Pseudo- S_6 Complex Cations of a Hexakis-*N*-methylformamide Nickel(II) Complex

Hiroshi SAKIYAMA,[†] Ryoji MITSUHASHI,^{**} and Masahiro MIKURIYA^{**}

^{*}Department of Material and Biological Chemistry, Faculty of Science, Yamagata University,
1-4-12 Kojirakawa, Yamagata 990-8560, Japan

^{**}Department of Applied Chemistry for Environment and Research Center for Coordination Molecule-based
Devices, School of Science and Technology, Kwansei Gakuin University, Gakuen 2-1, Sanda 669-1337,
Japan

The nickel(II) complex $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$ [NMF = *N*-methylformamide] [hexakis(*N*-methylformamide- κO)nickel(II) bis(tetraphenylborate)] was prepared, and characterized by a single-crystal X-ray method. The compound crystallizes in the triclinic space group $P\bar{1}$ and $Z = 2$ with the following cell parameters: $a = 10.680(2)\text{\AA}$, $b = 13.271(3)\text{\AA}$, $c = 19.960(4)\text{\AA}$, $\alpha = 86.043(6)^\circ$, $\beta = 84.483(6)^\circ$, $\gamma = 87.335(7)^\circ$, $V = 2807.0(10)\text{\AA}^3$. Two types of $[\text{Ni}(\text{NMF})_6]^{2+}$ cations are found in a crystal, but both have a *pseudo-S*₆ symmetry.

(Received June 22, 2015; Accepted July 15, 2015; Published on web September 10, 2015)

Nickel(II) complexes are typical good examples for studying any magnetostructural relationship. A slight distortion around the nickel(II) center influences the sign of the zero-field splitting, which will determine the magnetic behavior.¹ We previously determined the crystal structures of nickel(II) complexes $[\text{Ni}(\text{DMF})_6](\text{BPh}_4)_2$ [hexakis(*N,N*-dimethylformamide- κO)nickel(II) bis(tetraphenylborate)]² and $[\text{Ni}(\text{DMSO})_6](\text{BPh}_4)_2$ [hexakis(dimethylsulfoxide- κO)nickel(II) bis(tetraphenylborate)]³, where DMF and DMSO represent *N,N*-dimethylformamide and dimethylsulfoxide, respectively. The $[\text{Ni}(\text{DMF})_6]^+$ complex cations were found to take a trigonally compressed *pseudo-S*₆ structure, while the $[\text{Ni}(\text{DMSO})_6]^+$ complex cations were found to take both a trigonally compressed *pseudo-S*₆ structure and a *pseudo-S*₄ structure. For the purpose of gaining further examples, in this study, we prepared a nickel(II) complex, $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$ [hexakis(*N*-methylformamide- κO)cobalt(II) bis(tetraphenylborate)] [NMF = *N*-methylformamide], and elucidated the crystal structure.

The nickel(II) complex $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$ was prepared by the addition of a 2-propanol solution (2.0 mL) of sodium tetraphenylborate (~1.1 mmol, 0.37 g) to an NMF solution (1.0 mL) of nickel(II) nitrate hexahydrate (~0.5 mmol, 0.15 g). Slow

evaporation of the resulting green solution gave a green single crystal suitable for X-ray analysis.

Crystal data are included in Table 1. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. The final cycle of a full-matrix least-squares refinement on F^2 was allowed to satisfactory converge with $R_1 = 0.0460$ [$I > 2\sigma(I)$].

The crystal consists of complex cations, $[\text{Ni}(\text{NMF})_6]^{2+}$, and

Table 1 Crystal and experimental data

Empirical formula: $\text{C}_{60}\text{H}_{70}\text{B}_2\text{N}_6\text{NiO}_6$	
Formula weight = 1051.55	
$T = 90\text{ K}$	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 10.680(2)\text{\AA}$	$\alpha = 86.043(6)^\circ$
$b = 13.271(3)\text{\AA}$	$\beta = 84.483(6)^\circ$
$c = 19.960(4)\text{\AA}$	$\gamma = 87.335(7)^\circ$
$V = 2807.0(10)\text{\AA}^3$	$Z = 2$
$D_x = 1.244\text{ g/cm}^3$	
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K_\alpha) = 0.401\text{ mm}^{-1}$	$F(0\ 0\ 0) = 1116$
Crystal size = $0.25 \times 0.20 \times 0.20\text{ mm}^3$	
No. of reflections collected = 17686	
No. of independent reflections = 12566 [$R(\text{int}) = 0.0248$]	
θ range for data collection: 1.794 to 28.647°	
Data/Restraints/Parameters = 12566/0/685	
Goodness-of-fit on $F^2 = 0.973$	
R indices [$I > 2\sigma(I)$]: $R_1 = 0.0460$, $wR_2 = 0.0886$	
R indices (all data): $R_1 = 0.0702$, $wR_2 = 0.0955$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.491\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.346\text{ e}\text{\AA}^{-3}$
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: Direct methods (SHELXT 2014/5)	
Refinement: full matrix least-squares (SHELXL-2014/7)	
CCDC deposition number: 1407421

Fig. 1 Chemical structure of $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$.

[†] To whom correspondence should be addressed.
E-mail: saki@sci.kj.yamagata-u.ac.jp

Fig. 2 ORTEP view of $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$ with atom labeling. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond distances and bond angles

Atom	Atom	Distance (Å)		Atom	Atom	Distance (Å)	
Ni(1)	O(1)	2.0601(13)		Ni(1)	O(2)	2.0183(14)	
Ni(1)	O(3)	2.0456(14)		Ni(2)	O(4)	2.0120(14)	
Ni(2)	O(5)	2.0357(13)		Ni(2)	O(6)	2.0610(14)	
Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O(1)	Ni(1)	O(1*)	180	O(1)	Ni(1)	O(2)	90.19(5)
O(1)	Ni(1)	O(2*)	89.81(5)	O(1)	Ni(1)	O(3)	90.84(6)
O(1)	Ni(1)	O(3*)	89.16(6)	O(2)	Ni(1)	O(2*)	180
O(2)	Ni(1)	O(3)	90.04(6)	O(2)	Ni(1)	O(3*)	89.96(6)
O(3)	Ni(1)	O(3*)	180	O(4)	Ni(2)	O(4*)	180
O(4)	Ni(2)	O(5)	90.52(5)	O(4)	Ni(2)	O(5*)	89.48(5)
O(4)	Ni(2)	O(6)	88.93(6)	O(4)	Ni(2)	O(6*)	91.07(6)
O(5)	Ni(2)	O(5*)	180	O(5)	Ni(2)	O(6)	89.50(6)
O(5)	Ni(2)	O(6*)	90.50(6)	O(6)	Ni(2)	O(6*)	180

^a Symmetry code: * (1-x, 1-y, 1-z)

tetraphenylborate anions in a 1:2 molar ratio. The chemical structure and an ORTEP view are shown in Figs. 1 and 2, respectively, and the selected distances and angles are summarized in Tables 2 and 3S. In the crystal, there are two unique $[\text{Ni}(\text{NMF})_6]^{2+}$ cations. Hereafter, cations including Ni(1) or Ni(2) are called cations A and B, respectively. Each complex cation is centrosymmetric, and six NMF molecules coordinate to each nickel(II) ion to form an octahedral coordination geometry. The Ni(1)-O and the Ni(2)-O distances fall in the ranges of 2.0120(14) – 2.0610(14) Å (Table 2). The structures of cations A and B can both be considered to have *pseudo-S₆* symmetry (Fig. 3), as well as the previously reported hexakis-DMF nickel(II) cation $[\text{Ni}(\text{DMF})_6]^{2+}$.² Although the NiO_6 coordination geometry of $[\text{Ni}(\text{DMF})_6]^{2+}$ was trigonally compressed along the *pseudo-S₆* axis by 3.0%, neither cations A

Fig. 3 Two types of $[\text{Ni}(\text{NMF})_6]^{2+}$ cations projected along their each *pseudo-S₆* axis.

nor B showed such significant compression; only cation B showed trigonal compression along a different axis by 1.2% in the coordination geometry (Table 3S). If we focus on any tetragonal distortion of the NiO_6 coordination geometry, cation A can be seen to be tetragonally compressed along the O(2)-O(2*) direction by 1.1%, and tetragonally elongated along the O(1)-O(1*) direction by 0.9%. In the case of cation B, the geometry is tetragonally elongated along the O(6)-O(6*) direction by 1.2% and tetragonally compressed along the O(4)-O(4*) direction by 1.4%. Consequently, neither the trigonal distortion nor the tetragonal distortion is significant in both cations A and B. In the case of a related cobalt(II) complex, $[\text{Co}(\text{NMF})_6](\text{BPh}_4)_2$,⁴ two types complex cations, *pseudo-S₆* cations and *pseudo-C₂* cations, were found, and the present $[\text{Ni}(\text{NMF})_6]^{2+}$ cations were found to be less distorted [tetragonal distortion -1.19~+1.22%; trigonal distortion -1.22~+0.63%] than the $[\text{Co}(\text{NMF})_6]^{2+}$ cations [tetragonal distortion -1.40~+0.95%; trigonal distortion -2.40~+1.84%], which showed complicated distortion.

In conclusion, two types of $[\text{Ni}(\text{NMF})_6]^{2+}$ complex cations were found in the $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$ crystal; both cations have a *pseudo-S₆* symmetry. The distortion of the coordination geometry was not significant in the both cations.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Number 15K05445. Financial support by Yamagata University is also acknowledged.

Supporting Information: A CIF format file and Table 3S. These materials are available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

References

1. R. Boča, *Coord. Chem. Rev.*, **2004**, 248, 757.
2. R. Yamaguchi, M. Yamasaki, and H. Sakiyama, *X-ray Struct. Anal. Online*, **2011**, 27, 71.
3. R. Sudo, D. Yoshioka, M. Mikuriya, and H. Sakiyama, *X-ray Struct. Anal. Online*, **2013**, 29, 17.
4. R. Yamaguchi, D. Yoshioka, M. Mikuriya, and H. Sakiyama, *X-ray Struct. Anal. Online*, **2015**, 31, 7.