



Short communication

## Two cobalt complexes containing different nitronyl nitroxide radicals: Structure and magnetic properties

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## ABSTRACT

Two Co(II) complexes based on different nitronyl nitroxide radicals were synthesized and characterized structurally and magnetically: [Co(hfac)<sub>2</sub>(NITPh-*p*-Cl)(phenol)] (**1**) and [(Co(hfac)<sub>2</sub>(NITPh-(OCH<sub>3</sub>)<sub>3</sub>)(Co(hfac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>)] (**2**) [hfac = hexafluoroacetylacetonate, NITPh-*p*-Cl = 2-(4'-chlorophenyl)-4,4,5,5-tetramethylimidazole-1-oxyl-3-oxide, NITPh(OCH<sub>3</sub>)<sub>3</sub> = 2-(3',4',5'-trimethoxyphenyl)-4,4,5,5-tetramethylimidazole-1-oxyl-3-oxide]. X-ray crystal structure analysis revealed that the Co(II) ions in complexes **1** and **2** are six-coordinated with slightly distorted octahedral geometry. The packing diagram of complex **2** shows a 3D supermolecular structure formed by intermolecular hydrogen bond interactions. Variable temperature magnetic susceptibility measurement studies revealed that complexes **1** and **2** exhibit antiferromagnetic interactions between Co(II) and radicals with  $J = -0.1 \text{ cm}^{-1}$  (**1**) and  $J = -3.43 \text{ cm}^{-1}$  (**2**), respectively.

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In recent years, more and more attention has focused on design and synthesis of molecule magnet and the search for magnetic materials [1]. In this area, organic radicals are largely used as ligands and many compounds displaying interesting magnetic properties were obtained [2–4]. Nitronyl nitroxide, as organic radicals, play a significant role in molecular magnet [5–7]. The nitronyl nitroxide is a stable spin system which can be linked with the metal center through the O–N groups to produce metal–radical complexes [8–10]. Metal–radical complexes which have definite geometry are in favor of the fundamental studies of magneto-structural correlation, especially the way how structural factors affect the metal–organic radical interaction [11–14]. These investigations are necessary not only for understanding the spin–coupling behaviors between the metal ion and the organic radical but also for the development of new molecular magnetic materials [15,16].

Considering the weak coordination ability of nitronyl nitroxide, hexafluoroacetylacetonate–metal or trifluoroacetate–metal complexes are present to guarantee the Lewis acidity necessary for the coordination of these radicals to the metallic center [17,18]. A large number of transition metal–radical complexes with various structures and magnetic properties were synthesized and characterized [1,7,9,13,19,20]. A series of zero, one dimensional and multidimensional complexes based on transition metal were reported [6,11,17,18,21–23]. Cobalt (II) complexes have been researched rarely because of large spin-orbital coupling, although cobalt (II) ion is a very effective spin carrier [1,3,5]. To our knowledge, altering the substituent group of nitronyl nitroxide can sometimes result in dramatic changes in magnetic

properties [7,16]. But the influence of substituent on compound property is not clear. Along this line, we synthesized two kinds of nitronyl nitroxide radicals: NITPh-*p*-Cl and NITPh-(OCH<sub>3</sub>)<sub>3</sub> (The structures of these radicals are shown in Scheme S1), and two compounds based cobalt (II) were synthesized: [Co(hfac)<sub>2</sub> [NITPh-*p*-Cl](Phenol)] (**1**) and [(Co(hfac)<sub>2</sub> (NITPh-(OCH<sub>3</sub>)<sub>3</sub>)(Co(hfac)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>)] (**2**). In this paper, the synthesis, crystal structure and magnetic properties of the two complexes were reported. All reagents and solvents were purchased from commercial sources and used without purification. Co(hfac)<sub>2</sub>·2H<sub>2</sub>O, NITPh-(OCH<sub>3</sub>)<sub>3</sub> and NITPh-*p*-Cl were synthesized as described elsewhere [8,24,25]. Infrared spectra were recorded with a BRUKER FT-IR EQUINOX 55 using KBr pellets in the region 4000–400 cm<sup>-1</sup>. The C, H, and N elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Magnetic susceptibilities were measured with a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

The X-ray powder diffraction patterns (PXRD) of complexes **1** and **2** were recorded on a Shimadzu LabX XRD-6100 diffractometer, operated at 40.0 kV and 30.0 mA, using a Cu target tube and graphite monochromator. The intensity data were recorded by continuous scan in  $2\theta/\theta$  mode from 5° to 50° with a step size of 0.02° and a scan speed of 5° min<sup>-1</sup>.

The complex of the thermogravimetry-differential thermal analysis (TG-DTA) was studied by SDT-Q600 at a heating rate of 20 °C · min<sup>-1</sup> in a nitrogen atmosphere, and nitrogen gas of high purity (>99.999%) with a flow rate of 100 ml min<sup>-1</sup> was used as carrier gas. The sample was heated from ambient temperature to 600 °C.

The single crystal samples of **1** and **2** suitable for X-ray diffraction were successfully synthesized by using NITPh-*p*-Cl and NITPh(OCH<sub>3</sub>)<sub>3</sub>

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with  $\text{Co}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$  [26]. Single-crystals of the two Co–nitronyl nitroxide complexes were obtained 3 days later. Single-crystal X-ray diffraction analysis (crystal parameters, the measurement detail) of complexes **1**, **2** are listed in Table S1.

Complex **1** crystallizes in the Monoclinic,  $P2_1/c$  space group, while the complex **2** in Triclinic,  $P-1$  space group. The structures of complex **1** and complex **2** are shown in Figs. 1 and 2. The selected bond lengths and angles for complexes **1** and **2** are shown in Table S2. For complex **1**, the Co(II) ions are six-coordinated with slightly distorted octahedral geometry, which are occupied by four oxygen atoms (O3, O4, O5, O6) from two hfac units, one oxygen atom (O1) from nitronyl nitroxide and one from Phenol (O7). The bond length of Co1–O1 (radical) is 2.0483(2) Å, while the distance of Co1–O7 (Phenol) is 2.166(2) Å. The bond lengths of Co–O (hfac) are in the range of 2.0316(2)–2.090(2) Å. These bond lengths are comparable to the reported cobalt(II) nitronyl nitroxide complexes [1–3,7,8,28]. The dihedral angle between the benzene ring and the imidazoline ring (O2–N2–C1–N1–O1) is 26.688°. There are no hydrogen bond interactions in complex **1**.

For complex **2**, there are two crystallographically independent and chemically different molecules in the asymmetric unit: one is  $[\text{Co}(\text{hfac})_2(\text{NITPh}-(\text{OCH}_3)_3)_2]$ , the other is  $[(\text{Co}(\text{hfac})_2(\text{H}_2\text{O})_2)]$ . For Co1, the Co(II) ion is the center of a slightly distorted octahedron, and coordinated by four oxygen atoms from two hfac ligands with the Co–O bond lengths in the range of 2.0551(2)–2.0557(2) Å and two oxygen atoms from two nitronyl nitroxide radicals, with the Co–O bond lengths of 2.0935(2) Å. The fragment O1–N2–C6–N3–O2 is nearly coplanar as expected, indicating the easy delocalization of single electron within this moiety. The dihedral angle between the benzene ring and the imidazoline ring (O1–N1–C1–N2–O2) is 16.062°. For Co2, the Co(II) ion is six-coordinated by four oxygen atoms from two hfac ions and two oxygen atoms from two  $\text{H}_2\text{O}$  molecules.

Intermolecular hydrogen bonds are found in the crystal of complex **2**. There are two kinds of O–H–O hydrogen bonds in the complex **2** (Table S3). The molecular arrangement of complex **2** is shown in Fig. S1. The hydrogen bonding interactions exist between two oxygen atoms from one coordinated water molecule and one uncoordinated nitronyl nitroxide (O10---O2, 2.6602 Å). As a result, molecules are linked by weak interactions to form 1D chain. The intermolecular interactions also occur between one oxygen atom from  $\text{OCH}_3$  group of nitronyl nitroxide and H–O from one coordinated water molecule (O10---O4, 2.9377 Å) (O10---O5, 2.7769 Å), which leads to the formation of a 3D supermolecular structure, as depicted in Fig. 3.

To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments have been carried out for complexes **1** and **2**. The experimental and computer-simulated PXRD patterns are shown in Figs. S2 and S3. These patterns indicate that the bulk-synthesized materials and as-grown crystals can be considered homogeneous for the two complexes.

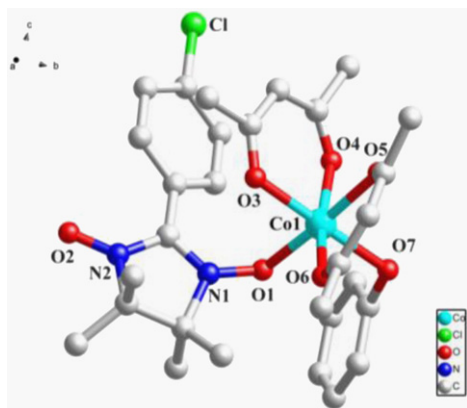


Fig. 1. Crystal structure of  $[\text{Co}(\text{hfac})_2(\text{NITPh-Cl})(\text{Phenol})]$  (**1**). All hydrogen and fluorine atoms and solvent molecules are omitted for clarity.

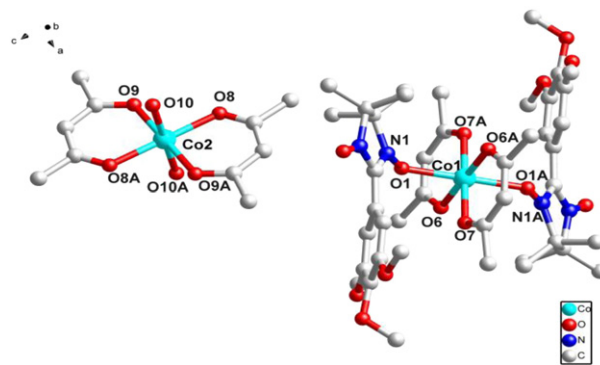


Fig. 2. Crystal structure of  $[(\text{Co}(\text{hfac})_2(\text{NITPh}-(\text{OCH}_3)_3)_2)(\text{Co}(\text{hfac})_2(\text{H}_2\text{O})_2)]$  (**2**). All hydrogen and fluorine atoms and solvent molecules are omitted for clarity.

In order to investigate the thermal stability of the complex **1** and **2**, thermogravimetric analysis was carried out and the TG-DTA curves are depicted in Figs. S4 and S5. For complex **1**, the decomposition takes place from 25.00 to 500 °C (the peak of DTA at 178.41 °C) with the weight loss of 71%, corresponding to the skeleton of compound begins collapsed, implying the decomposition of hfac and NITPhp-Cl (except the six oxygen atoms to coordinated Co(II) ion form CoO). For complex **2**, the decomposition takes place from 25.00 to 500 °C (the peak of DTA at 249.6 °C) with the weight loss of 87.23%, corresponding to the skeleton of compound begins collapsed, implying the decomposition of hfac and  $(\text{NITPh}-(\text{OCH}_3)_3)_2$  (except the six oxygen atoms to coordinated Co(II) ion form CoO).

The temperature dependence of the magnetic susceptibilities of complexes **1** and **2** were measured for polycrystalline sample in the range 2–300 K in an applied magnetic field of 1 kOe. The magnetic result of complex **1** is shown in Fig. 4. At room temperature the value of  $\chi_{\text{M}}T$  is 2.67  $\text{cm}^3 \text{K mol}^{-1}$ . These values is close to the expected values of (2.63  $\text{cm}^3 \text{K mol}^{-1}$ ) for an uncoupled system of one Co(II) ion ( $S = 3/2$ ) plus one radical ( $S = 1/2$ ). Upon cooling, the  $\chi_{\text{M}}T$  values decrease gradually and reach a minimum of 1.17  $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 5 K. This behavior indicates that the existence of antiferromagnetic exchange interactions between the Co(II) ion and radical. The isotropic Hamiltonian  $\hat{H} = -2J S_{\text{Co}} S_{\text{R}}$  is introduced to analyze the magnetic coupling strength, where  $J$  represents the magnetic coupling for the Co–radical. For Radical–Co(II) complexes, the theoretical expression of the magnetic susceptibility is:

$$\chi_{\text{Co}} = \frac{Ng^2\beta^2}{KT} \left[ \frac{10 + 2 \exp(-4/JKT)}{5 + 3 \exp(-4/JKT)} \right].$$

A mean-field parameter  $zJ'$ , was added in the formula for taking into account the magnetic interaction between units of Radical–Co(II). The theoretical expression of the molar magnetic susceptibility is:

$$\chi_{\text{M}} = \frac{\chi_{\text{Co}}}{1 - 2zJ' \chi_{\text{Co}} / Ng^2\beta^2}.$$

The best fitting results give coupling parameters  $g = 2.02$ ,  $J = -0.10 \text{ cm}^{-1}$ ,  $zJ' = 0.01 \text{ cm}^{-1}$ , which is in the range for other similar Co–radical compounds. The negative value of  $J$  shows the antiferromagnetic coupling between the Co(II) ion and nitronyl nitroxide radical. The plot of  $\chi_{\text{M}}^{-1}$  vs.  $T$  obeys the Curie–Weiss law  $1/\chi_{\text{M}} = (T - \theta) / C$  between 300 and 2.0 K, and yields  $C = 23.96 \text{ cm}^3 \text{mol}^{-1} \text{K}$  with  $\theta = -2.45 \text{ K}$ . The negative value of  $\theta$  also confirms the result of the existence of antiferromagnetic coupling between Co(II) ion and nitronyl nitroxide radical.

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