Synthesis, Structure and Magnetic Properties of a Novel Nickel(II) Radical Heterospin Complex with Salicylaldoxime

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Abstract. A novel heterospin complex containing both Ni^{II} and nitroxide radical ligands: $[Ni(salox)_2(NIT4Py)_2]$ (**1**) (salox = salicylaldoxime, NIT4Py = 2-(4′-pyridyl)-4,4,5,5- tetramethyl-imidazoline-1-oxyl-3-oxide) has been synthesized and structurally characterized. The structure consists of neutral $Ni(salox)_2$-$(NIT4Py)_2$ moieties bridged by intermolecular hydrogen bonds, for-ming a one-dimensional chain structure. Magnetic measurements show intramolecular antiferromagnetic interactions between NIT4Py and Ni^{2+} ion.

Keywords: Nickel; Salicylaldoxime; Nitronyl nitroxide radical; Crystal structure; Magnetic properties

Introduction

Pyridyl-substituted nitroxide radicals have attracted considerable attention in recent years in the design and construction of molecular magnetic materials. These stable and easy coordinating radicals can act not only as good building blocks for metal ions but also spin carriers themselves [1, 2]. By using the pyridyl-substituted nitroxide radicals as NIT4Py [3−10], NIT3Py [11-16], NIT2Py [17−19], a great many of novel heterospin functional materials exhibiting interesting magnetic behaviors, optical properties and a variety of structural topology have been obtained and studied.

On the other hand, $3d$ transition-metal complexes based on phenolic oximes derived from salicylaldehydes have also been greatly studied because of their analytical and biological importance [20−24], as well as their function in the hydrometallurgical processes for Cu^{2+} and Ni^{2+} ions based on solvent extraction [25]. However, pyridyl-substituted nitroxide radicals as co-ligand for $M(salox)_2$ has never been reported to the best of our knowledge. In this work we utilized NIT4Py as the co-ligand for $M(salox)_2$ fragment, and obtained a heterospin complex $[Ni(salox)_2(NIT4Py)_2]$ with three paramagnetic centers (NIT4Py -Ni- NIT4Py). The complex shows intramolecular antiferromagnetic inter-actions between the Ni^{2+} ion and NIT4Py, and forms one-dimensional chain structure with hydrogen bonding link-ages.

Experimental Section

General

All starting materials were analytical grade and used without further purification. Elemental analysis for C, H and N were car-ried out on a Perkin-Elmer elemental analyzer (model 240). The infrared spectrum was obtained on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the $4000−400 \, cm^{-1}$ regions, using KBr pellets. Variable temperature magnetic susceptibility measurements were carried out on a SQUID MPMS5 magnet-ometer between $2.0−300 \, K$ in a magnetic field of 5000 Oe. The molar magnetic susceptibility was corrected from the sample holder and diamagnetic contributions ($−3.0 \times 10^{-4} \, cm^3 \, mol^{-1}$) of all con-stituent atoms by using Pascal's constants.

Synthesis

2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide NIT4Py [26] and $Ni(salox)_2(py)_2$ [27] were prepared according to previous published methods.

Preparation of [Ni(salox)₂(NIT4Py)₂]

$Ni(salox)_2(py)_2$ (25 mg, 0.05 mmol) and NIT4Py (23.4 mg, 0.1 mmol) were dissolved in 5 ml CH_2Cl_2 and stirred for 1 hours at RT. The clear solution was then placed in a tube and layered with n-hexane (5 ml), staying without disturbance. After one week, dark blue crystals suitable for X-ray structure analysis were ob-tained (yield 60 %). Anal. Calcd for $C_{38}H_{44}N_8NiO_8$: C, 57.09; H,

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Table 1 Summary of crystallographic data for complex **1**.

Empirical formula	$C_{38}H_{44}N_8NiO_8$
Formula weight	799.52
Temperature /K	294(2)
Wavelength /Å	0.71073
Crystal system, space group	monoclinic, $P2_1/c$
a /Å	9.401(4)
b /Å	10.750(5)
c /Å	19.137(8)
α /°	90
β /°	91.888(8)
γ /°	90
Volume /Å³	1932.9(14)
Z, Calculated density /(Mg / m³)	2, 1.374
Absorption coefficient /mm⁻¹	0.564
$F(000)$	840
Crystal size /mm³	0.24 x 0.20 x 0.14
θ Range /°	2.13 to 25.01
Limiting indices	$-10 \leq h \leq 11, -12 \leq k \leq 12,$ $-18 \leq l \leq 22$
Reflections collected / unique	9606 / 3393 [R (int) = 0.0815]
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	0.9252 and 0.8765
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.055
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0557, \omega R_2 = 0.1263$
Largest diff. peak and hole	0.529 and -0.426 e. Å³

Table 2 Selected bond lengths /Å and angles /° for complex **1**.

|			
Ni(1)-O(1)#1	1.980(3)	Ni(1)-N(2)#1	2.174(4)
Ni(1)-O(1)	1.980(3)	O(3)-N(4)	1.282(4)
Ni(1)-N(1)#1	2.003(4)	O(4)-N(3)	1.287(5)
Ni(1)-N(1)	2.003(4)	O(2)-N(1)	1.410(4)
Ni(1)-N(2)	2.174(4)	O(1)-C(1)	1.310(5)
O(1)#1-Ni(1)-O(1)	180.0	N(1)#1-Ni(1)-N(2)#1	91.12(14)
O(1)#1-Ni(1)-N(1)#1	91.61(14)	N(1)-Ni(1)-N(2)#1	88.88(14)
O(1)-Ni(1)-N(1)#1	88.39(14)	N(2)-Ni(1)-N(2)#1	179.998(1)
O(1)#1-Ni(1)-N(1)	88.39(14)	C(1)-O(1)-Ni(1)	127.5(3)
O(1)-Ni(1)-N(1)	91.61(14)	C(7)-N(1)-Ni(1)	128.0(3)
N(1)#1-Ni(1)-N(1)	179.999(1)	O(2)-N(1)-Ni(1)	118.8(3)
O(1)#1-Ni(1)-N(2)	90.05(14)	C(8)-N(2)-Ni(1)	121.0(3)
O(1)-Ni(1)-N(2)	89.95(14)	C(12)-N(2)-Ni(1)	123.1(3)
N(1)#1-Ni(1)-N(2)	88.88(14)	O(4)-N(3)-C(13)	125.2(4)
N(1)-Ni(1)-N(2)	91.12(14)	O(4)-N(3)-C(17)	122.1(4)
O(1)#1-Ni(1)-N(2)#1	89.95(14)	O(3)-N(4)-C(13)	124.8(4)
O(1)-Ni(1)-N(2)#1	90.05(14)	O(3)-N(4)-C(14)	121.6(4)

Symmetry transformations, #1 $-x+1,-y+1,-z+1$

5.55; N, 14.02 %; Found: C, 57.25 H, 5.45; N, 13.94 %. IR (KBr disc, cm⁻¹): (1644 w δ_{OH}, 1184 m 908 s ν_{N-O}, 1311 s, 998 s ν_{C-O}, 1370 s ν_{N-O})

X-ray crystallography

X-ray diffractions were measured on an APEX II CCD area detector equipped with a graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). A summary of crystallographic data is given in Table 1. The structure was solved by direct methods using SHELXS-97 program and refined with SHELXL-97 [28, 29] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. The selected bond lengths and angles are listed in Tables 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre,
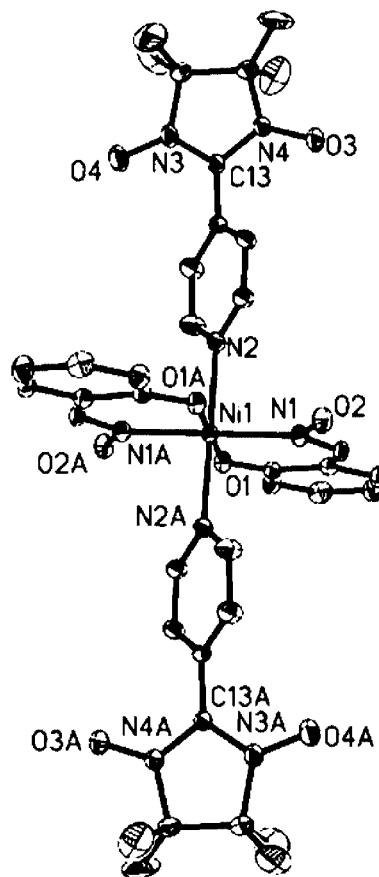
Fig. 1 ORTEP drawing of **1** with 30 % thermal ellipsoids.

CCDC No 611021. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk)

Results and Discussion

Crystal Structure of 1

The ORTEP drawing of **1** is shown in Figure 1. Ni²⁺ ion is located on an inversion center and adopts distorted octahedral geometry, completed by two deprotonated phenolic oxygen atoms (O1, O1A) and two nitrogen atoms (N1, N1A) both from salicylaldoxime ligands, forming the basal plane O1-N1-O1A-N1A (with the bond lengths of Ni−O1, 1.980(3), Ni−N1, 2.003(4) Å), the Ni²⁺ ion is absolutely coplanar with the basal plane with a displacement of 0 Å. While the axial positions are occupied by two nitrogen atoms (N2, N2A) from pyridyl rings of NIT4Py radicals (with the bond length of Ni−N2, 2.174(4) Å). The dihedral angle between pyridine ring and nitroxide group (O3−N4−C13−N3−O4) in the radical is 46.9°.

The intermolecular hydrogen bonds between O2 (from oximic) and O4 (from NIT4Py) connect the Ni(salox)₂(NIT4Py)₂ moieties to form a 1-D chain, as shown in Figure 2, with the bond length of O2···O4,
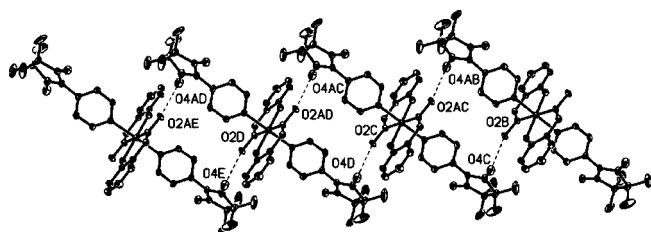
Fig. 2 Packing diagram for [Ni(salox)$_2$(NIT4Py)$_2$], a 1-D chain formed by intermolecular hydrogen bond interactions. Hydrogen atoms are omitted for clarity.
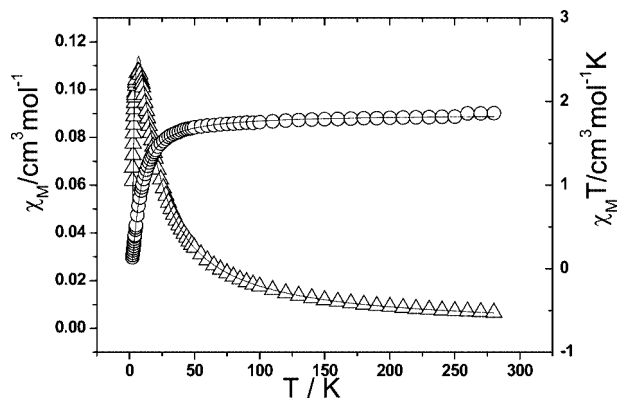
Fig. 3 Temperature dependence of the molar susceptibility (χ_M, $\triangle$) and $\chi_M T$, o versus T

2.920 Å. There are also intramolecular hydrogen bond interactions between phenolic oxygen O1 and oximic oxygen O2 from two salicylaldoximes in one Ni(salox)$_2$(NIT4Py)$_2$ moiety (O2···O1, 2.730 Å).

Magnetic Properties

Variable temperature magnetic susceptibility measurements were carried out with a SQUID MPMS5 magnetometer in the temperature range 2.0–300 K at a magnetic field of 5000 Oe. The magnetic properties of **1** in the forms of both $\chi_M T$ versus T and χ_M versus T plots are presented in Figure 3. At room temperature, the $\chi_M T$ is 1.87 cm^3 mol^{-1} K, which is slightly higher than the value (1.75 cm^3 mol^{-1} K) expected for an uncoupled system with one Ni^{2+} ion (S = 1) and two NIT4Py (S = 1/2), probably due to the mixing of an angular momentum from an excited state of Ni^{2+} ion ($^3T_{2g}$) via spin-orbit coupling. For the plot of $\chi_M T$ versus T, at higher temperature the $\chi_M T$ decreases very slowly with the decrease of the temperature, while at lower temperature $\chi_M T$ decreases sharply to 0.11 cm^3 K mol^{-1} around 2.0 K. In the case of χ_M versus T, the χ_M increases with the decrease of the temperature until getting a maximum at 7 K, then decreases sharply down with the temperature decreasing. All the above magnetic behaviors suggest the existence of antiferromagnetic interaction in the system [30].

From the structural features of complex **1**, the following magnetic interactions can exist in the system, (i) intra-molecular antiferromagnetic interactions between Ni(II) ions and NIT4Py (ii) intermolecular interactions between Ni(salox)$_2$(NIT4Py)$_2$ moieties and/or the zero-field splitting (ZFS) of Ni^{2+} ion (S = 1).

Considering all the above, using the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{Ni}\cdot\hat{S}_{Rad1} + \hat{S}_{Ni}\cdot\hat{S}_{Rad2})$ and Van Vleck equation, a theoretical expression of the magnetic susceptibility can be derived as Eq. (1) [1].

$$\chi_{tri} = \frac{2N\beta_2}{k(T-\theta)}\left[\frac{g_{21}^2 + g_{11}^2\, 5\exp\left(\frac{4J}{kT}\right) + g_{10}^2\exp\left(\frac{2J}{kT}\right)}{3 + 5\exp\left(\frac{4J}{kT}\right) + \exp\left(\frac{-2J}{kT}\right) + 3\exp\left(\frac{2J}{kT}\right)}\right]$$

The molecular $g_{s,s*}$ factors ($S^* = S_{R1} + S_{R2}$, $S = S_{Ni} + S^*$) have been related to the local g_R and g_{Ni} and shown as follows:

$$g_{21} = \tfrac{1}{2}g_{Rad} + \tfrac{1}{2}g_{Ni}$$

$$g_{11} = \tfrac{1}{2}g_{Rad} + \tfrac{1}{2}g_{Ni} \qquad\qquad (1)$$

$$g_{10} = g_{Ni}\,,\; g_{Rad} = 2$$

J is the magnetic exchange coupling constant between Ni^{2+} ion and NIT4Py. A weiss constant θ is included to describe phenomenologically the decrease of $\chi_M T$ at low temperature, which is caused by intermolecular magnetic interactions in **1** and/or zero-field splitting (ZFS) of Ni^{2+} ion (S = 1) [31]. The best fitting parameters were obtained as, $J = -2.51$ cm^{-1}, $g_{Ni} = 2.10$, $\theta = -0.40$ K, $R = 4.6\times10^{-3}$ (R value is defined as $R = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \Sigma[(\chi_M)_{obs}]^2$). The fitted J value -2.51 cm^{-1} is similar as those in other Ni^{II}-NIT4Py complexes (-3.45 and -5.0 cm^{-1}) [4, 5], which confirms the weak intramolecular antiferromagnetic coupling between Ni^{II} and NIT4Py. The g_{Ni} value is also in the range of g_{Ni} in Ni^{II}-NIT4Py systems (2.05-2.16) [5, 6]. $\theta = -0.40$ K shows the existence of intermolecular magnetic interactions between Ni(salox)$_2$(NIT4Py)$_2$ moieties and/or zero-field splitting (ZFS) of Ni^{2+} ion (S = 1).

The antiferromagnetic coupling between Ni^{II} atom and NIT4Py can be explained by a spin polarization mechanism of the π-electrons and the orthogonality of 3d magnetic orbital of Ni^{2+} ion and the 2$p\pi$ orbital on the pyridine rings, which have also been used to explain the magnetic properties of other pyridyl-substituted nitroxide radical-metal complexes [32–34]. Owing to spin polarization by the positive spin of radical center (Scheme 1), the sign alternation of spin density leads to significant negative spin density at N atom of pyridine. Furthermore, as the crystal structure shows in Figure 1, NIT4py radicals coordinate to Ni^{2+} ion via the axial positions, consequently, 2$p\pi$ orbital at the nitrogen of the pyridine ring and the magnetic orbital $d_{x^2-y^2}$ and d_{z^2} of Ni^{2+} ion have no significant overlap. Thus, their orthogonality leads to the same negative spin density at Ni^{2+} ion as that on N atom of pyridine, while the spin sign of radical center is posi-
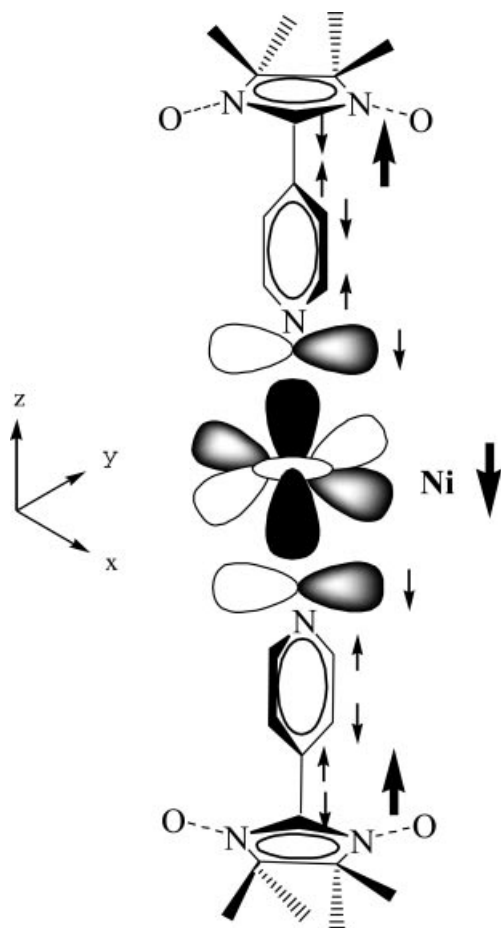
Scheme 1

tive, then the antiferromagnetic interaction between Ni^{2+} ion and NIT4Py will occur.

In summary, we have studied a new Ni^{II}-pyridyl-substituted nitronyl nitroxides complex with salicylaldoxime $[Ni(salox)_2(NIT4Py)_2]$. The complex forms one-dimensional chain structure with hydrogen bonding linkages, and shows intramolecular antiferromagnetic interactions between the Ni^{2+} ion and NIT4Py.

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