

Synthesis and Crystal Structure of Tetrakis(2-ethylimidazole)bis(thiocyanate-*N*)nickel(II) Complex

Inn Hoe Kim*, Ji Youn Cho, Chong-Hyeak Kim^a, Jong Seung Kim and Il-Hwan Suh^{b*}

Department of Chemistry, Konyang University, Nonsan 320-711, Korea

^aChemical Analysis Laboratory, Korea Research Institute of Chemical Technology, Daejeon 305-606, Korea

^bDepartment of Physics, Chungnam National University, Daejeon 305-764, Korea

Tetrakis(2-ethylimidazole)bis(thiocyanate-*N*)nickel(II)

착물의 합성 및 결정구조

김인회* · 조지연 · 김종혁^a · 김종승 · 서일환^{b*}

전양대학교 화학과, ^a한국화학연구원 분석실, ^b충남대학교 물리학과

Abstract

The title complex, Ni(L)₄(NCS)₂ (1) (L = 2-ethylimidazole), has been synthesized and characterized by X-ray single crystallography. The complex 1 crystallizes in the tetragonal system, *P4nc* space group with *a* = 10.587(2), *c* = 12.927(3) Å, *V* = 1448.9(4) Å³, *Z* = 2, *R*₁ = 0.0581 and *ωR*₂ = 0.1675 for 676 independent reflections. The central Ni(II) atom of this complex has a regular octahedral coordination geometry, with the 2-ethylimidazole ligands bonding through nitrogen atom and the isothiocyanate ligands bonding through nitrogen atom in a *trans* arrangement.

요 약

Ni(L)₄(NCS)₂ (1) (L = 2-ethylimidazole) 착물을 합성하고 단결정 구조를 규명하였다. 이 착물은 정방정계, 공간군 *P4nc*, *a* = 10.587(2), *c* = 12.927(3) Å, *V* = 1448.9(4) Å³, *Z* = 2로 결정화되었으며, 676개의 독립적인 회절반점에 대한 최종 신뢰도 인자 *R*₁ 및 *ωR*₂ 값은 각각 0.0581 및 0.1675이었다. 이 착물의 결정 구조는 Ni(II) 금속 원자에 4개의 2-ethylimidazole 리간드의 질소 원자가 *xy* 평면에 배위되어 있고, 2개의 isothiocyanate 리간드의 질소 원자가 *z* 축 방향에서 트랜스 형태로 배위되어 균일한 팔면체 구조의 단핵 착물을 형성한다.

1. Introduction

The design and architecture of infinite multi-dimensional structures by crystal engineering have become of particular interest recently.¹⁻²⁾ Because they have useful properties for catalytic, electronic, magnetic, and optical materials,³⁻⁴⁾ it is important to make multi-dimensional systems. To design architectures of multi-dimensional frameworks, one of us⁵⁾ and other workers⁶⁻⁷⁾ have used the coordination properties of various pseudohalide ions such as CN⁻,

SCN⁻, OCN⁻, SeCN⁻, CNO⁻, N₃⁻, and complementary organic ligands. The pseudohalide ions are known to build up one-, two-, and three-dimensional framework linking one metal atom M to another metal atom M' alternately.⁸⁾ The complementary organic ligands such as aliphatic and aromatic amines are known to play an important role in stabilizing the multi-dimensional structures.

On the other hand, aromatic nitrogen heterocycles such as imidazole derivatives represent an important class of ligands in coordination chemistry. They

have a good π -donors and can also exist as anionic ligands by deprotonation of acidic N-H groups in the free ligand. Especially, binding of imidazole derivatives to various metal complexes has been of great interest because of biological importance of the metal complexes. A number of metal complexes of various imidazole derivatives have been synthesized and characterized by X-ray single crystallography.⁹⁻¹⁷⁾ Our interest in this area is focused on the development of novel multi-dimensional framework structures using the terminal and bridging properties of the thiocyanate ligand and the coordination behaviour of the imidazole derivatives as a complementary organic ligands. In this paper, we report the synthesis and crystal structure of the nickel(II) isothiocyanate complex (**1**) with 2-ethylimidazole ligand.

2. Experimental Section

Preparation and Characterization of Ni(L)₄(NCS)₂ (1**).** The ethanolic solution (10 ml) of sodium thiocyanate (2 mmol, 0.16 g) was added to the ethanolic solution (10 ml) of NiCl₂ · 6H₂O (1 mmol, 0.24 g). To this mixture solution, the ethanolic solution (20 ml) of 2-ethylimidazole (4 mmol, 0.38 g) was introduced with stirring. From the resulting solution, a small amount of green precipitates was formed and was filtered off. The filtered ethanolic solution was allowed to stand in a refrigerator at 5°C. After a few weeks, the pale blue block crystals suitable for X-ray analysis were obtained.

IR spectrum of the crystal was recorded with a BioRad Digilab FTS-165 infrared spectrophotometer. The 2-ethylimidazole and isothiocyanate ligand were assigned by the relevant IR absorption bands, respectively.¹⁸⁾ The contents of the carbon, hydrogen, nitrogen, and sulfur were analyzed by a CE EA-1110 elemental analyzer. The content of the nickel was analyzed by a Perkin-Elmer 2380 atomic absorption spectrometer. The composition of the crystal **1** was deduced from the elemental analyses; the formula of Ni(L)₄(NCS)₂ is consistent with the results of X-ray single crystallography. *Anal. Found:* C, 47.24; H, 5.71; N, 24.88; S, 11.38; Ni, 10.3%. *Calc. for* NiC₂₂H₃₂N₁₀S₂: C, 47.24; H, 5.77; N, 25.04; S, 11.46; Ni, 10.49%.

X-ray Crystallography. A pale blue block crystal (0.33 × 0.33 × 0.23 mm) was coated with epoxy glue in order to prevent degradation of the specimen under ambient conditions. The crystal was mounted on an Enraf-Nonius CAD4 X-ray diffractometer and the intensity data were collected in the ω -2 θ scan mode using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). The cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections in the θ range of 11.26 to 14.07°.¹⁹⁾ One orientation reflection was checked every 200 reflections and three standard reflections were monitored every 300 minutes. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the ϕ -scans was applied.

All calculations were carried out using the Siemens SHELXTL crystallographic software programs.²⁰⁾ The space group was assigned on the basis of the

Table 1. Crystallographic and experimental data for **1**

| | |
|--|---|
| Empirical formula | C ₂₂ H ₃₂ N ₁₀ NiS ₂ |
| Formula weight | 559.41 |
| Temperature | 291(2) K |
| Crystal system | Tetragonal |
| Space group | <i>P4nc</i> |
| Unit cell dimensions | <i>a</i> = 10.587(2) Å <i>c</i> = 12.927(3) Å |
| Volume | 1448.9(4) Å ³ |
| <i>Z</i> | 2 |
| Density (calculated and measured*) | 1.282 and 1.28 g/cm ³ |
| Absorption coefficient | 0.842 mm ⁻¹ |
| <i>F</i> (000) | 588 |
| θ range for data collection | 2.49 to 24.99° |
| Limiting indices | 0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 15 |
| Reflections collected/unique | 1290/676 (<i>R</i> _{int} = 0.0576) |
| Data/restraints/parameters | 676/2/75 |
| Goodness-of-fit on <i>F</i> ² | 1.101 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0581 <i>wR</i> ₂ = 0.1675 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0806 <i>wR</i> ₂ = 0.1868 |
| Largest diff. peak and hole | 0.509 and -0.292 eÅ ⁻³ |
| Absolute structure (Flack, 1983)Flack parameter | = 0.05(7) |

*The density was measured by using the flotation method in bromoform-mesitylene.

systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method²¹⁾ and refined by successive least-squares methods followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at calculated positions with isotropic thermal parameters were included in the final structure-factor calculations. The final difference electron density map contained no significant features. The crystallographic and experimental data are summarized in Table 1.

3. Results and Discussion

The title complex, Ni(L)₄(NCS)₂ (**1**), crystallizes in the tetragonal system with *P4nc* space group. The molecular structure of **1** with the atomic numbering scheme is shown in Fig. 1. The refined atomic parameters and the selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. All the atoms of two isothiocyanate groups occupy special positions with 4-fold rotation symmetry along [001] direction and the central nickel(II) atom is hexa-coordinated by four nitrogen atoms from 2-ethylimidazole ligands and by two nitrogen atoms from the two isothiocyanate groups.

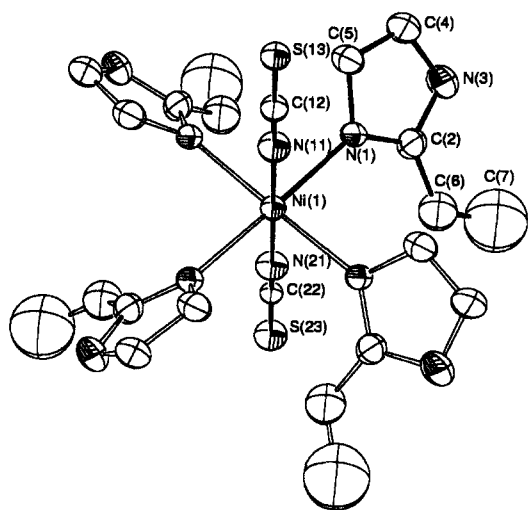


Fig. 1. An ORTEP²²⁾ drawing of **1** with the atomic numbering scheme. The displacement ellipsoids are shown at the 30% probability level.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

| atom | x | y | z | U_{eq} |
|-------|-----------|----------|----------|----------|
| Ni(1) | 0 | 0 | 5292(2) | 39(1) |
| N(11) | 0 | 0 | 3683(19) | 59(7) |
| C(12) | 0 | 0 | 2720(20) | 43(8) |
| S(13) | 0 | 0 | 1489(5) | 42(2) |
| N(21) | 0 | 0 | 6914(17) | 53(6) |
| C(22) | 0 | 0 | 7710(20) | 34(6) |
| S(23) | 0 | 0 | 9022(8) | 67(3) |
| N(1) | -1584(6) | 1237(5) | 5252(12) | 51(2) |
| C(2) | -1903(9) | 2244(9) | 5762(12) | 67(3) |
| N(3) | -3031(8) | 2689(8) | 5483(15) | 90(4) |
| C(4) | -3437(10) | 1922(12) | 4670(17) | 97(4) |
| C(5) | -2561(9) | 1026(9) | 4551(13) | 69(3) |
| C(6) | -1213(12) | 2809(13) | 6618(14) | 105(4) |
| C(7) | -1560(20) | 3910(20) | 7280(30) | 281(16) |

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Four 2-ethylimidazole ligands take equatorial positions. On the other hand, two isothiocyanate groups take axial positions with *trans*-configurations [N_{NCS} -Ni- N_{NCS} bond angle 180.0(4)]. Therefore, the coordination geometry of the central nickel(II) atom adopts a regular octahedral environment with NiN_6 composition. The Ni- $N_{2\text{-ethylimidazole}}$ bond length of 2.128(6) \AA and the average Ni- N_{NCS} bond length of 2.09(2) \AA are similar to that observed in the nickel(II) isothio-

Table 3. Bond lengths (\AA) and angles ($^\circ$) for **1**

| | | | |
|---|-----------|------------------------------|-----------|
| Ni(1)-N(11) | 2.08(2) | Ni(1)-N(21) | 2.10(2) |
| Ni(1)-N(1) | 2.128(6) | N(11)-C(12) | 1.24(5) |
| C(12)-S(13) | 1.59(3) | N(21)-C(22) | 1.03(4) |
| C(22)-S(23) | 1.69(3) | N(1)-C(2) | 1.30(1) |
| C(2)-N(3) | 1.33(1) | N(3)-C(4) | 1.40(2) |
| C(4)-C(5) | 1.34(2) | C(5)-N(1) | 1.39(1) |
| C(2)-C(6) | 1.46(2) | C(6)-C(7) | 1.49(2) |
| N(11)-Ni(1)-N(21) | 180.0(4) | N(11)-Ni(1)-N(1) | 88.6(4) |
| N(21)-Ni(1)-N(1) | 91.4(4) | N(1)-Ni(1)-N(1) ⁱ | 89.97(2) |
| N(1) ⁱ -Ni(1)-N(1) ⁱⁱ | 177.3(7) | Ni(1)-N(11)-C(12) | 180.0(2) |
| Ni(1)-N(21)-C(22) | 180.0(6) | Ni(1)-N(1)-C(2) | 134.3(6) |
| Ni(1)-N(1)-C(5) | 120.2(6) | N(11)-C(12)-S(13) | 180.0(2) |
| N(21)-C(22)-S(23) | 180.0(4) | N(1)-C(2)-N(3) | 112.8(10) |
| C(2)-N(3)-C(4) | 105.9(10) | N(3)-C(4)-C(5) | 106.6(10) |
| C(4)-C(5)-N(1) | 109.1(10) | C(5)-N(1)-C(2) | 105.5(7) |
| N(1)-C(2)-C(6) | 126.4(10) | N(3)-C(2)-C(6) | 120.6(11) |
| C(2)-C(6)-C(7) | 129.4(17) | | |

Symmetry code : (i) $-y, x, z$; (ii) $y, -x, z$.

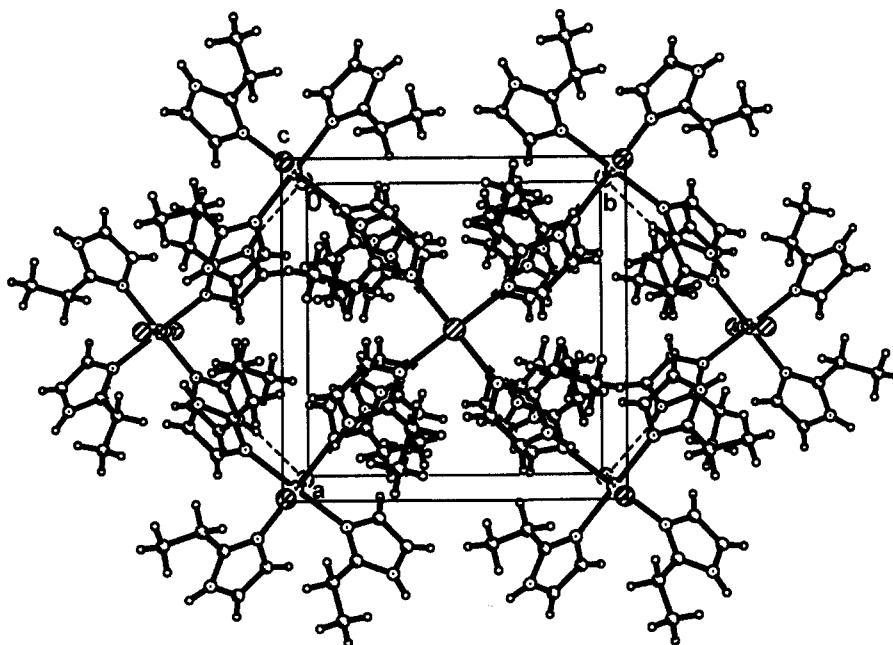


Fig. 2. A perspective view of the unit cell of 1 along the *c*-axis.

cyanate complexes with imidazole derivative ligands.^{14,23} The average $N_{NCS}-Ni-N_{2-ethylimidazole}$ bond angle is $90.0(4)^\circ$ and the $N_{2-ethylimidazole}-Ni-N_{2-ethylimidazole}$ bond angles are $89.97(2)^\circ$ and $177.3(7)^\circ$. All bond lengths and angles of 2-ethylimidazole ligands are roughly similar to the other reported compound, (2-ethylimidazole)(*N*-salcylidene-glycinato)copper(II).²⁴

A perspective view of 1 along the *c*-axis is shown in Fig. 2. The molecular packing of the title complex lies on an array parallel to the *ab*-plane. The nitrogen atoms of the isothiocyanate ligands are coordinated to the octahedral nickel(II) atoms, while the sulfur atoms of the isothiocyanate ligands are uncoordinated. This is quite different from other transition metal(II) isothiocyanate complexes^{17,25-26} that are doubly bridged by isothiocyanate (SCN^-) group and isothiocyanate (NCS^-) group through both ends. The nitrogen atoms of the 2-ethylimidazole ligands are coordinated to central nickel(II) atoms with equatorial positions, and their ethyl groups directed toward the upper positions of the *ab*-plane. The N atoms of 2-ethylimidazole and the S atoms of isothiocyanate are linked together in intermolecular hydrogen-bonding along *ab*-plane by the weak

$N3-H \cdots S13$ hydrogen bond [$3.47(1) \text{ \AA}$, 169.6°]. This $N_{2-ethylimidazole}-H \cdots S_{isothiocyanate}$ hydrogen-bonding may have fundamental importance in biochemical research to understanding of biomolecular interactions.²⁷ In summary, the central Ni(II) atom of the title compound 1 has a regular octahedral coordination geometry with the 2-ethylimidazole ligands bonding through nitrogen atom and the isothiocyanate ligands bonding through nitrogen atom in a *trans* arrangement. The weak $N_{2-ethylimidazole}-H \cdots S_{isothiocyanate}$ hydrogen-bonding contributes to stabilization of the crystal structure.

4. Supplementary Material

Tables of atomic coordinates, bond lengths and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors are available from I. H. Kim.

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