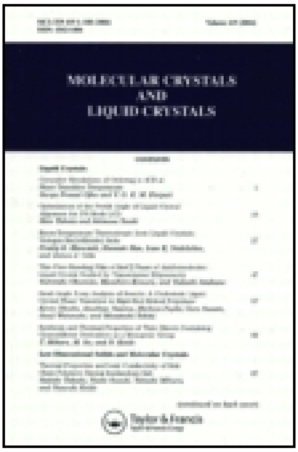

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First Isolation and Characterization of an HIN Complex, CdCl 2 (HIN) 4 (HIN=4,4,5,5-Tetramethylimidazolin-1-oxyl)

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First Isolation and Characterization of an HIN Complex, $CdCl_2(HIN)_4$ (HIN = 4,4,5,5-Tetramethylimidazolin-1-oxyl)

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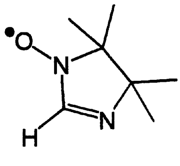
We report here for the first time the X-ray crystal structure and magnetic properties of an HIN complex, $CdCl_2(HIN)_4$, showing very strong antiferromagnetic interaction. X-ray crystal structure analysis reveals that intermolecular O···N distance (2.33 and 2.42 Å) are considerably short.

Keywords: X-ray diffraction, diamagnetic metal, unstable organic radicals, metal-radical complex

INTRODUCTION

The metal-radical approach is a promising strategy for molecule-based magnetic materials[1]. The imino- and nitronylnitroxide radical derivatives have been known as available ligands for magnetic materials and a large number of complexes have been developed as ferro- or ferrimagnets[2]. We assume that the choice of small ligands and anions is crucial in order to bestow strong magnetic interaction and raise magnetic phase transition temperatures in the metal-radical approach. We chose α-hydroiminonitroxide (HIN) as a ligand, which is the smallest derivative in the imino- and nitronylnitroxide family.



HIN

Although the isolation of HIN was

claimed to be difficult because of its instability[3], complexation affords a chance to purify and characterize HIN compounds. Stabilization based on complex formation is widely utilized for preparation of low-valent main group element compounds[4]. We report here for the first time the X-ray crystal structure and magnetic properties of an HIN complex, $CdCl_2(HIN)_4$. Extraordinary strong magnetic interaction was observed as expected from the small size of the ligand.

EXPERIMENTAL

4,4,5,5-Tetramethylimidazolin-1-oxyl (HIN) was prepared according to the procedure previously reported[3]. Solutions of HIN (100 mg, 0.71 mmol) in H_2O (1.5 ml) and of $CdCl_2{\cdot}2.5H_2O$ (162 mg, 0.71 mmol) in H_2O (0.5 ml) were mixed, the combined solution was allowed to stand in a cool and dark place for 2 h, and orange crystals of $CdCl_2(HIN)_4$ were precipitated. Elemental analysis (C, H, N) of this complex on a Fisons EA-1108 by a usual combustion method revealed that the metal/ligand ratio is 1:4. X-Ray diffraction data were collected on a Rigaku Raxis-Rapid IP diffractometer with monochromated Mo$K\alpha$ radiation. Structure was solved by direct methods and refined using all of the reflections. Magnetic susceptibility was measured on a Quantum Design MPMS SQUID magnetometer.

RESULTS AND DISCUSSION

X-Ray Crystal Structure Analysis

Table 1 summarizes the X-ray crystallographic data for $CdCl_2(HIN)_4$. Figure 1 shows that $CdCl_2(HIN)_4$ is a mononuclear complex. There are two crystallographically independent HIN units in a molecule. The imino nitrogen atoms N(1) and N(3) are coordinated to the Cd ion whereas the nitroxide oxygen atoms O(1) and O(2) remain uncoordinated. The strong coordination ability of the imino nitrogen atoms can be understood in view of the steric congestion around imino nitrogen and nitroxide oxygen atoms.

This complex does not form any covalent network in the crystal. However, as Figure 2 shows, considerably short intermolecular distances of 2.33(2) and 2.41(8) Å are found between O(1)···N(2*) and O(2)···N(4*), respectively. These distances are much shorter than the sum of the van der Waals radii of oxygen and nitrogen (3.07 Å)[5]. We assumed that HIN groups formed a dimer by contacting nitroxide groups in an intermolecular fashion.

TABLE 1 Selected X-ray crystallographic data of $CdCl_2(HIN)_4$.

Formula	$CdCl_2(C_7H_{13}N_2O)_4$
Space group	$P\bar{1}$
a/ Å	10.417(4)
b/ Å	10.591(1)
c/ Å	9.455(8)
α/ degrees	105.78(6)
β/ degrees	103.25(2)
γ/ degrees	115.56(2)
V/ Å^3	830.3(1)
Z	1
D_{calc}/ g cm^{-3}	1.50
T/K	100
$R(I>2\sigma(I))$	0.025

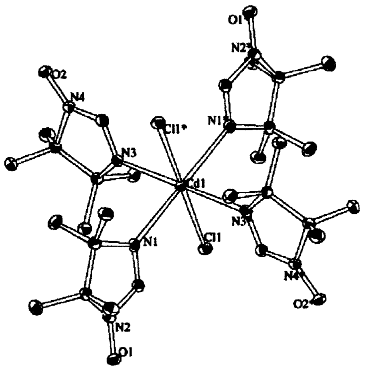


FIGURE 1 Molecular structure of $CdCl_2(HIN)_4$. Methyl hydrogen atoms are omitted for clarity.

Magnetic properties

Temperature dependences of the molar magnetic susceptibility χ_m and the product $\chi_m T$ are shown in Figure 3. Since some metal complexes with organic paramagnetic ligands and diamagnetic metals have been reported to show magnetic interactions through the diamagnetic metal

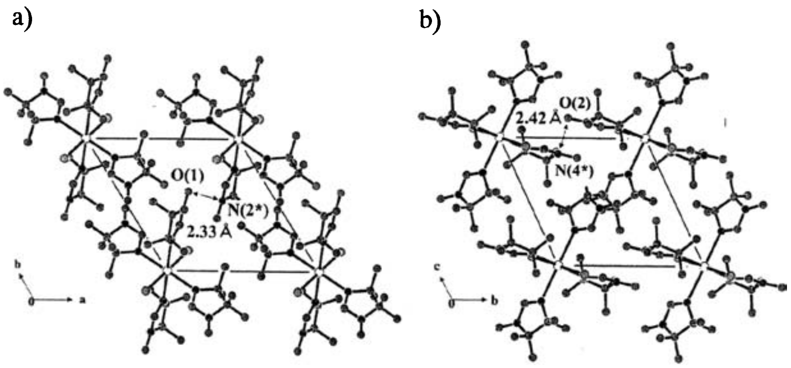


FIGURE 2 Molecular arrangement in the crystal of $CdCl_2(HIN)_4$. Short intermolecular contacts are indicated. a) Viewed along the *c* axis. b) Viewed along the *a* axis.

ion[6], the present complex also attracts attention to intra- and intermolecular magnetic interactions. The $\chi_m T$ value at 300 K was 0.04 emu K mol^{-1} while the calculated value of a paramagnetic four-spin system is 1.5 emu K mol^{-1}. The $\chi_m T$ value hardly changes on lowering the temperature. The above structural analysis of $CdCl_2(HIN)_4$ clarified that every two HIN moieties formed a dimer. In this complex, there are two possible pathways of magnetic interactions; one is intramolecular interaction through the Cd ion and the other intermolecular interaction through the nitroxide contacts. We assume that the latter is stronger than the former viewing from considerably short intermolecular contacts.

There are two crystallographically independent dimers in a unit cell. We attempted to fit the result of the magnetic measurements by using a combined dimer model given by eq 1, based on the spin Hamiltonian $H = -2J_1S_1 \bullet S_2 - 2J_2S_3 \bullet S_4$, where all symbols have their usual meaning. The symbol α in eq1 means the ratio of S=1/2 paramagnetic impurity contained. The exchange parameters J_1 and J_2 are the spin-spin coupling constants between O(2)···N(4) and O(1)···

N(2), respectively. The estimated values of $|J_1/k|$ and $|J_2/k|$ are larger than 700 K, and paramagnetic impurity component is about 2%.

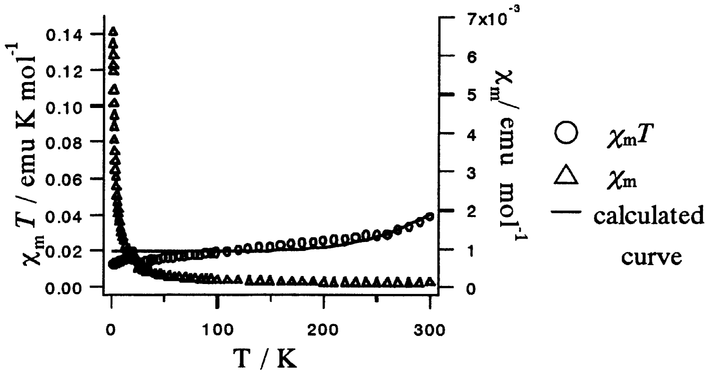


FIGURE 3 Temperature dependence of the molar magnetic susceptibility χ_m and the product $\chi_m T$ of $CdCl_2(HIN)_4$.

$$\chi = (1-\alpha)\left[\frac{2Ng^2\mu_B^2}{kT}\frac{1}{3+\exp(-2J_1/kT)} + \frac{2Ng^2\mu_B^2}{kT}\frac{1}{3+\exp(-2J_2/kT)}\right] + 2\alpha\frac{N^2g^2\mu_B^2}{3kT} \qquad (1)$$

These results show that $CdCl_2(HIN)_4$ is practically diamagnetic below 300 K, and contains a small amount of monomeric impurities.

The α-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide (α-HNN)[3] has been known as the smallest nitronylnitroxide radical. The α-HNN forms a dimer structure in the crystal, and exhibits large intermolecular antiferromagnetic interaction (J/k= -22 K) due to the close spacing between the ONCNO moieties[7]. The shortest intermolecular atomic distance between the ONCNO groups is 3.376(3) Å[7], whereas we can find much shorter distances (2.33(2) and 2.41(8) Å) in $CdCl_2(HIN)_4$. Therefore, the magnetic interaction of $CdCl_2(HIN)_4$ is reasonably attributed to intermolecular interaction.

This result indicates that the HIN ligands can be used for achieving the strong intermolecular exchange interaction.

CONCLUSION

We have demonstrated the preparation and full characterization of $CdCl_2(HIN)_4$. Considerably strong antiferromagnetic coupling ($|J/k|$>700K) was observed and assigned to intermolecular interactions.

Acknowledgments
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