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Synthesis and Crystal Structures of Cobalt(II) and Nickel(II) Complexes Containing Nitronyl Nitroxide Radical and Dicyanamide[1]

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Abstract—Two new complexes $[Co(NIT\text{-}1'\text{-}MeBzIm)_2(Dca)_2]$ (**I**) and $[Ni(NIT\text{-}1'\text{-}MeBzIm)_2(Dca)(H_2O) \cdot NO_3 \cdot H_2O$ (**II**) (NIT-1'-MeBzIm = 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide; Dca = $N(CN)_2$) were prepared and structurally characterized by single-crystal X-ray diffraction. Relevant crystallographic parameters are as follows: monoclinic, $P2_{1/c}$ space group, $Z = 4$; crystal data: $C_{34}H_{38}N_{14}O_4Co$, $M = 765.71$, $a = 14.343(4)$, $b = 14.322(4)$, $c = 18.626(5)$ Å, $\beta = 105.956(3)°$ for **I**. Orthorhombic $Pna2_1$ space group, $Z = 4$; crystal data: $C_{32}H_{42}N_{12}O_9Ni$, $M = 797.49$, $a = 24.426(4)$, $b = 11.0326(18)$, $c = 13.980(2)$ Å for **II**. The X-ray analysis reveals that Co^{2+} ion and Ni^{2+} ion resides in a approximate sdistorted octahedron center. In **I**, the complex was linked by intermolecular hydrogen bonds, resulting in a 1D chain configuration. In **II**, the complex was linked by intermolecular hydrogen bonds, resulting in a 2D network configuration.

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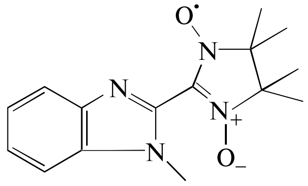
INTRODUCTION

The design and synthesis of molecule-based magnetic materials is one of the major challenges of materials science. The major research aims in the field of molecular magnetism are either the chemical design of molecular assemblies that exhibit a spontaneous magnetization, or the rationalization of magneto-structural correlation [1–8]. In many different types of organic radicals, research has focused on the nitronyl nitroxide radicals (NITR) family because of their good stable spin carriers even coordinated to metal ions. So far, there have been many investigations concerning paramagnetic metal complexes with the organic radicals. In the same frontier field, the dicyanamide anionic ligand has aroused much interest, especially in the form of $M(II)(Dca)_2$ compounds, where M = Ni, Co, Cu and Dca = $N(CN)_2$, as a new class of molecule-based magnetic materials [9–14]. Dicyanamide, is a versatile ligand which has been shown to coordinate to metal ions in various modes.

In the present work, we have synthesized two metal–radical complexes with dicyanamide anions $[Co(NIT\text{-}1'\text{-}MeBzIm)_2(Dca)_2]$ (**I**) and $[Ni(NIT\text{-}1'\text{-}MeBzIm)_2(Dca)(H_2O)] \cdot NO_3 \cdot H_2O$ (**II**) (NIT-1'-MeBzIm = 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide).



NIT-1'-MeBzIm

In addition, we extend to report the hydrogen-bonded molecular structure of the complex which is 1D chain configuration for **I** and 2D network configuration for **II**.

EXPERIMENTAL

All chemicals and solvents purchased were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 cm^{-1}) were recorded by using KBr pellet on an Avatar^{TM} 360 E.S.P. IR spectrometer. The crystal determination was performed on a Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å).

Synthesis. The nitronyl nitroxide radical, NIT-1'-MeBzIm, was prepared according to the literature method [15, 16]. The complex **I** was synthesized by adding dropwise an orange methanol solution (5 mL) of NIT-1'-MeBzIm (0.289 g, 1 mmol) into 5 mL

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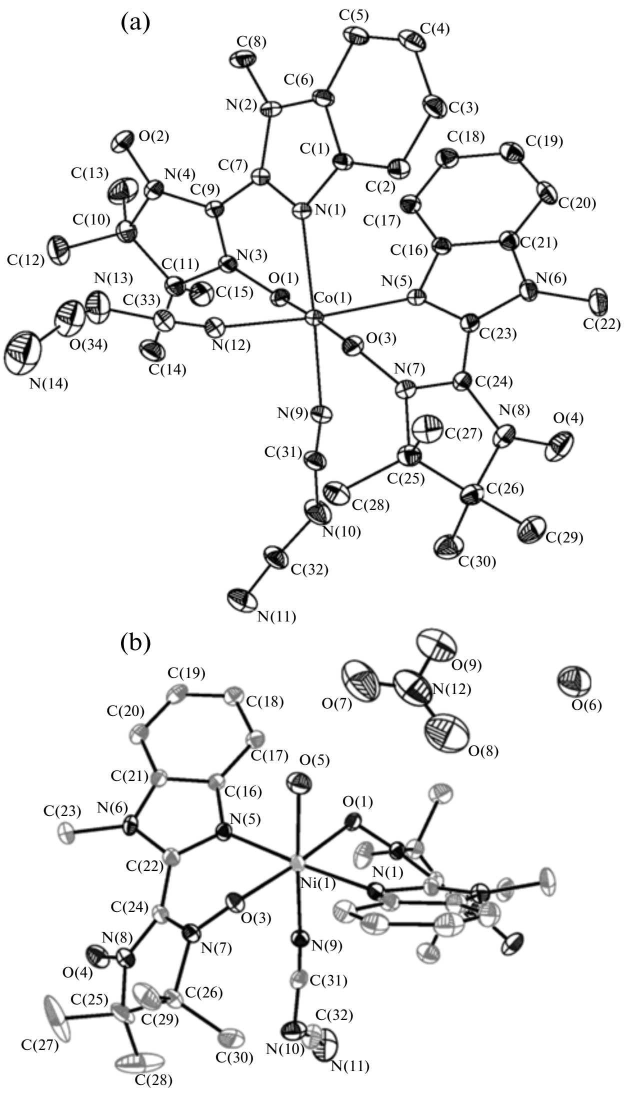

Fig. 1. Molecular structure of **I** (a) and **II** (b) with 25% probability ellipsoids (the hydrogen atoms have been omitted).

methanol solution of $Co(NO_3)_2 \cdot 3H_2O$ (0.210 g, 0.5 mmol). After 2 h, 0.265 g (0.2 mmol) of sodium dicyanamide dissolved in 5 mL methanol was added to the resulting solution. The mixture was stirred for 6 h at room temperature and then filtered. The clear orange filtrate was diffused with diethyl ether vapour at room temperature and darkpurple block crystals were obtained after one week. The yield was 54.4%.

For $C_{34}H_{38}N_{14}O_4Co$ (**I**)			
anal. calcd., %:	C, 53.39	H, 5.01	N, 25.65.
Found, %:	C, 53.31	H, 5.18	N, 26.09.

IR (KBr; ν, cm^{-1}): 1373.25 ν(N–O), 1377.62 ν(C–N), 1482.13 $\delta(CH_3)$, 1378.2 $\omega(CH_3)$; 1618.36—the framework vibration of benzimidazole; the present of $[N(CN)_2]^{-1}$ ligand (1352 ν_s(C≡N) 2195, ν_{as}(C≡N) 2266, ν_{as}(C≡N)).

Complex **II** was prepared by a way similar to that of **I**.

For $C_{32}H_{42}N_{12}O_9Ni$ (**II**)			
anal. calcd., %:	C, 48.20;	H, 5.31;	N, 21.08.
Found, %:	C, 48.22;	H, 5.28;	N, 21.21.

IR (KBr; ν, cm^{-1}): 1374.54 ν(N–O), 1377.48 ν(C–N), 1481.45 $\delta(CH_3)$, 1377.1 $\omega(CH_3)$; 1618.32—the framework vibration of benzimidazole; the present of $[N(CN)_2]^{-1}$ ligand (1354 ν_s(C≡N) 2194, ν_{as}(C≡N) 2265, ν_{as}(C≡N)).

X-ray diffractions analysis of I and II. A darkpurple single crystal of complex **I** or **II** was put on a Bruker SMART APEX II CCD diffractometer equipped with a

Table 1. Crystallographic data and experimental details for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	765.71	797.49
T, K	291(2)	291(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a, Å	14.343(4)	24.426(4)
b, Å	14.322(4)	11.0326(18)
c, Å	18.626(5)	13.980(2)
β, deg	105.956(3)	90
V, Å^3	3678.6(16)	3767.4(10)
Z	4	4
μ, mm^{-1}	0.525	0.583
ρ_{calcd}, g cm^{-3}	1.383	1.429
F(000)	1596	1972
Cryst size, mm	0.49 × 0.38 × 0.29	0.38 × 0.33 × 0.33
θ Range for data collection, deg	2.53–25.50	2.29–25.49
Limiting indices	$-17 \le h \le 17$, $-17 \le k \le 17$, $-22 \le l \le 22$	$-29 \le h \le 29$, $-13 \le k \le 13$, $-16 \le l \le 16$
Collected reflections	25647	21529
Independent reflections, R_{int}	6829 (0.0724)	6978 (0.0588)
Reflections with $I > 2\sigma(I)$	3545	4893
Data/restraints/parameters	6829/223/488	6978/61/497
Max and min transmission	0.8626 and 0.7841	0.8331 and 0.8097
$R(F_o)$, $I > 2\sigma(I)$	0.0655, 0.1646	0.0561, 0.1544
Largest diff. peak and hole, e Å^{-3}	0.914 and –0.425	0.608 and –0.450

Table 2. Selected bond lengths (Å) and angles (deg) for structure **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Co(1)N(9)	2.059(5)	Co(1)O(1)	2.114(4)
Co(1)O(3)	2.082(4)	Co(1)N(5)	2.135(4)
Co(1)N(12)	2.090(5)	Co(1)N(1)	2.142(4)
		II	
Co(1)N(9)	2.059(5)	Co(1)O(1)	2.114(4)
Co(1)O(3)	2.082(4)	Co(1)N(5)	2.135(4)
Co(1)N(12)	2.090(5)	Co(1)N(1)	2.142(4)
Angle	ω, deg	Angle	ω, deg
		I	
N(9)Co(1)O(3)	90.46(17)	O(3)Co(1)N(1)	99.50(15)
N(9)Co(1)N(12)	95.19(19)	N(12)Co(1)N(1)	86.28(17)
O(3)Co(1)N(12)	87.93(18)	O(1)Co(1)N(1)	84.05(15)
N(9)Co(1)O(1)	85.98(16)	N(5)Co(1)N(1)	87.07(15)
O(3)Co(1)O(1)	176.40(14)	N(3)O(1)Co(1)	116.0(3)
N(12)Co(1)O(1)	92.97(18)	N(7)O(3)Co(1)	115.7(3)
N(9)Co(1)N(5)	92.97(16)	C(7)N(1)Co(1)	122.3(3)
O(3)Co(1)N(5)	84.02(15)	C(1)N(1)Co(1)	130.7(3)
N(12)Co(1)N(5)	168.58(18)	C(23)N(5)Co(1)	123.6(3)
O(1)Co(1)N(5)	95.56(15)	C(31)N(9)Co(1)	164.2(5)
N(9)Co(1)N(1)	169.99(18)	C(33)N(12)Co(1)	164.3(5)
		II	
N(9)Co(1)O(3)	90.46(17)	O(3)Co(1)N(1)	99.50(15)
N(9)Co(1)N(12)	95.19(19)	N(12)Co(1)N(1)	86.28(17)
O(3)Co(1)N(12)	87.93(18)	O(1)Co(1)N(1)	84.05(15)
N(9)Co(1)O(1)	85.98(16)	N(5)Co(1)N(1)	87.07(15)
O(3)Co(1)O(1)	176.40(14)	N(3)O(1)Co(1)	116.0(3)
N(12)Co(1)O(1)	92.97(18)	N(7)O(3)Co(1)	115.7(3)
N(9)Co(1)N(5)	92.97(16)	C(7)N(1)Co(1)	122.3(3)
O(3)Co(1)N(5)	84.02(15)	C(1)N(1)Co(1)	130.7(3)
N(12)Co(1)N(5)	168.58(18)	C(23)N(5)Co(1)	123.6(3)
O(1)Co(1)N(5)	95.56(15)	C(31)N(9)Co(1)	164.2(5)
N(9)Co(1)N(1)	169.99(18)	C(33)N(12)Co(1)	164.3(5)

graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using ϕ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97 [17]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [18]. The final agreement factor values are: $R = 0.0655$ and $wR = 0.1646$ ($w = 1/[\sigma^2(F_o^2) + (0.0937P)^2 + 2.0697P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.097$, $(\Delta/\sigma)_{max} = 0.061$ for complex **I** and $R = 0.0561$ and $wR = 0.1544$ ($w = 1/[\sigma^2(F_o^2) + (0.1125P)^2 + 0.1032P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.056$, $(\Delta/\sigma)_{max} = 0.002$ for complex **II**. Table 1 shows crystallographic data of the complexes **I** and **II**. Selected bond lengths and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 669672 for **I** and 666956 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

RESULTS AND DISCUSSION

The ORTEP drawing of complex **I** is shown in Fig. 1a. The Co^{2+} ion resides in a distorted octahedron center and is coordinated by two NN oxygen atoms O(1), O(3), one nitrogen atom N(12) from the dicyanamide ligand and one benzimidazolyl nitrogen atoms N(5) of NIT-1'-MeBzIm radicals from the equatorial position to form a *trans* configuration. The Co^{2+} ion is highly coplanar with the basal plane with a displacement of 0.052 Å (with the bond lengths of 2.114(4) Co(1)–O(1), 2.082(4) Co(1)–O(3), 2.135(4) Co(1)–N(5), 2.090(5) Å Co(1)–N(12)). The axial positions are occupied by one benzimidazolyl nitrogen atoms N(1) of NIT-1'-MeBzIm radicals (the bond length is 2.142(4) Å for Co(1)–N(1)) and one nitrogen atom N(9) (the bond length is 2.059(5) Å for Co(1)–N(9)) from the dicyanamide ligand. The axial direction is slightly deviated from the normal of the equatorial plane as indicated by the average angles of 84.59°, O(1)Co(1)N(9) 85.98(16)°, N(5)Co(1)O(3) 84.02(2)°, N(1)Co(1)O(1) 84.05(2)°.

The intermolecular H bonds occur between oxygen atoms of the uncoordinated NO moiety of nitronyl nitroxide and H–C from the NN (O(2)–H(19)···C(19) 3.078 Å). In the unit cell, the single hydrogen bond is alternatively arranged, resulting in a 1D chain configuration (Fig. 2a).

The ORTEP drawing of complex **II** is shown in Fig. 1b. The Ni^{2+} ion resides in a distorted octahedron center and is coordinated by two NN oxygen atoms O(1), O(3) and two benzimidazolyl nitrogen atoms

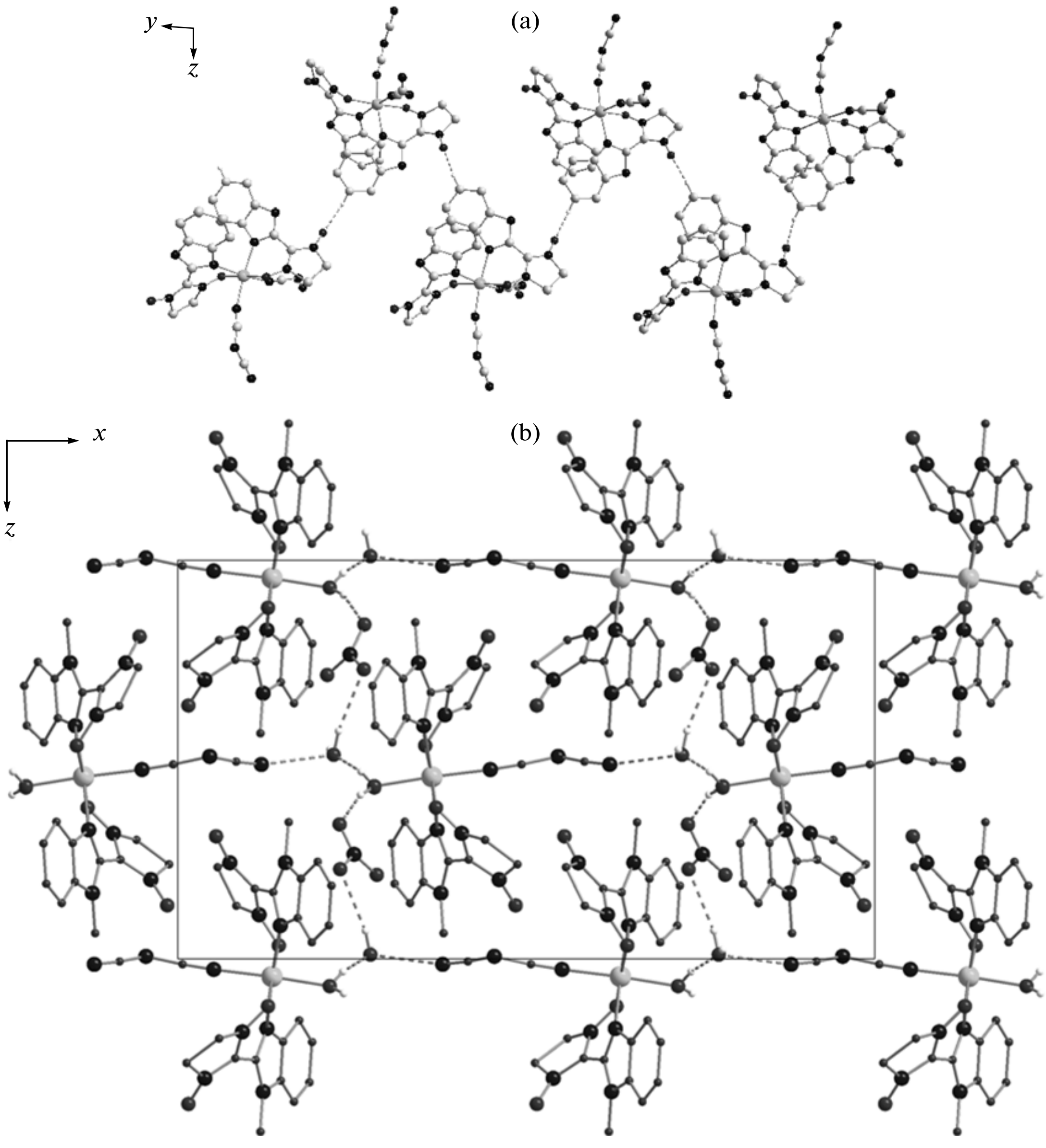

Fig. 2. A sketch of the intermolecular hydrogen bond of **I** (a) and **II** (b) (part of hydrogen atoms and methyls are deleted for clarity).

N(1), N(5) of NIT-1'-MeBzIm radicals from the equatorial position to form a *trans* configuration. The Ni^{2+} ion is highly coplanar with the basal plane with a displacement of 0.069 Å (with the bond lengths of 2.089(5) Ni(1)–O(1), 2.055(5) Ni(1)–O(3), 2.077(6) Ni(1)–N(1), 2.068(6) Å Ni(1)–N(5)). The axial positions are occupied by one water molecular oxygen atom O(5) (the bond length is 2.100(3) Å for Ni(1)–O(5)) and one nitrogen atom N(9) (the bond length is 2.155(13) Å for Ni(1)–N(9)) from the dicyanamide ligand. The axial direction is slightly deviated from the normal of the equatorial plane as indicated by the average angles of 96.21°, O(1)Ni(1)N(9) 89.2(3)°, N(5)Ni(1)O(3) 86.9(2)°, N(1)Ni(1)O(5) 89.7(8)°. The fragment O(3)–N(7)–C(24)–N(8) is nearly coplanar but forms a dihedral angle of 15.42(23)°.

The intermolecular H bonds occur between oxygen atoms of the uncoordinated NO moiety of nitronyl nitroxide and H–O from the NN (O(6)–H(3*w*)···O(8) 3.212(16) Å, O(6)–H(3*w*)···O(9) 3.197(15) Å). In the unit cell, the single hydrogen bond is alternatively arranged, resulting in a 2D network configuration (Fig. 2b).

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