

# Synthesis and Crystal Structures of Two Metal-Radical Complexes

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## Abstract

Two new M(II)-radical complexes [M(hfac)<sub>2</sub>(IM-*o*-QN)] (M = Ni(1), Zn(2); IM-*o*-QN = 4'-quinoxaliny-substituted imino nitroxide; hfac = hexafluoroacetylacetonate) have been synthesized and characterized by X-ray diffraction analysis, element analyses, IR and UV-Visible spectroscopy. X-ray analysis reveal that the structures of both complexes are similar configuration and differently spatial symmetries. The complex 1 crystallizes in the triclinic *P*1 space group with the respective cell parameters:  $a = 9.1189(18) \text{ \AA}$ ,  $b = 9.836(2) \text{ \AA}$ ,  $c = 18.537(4) \text{ \AA}$ ,  $\alpha = 75.92(3)^\circ$ ,  $\beta = 81.95(3)^\circ$ ,  $\gamma = 69.32(3)^\circ$ ,  $V = 1506.1(5) \text{ \AA}^3$ ,  $Z = 2$ , whereas the complex 2 is in monoclinic *C*2/*c* space group with the respective cell parameters:  $a = 26.996(5) \text{ \AA}$ ,  $b = 9.5223(19) \text{ \AA}$ ,  $c = 23.961(5) \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 91.07(3)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 6158(2) \text{ \AA}^3$ ,  $Z = 8$ . In two new M(II)-radical complexes, the central M(II)(Ni(1) and Zn(2)) ions are coordinated by four oxygen atoms from two hfac and two nitrogen atoms from imino nitroxide radicals to form a distorted octahedron. Additionally, the optical properties and thermal analysis of the two complexes are reported.

## Keywords

M(II)-Radical Complex, Quinoxaliny-substituted Imino Nitroxide, Synthesized, Characterized

## 1. Introduction

Much of the popularity of nitronyl nitroxide radicals (NIT) stems from their intriguing structural diversity and their attracting stability in ambient condition [1] [2]. Recently, as stable spin carriers, they are now widely used in coordination che-

mistry and interest in paramagnetic and diamagnetic species is increasing [3] [4] [5] [6]. Interest in the magnetochemistry of metal complexes with organic radicals comes from the discovery of the molecule-based magnets [Mn(hfac)<sub>2</sub>(NIT-R)], and NIT-R (nitronyl nitroxide) contains an isopropyl group. In the last few years, much attention has been paid to metal-radical complexes for the design of molecular based magnetic materials in terms of the so-called radical approach [7] [8]. Previous investigations reveal that magnetic interactions between a metal ion and an organic radical depend on the magnetic orbital of the metal ion and coordination mode, and display that the ligands have strong donor properties and peculiar bonding geometries. Similar features are found in the imino nitroxides [9] [10]; the imino nitrogen atom has a pronounced basic character and some preliminary investigations showed that the magnetic behavior of these free radicals is markedly different from that of the nitronyl nitroxides and related to different binding geometries. In the last two decades, the chemistry and magnetic properties of transition metal complexes containing imidazolin-1-oxyl 3-oxide (NIT) or imidazolin-1-oxyl (IM) radicals have been examined extensively.

According to the thinking, we devote ourselves to synthesize NIT and /or IM radicals and prepare new metal-radical complexes. Herein, we describe the preparation and the crystal structure of [M(hfac)<sub>2</sub>(IM-o-QN)] (M = Ni(1), Zn(2)) complexes containing IM-o-QN as such building block. The optical properties and thermogravimetric analysis of the two complexes are reported.

## 2. Experimental

### 2.1. Materials and Measurements

All chemicals and solvents used for the syntheses were of reagent grade and were used without further purification. The radical ligand and M(hfac)<sub>2</sub>·H<sub>2</sub>O (M = Ni(1), Zn(2)) have been performed according to the literature methods [11] [12]. All reactions were conducted in aerobic conditions. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. Infrared spectra were taken on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the region 4000 - 400 cm<sup>-1</sup>, using KBr pellets. Ultraviolet-visible spectra were recorded on a Cary 50 UV-Vis spectrophotometer in stated solvent.

### 2.2. Synthesis of [Ni(hfac)<sub>2</sub>(IM-o-QN)] (1)

Ni(hfac)<sub>2</sub>·2H<sub>2</sub>O (0.1 mmol) was refluxed at 80°C for 30 minutes in 10 mL *n*-heptane. Then the reactant was cooled to 60°C, 6 mL of dichloromethane solution containing 0.1 mmol *o*-quinoxaline imino nitroxide (IM-o-QN) was added, and stirring was continued for 30 minutes. Then, it was cooled to the room temperature, and filtered. One week later, block red-orange crystals suitable for single crystal diffraction had been obtained. Anal. Calcd. (%) for C<sub>25</sub>H<sub>19</sub>F<sub>12</sub>N<sub>4</sub>O<sub>5</sub>Ni (742.13): C, 40.45; N, 7.55; H, 2.58; Found: C, 40.51; N, 7.49; H, 2.71%. FTIR (KBr, cm<sup>-1</sup>): 1639 (s), 1530 (s), 1476 (m), 1352 (m), 1253 (s), 1204 (m), 1138 (s), 1096 (s), 799 (s), 670 (s). UV-Vis (nm): 243 and 313 nm.

### 2.3. Synthesis of [Zn(hfac)<sub>2</sub>(IM-*o*-QN)] (2)

The complex **2** was obtained in the similar manner using Zn(hfac)<sub>2</sub>·2H<sub>2</sub>O instead of Ni(hfac)<sub>2</sub>·2H<sub>2</sub>O. A few days later, block red-orange crystals suitable for single crystal diffraction had been obtained. Anal. Calcd. (%) for C<sub>25</sub>H<sub>19</sub>F<sub>12</sub>N<sub>4</sub>O<sub>5</sub>Zn (748.83): C, 40.01; N, 7.48; H, 2.56; Found: C, 40.06; N, 7.46; H, 2.49%. FTIR (KBr, cm<sup>-1</sup>): 1640 (s), 1529 (s), 1488 (m), 1355 (m), 1255 (s), 1196 (m), 1135 (s), 1094 (s), 796 (s), 664 (s). UV-Vis (nm): 242 and 307 nm.

### 2.4. X-Ray Crystallography

The diffraction data were collected at room temperature with Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation using a Bruker CCD APEX-II diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares methods on F<sup>2</sup> by using the SHELXL-97 program package [13]. Empirical absorption corrections from  $\varphi$  and  $\omega$  scan were applied. Metal atoms in each compound were located from the E-maps.

All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were added theoretically. The crystal parameters, data collection procedure, and refinement results for the two complexes **1** and **2** are summarized in detail in **Table 1**. Selected bond lengths and angles for the two complexes are listed in **Table 2**.

**Table 1.** Crystallographic data and structure refinement details for **1-2**.

Empirical formula	C <sub>25</sub> H <sub>19</sub> F <sub>12</sub> N <sub>4</sub> O <sub>5</sub> Ni( <b>1</b> )	C <sub>25</sub> H <sub>19</sub> F <sub>12</sub> N <sub>4</sub> O <sub>5</sub> Zn( <b>2</b> )
Wavelength	0.71073	0.71073
Temperature/K	296	296
Formula weight	742.13	748.83
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	C2/c
a/Å	9.1189(18)	26.996(5)
b/Å	9.836(2)	9.5223(19)
c/Å	18.537(4)	23.961(5)
$\alpha$ /°	75.92(3)	90
$\beta$ /°	81.95(3)	91.07(3)
$\gamma$ /°	69.32(3)	90
Volume/Å <sup>3</sup>	1506.1(6)	6158(2)
Z	2	8
$\rho_{\text{calc}}$ g/cm <sup>3</sup>	1.637	1.615
$\mu$ /mm <sup>-1</sup>	0.761	0.912
F(000)	746.0	3000.0
Crystal size/mm <sup>3</sup>	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ Å)	MoK $\alpha$ ( $\lambda = 0.71073$ Å)
Final R <sub>1</sub> , wR <sub>2</sub> [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0587 wR <sub>2</sub> = 0.1486	R <sub>1</sub> = 0.0510 wR <sub>2</sub> = 0.1530
R indices (all data)	R <sub>1</sub> = 0.1149 wR <sub>2</sub> = 0.1800	R <sub>1</sub> = 0.0762 wR <sub>2</sub> = 0.1782

**Table 2.** Crystallographic data and structure refinement details for **1-2**.

Complex 1 C <sub>25</sub> H <sub>19</sub> F <sub>12</sub> N <sub>4</sub> O <sub>5</sub> Ni(1) Ni(hfac) <sub>2</sub> (IM- <i>o</i> -QN)			
Bond	Length/Å	Bond	Length/Å
Ni1-O4	2.009(3)	N3-C9	1.292(5)
Ni1-O5	2.023(4)	O4-C21	1.257(5)
Ni1-O2	2.029(3)	O3-C18	1.237(6)
Ni1-O3	2.030(3)	N4-O1	1.263(5)
Ni1-N3	2.056(4)	N4-C9	1.384(5)
Ni1-N1	2.166(4)	N1-C8	1.339(5)
N1-C6	1.365(5)	O5-C23	1.250(6)
O2-C16	1.256(5)	C5-N2	1.352(6)
Bond	Angle/°	Bond	Angle/°
O4-Ni1-O5	90.57(14)	N3-Ni1-N1	78.61(14)
O4-Ni1-O2	89.28(13)	C23-O5-Ni1	124.3(4)
O5-Ni1-O2	84.46(14)	N3-C9-N4	113.3(4)
O4-Ni1-O3	177.55(13)	N3-C9-C8	121.1(4)
O5-Ni1-O3	89.19(14)	N4-C9-C8	125.5(4)
O2-Ni1-O3	88.27(13)	C8-N1-C6	116.4(4)
O4-Ni1-N3	94.57(14)	C8-N1-Ni1	111.7(3)
O5-Ni1-N3	96.44(15)	C6-N1-Ni1	131.8(3)
O2-Ni1-N3	176.03(13)	C16-O2-Ni1	123.3(3)
O3-Ni1-N3	87.87(13)	C9-N3-C11	109.1(4)
O4-Ni1-N1	92.98(13)	C9-N3-Ni1	112.9(3)
O5-Ni1-N1	174.12(13)	C11-N3-Ni1	136.7(3)
O2-Ni1-N1	100.26(14)	C21-O4-Ni1	123.4(3)
O3-Ni1-N1	87.46(13)	C18-O3-Ni1	123.5(3)
Complex 2 C <sub>25</sub> H <sub>19</sub> F <sub>12</sub> N <sub>4</sub> O <sub>5</sub> Zn(2) Zn(hfac) <sub>2</sub> (IM- <i>o</i> -QN)			
Bond	Length/Å	Bond	Length/Å
O3-C16	1.252(4)	N3-C9	1.280(3)
O3-Zn1	2.062(2)	N3-C11	1.490(3)
Zn1-N3	2.079(2)	O5-C21	1.248(4)
Zn1-O5	2.088(2)	O4-C18	1.245(4)
Zn1-O6	2.098(2)	O6-C23	1.238(4)
Zn1-O4	2.107(2)	N1-C8	1.315(4)
Zn1-N1	2.258(2)	N1-C6	1.375(3)
N4-C10	1.487(4)	O2-N4	1.260(3)
N2-C5	1.348(5)	N4-C9	1.381(4)
Bond	Angle/°	Bond	Angle/°
C16-O3-Zn1	122.3(2)	O2-N4-C9	126.5(2)
O3-Zn1-N3	104.00(9)	O2-N4-C10	123.4(3)
O3-Zn1-O5	84.50(10)	C9-N4-C10	109.7(2)

## Continued

N3-Zn1-O5	169.82(9)	O4-C18-C17	128.3(3)
O3-Zn1-O6	166.92(9)	O4-C18-C20	114.0(3)
N3-Zn1-O6	88.64(9)	N3-C9-N4	113.1(2)
O5-Zn1-O6	83.27(9)	N3-C9-C8	121.5(2)
O3-Zn1-O4	85.33(9)	N4-C9-C8	125.4(2)
N3-Zn1-O4	98.87(9)	N1-C8-C7	122.2(3)
O5-Zn1-O4	87.26(10)	N1-C8-C9	114.2(2)
O6-Zn1-O4	89.46(10)	O6-C23-C22	128.1(3)
O3-Zn1-N1	87.82(9)	O6-C23-C25	113.9(3)
N3-Zn1-N1	76.50(9)	O5-C21-C22	127.6(3)
O5-Zn1-N1	98.54(9)	O5-C21-C24	112.3(4)
O6-Zn1-N1	98.55(9)	C7-N2-C5	117.5(3)
O4-Zn1-N1	170.57(9)	N1-C6-C1	121.0(3)
C9-N3-C11	109.9(2)	N1-C6-C5	119.6(3)
C9-N3-Zn1	115.31(18)	N2-C7-C8	121.5(3)

### 3. Results and Discussion

#### 3.1. Crystal Structure

##### 3.1.1. The Complex Ni(hfac)<sub>2</sub>(IM-o-QN) (1)

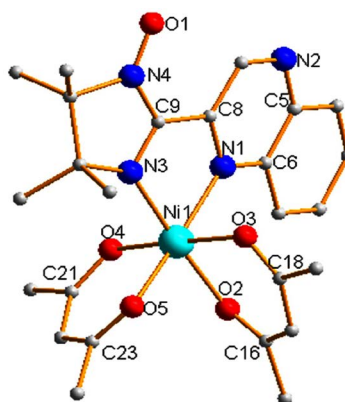
Complex **1** crystallizes in the triclinic *P*<sub>1</sub> space group. The molecular structure of the complex **1** (Ni(hfac)<sub>2</sub>(IM-o-QN)) is given in **Figure 1**.

The complex **1** is a discrete monomer as a two-spin system (*s* = 3/2). Each nickel ion is a distorted octahedral configuration. Six-coordinated geometry is formed by four oxygen atoms from two hfac and two nitrogen atoms from the bidentate imino nitroxide ligand. The hfac ions act as typical chelating ligands to form a mononuclear structure. The bond distance of the Ni1-N1(quinoxalinylyl) is 2.166(4) Å, which is slightly longer than the Ni-N(imino) bond distances (2.056(4) Å). The bond distances of all Ni1-O(hfac) are 2.029(3) Å (Ni1-O2), 2.030(3) Å (Ni1-O3), 2.009(3) Å (Ni1-O4) and 2.023(4) Å (Ni1-O5), respectively. The quinoxalinylyl rings of the IM-o-QN ligands are planar as expected. The equatorial plane comprises one nitrogen atom (N3) from the ONCN imino nitroxide fragment and three oxygen atoms (O2, O3, O4) from two hfac coligands. The axial positions are occupied by one nitrogen atom from the quinoxalinylyl section and one oxygen atom from one hfac coligand. The axial Ni1-N1 bond distance (2.166(4) Å) is longer than the equatorial Ni1-N3 bond lengths (2.056(4) Å). The dihedral angle between the NO-C-N moieties and quinoxalinylyl rings for the IM-o-QN ligands is 8.3°. The dihedral angle between the imino nitroxide fragment (O1, N4, C9, N3) and the equatorial plane (N3, O2, O3, O4) is 76.7°. All Ni-N and Ni-O bond lengths are as well as the bond angles around each central Ni(II) atom are in the expected range [14] [15]. The N4-O1 bond length is 1.263(5) Å, which means that the oxygen atom from ONCN is uncoordinated to the Ni(II) ion.

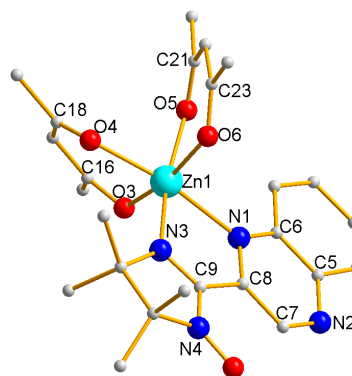
### 3.1.2. The Complex $\text{Zn}(\text{hfac})_2(\text{IM-}o\text{-QN})$ (**2**)

Complex **2** crystallizes in the monoclinic  $C2/c$  space group. The molecular structure of the complex **2** ( $\text{Zn}(\text{hfac})_2(\text{IM-}o\text{-QN})$ ) is shown in **Figure 2**.

The complex **2** forms a mononuclear structure as a two-spin system ( $s = 1/2$ ). Similar to the complex **1**, the coordination geometry about the zinc(II) ion is distorted octahedral with the six coordination sites being occupied by four oxygen atoms (O3, O4, O5 and O6) from the two hfac and two nitrogen atoms (N1, N3) of the bidentate quinoxaliny-substituted imino nitroxide groups. The bond distance of the Zn1-N1 (quinoxaliny) is 2.258(2) Å, which is slightly longer than the Zn-N3 (imino) bond distances (2.079(2) Å). The bond distances of all Zn1-O (hfac) are 2.062(2) Å (Zn1-O3), 2.107(2) Å (Zn1-O4), 2.088(2) Å (Zn1-O5) and 2.098(2) Å (Zn1-O6), respectively. The quinoxaliny rings of the IM-*o*-QN ligands are coplanar as expected. The dihedral angle between the NO-C-N moieties and quinoxaliny rings for the IM-*o*-QN ligands is 7.9°. The dihedral angle between the imino nitroxide fragment (O2, N4, C9, N3) and the equatorial plane (N3, O3, O5, O6) is 94.7°. All Zn-N and Zn-O bond lengths are as well as the bond angles around each central Zn(II) atom are in the expected range [15] [16]. The N4-O2 bond lengths are 1.260(3) Å, which is consistent with the free radical (NO-C-N).



**Figure 1.** Crystal structure of dimer complex **1**. All of the hydrogen atoms and fluorine atoms are omitted for clarity.



**Figure 2.** Crystal structure of dimer complex **2**. All of the hydrogen atoms and fluorine atoms are omitted for clarity.

### 3.2. IR Spectrum of the Two Complexes

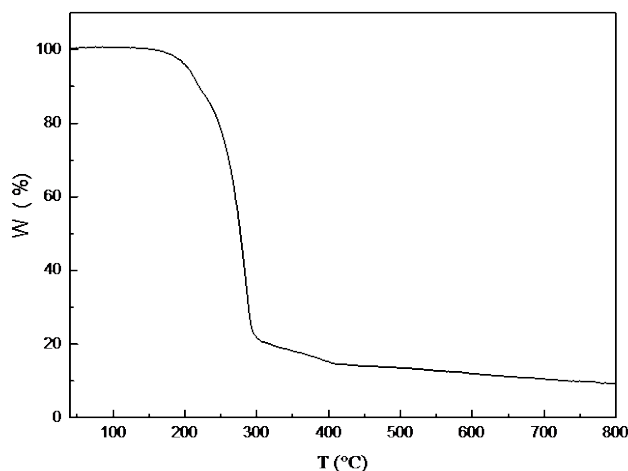
In IR spectra of the two complexes, the characteristic strong bands around 1253, 1204, 1138  $\text{cm}^{-1}$  for the complex **1** and 1256, 1196, 1135  $\text{cm}^{-1}$  for complex **2** can be assigned to the stretching vibrations of the  $\nu(\text{C-F})$  of the *hfac*. The strong absorptions around 1640  $\text{cm}^{-1}$  for the two complexes are ascribed to the  $\nu(\text{C-O})$  of the *hfac*, indicating that the hexafluoroacetone is coordinated to the metal by enol form. The N-O stretching vibrations at 1352  $\text{cm}^{-1}$  (for **1**) or 1355  $\text{cm}^{-1}$  (for **2**) of the imino radical ligands, which indicate the existence of uncoordinated N-O group of IM-o-QN radical ligands. In addition, peaks around 799/670  $\text{cm}^{-1}$  (for **1**) and 796/664  $\text{cm}^{-1}$  (for **2**) can be attributed to aromatic benzene.

### 3.3. UV-Vis Spectrum of the Two Complexes

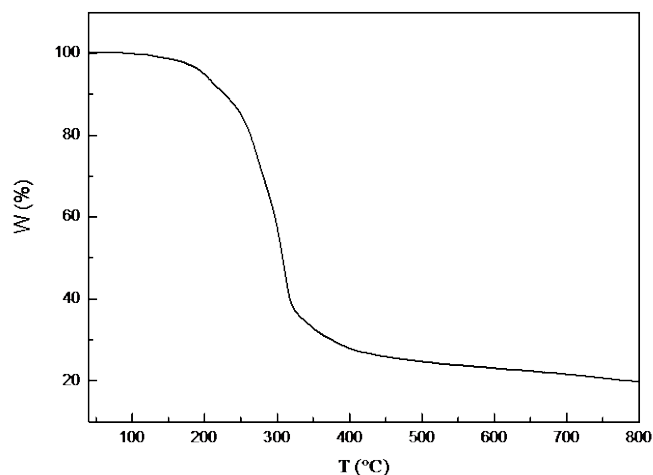
The UV-Vis spectra for the two complexes are measured in methyl alcohol solvent. The absorptions around 313 nm for **1** and 307 nm for **2** can be attributed to  $\pi \rightarrow \pi^*$  of the ONCN conjugate groups of the quinoxaliny-substituted imino nitroxide radicals and the absorptions around 243 nm for **1** and 242 nm for **2** should be attributed to  $\pi \rightarrow \pi^*$  of quinoxaliny group.

### 3.4. Thermogravimetric Analysis of the Two Complexes

TGA (Thermogravimetric analysis) of the two complexes are conducted under  $\text{N}_2$  atmosphere in the temperature range of 40  $^{\circ}\text{C}$  - 800  $^{\circ}\text{C}$  at the heating rate of 10  $^{\circ}\text{C}/\text{min}$ . The thermal decomposition curves of the complex **1** and **2** are as shown in **Figure 3** and **Figure 4**, respectively. As can be seen from the **Figure 3**, the thermal decomposition process of the complex **1** is mainly concentrated in 187  $^{\circ}\text{C}$  - 400  $^{\circ}\text{C}$ , which can be roughly divided into two parts. In the first stage, the complex **1** decomposes and significant weight loss is 79.65% at 167  $^{\circ}\text{C}$  - 312  $^{\circ}\text{C}$ , which corresponds to loss of two *hfac* molecules and a few imino nitroxide section. In the second stage, the fragment for the imino nitroxide ligand further decomposes. The weight loss is about 12.14%. Considered from the ratio, the last residue should be the nitride of nickel.



**Figure 3.** The thermal decomposition curves of the complex **1**.



**Figure 4.** The thermal decomposition curves of the complex **2**.

Seen from **Figure 4**, the thermal decomposition process of the complex **2** is mainly concentrated in 168°C - 450°C, which can be also roughly divided into two parts. In the first stage, the complex **2** decomposes and significant weight loss is 69.98% at 168°C - 365°C which corresponds to loss of two *hfac* molecules and NO of the imino nitroxide section. In the second stage, the fragment for the imino nitroxide ligand further decomposes. The weight loss is about 13.29%. Thinking to the ratio, the last residue should be the nitride of zinc.

#### 4. Conclusion

In summary, two novel nickel(II) and zinc(II) complexes with IM-o-QN were obtained at room temperature, the IM-o-QN ligand is coordinated to metal with the N(quinoxaliny) and N(IM) mode to avoid steric hindrance. Those have been characterized structurally by X-ray diffraction analysis, element analyses, IR and UV-Visible spectroscopy. In two new M(II)-radical complexes, the central M(II) (Ni(**1**) and Zn(**2**)) ions are coordinated by four oxygen atoms from two *hfac* and two nitrogen atoms from imino radicals to form a distorted octahedron. Additionally, the optical properties of the two complexes are reported. The magnetic properties of the two complexes **1** and **2** are under researching.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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