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Synthesis, Crystal Structure and Physical Properties of Charge Transfer Coordination Complex, $[Pt(H_2DAG)(HDAG)][Ni(dmit)_2].1/2H_2O.CH_3CN.CH_3OH$

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SYNTHESIS, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES OF CHARGE TRANSFER COORDINATION COMPLEX, [Pt(H2DAG)(HDAG)][Ni(DMIT)2].1/2H2O.CH3CN.CH3OH

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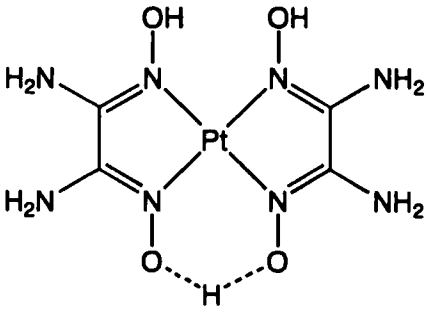
Abstract A low-dimensional charge transfer coordination complex, [Pt(H2dag)(Hdag)][Ni(dmit)2].1/2H2O.CH3CN.CH3OH (H2dag=diamino-glyoxime; dmit=1,3-dithiol-2-thione- 4,5- dithiolate) has been synthesized. In the crystal, [Pt(H2dag)(Hdag)] molecules and [Ni(dmit)2] molecules are dimerized, respectively, and the dimerized molecules are stacked alternatively, forming a linear chain structure. The intermolecular S...S contacts between [Ni(dmit)2] molecules in the neighboring linear chains are observed, and moreover intermolecular hydrogen-bonds between S of dmit and H of dag ligands in the neighboring linear chains are also observed, resulting in the two-dimensional network. Single-crystal electrical conductivity, absorption spectrum and magnetic susceptibility have been measured and their results are discussed.

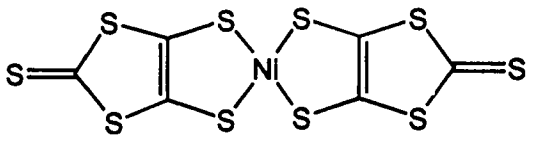
INTRODUCTION

So far low-dimensional organic charge transfer complexes have been extensively investigated to create interesting physical properties such as Peierls transition, CDW, SDW, neutral-ion transition, superconductivity, etc..[1] However, only a few charge

transfer complexes composed of both donor and acceptor coordination compounds have been synthesized. Since the electronic states and structures in coordination compounds can be designed more widely and intensionally, compared with those of the inorganic and organic compounds, the charge transfer coordination compounds are more promissing to create the interesting physical properties.[2] Moreover, in this system we introduce the hydrogen-bonds between a donor coordination molecule and an acceptor coordination molecule because we can anticipate more interesting physical properties by the cooperative interaction between hydrogen-bonds and electron transfer. Recently, such cooperative interactions have been observed in [M(H2dag)(Hdag)]TCNQ (M=Pt, Pd and Ni)[3,4] and some Ni(dmit)2 compounds.[5] As is well known, bis-dioxime (H2L) coordination compounds with d^8 metal ions form linear chain structures and they have three types of formula such as [M(H2L)2], [M(H2L)(HL)], and [M(HL)2] depending on the dissociation of hydrogen atoms of oxime sites. These three compouds have possibilities of donor molecules. Among the bis-dioxime coordination compounds, bis-diaminoglyoxime coordination compounds have two parts capable of hydrogen-bonding, that is, oxime and amino sites.[6] Accordingly the intermolecular hydrogen bond systems lead to rich structural chemistries as well as physical properties in the solid states. On the other hand, the dmit coordination compounds are acceptors, which show various electrical conducting behaviors from insulators to superconductors.[7] Moreover, the dmit moieties have proton acceptor sites (=thiocarbonyl group). According to the strategy mentioned above, we have synthesized, determined the crystal structure and investigated the properties of [Pt(H2dag)(Hdag)][Ni(dmit)2].1/2H2O.CH3CN. CH3OH.



[Pt(H_2dag)(Hdag)]



[Ni($dmit)_2$]

EXPERIMENTAL

The compound was synthesized by mixing of equimolar [Pt(Hdag)2].2HCl and (n-Bu4N)[Ni(dmit)2] in methanol and acetonitrile (2:1) including 1% H_2O. Single-crystals were obtained by evaporation. Elemental analyses: Calcd(%) for $C_{13}H_{19}N_9O_{5.5}S_{10}NiPt$, C 16.19, H 1.98, N 13.08; Found (%), C 16.16, H 1.77, N 12.57.

Crystal structure was determined by single-crystal X-ray diffraction method. Crystal and intensity data were collected on Mac Science MXC18 four-circle diffractometer using graphite-monochromated Mo Kα radiation. Crystal data are monoclinic, space group A2, a=17.721(9), b=9.884(4), c= 17.467(7) Å, β = 97.86(4)°, V=3030(2) $Å^3$, and Z=2. Independent 3548 reflections were used for the structure analysis. The structure was solved by the heavy-atom method, and the final R and Rw values are 0.072 and 0.098, respectively.

The absorption spectra were measured at room temperature using powdered pellet samples diluted with KBr on JASCO CT-25C spectrometer.

Electrical conductivities were measured along the elongated direction of the sample using four-probe method. Contacts of gold wire were made by gold paint.

Magnetic susceptibilities were measured by SQUID QUANTUM MPMS.

RESULTS AND DISCUSSION

Figure 1 shows the crystal structure along the c axis. In the crystal, [Pt(H2dag)(Hdag)] molecules and [Ni(dmit)2] molecules are dimerized respectively, and the dimerized molecules are stacked alternatively, forming a linear chain structure. In the [Ni(dmit)2] molecule, the Ni atom is a little deviated from S4 plane toward the adjacent molecule in the dimer. The average Ni-S bond distance in this molecule (ca. 2.17 Å) is shorter than that in the (n-Bu4N)2[Ni^{II}(dmit)2] (ca. 2.22 Å)[8] and a little longer than that in (n-Bu4N)- [Ni^{III}(dmit)2] (ca. 2.16 Å).[9] The C=C bond distances in dmit moieties in this complex (ca. 1.37 Å) is between those in the Ni^{II} compound (ca. 1.39 Å) and those in the Ni^{III} compound (ca. 1.35 Å). Accordingly, the fractional oxidation state between + 2

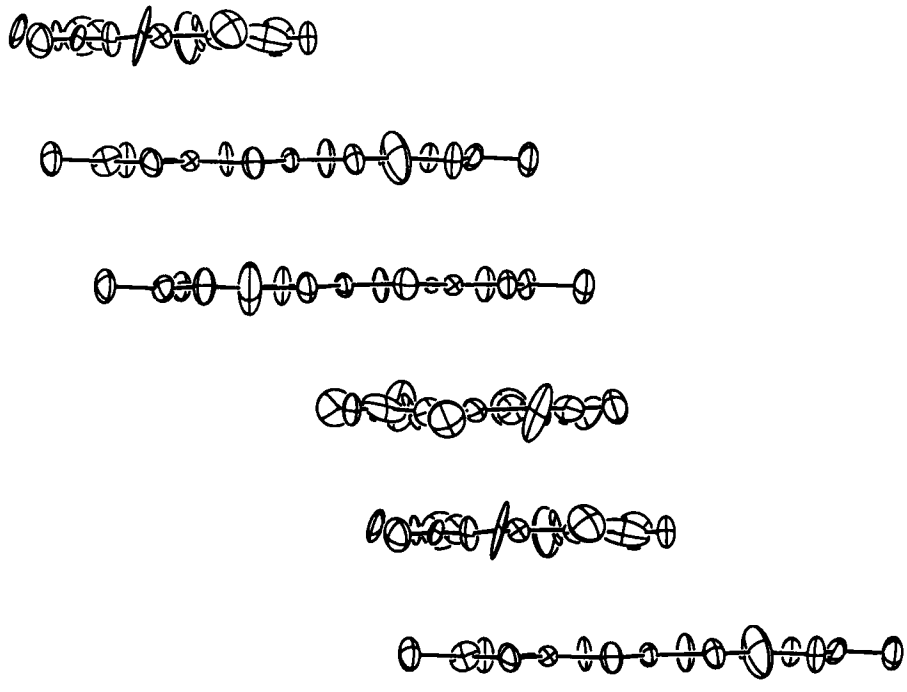


FIGURE 1 Crystal Structure of [Pt(H2dag)2][Ni(dmit)2] without solvent molecules.

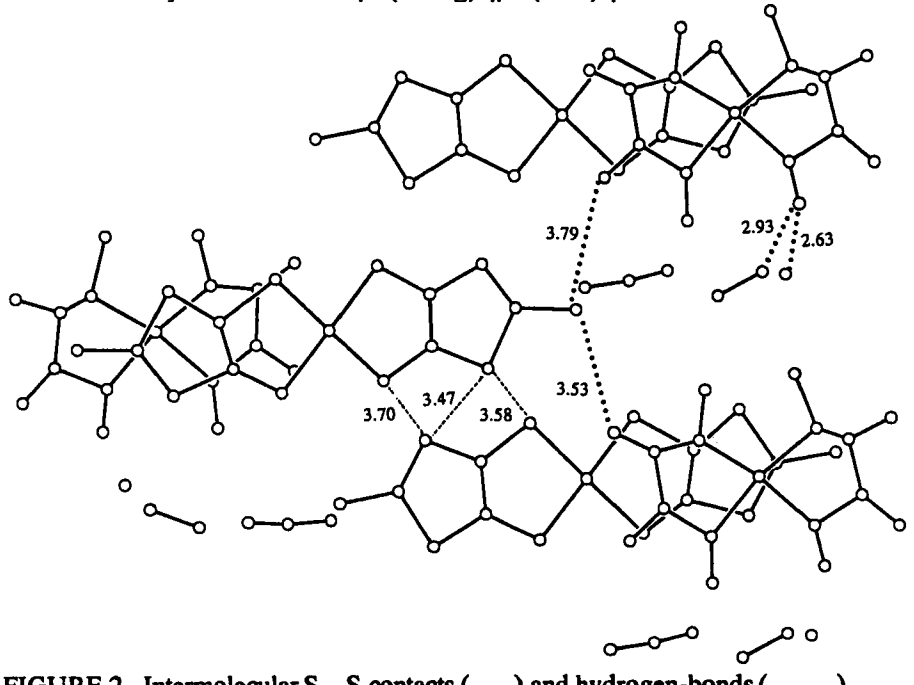


FIGURE 2 Intermolecular S...S contacts (.....) and hydrogen-bonds (. . . . .).

and +3 is considered to be taken in this molecule. Each [Ni(dmit)2] molecule in the dimer is slipped and stacked to each other, and the Ni...Ni and intermolecular distances in the dimerized [Ni(dmit)2]2 units are 3.94 and 3.63 Å, respectively. In the [Pt(H2dag)(Hdag)] molecule, the Pt atom is a little deviated from N4 plane apart from the adjacent molecule in the dimer. Since this molecule has one strong hydrogen-bond (O...O=2.65 Å) between two diaminoglyoxime ligands, the two Pt-N bond distances in the hydrogen-bonding site are forced to be shortened, compared with those of the other site. Such geometry is also observed in [Pt(H2dag)(Hdag)]I.2H2O by Endres.[6] The average Pt-N distance of this compound (ca. 2.06 Å) is longer than that of [Pt(H2dag)(Hdag)]I.2H2O (ca. 1.99 Å). This might be due to the contamination of $[Pt(H2dag)_2]^{2+}$ into $[Pt(H2dag)(Hdag)]^{+}$. In this way, the fractional charge is considered to be adjusted between the donor molecules and acceptor molecules. Similar phenomena are observed in [M(H2dag)(Hdag)]TCNQ.[10] Each [Pt(H2dag)(Hdag)] molecule in the dimer is slipped and stacked to each other , and the Pt...Pt and intermolecular distances in the dimerized [Pt(H2dag)(Hdag)]2 units are 3.68 and 3.47 Å, respectively. The adjacent [Pt(H2dag)(Hdag)] and [Ni(dmit)2] molecules are also slipped and stacked, and the Ni...Pt and intermolecular distances between [Pt(H2dag)(Hdag)] and [Ni(dmit)2] molecules are 5.26 and 3.57 Å, respectively.

There are three S..S contacts between [Ni(dmit)2] molecules in the neighboring chains. The weak hydrogen-bonds between thiocarbonyl groups of [Ni(dmit)2] and amino-hydrogens of [Pt(H2dag)2(Hdag)] in the neighboring chains are also observed. As a result, the two-dimensional networks are formed, as shown in Figure 2. The hydrogen-bonds between hydrogen atoms of the oxime sites in [Pt(H2dag)(Hdag)] and solvents are also formed.

In the absorption spectra, the broader band in the complex is observed around 1 eV, compared with those in the starting compounds, (n-Bu4N)[Ni(dmit)2] and [Pt(Hdag)2].2HCl (Figure 3). Accordingly, the charge transfer transition is considered to occur in this complex by forming a linear chain structure. This might be attributable to the charge transfe between donor molecules and acceptor molecules, or between acceptor molecules.

Figure 4 shows the temperature dependence of resistivity. The resistivity at room

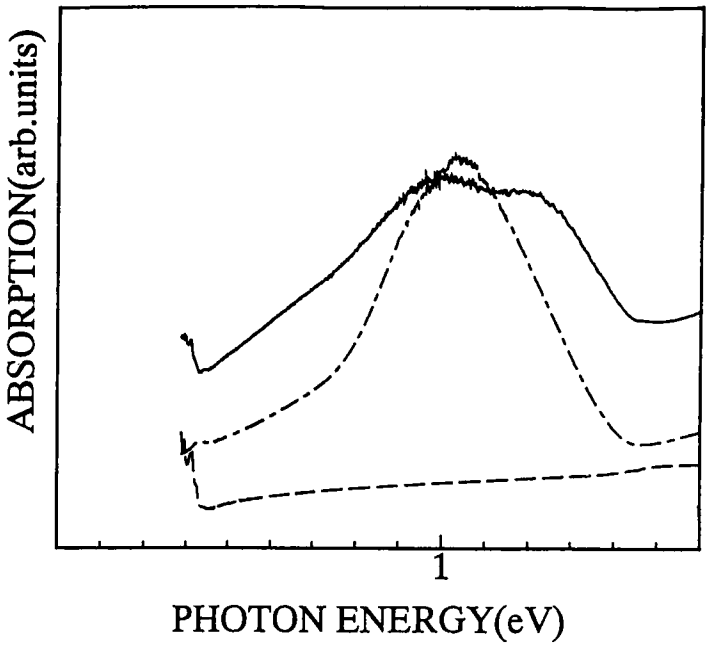


FIGURE 3 Absorption spectra of the complex (—), [Pt(Hdag)2].2HCl (---), and (n-Bu4N)[Ni(dmit)2] (-----)

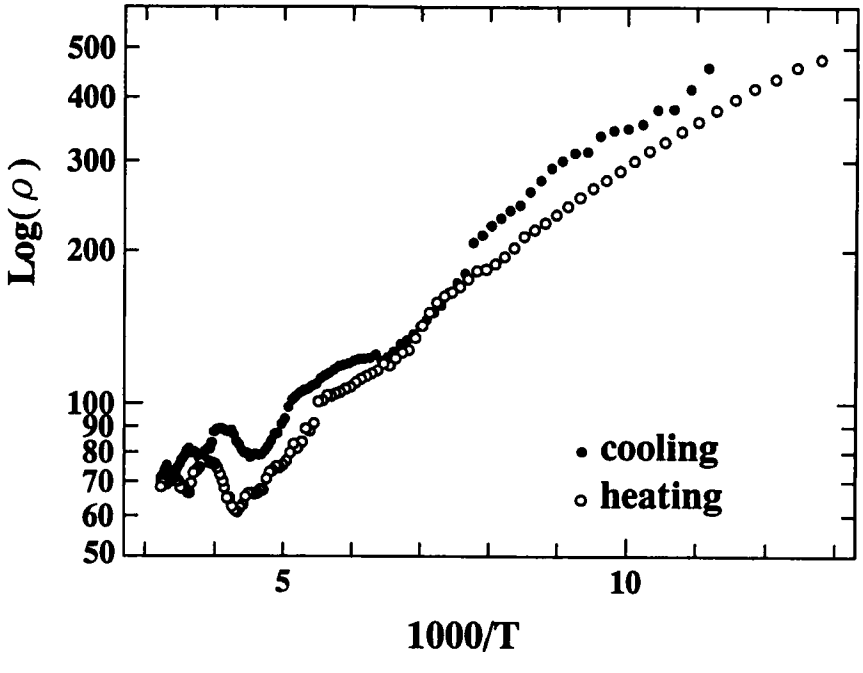


FIGURE 4 Temperature-dependence of resistivity of the complex.

temperature is ca. 70 Ω.cm. On both cooling and heating between the room temperature and ca. 200K, the small fluctuation of the resistivity is observed, which may look like semi-metallic behavior. Below 200K, the semiconducting behavior with a small activation energy (ca. 0.05 eV) is observed. Since the structure is already dimerized at room temperature, the anomalous behavior might be correlated with the two-dimensional interaction formed by not only S...S contacts but also hydrogen-bonds between neighboring chains. Since the (n-Bu4N)[Ni^{III}(dmit)] is an insulator with the room temperature conductivity of $3x10^{-8}$ $(\Omega cm)^{-1}$, the conductivity of this compoud is consistent with being a charge transfer complex, which is also consistent with the results of the crystal structure and absorption spectra.

Preliminary magnetic susceptibility measurements have been carried out. The χT vs T date are shown in Figure 5. The χT values are almost constant down to 40 K and approach to zero below 40 K. The 0.71 spin per unit formula is estimated to exsit down to 40K. This might be due to the magnetic dimer [Ni(dmit)2] with the fractional oxidation state which are separated by the diamagnetic dimer [Pt(H2dag)(Hdag)] units along the chain. The behavior below 40 K is understood by the interchain antiferromagnetic interactions.

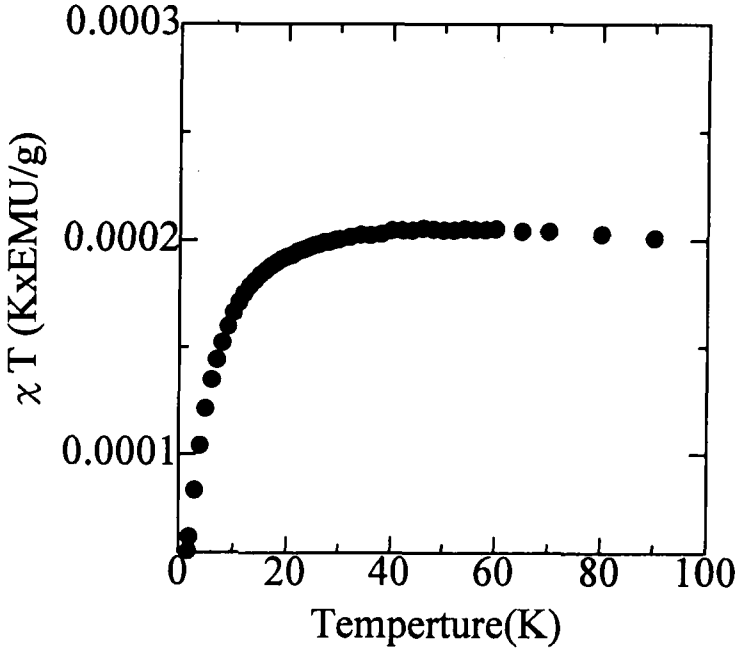


FIGURE 5 Temperature-dependence of magnetic susceptibilities of the complex.

More detailed investigations are necessary and now in progress.

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