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A Novel Five-Coordinated Sodium Ion Captured in $Na_2[Ni(succim)_4]\cdot 2H_2O$ (succim = succinimidate) Complex: Crystal Structure and Crystal Polarized Electronic Spectra.

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The crystal structure of $Na_2[Ni(succim)_4]\cdot 2H_2O$ complex having four monodentate succinimidate (succim) ligands was determined by X-ray structural analysis. The host complex captures five-coordinated guest sodium ion, which is the first example of a podand complex formed in a crystal. Polarized crystal electronic spectra of the complex were measured with parallel and perpendicular to *b* axis polarization.

Host-guest recognition is a subject of great interest in recent supramolecular chemistry.[1] Receptors to capture specific substrates, for instance cryptates and crown ethers, lead to supramolecular crystalline architectures. Especially, half-opened podands[2] would be expected as a host complex for induced fitting.[3] We have systematically studied about complexes having monodentate imidate and amine ligands. The flexibility of $3d^9$ copper(II) complexes results in a variety of coordination geometries such as square planar $[CuN_4]$,[5,6] distorted square planar $[CuN_4]$,[6,7] or square pyramidal $[CuN_4O]$[8,9] depending on steric factors of ligands or counter ions. Rigid $4d^8$ palladium(II) complexes, however, usually afford a square planar $[PdN_4]$ geometry.[10] Herein, we report crystal structure and polarized crystal electronic spectra of $3d^8$ nickel(II) complex, $Na_2[Ni(succim)_4]\cdot 2H_2O$. Surprisingly, five-coordinated sodium ion captured by the host podand complex has been found for the first time, while crown ethers are known to capture a sodium ion selectively.

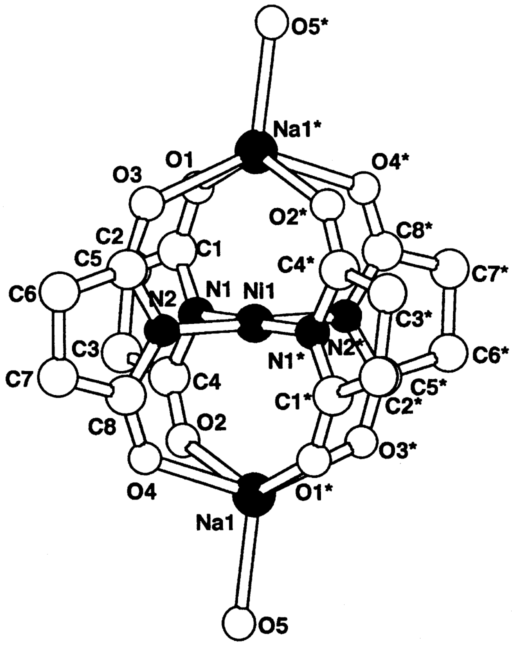

Fig. 1. Molecular structure of $Na_2[Ni(succim)_4]\cdot 2H_2O$. Selected bond distances (Å) and angles (°): Ni1–N1 1.898(3), Ni1–N2 1.901(4), Na1–O1 2.347(4), Na1–O2 2.420(4), Na1–O3 2.347(4), Na1–O4 2.416(4), Na1–O5 2.311(4), N1–Ni1–N1* 180.0, N2–Ni1–N2* 180.0, N1–Ni1–N2 90.1(1), N1–Ni1–N2 89.9(1), O1–Na1–O2 140.1(1), O1–Na1–O3 81.0(2), O1–Na1–O4 84.2(1), O1–Na1–O5 107.0(1), O2–Na1–O3 80.1(2), O2–Na1–O4 89.2(2), O2–Na1–O5 111.2(1), O3–Na1–O4 141.5(1), O3–Na1–O5 102.5(1), O4–Na1–O5 115.8(1). The atoms marked with *'s are expanded by symmetry operation ($-x$, $-y$, $-z$).

Figure 1 shows the complex which affords a square planar $[NiN_4]$ coordination geometry with Ni1–N1 1.898(3) and Ni1–N2 1.901(4) Å. Four succinimidate ligands are almost perpendicular to the $[NiN_4]$ coordination plane, which enables the ligands to capture a sodium ion as a podand. Though several cationic nickel(II) complexes have been reported as monodentate neutral pyridine derivative ligands,[11–13] this is the first example for an anionic complex. The Ni–N bond lengths are slightly shorter than that of the neutral ligand complexes (average 1.95 Å), however, they are considerably shorter than that of the related copper(II) complexes (average 2.02 Å) in agreement with the ionic radii of nickel(II) and copper(II). No interaction may be expected at the bond length Ni1–Na1 3.047 Å. The sodium ion is five-coordinated with a distorted square pyramidal geometry. Four of the five oxygens are carbonyls of imidates and the other is a crystalline water, and Na–O bond lengths range from 2.311(4) to 2.420(4) Å. As far as we know, this is the first five-coordinated sodium ion captured in a podand complex. The coordination number of guest ion (crystalline water) is crucial for symmetry of host complexes in crystals. Depending on the size of counter alkali ions (M^+), $M_2[Cu(succim)_4]$ complexes are tunable to form various crystal structures from the same host complexes. The coordination features are as follows: Li^+4 (tetrahedral), K^+6 (octahedral), Cs^+6 (octahedral) and 8 (cubic) , and Rb^+6 (octahedral) and 8 (cubic).[5,6]

The present yellow complex shows a broad ligand field band with a peak at 24000 cm^{-1} with E//*b* and E⊥*b* polarization

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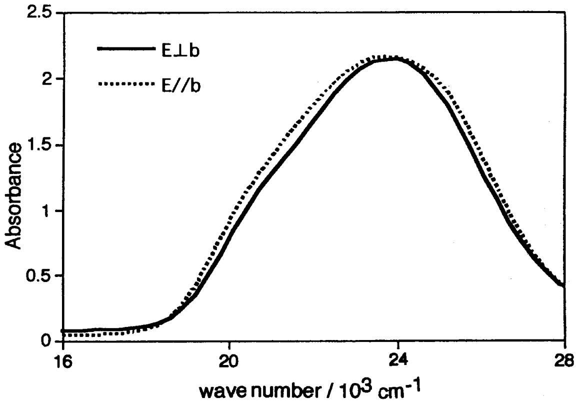

Fig. 2. Polarized crystal spectra of $Na_2[Ni(succim)_4]\cdot 2H_2O$ from (001) face with E//*b* and E⊥*b* polarization.

(Fig. 2). The peak is characteristic for square planar $[NiN_4]$ complexes.[14] The projections of electric vector onto a $[NiN_4]$ coordination plane are $0.1253x^2 + 0.0416y^2 + 0.8331z^2$ (E // *b*) and $0.7939x^2 + 0.1369y^2 + 0.0692z^2$ (E⊥*b*), because the present crystal shows little anisotropic spectra by polarization. Complexes of this type would be a good example to tune optical anisotropy or other crystalline properties. Further studies on polarized crystal spectra are in progress, for example separate observation of a certain transition.

Experimental

Preparation of $Na_2[Ni(succim)_4]\cdot 2H_2O$. The complex was prepared from the reaction of nickel(II) acetate tetrahydrate (0.625 g, 2.51 mmol) in water (25 cm³), an aqueous solution (3 cm³) of sodium hydroxide (0.625 g, 15.6 mmol) and succinimide (1.50 g, 15.0 mmol) for 30 min at 50 °C. The resulting yellow precipitates were washed with ethanol and recrystallized from aqueous solution (7 cm³) of sodium hydroxide (1.00 g, 25.0 mmol) and succinimide (4.00 g, 40.0 mmol). $Na_2[Ni(succim)_4]$: Anal. Calcd for $C_{16}H_{16}N_4Na_2NiO_8$: C, 38.62; H, 3.24; N, 11.27%. Found: C, 38.42; H, 3.33; N, 11.23%. Yellow plate-like crystals of $Na_2[Ni(succim)_4]\cdot 2H_2O$ were obtained from the resulting solution at room temperature.

Measurement. The polarized crystal electronic spectra were recorded with a Hitachi U-3400 UV/VIS/NIR spectrophotometer with originally designed attachments for polarized crystal spectra. The light beam passed though a PM-8AS 8 × 8 polarizer (effective from 320 to 2300 nm, 90% transmittance) onto a pinhole (0.40 mm in diameter) in an aluminum plate where a thin crystal was mounted. The polarized crystal spectra were determined with the electronic vector parallel and perpendicular to the *b* axis on (001) face. The orientations of crystal axes and shapes were confirmed by X-ray diffraction measurements. Elemental analysis was performed by the Liberal Arts and Sciences Organization, Osaka University.

X-ray Crystallography. Intensity data were collected on a Rigaku AFC-5R four-circle diffractometer with nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). The structure was solved by a direct method using SIR92[15] and refined by a full-matrix least-squares method with a teXsan program package[16] on a SGI O2 workstation. Crystal data for $Na_2[Ni(succim)_4]\cdot 2H_2O$: $C_{16}H_{20}N_4Na_2NiO_{10}$; FW = 533.03; $T = 300$ K; Cu$K\alpha$ 1.54178 Å; Monoclinic; $P2_1/c$; $a = 8.792(2)$ Å; $b = 13.356(2)$ Å; $c = 9.827(2)$ Å; $\beta = 113.19(2)$; $V = 1060.8(4)$ Å³; $Z = 2$; $D_{calc} = 1.669$ g cm⁻³; $\mu = 23.05$ cm⁻¹; $F(000) = 548$; (0.20 × 0.20 × 0.30 mm); Rigaku AFC5R; $2\theta_{max} = 119.9°$; Measured reflections: 1770; Independent reflections: 1653 (R_{int} 0.039); Used reflections: [$I > 2.0\ \sigma(I)$] 1458; Parameters: 151; Full-matrix least-squares on F. R = 0.050; $R_w = 0.065$. List of atomic coordinates, anisotropic thermal parameters, and bond distances and angles are deposited as Document No.74015 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 154895.

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