at the Computer Center of the University of Tokyo, using the local version of UNICS.[12] The scattering factors were taken from Reference 13.

The structure was solved by the heavy-atom method. The positional parameters of all the non-hydrogen atoms converged, but as the equivalent isotropic temperature factors of C(35), C(36), and C(37) were found to be large, at the final refinement process, the positions of these three atoms were fixed at respective positions assuming their B_{iso} to be 15.0. Applying the anisotropic temperature factors for the other atoms, the final R value,[14] thus obtained, was 0.086.

Results and Discussion

The selected bond lengths and bond angles are shown in Table 1.[15] A projection of the complex together with the numbering scheme of the atoms is shown in Fig. 1, and the crystal packing diagram in Fig. 2.

The metal atom is hexa-coordinated and is in an octahedral geometry. Two nickel atoms are bridged by two SCN ions, where each nickel atom is ligated by the nitrogen atom of one ligand and the sulfur atom of the other. The eight-membered ring, which consists of

Table 1. Selected Bond Lengths and Bond Angles with Estimated Standard Deviations in Parentheses

Bond length (l/Å)					
Ni-S(1)	2.639(3)	Ni-N(1^{i})	2.050(6)	Ni-N(2)	2.048(6)
Ni-N(11)	2.101(7)	Ni-N(21)	2.127(6)	Ni-N(31)	2.126(9)
S(1)-C(1)	1.638(7)	C(1)-N(1)	1.139(8)	S(2)-C(2)	1.623(7)
C(2)-N(2)	1.140(10)	N(11)-C(11)	1.499(10)	C(11)-C(12)	1.512(14)
N(21)-C(21)	1.471(9)	C(21)-C(22)	1.532(13)	N(31)-C(31)	1.35(2)
C(31)-C(32)	1.52(2)	Ni···Ni^{i}	5.717(3)	Ni···Ni^{ii}	6.515(3)
Bond angle (ϕ/°)					
S(1)-Ni-N(1^{i})	92.05(17)	S(1)-Ni-N(2)	86.19(19)	S(1)-Ni-N(11)	84.4(2)
S(1)-Ni-N(31)	86.1(3)	N(1^{i})-Ni-N(2)	177.9(3)	N(1^{i})-Ni-N(11)	94.7(3)
N(1^{i})-Ni-N(21)	86.6(2)	N(1^{i})-Ni-N(31)	90.9(3)	N(2)-Ni-N(11)	86.3(3)
N(2)-Ni-N(21)	95.2(2)	N(2)-Ni-N(31)	87.8(3)	N(11)-Ni-N(21)	93.5(3)
N(21)-Ni-N(31)	96.1(3)	Ni-S(1)-C(1)	102.2(3)	Ni-N(1^{i})-C(1^{i})	164.9(6)
Ni-N(2)-C(2)	179.0(6)	S(1)-C(1)-N(1)	179.0(6)	S(2)-C(2)-N(2)	179.9(7)

Key to the symmetric operations: i, $1-x$, $1-y$, $1-z$, ii, x, y, $1+z$.

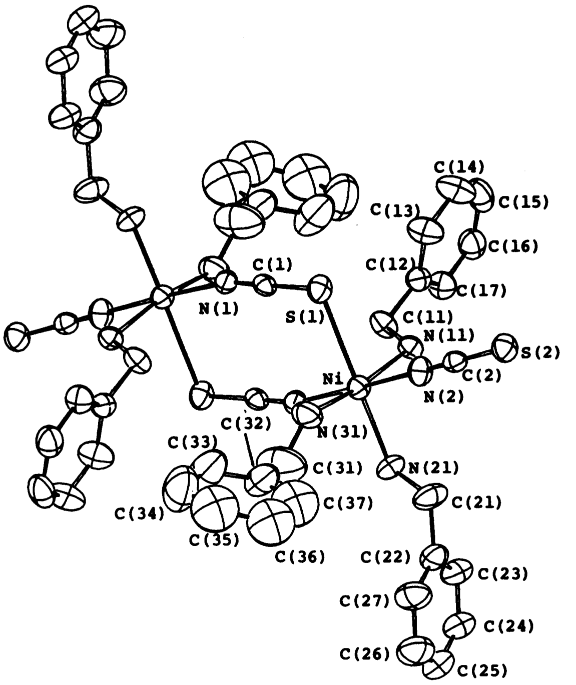

Fig. 1. A projection of the dimeric complex with the numbering scheme.

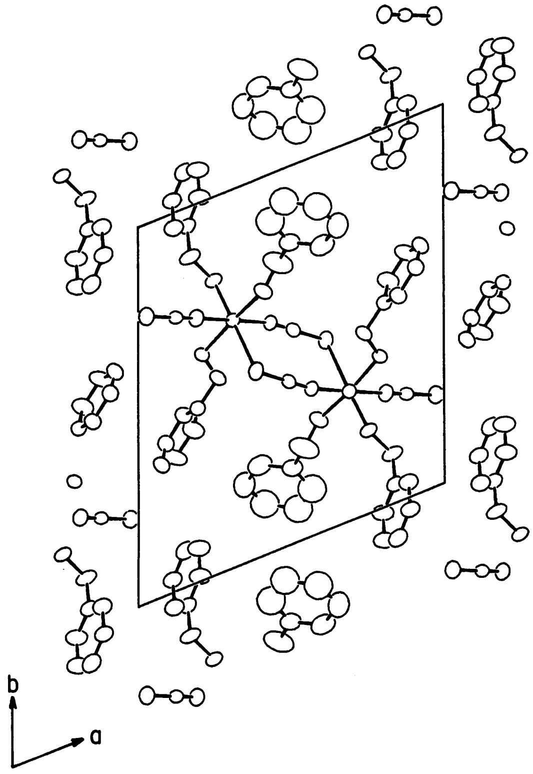

Fig. 2. Crystal packing diagram.

two nickel atoms and two bridging SCN ions, is about on a plane (average deviations of the atomic positions is 0.008 Å). A nitrogen atom of another SCN ion, as well as three bza nitrogen atoms, are coordinated to each metal atom. Each dimer complex is discrete in the crystal; neither ligand bridgings nor hydrogen bondings are found between them. Two SCN nitrogen atoms take trans configuration, and the sulfur atom of SCN ion is in the cis orientation from both of these nitrogen atoms; the other three positions are occupied by the bza nitrogen atoms. The bond length Ni–S(1) is 2.639(3) Å, which is a little longer than the sum of the Shannon's ionic radii, 2.53 Å (r_{Ni}=0.690 and r_{S}=1.84 Å).[16] The bond length Ni–N(bza) is 2.118 Å on the average, a little longer than that for Ni–N(SCN), 2.049 Å on the average. The latter value is a little shorter than the sum of the Shannon's ionic radii, 2.15 Å (where r_{N}=1.46 Å), probably due to the delocalization of the charge on the nitrogen atoms of the SCN ions.

Although the properties of bza and pic are quite different and their adducts of the metal complexes are expected to take different structures from each other, the structure of **1** is essentially similar to that of **2**: the orientation of the ligated atoms around the metal atom is the same in **1** and **2**.

However, in **2**, the Ni–S bond length (2.583 Å), as well as the Ni–N(pic) ones (2.085 Å on the average), are much shorter than the corresponding bond lengths of **1**, while those of Ni–N(SCN) are about the same.[11] Therefore, in **1** the Ni–S and Ni–N(Lewis base) bonds are thought to be weaker than the corresponding bonds of **2**. This fact may be, at least partially, due to the bulkiness of the bza ligand, which has a methylene group between the ligand nitrogen atom and the phenyl group; the ligand is not planar and it is hardly packed into a crystalline space, while the pic molecule is planar except for the methyl hydrogen atoms. Therefore, in the crystal packing, the steric hindrance of the Lewis base ligands makes the approach of the ligated atoms to the metal atoms in **1** more difficult than in **2**.

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14) $R=\sum||F_o|-|F_c||/\sum|F_o|$.

15) The final atomic and thermal parameters, the final F_o-F_c table, and some additional data about the bond lengths and bond angles are deposited as Document No. 8644 at the Office of the Bull. Chem. Soc. Jpn.

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