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Synthesis and characterisation of a new six-coordinated thermochromic Ni complex

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1. Introduction

Chromotropism is defined as a reversible colour change induced by an external stimulus [1,2]. For example, Irie et al. and Abe et al. described photochromic organic molecules that changed colour when they were irradiated with light [3,4]. Tsuji et al. described electrochromic organic molecules that changed colour when a potential was applied [5].

Moreover, in the field of coordination compounds, there are many complexes that change colour reversibly because of external stimuli [6]. Thermochromic behaviour is chromotropism induced by a temperature change. Thermochromism in Ni(II) complexes can be divided into three types from the viewpoint of the reason for change in colour of complexes. A type (i) complex changes colour because the coordination number changes between six (giving an octahedral structure) and four (giving a square planar structure) in solution because of the complex being coordinated and un-coordinated of solvent [7–9]. A type (ii) complex changes colour because the coordination structure changes between a square planar structure and a tetrahedral structure in the solid state [10–12]. Type (iii) complexes are those that change colour for other reasons such as isomerization [13]. Some square planar Ni(II) complexes that show type (i) thermochromism are interesting because they not only change colour but also change spin

ABSTRACT

The Ni(II) complex [Ni(diethylenetriamine)(2,6-bis(hydroxymethyl)pyridine)]·PF₆·CF₃COO·H₂O is described here. A single crystal X-ray crystallographic study revealed that the Ni(II) in the complex has a six-coordinated octahedral structure. The complex shows thermochromic behaviour in the solid state. X-ray crystallographic studies at various temperatures suggested that the thermochromism is caused by anisotropic structural change. The relationship between the structural change and the colour change was confirmed by absorption spectrum and TD-DFT calculation.

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state. However, types (i) and (ii) are the dominant thermochromic Ni(II) complexes. As far as we know, occurrence of thermochromism due to a change in the coordination number in the solid state is quite rare.

Taki et al. recently described the thermochromic square planar Ni(II) complex **1**, which is illustrated in Scheme **1** [14]. Complex **1** has one aromatic N atom and three aliphatic N atoms. The central Ni(II) atom has a slightly distorted square planar coordination environment in the solid state. In solution, such as CH₃CN or acetone, complex **1** changes from a square planar structure into an octahedral structure because of solvent molecules become coordinated to it. The solvent coordination in equilibrium at the temperature, as shown in Scheme 2, and the equilibrium shifts to the right with lowering temperature.

Accordingly, a novel type of thermochromism could occur because of a change in the coordination number in the solid state. Covalently linking extra donor atoms to the ligand in complex **1** could provide an alternative source of coordinating atoms (which would still be present in the solid state) to the coordinating solvent, required to change the coordination number in the original complex **1**. Such a derivative of complex **1** might be thermochromic because of the coordination and un-coordination of these donor atoms even in the solid state. In this study, we synthesised a complex with linked donor atoms. Here, we describe the crystal structure and thermochromic behaviour of [Ni(dien) (py(CH₂OH)₂)]·PF₆·CF₃COO·H₂O (dien: diethylenetriamine; py(CH₂OH)₂: 2,6-bis(hydroxymethyl)pyridine) (**2**), which is shown in Scheme **1**.







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Scheme 1. Molecular structure of complexes 1 and 2.

2. Experimental

2.1. Materials

All materials were purchased from commercial suppliers (Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd.) and were used without further purification.

2.2. Instrumentation

Organic elemental analysis (C, H and N) was performed by the elementary analysis of organic compounds service centre at Kyushu University. Thermogravimetry was performed using an SII TG/DTA6300 thermogravimetric analyser in a flowing N₂ atmosphere, with a heating rate of 10 K min⁻¹. Differential scanning calorimetry (DSC) was performed using an SII DSC6220N instrument, with a heating and cooling rate of 2 K min⁻¹, and photographs were taken during the DSC analyses. Electrospray ionisation mass spectrum was obtained using a JEOL JMS-T100CS mass spectrometer. Absorption spectra were recorded using a SHIMADZU UV-3600 UV–Vis–NIR spectrophotometer, with an optical path length of 1 cm. Absorption spectra were measured at various temperatures using the spectrophotometer equipped with an OXFORD CF1104 continuous flow cryostat, and the samples were prepared as KBr pellets.

2.3. Synthesis

A solution of dien (0.390 g, 3.78×10^{-3} mol) in MeOH (4 cm³) was added dropwise into an aqueous solution of NiSO4·6H2O (0.995 g, 3.79×10^{-3} mol) in H₂O (8 cm³), then a solution of $py(CH_2OH)_2$ (0.599 g, 4.30×10^{-3} mol) in MeOH (4 cm³) was added to the mixture. After several days, an excess of NH₄PF₆ was added to the mixture, then the solution was concentrated to ca. 5 cm^3 using a rotary evaporator. The precipitate formed was collected by filtration, and the crude product was purified by recrystallizing it from an excess of a mixture of CF₃COONa, H₂O and acetone. Red-purple block-shaped crystals, that would be $[Ni(dien)_2]^{2+}$ complex, first recrystallized and were separated from the solution by filtration. Blue-purple pillar-shaped crystals recrystallized next, and these were also collected by filtration; their yield was 0.632 g (29.9%). Anal. Calc. for $C_{13}H_{24}F_9N_4NiO_5P_1$: C, 27.06; H, 4.19; N, 9.70. Found: C, 27.04; H, 4.16; N, 9.82%. UV-Vis λ_{max} (CH₃CN)/nm 302 (ϵ /dm³ mol⁻¹ cm⁻¹ 66), 549 (5.8), 758 (12) and 803 (12). ESI-MS: *m*/*z* 299 (calc. for M-H₂O-PF₆- $CF_3COO-H = 299$).

2.4. X-ray crystallography

Single crystals of **2** suitable for single-crystal X-ray analysis were obtained by slowly recrystallizing **2** from a mixture of CF₃COONa, H_2O and acetone at room temperature. X-ray diffraction data were collected using a RIGAKU R-AXIS RAPID II IP



Scheme 2. Thermochromic behaviour of complex 1.

diffractometer, with graphite-monochromated Mo K α radiation (λ = 0.71070 Å). Multi-scan absorption correction was applied to the intensity data. The structure was solved using the direct method (using siR-2011) [15] and refined using the full-matrix least-squares method using F^2 (SHELXL-2013) [16]. All non-hydrogen atoms were refined using a nisotropic parameters. H atoms in O–H groups were located using a difference Fourier map, and the coordinates were fixed. Other H atoms were included in the calculated positions and refined using a riding model. Crystallographic diagrams were obtained using the ortep program [17]. Crystal data are shown in Table 1.

2.5. Computational details

The GAUSSIAN 09 program package [18] was used for the calculations undertaken at the Research Institute for Information Technology, Kyushu University. The TD-DFT calculations [19] at the B3LYP [20]/LANL2DZ [21] level of theory were performed to calculate the excited states in the gas phase. All calculations were performed for the complex cation of which geometry was obtained from the X-ray crystallography.

3. Results and discussion

3.1. Molecular design

Complex **2** has one N atom in a pyridine ring and three N atoms in dien; hence, **2** has approximately the same N_4 coordination environment as that of **1**. In addition, **2** has extra O donor atoms linked to the pyridine ring. The extra O donor atoms in **2** can act as the solvent molecules in complex **1**. Therefore, **2** could be exhibit thermochromism depending on coordination of the O donor atom in the solid state.

Empirical formula	$C_{13}H_{24}F_9N_4Ni_1O_5P_1$	
Formula weight	577.04	
Crystal size (mm ³)	$0.48 \times 0.16 \times 0.10$	
Т	100(2)	300(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	Pnma
a (Å)	8.4710 (3)	13.7521 (7)
b (Å)	13.7247 (5)	8.6463 (4)
c (Å)	19.7789 (7)	20.2107 (9)
β (°)	94.8489 (11)	90
V (Å ³)	2291.30 (14)	2403.1 (2)
Ζ	4	4
D_{calc} (g cm ⁻³)	1.673	1.595
μ (mm ⁻¹)	1.021	0.974
Goodness-of-fit on F^2	1.160	1.087
$R_1^{a}, w R_2^{b} (I > 2\sigma(I))$	0.0450, 0.119	0.0720, 0.221
R_1^{a} , wR_2^{b} (all data)	0.0524, 0.123	0.0917, 0.239
Reflections collected	35651	37 599
Reflections unique, R _{int}	5215, 0.0399	2933, 0.0480

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$

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