Inorganic Chemistry

COMMUNICATION

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Paramagnetic−Diamagnetic Phase Transition Accompanied by Coordination Bond Formation−Dissociation in the Dithiolate Complex $Na[Ni(pdt)_2]\cdot 2H_2O$

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Supporting Information

ABSTRACT: Bis(2,3-pyrazinedithiolate)nickel complex $Na[Ni(pdt)_2]\cdot 2H_2O$ formed one-dimensional stacks of the $Ni(pdt)_2$ units and showed strong antiferromagnetic interactions along the stacking direction. A first-order phase transition between the paramagnetic and diamagnetic states, which was driven by dimerization of the $Ni(pdt)_2$ units, accompanied by coordination bond formation, was observed.

Electronic properties of bis(*o*-dithiolate) metal complexes, such as superconductivity,[1] spin liquid phenomena,[2] single-component molecular metal behavior,[3] etc., have been extensively studied in relation to conducting and magnetic materials because of their redox activity and π-extended molecular orbitals. Some bis(*o*-dithiolate) metal complexes with a one-dimensional electronic structure undergo a phase transition caused by electronic instability or bistability via a strong electron−lattice interaction, such as a charge-transfer (CT) phase transition,[4] Peierls transition,[5] etc. In the present Communication, we report that the bis(*o*-dithiolate)nickel complex $Na[Ni(pdt)_2]\cdot 2H_2O$ (pdt = 2,3-pyrazinedithiolate) undergoes a phase transition between the paramagnetic and diamagnetic states, which is driven by dimerization of the $Ni(pdt)_2$ units, accompanied by coordination bond formation−dissociation.

$Na[Ni(pdt)_2]\cdot 2H_2O$ was synthesized by the electrochemical oxidation of $Na_2[Ni(pdt)_2]$ in 5:1 (v/v) H_2O/MeOH with a constant current of 5 μA. After 1 week, black needle-shaped crystals formed on the anode. Elem anal. Calcd for $C_8H_8N_4Na_1Ni_1O_2S_4$: C, 23.89; H, 2.01; N, 13.93. Found: C, 23.895; H, 1.962; N, 13.994. The magnetic susceptibility of the polycrystalline sample was measured in a 1 T field using a Quantum Design MPMS susceptometer. Single-crystal structures were determined on a Rigaku CCD diffractometer with a VariMax microfocus X-ray source of graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The electrical resistivity was measured by using a two-probe method with a constant voltage of 1.0 V on a Keithley 6211 system sourcemeter.

Figure 1 shows the crystal structure of $Na[Ni(pdt)_2]\cdot 2H_2O$ at 230 K. The $Ni(pdt)_2$ units had square-planar geometries. In the *bc* plane, the $Ni(pdt)_2$ units are arranged in a herringbone motif. Each $Ni(pdt)_2$ unit is connected to each other via weak N−Na coordination bonds (N−Na distance = 2.586 Å). $Ni(pdt)_2$ units

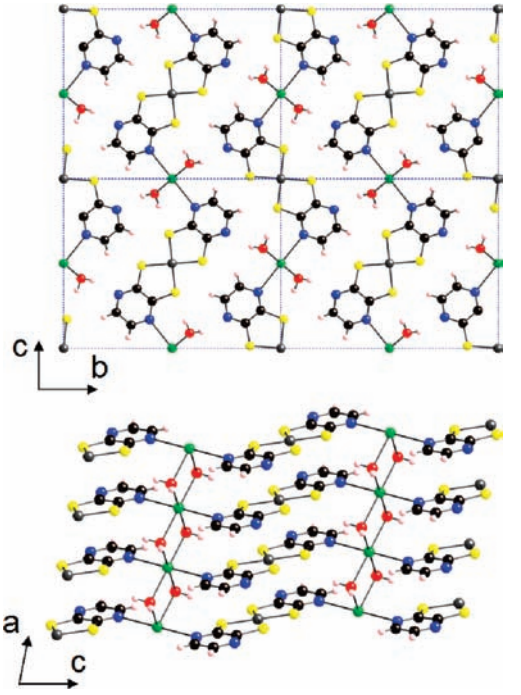

Figure 1. Crystal structure of $Na[Ni(pdt)_2]\cdot 2H_2O$ at 230 K: (a) top view; (b) side view. Color code: gray, Ni; yellow, S; green, Na; red, O; blue, N; black, C; pink, H.

are one-dimensionally stacked through an infinite number of $\cdots Na-(\mu\text{-}O_{aq})_2-Na\cdots$ coordination bonds along the *a* axis with a distance of 3.54 Å, indicating that there are $\pi-\pi$ interactions between the neighboring $Ni(pdt)_2$ units. The structure is almost the same as that previously reported for $Na[Cu(pdt)_2]\cdot 2H_2O$.[6] However, the nickel complex is spin $^1/_2$, whereas the copper complex is spinless.

Figure 2 shows molecular orbitals of $[Ni(pdt)_2]^-$ calculated using density fundtional theory (DFT) at the UB3LYP level with the 6-31G* basis set. The X-ray data were used for the calculations, and point charges of 0.5+ were added at the positions of the Na ions. On the basis of the DFT calculations, the lowest unoccupied molecular orbital (LUMO) is comprised of an antibonding Ni $d_{x^2-y^2}$ orbital and an S p_σ orbital. The singly

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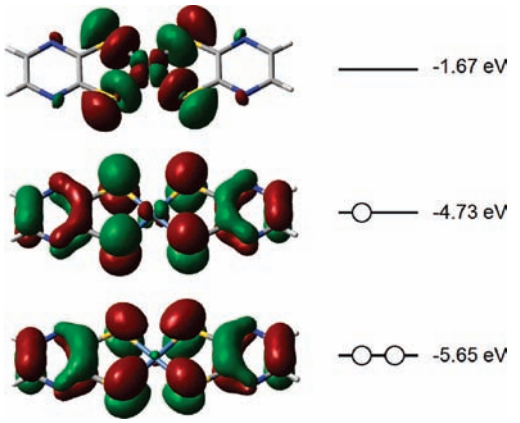

Figure 2. Frontier molecular orbitals of $Ni(pdt)_2^-$.

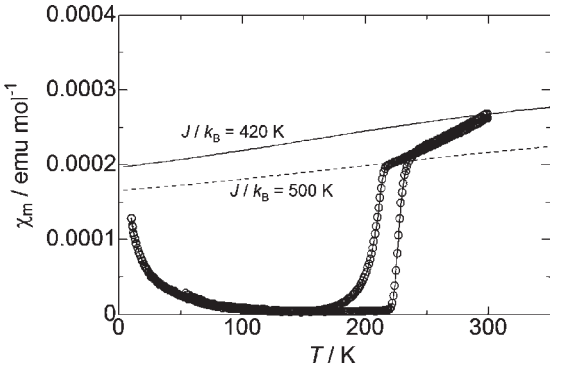

Figure 3. Magnetic susceptibility of $Na[Ni(pdt)_2]\cdot 2H_2O$. Solid and broken lines show a Bonner–Fisher curve with J/k_B = 420 and 500 K, respectively. An isotropic g value (=2.108) was determined by an electron spin resonance spectrum with a methanol solution of $Na[Ni(pdt)_2]\cdot 2H_2O$.

occupied molecular orbital (SOMO) is comprised of p_π orbitals on the pdt ligands with a nonnegligible contribution from the metal ion. The highest occupied molecular orbital (HOMO) is mainly comprised of p_π orbitals on the pdt ligands. From the crystal structure, the distance between the nearest $Ni(pdt)_2$ planes was 3.54 Å, which means that the SOMOs of each unit $Ni(pdt)_2$ overlap, causing antiferromagnetic interactions. We also made conventional band calculations with a combination of the extended Hückel method and the tight binding model. The overlap integral (S) between the neighboring $Ni(pdt)_2$ molecules along the stacking direction ($=-1.05 \times 10^{-2}$) is much larger than that along the other direction ($<1.5 \times 10^{-3}$), indicating that the present compound is nearly in a one-dimensional system.

Figure 3 shows a plot of the magnetic susceptibility of $Na[Ni(pdt)_2]\cdot 2H_2O$. The magnetic susceptibility above 215 K gradually decreased upon cooling, indicating that strong antiferromagnetic interactions were present. The susceptibility could not be reproduced by fitting with a spin $^1/_2$ one-dimensional antiferromagnetic model (Bonner–Fisher model)[7] with a unique J value. This is probably because the value of J itself changes with temperature between J/k_B = 420 and 500 K. The magnetic susceptibility showed hysteresis at critical temperatures (T_c) of 216 and 221 K upon cooling and heating, respectively. This

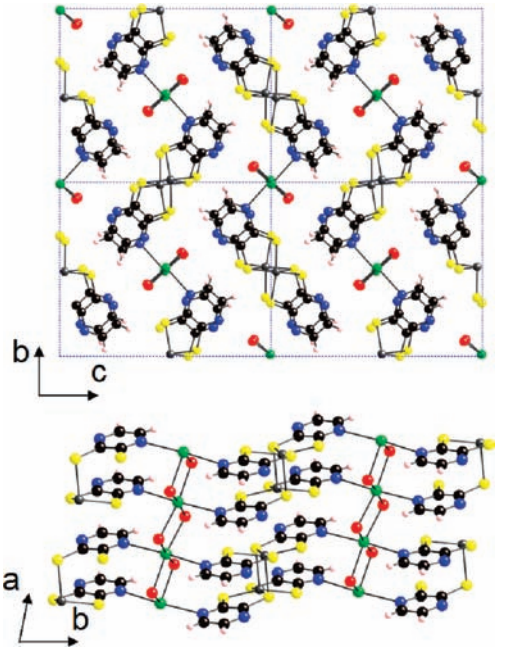

Figure 4. Crystal structure of $Na[Ni(pdt)_2]\cdot 2H_2O$ at 210 K. Color code: gray, Ni; yellow, S; green, Na; red, O; blue, N; black, C; pink, H.

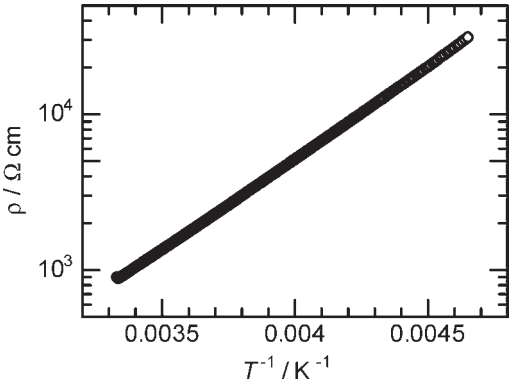

Figure 5. Electrical resistivity of $Na[Ni(pdt)_2]\cdot 2H_2O$.

indicates that some first-order phase transitions occur between the paramagnetic and diamagnetic states.

In order to clarify the origin of the phase transition, we performed X-ray crystal structure analysis below T_c (210 K). The temperature was decreased from 230 to 210 K at a rate of ≤0.5 K/min because the single crystal collapsed when we decreased the temperature quickly. Figure 4 shows the crystal structure of $Na[Ni(pdt)_2]\cdot 2H_2O$ at 210 K. There was a marked difference in the molecular geometry as well as its periodicity. At 230 K, the $Ni(pdt)_2$ molecules have a mostly planar structure and were arranged uniformly, forming one-dimensional columns. At 210 K, on the other hand, the molecules were distorted from the square-planar geometry and had dimerized, forming a Ni–S coordination bond (Ni–S distance = 2.413 Å). The abrupt decrease in the magnetic susceptibility is explained by dimerization of the $Ni(pdt)_2$ units, which gives rise to a spin singlet ground state. The contribution of $1/T$ at low temperature (the spin concentration is 0.37%) is probably due to the isolated unpaired electrons arising from a phase mismatch upon dimerization.

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The origin of this phase transition is qualitatively explained as follows. The tendency for dimerization in the bis(*o*-dithiolate) metal complexes highly depends on the metal ion. To the best of our knowledge, monoanionic nickel complexes have a moderate tendency to dimerize (lower than manganese, iron, and cobalt complexes and higher than copper complexes).[8] In the present compound, in addition, the molecules are originally arranged in a slipped stack motif to enable dimerization. Those conditions enable transformation between the monomer and dimer reversibly.

Figure 5 shows the electrical resistivity of $Na[Ni(pdt)_2]\cdot 2H_2O$. This compound showed semiconducting behavior with an activation energy of 0.23 eV above T_c. This energy gap is probably due to on-site Coulomb repulsion between the Ni-$(pdt)_2$ units. Below T_c, the electrical conductivity could not be measured because the resistivity was too high ($>10^9$ Ω cm).

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format and an electron spin resonance spectrum of $Na[Ni(pdt)_2]\cdot 2H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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