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Synthesis, crystal structure and magnetism of two cobalt(II) complexes with imino and nitronyl nitroxides

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Abstract Two new cobalt–radical complexes, namely $[Co(IM\text{-}5\text{-}Br\text{-}2Py)_2(N_3)_2]\cdot MeOH$ (**1**) and $[Co(NIT\text{-}5\text{-}Br\text{-}2Py)_2(N_3)_2]$ (**2**) (IM-5-Br-2Py = 2-(5-bromo-2-pyridyl)-4,4,5,5-tetramethyl-limidazoline-1-oxyl, NIT-5-Br-2Py = 2-(5-bromo-2-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) have been synthesized and characterized by magnetic and single-crystal X-ray diffraction studies. X-ray diffraction analysis indicates that both complexes possess mononuclear structures, in which two radical ligands coordinate to the Co(II) atom in chelating fashion and two azides act as terminal ligands. The magnetic properties for complexes **1** and **2** have been investigated in the temperature range 2–300 K. DC magnetic measurements show that the Co(II) atom of complex **1** interacts ferromagnetically with the directly bonding imino nitroxide, while the Co(II) atom strongly antiferromagnetically couples with the directly coordinated N–O group in complex **2**.

Introduction

The coordination complexes of paramagnetic metal atoms with nitroxide radical ligands have recently attracted considerable interest for the purpose of exploiting new molecular-based magnetic materials [1–4]. By using this approach, various highly interesting species such as molecular-based ferromagnets [5–7], single-chain magnets (SCMs) [8–13], single-molecule magnets (SMMs) [14–19] and molecule spin transition species [20–23] have been achieved so far. However, most of the work performed in this area has involved in copper(II), nickel(II), manganese(II) or lanthanide compounds, and the reported cobalt(II)–radical compounds are currently very scarce [24–26]. It is well known that the high-spin cobalt(II) atom may exhibit large magnetic anisotropy due to strong spin–orbital coupling. On the other hand, the direct binding of the nitroxide radicals with transition metal atoms can yield strong magnetic exchange coupling. Thus, the combination of the cobalt(II) atom and the nitroxide radical into a molecular entity will be an appealing way to obtain interesting magnetic materials. As part of our continuing interest in molecular-based magnetic materials by means of nitroxide radicals, here, we have chosen cobalt(II) atom and imino and nitronyl nitroxide radicals to construct new metal–radical complexes. In this paper, we report the crystal structures and magnetic properties of two cobalt(II)–radical complexes $[Co(IM\text{-}5\text{-}Br\text{-}2Py)_2(N_3)_2]\cdot MeOH$ (**1**) and $[Co(NIT\text{-}5\text{-}Br\text{-}2Py)_2(N_3)_2]$ (**2**) (IM-5-Br-2Py = 2-(5-bromo-2-pyridyl)-4,4,5,5-tetramethyl-limidazoline-1-oxyl, NIT-5-Br-2Py = 2-(5-bromo-2-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide).

Experimental section

Materials and general methods

All reagents and chemicals were purchased from commercial sources and used without further purification. The imino radical ligand IM-5-Br-2Py and radical ligand NIT-5-Br-2Py were prepared by the literature methods [27, 28].

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Elemental analysis for carbon, hydrogen and nitrogen were carried out on a PerkinElmer elemental analyzer model 240. The infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker Tensor 27 IR spectrometer. Variable-temperature magnetic susceptibilities were measured on a VSM SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants for all the constituent atoms.

Synthesis of [Co(IM-5-Br-2Py)$_2$(N$_3$)$_2$]·MeOH (1)

NaN$_3$ (0.065 g, 1.0 mmol) was added to a mixture of Co(ClO$_4$)$_2$·6H$_2$O (0.1829 g, 0.5 mmol) and IM-5-Br-2Py(0.3 g, 1.0 mmol) in methanol (25 mL) at room temperature. The resulting solution was stirred for 10 min to obtain a dark blue solution, filtered and the filtrate was evaporated at room temperature for 3 days to give deep-blue crystals suitable for X-ray analysis. Yield 0.18 g (48 %). Anal. calc. for C_{25} $H_{34}Br_2CoN_{12}O_3$ (%): C 39.02; H 4.45; N 21.84. Found: C 38.44, H 4.07, N 21.11. IR (KBr, cm^{-1}): 3414 (m), 2985 (m), 2030 (s), 1445 (s), 1363 (s), 1255 (s), 1161 (s), 1024 (s), 659 (m).

Synthesis of [Co(NIT-5-Br-2Py)$_2$(N$_3$)$_2$] (2)

An identical procedure as that for **1** was followed to prepare **2**, except that IM-5-Br-2Py was replaced by NIT-5-Br-2Py. Yield 0.23 g (60 %). Anal. calc. for $C_{24}H_{30}Br_2CoN_{12}O_4$ (%): C 37.46; H 3.93; N 21.84; Found: C 37.04; H 3.87; N 21.19. IR (KBr, cm^{-1}): 3117 (m), 2985 (m), 2040 (s),1574 (s),1555 (s), 1445 (s), 1349 (s), 1132 (s), 1028 (s), 845 (s).

X-ray crystallography

X-ray single-crystal diffractions of complexes **1** and **2** were performed on a Rigaku Saturn CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 113 K. The structures were solved by direct methods using the program SHELXS-97 and refined using full matrix least squares methods on F^2 with the use of the SHELXL-97 program package [29]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Detailed data collection and refinement of the compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1059321for **1**, and 1059322 for **2**. The copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: t44 1223336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and discussion

Structural description of [Co(IM-5-Br-2Py)$_2$(N$_3$)$_2$]·MeOH(1)

Complex **1** crystallizes in the monoclinic space group $P2_1/c$. An ORTEP drawing of **1** is shown in Fig. 1. The asymmetric unit of compound **1** contains one Co(IMNIT-5-Br-2Py)$_2$(N$_3$)$_2$ moiety and one methanol solvent molecule. The coordination geometry of the cobalt(II) atom is distorted octahedral with the six coordination sites being occupied by four nitrogen atoms [N(2), N(3), N(4), N(6)] of the two bidentate imino nitroxide radicals and two nitrogen atoms [N(7), N(10)] of two azide groups. Two radical ligands act as bidentate ligands in a chelating manner toward cobalt(II) through the nitrogen atoms of the pyridine ring and imino nitrogen atoms. The Co–N(pyridyl) bond distances are 2.150(5) and 2.130(6) Å for Co(1)–N(3) and Co(1)–N(6), respectively, which are slightly shorter than the Co–N(imino) bond distances [2.158(6) and 2.147(6) Å for Co(1)–N(2) and Co(1)–N(4), respectively]. The dihedral angles between the N–O–C–N moieties and pyridyl rings for the two im-2-py ligands are 2.733(5)° and 1.967(5)°, respectively. Two azide groups coordinate to metal atom as terminal ligands in *cis*-positions. The Co(1)–N(7) and Co(1)–N(10) bond lengths are 2.078(7) and 2.092(6) Å, respectively. The azide ligands are quasi-linear [177.4(8)° and 179.4(8)°for N(7)–N(8)–N(9) and N(10)–N(11)–N(12), respectively]. The packing arrangement of complex **1** is shown in Fig. S1. The shortest intermolecular contact between nitroxide groups of O(2)···O(2) is 4.857(9) Å, implying the complex units are well separated.

Structural description of [Co(NIT-5-Br-2Py)$_2$(N$_3$)$_2$] (2)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. An ORTEP drawing of **2** is shown in Fig. 2. The asymmetric unit of complex **2** is composed of two crystallographically independent Co$_{0.5}$(NIT-5-Br-2Py)(N$_3$) moieties. The cobalt atom lies on an inversion center and adopts a distorted octahedral coordination. The coordination sphere of the cobalt(II) atom is formed by two nitrogen atoms from two pyridyl rings, two oxygen atoms from two N–O groups and two nitrogen atoms of two azide ligands. The two azido anions acting as terminal ligands are ligated to a cobalt(II) atom at axial positions in the *trans*-form. The Co–O(nitroxide) distances are 2.115(4) and 2.107(4) Å for the two crystallographically independent moieties, respectively. The Co–N(pyridine) bond lengths are 2.144(5) and 2.127(5) Å

Table 1 Crystal data and structure refinements for complexes **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{25}H_{34}Br_2CoN_{12}O_3$	$C_{24}H_{30}Br_2CoN_{12}O_4$
Mr	769.37	769.33
T (K)	113(2)	113(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	9.5988(19)	9.6460(19)
b/Å	17.589(3)	12.191(2)
c/Å	20.473(6)	13.953(3)
α/°	90	91.85(3)
β/°	113.19(3)	96.25(3)
γ/°	90	107.80(3)
V/Å^3	3177.3(14)	1549.2(6)
Z	4	2
D_{calcd}/g cm^{-3}	1.608	1.649
μ/mm^{-1}	3.103	3.185
θ/°	2.45–25.01	1.47–25.03
F(000)	1556	774
Reflections collected/unique	24,989/5608	12,151/5477
R_{int}	0.1405	0.0704
GOF (F^2)	1.003	1.000
Limiting indices	$-10 \le h \le 11$, $-20 \le k \le 20$, $-24 \le l \le 17$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-16 \le l \le 16$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0765$, $wR_2 = 0.1800$	$R_1 = 0.0608$, $wR_2 = 0.1502$
R indices (all data)	$R_1 = 0.1157$, $wR_2 = 0.2064$	$R_1 = 0.0757$, $wR_2 = 0.1540$

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Bond distances			
Co(1)–N(7)	2.078(7)	Co(1)–N(10)	2.092(6)
Co(1)–N(6)	2.130(6)	Co(1)–N(3)	2.150(5)
Co(1)–N(4)	2.147(6)	Co(1)–N(2)	2.158(6)
O(1)–N(1)	1.269(7)	O(2)–N(5)	1.270(7)
Angles			
N(7)–Co(1)–N(10)	95.6(3)	N(7)–Co(1)–N(6)	90.9(2)
N(10)–Co(1)–N(6)	90.2(2)	N(7)–Co(1)–N(3)	89.8(2)
N(10)–Co(1)–N(3)	90.2(2)	N(6)–Co(1)–N(3)	179.2(2)
N(7)–Co(1)–N(4)	89.4(2)	N(10)–Co(1)–N(4)	165.4(2)
N(6)–Co(1)–N(4)	76.0(2)	N(3)–Co(1)–N(4)	103.5(2)
N(7)–Co(1)–N(2)	164.1(2)	N(10)–Co(1)–N(2)	90.1(2)
N(6)–Co(1)–N(2)	103.9(2)	N(3)–Co(1)–N(2)	75.4(2)
C(1)–N(3)–Co(1)	123.3(5)	C(5)–N(3)–Co(1)	116.6(4)

for Co(1)–N(1) and Co(2)–N(7), respectively, which are longer than the axial Co–N(azide) bond distances [2.090(5) and 2.101(5) Å], suggesting the coordination geometry is a compressed distorted octahedron. The coordinated N–O bond lengths of the nitronyl nitroxide radicals are 1.300(6) and 1.318(6) Å, indicating the existence of the nitronyl nitroxide radical. The dihedral angles defined by the pyridine ring and the O–N–C–N–O plane are 20.298(2)° for Co(1) and 18.568(3)° for Co(2). The packing arrangement of complex **2** is shown in Fig. S2. The shortest intermolecular contact between nitroxide groups of O(2)···O(4) is 4.184(6) Å, implying the complex units are well separated.

Magnetic properties

The temperature-dependent magnetic susceptibilities of the two complexes were measured in the range of 2–300 K in an external magnetic field of 1 kOe, and the plots of $\chi_M T$ versus T of the two compounds **1** and **2** are provided in Fig. 3, respectively. For compound **1,** the $\chi_M T$ values gradually increased as the temperature was lowered from 300 K, reaching a maximum value of 3.83 cm^3 K mol^{-1} at 64 K, and then decreased sharply to 1.19 cm^3 K mol^{-1} at 2.0 K. The $\chi_M T$ value (3.66 cm^3 K mol^{-1}) at 300 K is larger than the expected value (2.62 cm^3 K mol^{-1} with $g = 2$) for one uncoupled system for one cobalt(II) atom ($S = 3/2$) and two radicals ($S = 1/2$), which is due to the orbital contribution of

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

Bond distances			
Co(1)–O(1)	2.115(4)	Co(1)–N(4)	2.090(5)
Co(1)–N(1)	2.144(5)	Co(2)–N(10)	2.101(5)
Co(2)–N(7)	2.127(5)	Co(2)–O(3)	2.107(4)
N(3)–O(2)	1.269(6)	N(2)–O(1)	1.300(6)
N(9)–O(4)	1.295(6)	N(8)–O(3)	1.318(6)
Angles			
O(3)–Co(2)–N(7)#2	82.75(17)	O(3)–Co(2)–N(7)	97.25(17)
N(10)–Co(2)–N(7)	94.1(2)	N(10)–Co(2)–N(7)#2	85.9(2)
Co(1)–O(1)–N(2)	117.6(3)	N(10)#2–Co(2)–O(3)	91.97(18)
O(1)–Co(1)–N(1)#1	83.71(17)	N(10)–Co(2)–O(3)	88.03(18)
O(1)–Co(1)–N(1)	96.29(17)	N(4)–Co(1)–O(1)	86.44(19)
N(4)–Co(1)–O(1)#1	93.56(19)	N(4)–Co(1)–N(1)#1	86.0(2)
Co(2)–O(3)–N(8)	116.3(3)	N(4)–Co(1)–N(1)	94.0(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+1, -z+1$ #2 $-x, -y, -z$

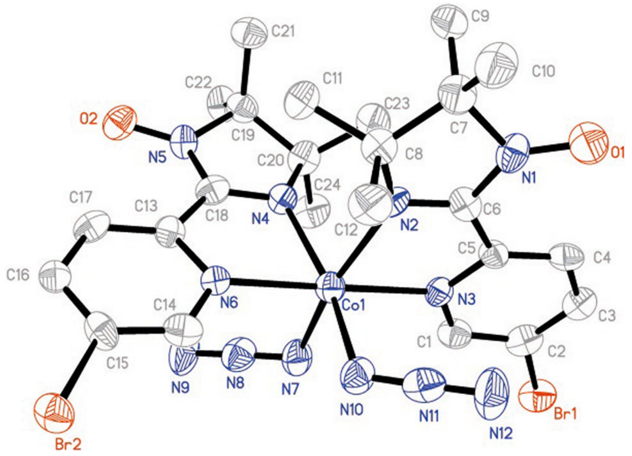

Fig. 1 An ORTEP drawing of complex **1** with atom labeling and 50 % thermal ellipsoids. Hydrogen atoms and methanol solvent molecule are omitted for clarity

the cobalt(II) atom. The gradual increase in the $\chi_M T$ value in the high-temperature region suggests the occurrence of an intramolecular ferromagnetic interaction between the cobalt(II) atom and the coordinated radical. The $\chi_M T$ value decreases rapidly in the low-temperature region, which can be attributed to the spin–orbit coupling of the cobalt(II) atom and/or the intermolecular antiferromagnetic interactions in the complex. It would be difficult to incorporate the spin–orbit coupling and magnetic interactions into a model to fit the magnetic data over the whole temperature range. However, the higher temperature magnetic data may be approximately interpreted by the isotropic spin Hamiltonian. For the present magnetic unit, the spin Hamiltonian can be expressed as $\hat{H} = -2J\sum(\hat{S}_{\mathrm{Co}}\hat{S}_R + \hat{S}_{\mathrm{Co}}\hat{S}_R)$, where J represents the magnetic interaction between cobalt(II) atom and the coordinated radical ligand. The expression of the magnetic susceptibility is given below [30]:

$$\chi_M = \frac{N\beta^2}{4kT}\,\frac{35{g_1}^2 + 10{g_2}^2\exp(-5x) + {g_3}^2\exp(-8x) + 10{g_4}^2\exp(-3x)}{3 + 2\exp(-5x) + \exp(-8x) + 2\exp(-3x)}$$

with $x = J/kT$, $g_1 = (3g_{\mathrm{Co}} + 2g_R)/5$, $g_2 = (11g_{\mathrm{Co}} + 4g_R)/15$, $g_3 = (5g_{\mathrm{Co}} - 2g_R)/3$ and $g_4 = g_{\mathrm{Co.}}$

The best fit for magnetic data (70–300 K) gave $g_{\mathrm{Co}} = 2.37$, $g_{\mathrm{rad}} = 2.00$, $J = 6.46\ \mathrm{cm}^{-1}$, $R = 1.20 \times 10^{-3}$ (the residual value R is defined as $\sum[(\chi_M)_{\mathrm{obs}} - (\chi_M)_{\mathrm{calc}}]^2/\sum[(\chi_M)_{\mathrm{obs}}]^2$). The fitting results indicate that the magnetic coupling between the cobalt(II) atom and the coordinated imino nitroxide radical is weakly ferromagnetic. Furthermore, the field dependence of magnetization has been determined at 2 K in the 0–70 kOe field range (Fig. 4). Upon increasing in the applied field, M increases up to 3.30 Nβ at 70 kOe, which does not reach the saturation, indicating the presence of magnetic anisotropy in the system [31, 32].

For compound **2,** the $\chi_M T$ value at room temperature is 2.34 $\mathrm{cm}^3\ \mathrm{K\ mol}^{-1}$, which is slightly lower than the spin-only value of 2.62 $\mathrm{cm}^3\ \mathrm{K\ mol}^{-1}$ for an uncoupled system for one cobalt(II) atom ($S = 3/2$) and two radicals ($S = 1/2$). Upon cooling, the $\chi_M T$ value decreases more and more rapidly to reach 0.64 $\mathrm{cm}^3\ \mathrm{K\ mol}^{-1}$ at 2.0 K. These indicate the presence of strong antiferromagnetic interactions in 2. Using the same magnetic model as in complex **1**, the least squares analysis of magnetic data (60–300 K) led to $g_{\mathrm{Co}} = 2.39$, $g_{\mathrm{rad}} = 2.00$, $J = -64.20\ \mathrm{cm}^{-1}$, $R = 3.68 \times 10^{-3}$. This shows that the cobalt(II)–nitronyl nitroxide interaction is a strong antiferromagnetic interaction. The

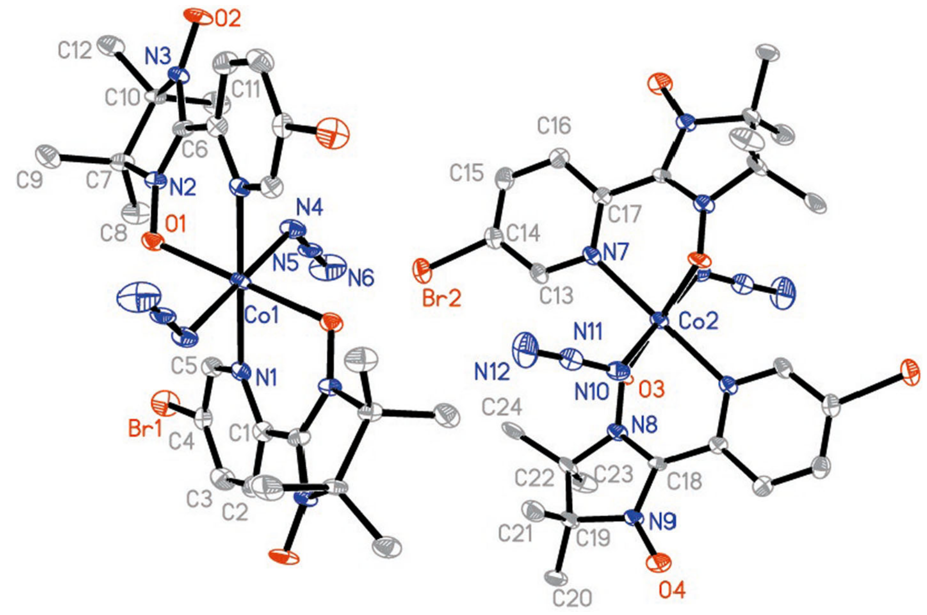

Fig. 2 An ORTEP drawing of complex **2** with atom labeling and 50 % thermal ellipsoids. Hydrogen atoms are not shown for the sake of clarity

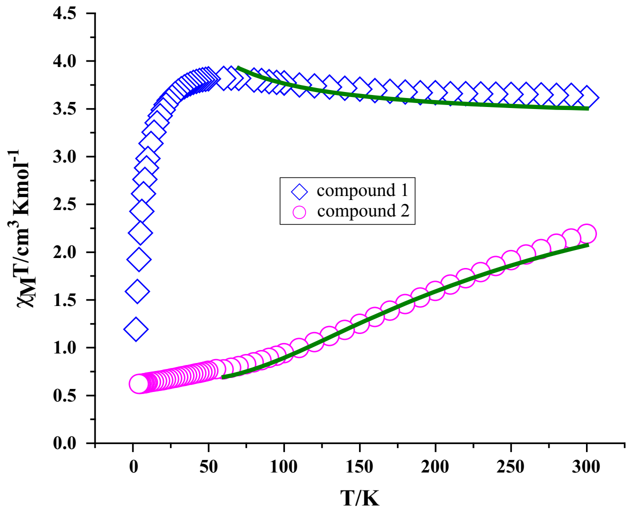

Fig. 3 Plots of $\chi_M T$ versus T for complexes **1** (*blue*) and **2** (*magenta*). The *solid lines* correspond to the best theoretical fit. (Color figure online)

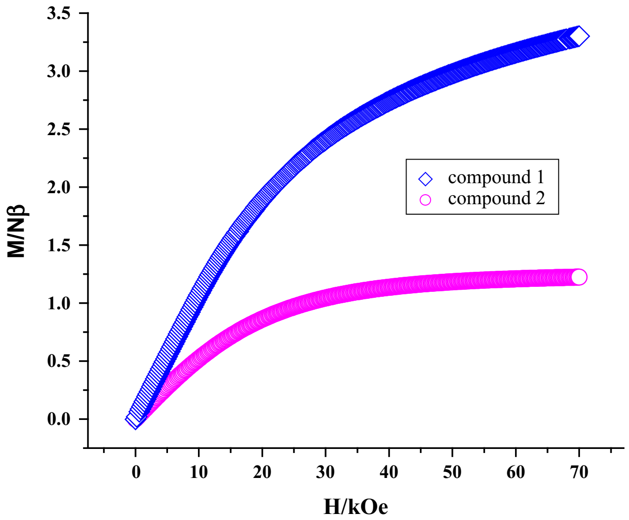

Fig. 4 Field dependence (H/kOe) of magnetization (M/μ_B) of complexes **1** (*blue*) and **2** (*magenta*) at 2.0 K. (Color figure online)

field-dependent magnetization had been determined at 2 K in the 0–70 kOe field range (Fig. 4), upon increasing in the applied field, M increases up to 1.22 Nβ at 70 kOe for complex **2**, suggesting the presence of a strong antiferromagnetic interaction in the complex.

As seen, the cobalt(II) atom ferromagnetically interacts with the imino nitroxide, whereas the antiferromagnetic interaction is observed between the cobalt(II) and nitronyl nitroxide. Because the imino and nitronyl nitroxides have similar related electronic structures, the reversal of the sign of the interaction should originate from the different coordination geometries around the cobalt(II) atoms. For the present two compounds, the magnetic orbitals of both imino and nitronyl nitroxide radicals are π^* orbitals. The cobalt(II) atom has two magnetic orbitals ($d_{x^2-y^2}$ and d_{z^2}) with σ symmetry and one magnetic orbital (either of d_{xy}, d_{xz}, d_{yz}) with π symmetry. Thus, the imino radical ligand and metal magnetic orbitals are orthogonal, which results in ferromagnetic coupling as observed in complex **1** [33, 34]. The observed weak ferromagnetic coupling can be attributed to the overlap of the π^* orbital and another magnetic orbital of cobalt(II) (either of d_{xy}, d_{xz}, d_{yz}) leading to antiferromagnetic coupling. This antiferromagnetic contribution will lead to the reduction in the ferromagnetic interaction. For complex **2**, two nitronyl nitroxide radicals are coordinated to the cobalt(II) atoms in equatorial positions. The Co–O–N angle is about 117°, which favors the overlap of the radical magnetic orbital (π^*) and the cobalt(II) magnetic orbitals ($d_{x^2-y^2}$ and d_{z^2}), resulting in strong antiferromagnetic interaction [35].

Conclusion

Two rare cobalt(II)-nitroxide complexes have been obtained by using imino and nitronyl nitroxide radicals. The radical ligands are bonded to the metal ion in a chelating fashion. Magnetic studies show that the cobalt(II) interacts ferromagnetically with the imino nitroxide. In contrast, antiferromagnetic coupling is observed between the cobalt(II) and nitronyl nitroxide. This can be ascribed to the different structural features for two complexes.

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