

DINUCLAR NICKEL(II) PIVALATE WITH μ -AQUA AND DI- μ -PIVALATO BRIDGES SHOWING A FERROMAGNETIC INTERACTION

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Abstract. Dinuclear nickel(II) complex, $[\text{Ni}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{OH}_2)\{\text{HO}_2\text{CC}(\text{CH}_3)_3\}_4]$ (**1**), was synthesized and characterized by elemental analysis, IR and UV-Vis-NIR spectroscopy, and temperature dependence of magnetic susceptibilities (4.5–300 K). Single-crystal X-ray crystallography revealed a dinuclear core with μ -aqua and di- μ -pivalato bridges having monodentate pivalato and monodentate pivalic acid molecules. Magnetic data analysis showed a ferromagnetic interactions between the two nickel atoms with $g = 2.251$, $J = 2.78 \text{ cm}^{-1}$, $D = 3.75 \text{ cm}^{-1}$, and $tip = 184 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$; $g = 2.253$, $J = 2.73 \text{ cm}^{-1}$, $D = -3.26 \text{ cm}^{-1}$, and $tip = 176 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

Keywords: nickel complex, dinuclear complex, magnetic property, ferromagnetic interaction.

Introduction

Copper(II) acetate is a well-known dinuclear metal complex, having a lantern-type (or paddlewheel-type) core composed of two copper(II) atoms and four acetato bridges as shown in Figure 1 (a) [1-9]. On the other hand, nickel(II) acetate is known as a mononuclear metal complex composed of one nickel(II) atom and two acetato and four aqua ligands shown in Figure 1 (b).

Although a lantern-type dinuclear core was also found in some adducts of nickel(II) pivalate [10-12], the structure of the parent complex, nickel(II) pivalate, has not been elucidated yet. Therefore, we tried to reveal the

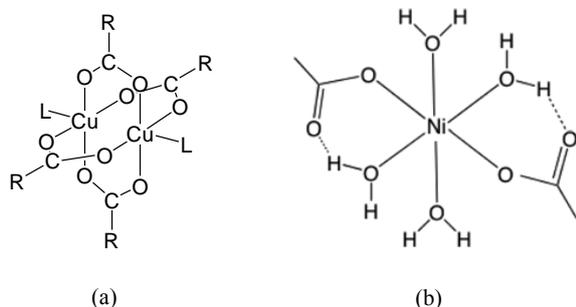


Figure 1. Molecular structures of copper(II) acetate monohydrate (R = CH₃) and nickel(II) acetate tetrahydrate.

molecular structure of nickel(II) pivalate by crystallizing the parent complex using various kinds of organic solvents. In this study, we isolated a crystalline material by recrystallizing the product from hexane. The isolated complex was characterized by elemental analysis, IR and UV-Vis-NIR spectroscopy, measurement of temperature dependence of magnetic susceptibilities (4.5-300 K), and single-crystal X-ray crystallography. The X-ray structure analysis of the complex revealed a different dinuclear core from the lantern-type dinuclear copper(II) complexes. Interestingly temperature dependence of magnetic susceptibilities (4.5-300 K) of the complex showed a ferromagnetic property. Herein, we report on the crystal structure, spectral features, and magnetic property of this complex.

Experimental

All reagents and solvents were obtained from commercial sources and were used without further purification. $[\text{Ni}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{OH}_2)\{\text{HO}_2\text{CC}(\text{CH}_3)_3\}_4]$ (**1**).

Nickel(II) carbonate hydroxide (0.358 g, 1.17 mmol) and pivalic acid (0.966 g, 9.45 mmol) were mixed at room temperature and then heated at 60°C with stirring for 1 hr. The resulting green product was dissolved in hexane (200 mL) and the solution was filtrated. The solution was concentrated by rotary evaporator to 5 mL and left in a refrigerator overnight. Green crystals that deposited were collected by filtration, washed with small amount of petroleum ether. Yield: 0.458 g (27.5%). Anal. Found: C, 51.08; H, 7.96%. Calcd for $\text{C}_{40}\text{H}_{78}\text{Ni}_2\text{O}_{17}$: C, 50.66; H, 8.29%. IR (KBr): $\nu(\text{OH})$ 3350sh, 3140sh; $\nu_{\text{as}}(\text{CO}_2^-)$ 1607, 1482; $\nu_{\text{s}}(\text{CO}_2^-)$ 1407, 1362. Diffuse reflectance spectrum: λ_{max} 390, 664, 740 sh, 1132 nm.

Measurements: Elemental analyses for carbon, hydrogen, and nitrogen were done using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm^{-1} region. Electronic spectra were measured with a Shimadzu UV-Vis-NIR Recording Spectrophotometer (Model UV-3100). Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5–300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828\sqrt{\chi_M T}$, where χ_M is the molar magnetic susceptibility per mole of dinuclear nickel molecule.

X-Ray crystallography: X-Ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer (Mo $K\alpha$ radiation) at 90 K and indexed using the SMART software. Crystal data and details concerning data collection are given in Table 1. The cell parameters were refined by full-matrix least-squares on F^2 . Integrated intensity information for each reflections was obtained and corrected using the SAINT+ program package including the reduction program SAINT and the empirical absorption correction program SADABS. The structure was solved using the SHELXTL program. The structure was solved by direct methods, and the residual non-hydrogen atoms were located by D-Fourier synthesis. All of non-hydrogen atoms were refined by full-matrix least-squares on F^2 . The hydrogen atoms except for those of water molecules were inserted at their ideal positions and fixed there. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software package. CCDC 997144 for **1** contains supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (internet.) +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1

Crystal and experimental data.

Parameter	Value
Chemical formula	$\text{C}_{40}\text{H}_{78}\text{Ni}_2\text{O}_{17}$
Formula weight	948.44
Temperature, (K)	90
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4
a, (Å)	11.920(3)
b, (Å)	19.811(4)
c, (Å)	22.746(5)
β , (°)	103.523(4)
V, (Å ³)	5222(2)
D_x , (g/cm ³)	1.206
Radiation: Mo $K\alpha$, λ , (Å)	0.71073
μ (Mo $K\alpha$), (mm ⁻¹)	0.781
F, (000)	2040
Crystal size, (mm ³)	0.66 × 0.39 × 0.34
No. of reflections collected	31122
No. of independent reflections	12083
θ range for data collection, (°)	1.78 - 28.44
Data/Restraints/Parameters	12083/0/551
Goodness-of-fit on F^2	0.974
R indices [$I > 2\sigma(I)$]	$R1 = 0.0368$, $wR2 = 0.0874$
R indices (all data)	$R1 = 0.0536$, $wR2 = 0.0921$
$(\Delta/\sigma)_{\text{max}}$	0.000
$(\Delta\rho)_{\text{max}}$, (eÅ ⁻³)	0.711
$(\Delta\rho)_{\text{min}}$, (eÅ ⁻³)	-0.233
Measurement	Bruker Smart APEX CCD diffractometer
Program system	SHELXTL
Structure determination	Direct methods (SHELXS-97)
Refinement	full matrix least-squares (SHELXL-97)
CCDC deposition number	997144

Results and discussion

Reaction of nickel(II) carbonate hydroxide with excess amount of pivalic acid gave green product. Successive recrystallization of the product from hexane afforded green crystals. The formulation of dinuclear species, $[\text{Ni}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{OH}_2)\{\text{HO}_2\text{CC}(\text{CH}_3)_3\}_4]$, was confirmed by the elemental analysis, infrared and electronic absorption spectroscopies, single-crystal X-ray structure analysis, and magnetic susceptibility measurement. In the infrared spectra of **1**, two strong bands assignable to antisymmetric $\nu_{\text{as}}(\text{CO}_2)$ stretching vibrations were observed at 1608 and 1483 cm^{-1} , whereas another two bands attributable to symmetrical $\nu_{\text{s}}(\text{CO}_2)$ stretching vibrations appear at 1407 and 1360 cm^{-1} . The Δ values of $\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$, $1607 - 1362 = 245 \text{ cm}^{-1}$ and $1482 - 1407 = 75 \text{ cm}^{-1}$, are in the ranges of monodentate and *syn-syn* bridging pivalato, respectively [7,13,14] (Figure 2). The shoulder bands at 3350 and 3140 cm^{-1} in **1** may be attributed to $\nu(\text{OH})$ stretching bands of pivalic acid and water molecules [13].

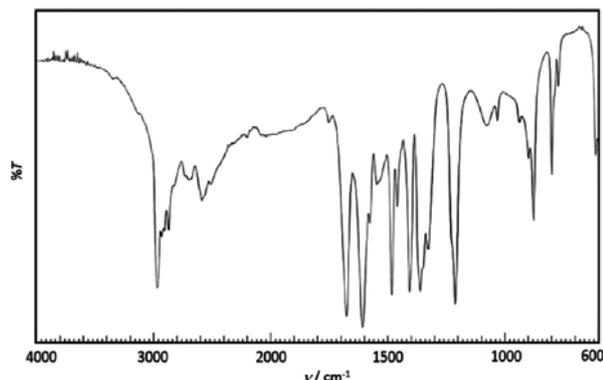


Figure 2. Infrared spectra of **1**.

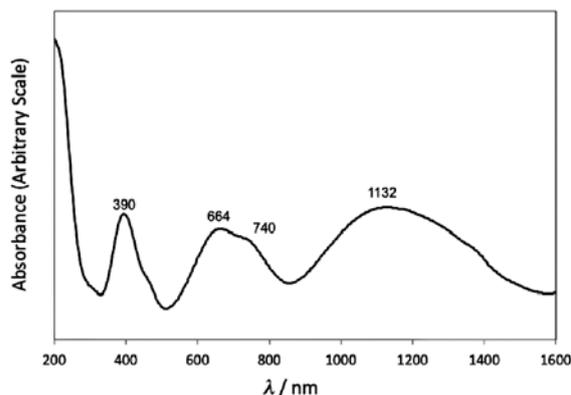


Figure 3. Diffused reflectance spectra of **1**.

The diffused reflectance spectra of **1** are shown in Figure 3. Four absorption bands appear at around 390, 664, 740 sh, and 1132 nm in solid. These bands can be attributed to d-d transitions of octahedral nickel(II) complex in origin. The first band at 1132 nm may be assigned to spin-allowed ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{2g}({}^3\text{F})$ transition, a shoulder at 740 nm to a spin-forbidden ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^1\text{E}_g({}^1\text{D})$ transition, a band at around 664 nm to spin-allowed ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{1g}({}^3\text{F})$ transition, and a band at 390 nm to spin-allowed ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{1g}({}^3\text{P})$ transition [15]. The spectral feature is in harmony with the presence of two octahedral nickel(II) ions.

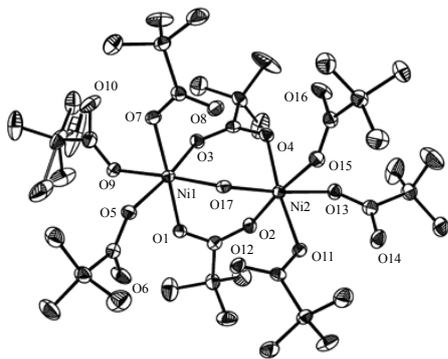


Figure 4. ORTEP drawing of the structure of the dinuclear nickel complex showing the 50% probability level thermal ellipsoids.

Selected bond lengths (Å) and angles (°): Ni1···Ni2 3.3969(7), Ni1-O1 2.0336(14), Ni1-O3 2.0194(13), Ni1-O5 2.0832(13), Ni1-O7 2.0577(14), Ni1-O9 2.0640(14), Ni1-O17 2.0319(13), Ni2-O2 2.0140(14), Ni2-O4 2.0284(13), Ni2-O11 2.0532(13), Ni2-O13 2.0715(14), Ni2-O15 2.0935(14), Ni2-O17 2.0823(13), Ni1-O17-Ni2 113.57(6).

Single crystals of **1** were obtained by recrystallization of the reaction product from hexane. X-ray crystal structure analysis revealed that the present complex has a dinuclear nickel(II) core being different a little from the lantern-type dinuclear metal complexes. The structure of the dinuclear complex drawn by ORTEP is shown in Figure 4. The Ni1 atom is coordinated by two pivalato-oxygen atoms (O1 and O3) of *syn-syn*-bridging, one monodentate pivalato-oxygen atom (O7), two oxygen atoms (O5 and O9) of monodentate pivalic acid molecules, and bridging aqua-oxygen atom (O17) in an octahedral geometry, whereas the Ni2 atom is coordinated by two bridging pivalato-oxygen atoms (O2 and O4), one monodentate pivalato-oxygen atom (O11), two oxygen atoms (O13 and O15) of monodentate pivalic acid molecules and μ -aqua-oxygen atom (O17) in an octahedral geometry. The Ni1···Ni2 distance is 3.3969(7) Å. There are hydrogen bonds between the monodentate pivalato ligand and the μ -aqua molecule [O17(H)···O8 2.539(2) Å, O17(H)···O12 2.526(2) Å]. Another hydrogen bonds can be found between the coordinating pivalic acid molecule and the bridging pivalato group or the neighboring pivalic acid molecule [O6(H)···O1 2.564(2) Å, O10(H)···O7 2.534(2) Å, O14(H)···O11 2.567(2) Å, O16(H)···O4 2.578(2) Å]. Almost same structure was reported by Eremenko et al. [16] and Winpenny et al. [17,18], although the preparative methods are different from the present preparation. The Eremenko's crystal structure was measured

at 230 K and is almost same as the present crystal structure taken at 90 K, whereas the Winpenny's structure at 150 K belongs to different crystal system and space group, orthorhombic *Pbca*, irrespective of the similar dinuclear structure.

Temperature dependence of effective magnetic moment of **1** is shown in Figure 5. The magnetic moment is 4.65 μ_B at 300 K per dinuclear nickel(II) molecule, which is significantly higher than the spin-only value (4.00 μ_B). The magnetic moment gradually increases with lowering of temperature until reaching 5.36 μ_B at 4.5 K, being typical of ferromagnetic behavior [19]. The magnetic data were analyzed with magnetic susceptibility Eq.(1) based on the Heisenberg model $H = -2J\mathbf{S}_{\text{Ni1}} \cdot \mathbf{S}_{\text{Ni2}}$ considering zero-field-splitting (D) by the Ginsberg's method [20].

$$\chi_M = (2Ng^2\mu_B^2/3)[F_1/(kT) + 2F_5] + tip \quad (1)$$

where

$$\delta = [(3J+D)^2 - 8JD]^{1/2}$$

$$c_1 = 2(2)^{1/2}D/[(9J-D+3\delta)^2 + 8D^2]^{1/2}$$

$$c_2 = (9J-D+3\delta)/[(9J-D+3\delta)^2 + 8D^2]^{1/2}$$

$$F_0 = 2 + \exp[D/(kT)] + \exp[J/(kT)] \exp[-\delta/(kT)] + \exp[J/(kT)] \exp[\delta/(kT)] + 2\exp[4J/(kT)] + 2\exp[4J/(kT)] \exp[D/(kT)]$$

$$F_1 = \{1 + \exp[4J/(kT)] + 4\exp[4J/(kT)] \exp[D/(kT)]\} / F_0$$

$$F_2 = \{2\exp[4J/(kT)] \exp[-D/(kT)] + \exp[D/(kT)] - 1 - 2\exp[4J/(kT)]\} / F_0$$

$$F_3 = \{\exp[4J/(kT)] - \exp[J/(kT)] \exp[\delta/(kT)]\} / F_0$$

$$F_4 = \{\exp[4J/(kT)] - \exp[J/(kT)] \exp[-\delta/(kT)]\} / F_0$$

$$F_5 = F_2/D + 3c_2^2F_3/(3J-\delta) + 3c_1^2F_4/(3J+\delta).$$

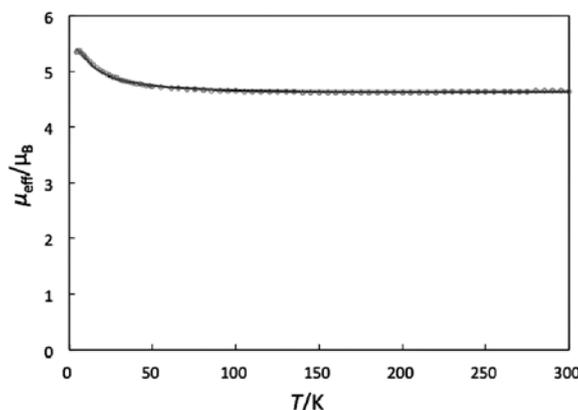


Figure 5. Temperature dependence of magnetic moment of **1**.

Best fitting curve was obtained for positive and negative D values, respectively: $g = 2.251$, $J = 2.78 \text{ cm}^{-1}$, $D = 3.75 \text{ cm}^{-1}$, and $tip = 184 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$; $g = 2.253$, $J = 2.73 \text{ cm}^{-1}$, $D = -3.26 \text{ cm}^{-1}$, and $tip = 176 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ [15,21]. This result shows that a considerable ferromagnetic interaction is operating between the two nickel atoms. Similar magnetic behavior was also reported by Eremenko [16] and Winpenny [17], although a smaller D value was found. The bridging angle between the two nickel atoms is $113.57(6)^\circ$ for Ni1-O17-Ni2 in the present crystal structure. The corresponding Ni-O-Ni angle is $112.8(2)^\circ$ in Eremenko's crystal structure [16], whereas $111.24(11)^\circ$ [17] or $111.53(10)^\circ$ [18] in Winpenny's crystal structures. From the magneto-structural relationship between exchange interaction and Ni-O-Ni angle, the observed Ni-O-Ni angles prefer antiferromagnetic interaction rather than ferromagnetic interaction [15,19]. In this regard, we should notice that a DFT calculation showed a positive J value of 3.6 cm^{-1} for the Ni-O-Ni angle of 111.53° [18]. This may come from the combination of the hydrogen-bonded aqua and two pivalato bridges.

Conclusions

Recrystallization of reaction product of pivalic acid and nickel(II) carbonate hydroxide from hexane gave a dinuclear nickel(II) complex, $[\text{Ni}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{OH}_2)\{\text{HO}_2\text{CC}(\text{CH}_3)_3\}_4]$. The crystal structure revealed a unique dinuclear core with μ -aqua- and di- μ -pivalato-bridges having monodentate pivalato and monodentate pivalic acid molecules. In contrast with the structural feature, a considerable ferromagnetic interaction was observed for the present complex.

Acknowledgements

During the course of publication, we became aware of the literatures on the present complex. We thank the referees for their pointing out. The present work was partially supported by Grant-in-Aid for Scientific Research No. 26410080 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan) and the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2010-2014.

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