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Synthesis, Crystal Structures, and Magnetic Properties of Cobalt(II)-Hexafluoro-Acetylacetonate Complexes with Two New Triazole-Substituted Nitronyl and Imino Nitroxide[1]

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Abstract—Two new chelating radical ligands, NITphtrz (4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3-triazole-4-yl)imidazoline-1-oxyl-3-oxide) and IMphtrz (4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3-triazole-4-yl)imidazoline-1-oxyl), and their cobalt(II) complexes [Co(Hfac)$_2$(NITphtrz)] (**I**) and [Co(Hfac)$_2$(IMphtrz)] (**II**) (Hfac = hexafluoroacetylacetonate) have been prepared and characterized by IR, magnetic, and single-crystal X-ray analysis. The magnetic behaviors of the lignad NITphtrz and complex **I** have been discussed.

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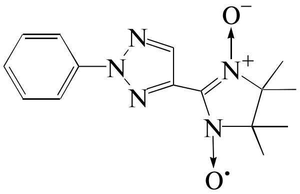
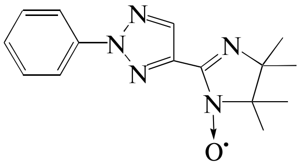
INTRODUCTION

Metal-radical hybrid solids have been well investigated toward molecule-based magnets, where a radical center is directly bonded to the metal ion, affording appreciable magnetic exchange coupling [1]. In the past decades, there has been a number of investigations concerning paramagnetic metal complexes with nitronyl nitroxide (NITR: 4,4,5,5-tetramethyl-2-R-imidazolin-1-oxyl-3-oxide) and imino nitroxide (IMR: 4,4,5,5-tetramethyl-2-R-imidazolin-1-oxyl) radicals in order to reveal the magnetic interactions between paramagnetic centres for the design of molecular-based ferromagnets [2–5]. As anticipated the feature of R-group linked to the nitronyl nitroxide not only influences the intermolecular spin-spin interactions, but also affects the coordination mode of the nitronyl nitroxides with metal ions. This is particularly true if there are potential coordination sites available in the R-group [6, 7]. Therefore, modification of the R-group would tune the coordination mode between the nitroxides and metal ions and thus alter the magnetic interaction between the nitroxides and metal ions.

In order to extend our knowledge of the extremely rich chemistry of such systems, we are devoted to the exploration of new building blocks for molecule-based magnetic materials. In this paper, we will report two new nitroxide ligands NITphtrz (L^1) and IMphtrz (L^2):



(L^1)



(L^2)

Due to the presence of the N-triazole moieties, L^1 and L^2 can coordinate to metal ions as chelate ligands. Reactions of L^1 and L^2 with Co(Hfac)$_2$ (Hfac = hexafluoroacetylacetonate) afforded two hetero-spin complexes. The crystal structures and magnetic characterizations of the related compounds will be described and discussed.

EXPERIMENTAL

Materials and equipment. 2-Phenyl-1,2,3-triazole-4-carboxaldehyde is prepared according to literature method [8]. Co(Hfac)$_2$ · 2H$_2$O (Hfac = hexafluoroacetylacetone) as prepared as the previous reported [9]. All the other chemicals purchased were of reagent grade and used without purification. Elemental analyses (C, H, and N) were carried out with a PerkinElmer 240C elemental analyzer. IR spectra were recorded in the region of 4000–400 cm^{-1} on an Avatar-360 spectrophotometer using KBr pellets. Variable-temperature magnetic susceptibilities were measured with a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

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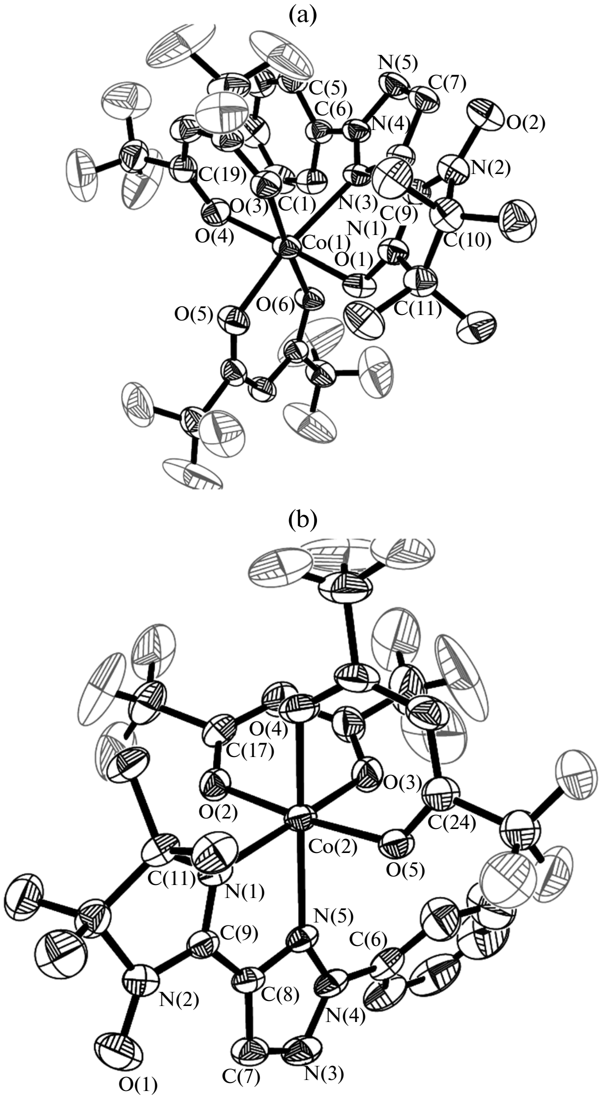

Fig. 1. ORTEP drawing of complexes **I** (a) and **II** (b) showing the atom labelling scheme with 30% thermal ellipsoids and H atoms omitted for clarity.

Ligands L^1 and L^2 were prepared as previously described in [10] and [11], respectively. The yields were 76 (L^1), 52% (L^2).

For $C_{15}H_{18}N_5O_2$ (L^1)
anal. calcd., %: C, 60.00; H, 6.00; N, 23.33.
Found, %: C, 60.31; H, 6.12; N, 23.18.

Important IR absorptions (KBr; ν, cm^{-1}): 1368 s ν(NO).

For $C_{15}H_{18}N_5O$ (L^2)
anal. calcd., %: C, 63.38; H; 6.34; N, 24.65.
Found, %: C, 63.51; H, 6.21; N, 24.50.

Important IR absorptions (KBr; ν, cm^{-1}): 1360 s ν(NO).

Synthesis of $[Co(Hfac)_2(L^1)]$ (I). $Co(Hfac)_2 \cdot 2H_2O$ (0.1 mmol) was dissolved in boiling *n*-heptane (30 mL). The solution was left to boil for 30 min and then cooled down to 60°C, whereupon 0.1 mmol of L^1 was added under stirring followed by the addition of 5 mL CH_2Cl_2. The mixture was stirred for 40 min, then filtered. The dack brown filtrate was set aside at a refrigerator for two weeks. Crystals of complex **I** suitable for X-ray crystallographic analysis were obtained and filtered. The yield was 58%.

For $C_{25}H_{22}N_5O_6F_{12}Co$ (**I**)
anal. calcd., %: C, 38.73; H, 2.86; N, 9.03.
Found, %: C, 38.68; H, 2.83; N, 8.95.

Important IR absorptions (KBr; ν, cm^{-1}): 1370 ν(NO).

Synthesis of complex $[Co(Hfac)_2(L^2)]$ (II) was carried out using the same procedure as that of complex **I**, which started from L^2 and $Co(Hfac)_2 \cdot 2H_2O$. The yield was 36%.

For $C_{25}H_{22}N_5O_5F_{12}Co$ (**II**)
anal. calcd., %: C, 39.55; H, 2.92; N, 9.22.
Found, %: C, 39.42; H, 2.83; N, 9.13.

Important IR absorptions (KBr; ν, cm^{-1}): 1345 ν(NO).

X-ray structure determination. Structure measurements of complexes **I** and **II** were performed on a Bruker Smart 1000 CCD X-ray single-crystal diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at 273 K. The intensity data were obtained in a range of $2.10° < \theta < 25.10°$ (for complex **I**) and $1.90° < \theta < 28.37°$ (for complex **II**) by using a scan technique. The corrections for the *Lp* factor and an empirical absorption correction were applied. The structure was resolved by a direct method using SHELXS-97 [12, 13]. All the non-hydrogen atoms were determined with successive difference Fourier syntheses and refined by full-matrix least squares on F^2 (SHELXL-97). All hydrogen atoms were located at the calculated positions. Crystal data and structure refinement details are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 895285 (**I**), 895284 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

ORTEP drawings of complex **I** and complex **II** are depicted in Fig. 1. In complex **I**, the Co atom is six-co-

Table 1. Crystal data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	775.11	759.106
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions:		
a, Å	10.208(2)	10.107(2)
b, Å	11.67892)	10.983(2)
c, Å	14.680(3)	15.168(3)
α, deg	79.02(3)	86.19(3)
β, deg	76.53(3)	76.17(3)
γ, deg	67.98(3)	77.53(3)
Volume, Å^3; Z	1567.4(5); 2	1596.2(5); 1
$F(000)$	1160	748
θ Range for data collection, deg	1.89–28.37	1.90–28.37
Limiting indices	$-13 \le h \le 13$, $-15 \le k \le 15$, $-19 \le l \le 19$	$-13 \le h \le 12$, $-14 \le k \le 14$, $-20 \le l \le 17$
Reflections collected	37545	28519
Independent reflections	7808	7899 ($R_{\text{int}} = 0.0223$)
Numder of refinement	442	433
Completeness, %	99.3	98.7
Goodness-of-fit on F^2	1.097	1.515
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0622$, $wR_2 = 0.1864$	$R_1 = 0.0621$, $wR_2 = 0.1973$
R indices (all data)	$R_1 = 0.0782$, $wR_2 = 0.2035$	$R_1 = 0.0781$, $wR_2 = 0.2100$
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	0.907 and –0.524	0.752 and –0.461

ordinated in a distorted octahedron NO_5 environment. The equatorial plane is formed by N(3) from L^1, O(3), O(5), and O(6) from two Hfac ligands. The Co–O bond lengths in the basal plane are 2.031(2), 2.057(2), 2.054(2) Å, respectively. The Co–N(3) distance is 2.251(2) Å. The axial positions are occupied by two oxygen atoms from Hfac and L^1, respectively. The Co–O bond lengths are 2.025(3) and 2.030(3) Å for $\mathrm{Co{-}O_{(NITphtrz)}}$ and $\mathrm{Co{-}O_{(Hfac)}}$, respectively. The O(4)CoO(1) angle is 177.82° and the N(3)CoO(1) angle is 91.03°. The dihedral angle between the triazole rings for L^1 and the O–N–C–N moieties (O(1), N(1), C(9), and N(2)) is 11.9°. The fragment O(1)–N(1)–C(9)–N(2)–O(2) forms a dihedral angle of 54.5° with the equatorial plane.

Table 2. Selected bond distances (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Co(1)–O(1)	2.025(3)	Co(1)–O(6)	2.031(2)
Co(1)–O(4)	2.030(3)	Co(1)–O(5)	2.054(2)
Co(1)–O(3)	2.057(2)	Co(1)–N(3)	2.251(2)
N(1)–O(1)	1.289(3)	N(2)–O(2)	1.265(4)
N(4)–N(3)	1.332(3)	N(3)–C(8)	1.346(4)
N(4)–N(5)	1.324(4)	N(4)–C(6)	1.423(4)
N(1)–C(9)	1.338(4)	N(2)–C(9)	1.349(4)
	II		
Co(2)–O(5)	2.028(2)	Co(2)–O(3)	2.045(2)
Co(2)–O(2)	2.044(2)	Co(2)–O(4)	2.069(2)
Co(2)–N(1)	2.088(2)	Co(2)–N(5)	2.287(2)
N(2)–O(1)	1.275(3)	N(3)–N(4)	1.342(3)
N(4)–N(5)	1.327(3)	N(5)–C(8)	1.341(4)
N(1)–C(9)	1.295(3)	N(2)–C(9)	1.366(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
	I		
O(1)Co(1)O(6)	89.30(10)	O(1)Co(1)O(4)	177.82(10)
O(6)Co(1)O(4)	91.26(10)	O(1)Co(1)O(5)	86.09(11)
O(6)Co(1)O(5)	88.57(9)	O(4)Co(1)O(5)	91.82(11)
O(1)Co(1)O(3)	91.03(10)	O(6)Co(1)O(3)	175.71(8)
O(4)Co(1)O(3)	88.57(10)	O(5)Co(1)O(3)	95.72(10)
O(6)Co(1)N(3)	82.19(10)	O(6)Co(1)N(3)	94.20(9)
O(4)Co(1)N(3)	99.86(10)	O(5)Co(1)N(3)	167.92(10)
O(3)Co(1)N(3)	81.62(9)	O(2)N(2)C(9)	125.3(3)
O(1)N(1)C(9)	125.8(3)		
	II		
O(5)Co(2)O(3)	89.69(9)	O(5)Co(2)O(2)	174.56(7)
O(3)Co(2)O(2)	85.86(9)	O(5)Co(2)O(4)	88.18(9)
O(3)Co(2)O(4)	87.28(11)	O(2)Co(2)O(4)	88.49(9)
O(5)Co(2)N(1)	98.16(9)	O(3)Co(2)N(1)	170.37(9)
O(2)Co(2)N(1)	86.58(9)	O(4)Co(2)N(1)	98.48(10)
O(5)Co(2)N(5)	87.69(8)	O(3)Co(2)N(5)	97.80(10)
O(2)Co(2)N(5)	95.99(8)	O(4)Co(2)N(5)	173.43(9)
N(1)Co(2)N(5)	77.07(9)		

In complex **II**, the Co^{2+} ion is also six-coordinated in a distorted octahedron N_2O_4 environment. The equatorial plane is formed by N(1) and N(5) from L^2, O(3) and O(4) from two Hfac molecules. The Co–O bond lengths in the basal plane are 2.045(2) and 2.069(2) Å, respectively. The Co–N distances are 2.287(2) and 2.088(2) Å, respectively. The axial positions are occupied by two oxygen atoms from two Hfac ligands. The Co–O bond lengths are 2.044(2) and 2.028(2) Å. The O(2)CoO(5) angle is 174.56° and the N(1)CoN(5) angle is 77.07°. The dihedral angle between the triazole rings for L^2 and the O–N–C–N moieties (O(1), N(2), C(9), and N(1)) is 1.4°. The fragment O(1)–N(2)–C(9)–N(1) forms a dihedral angle of 7.5° with the equatorial plane.

No short inter-atomic contacts exist in the crystal lattices of complexes **I** and **II**.

The temperature dependence of the magnetic susceptibility for radical ligand L^1 was investigated in the temperature range 1.8–300 K under a magnetic field of 2000 G. Figure 2 shows the variation of $\chi_M T$ and $1/\chi_M$ with temperature for ligand L^1, where χ_M is the molar magnetic susceptibility and T is the absolute temperature. The value of $\chi_M T$ at 300 K is 0.376 emu K mol^{-1}, which is close to that expected for $S = 1/2$ system (0.375 emu K mol^{-1}). As shown in Fig. 3, $\chi_M T$ kept unchanged from 300 to 50 K. Below 50 K, it decreased sharply, indicating the intermolecular antiferromagnetic interaction of nitronyl nitroxides. The temperature dependence of $1/\chi_M$ of L^1 follows the Curie–Weiss law in the whole temperature range between 1.8 and 300 K. The values obtained for Weiss constant (θ) in this manner is –2.83 K ($C = 0.381$ emu K mol^{-1}). The negative value θ, which reflects the intermolecular spin interaction, indicates the weak anti-ferromagnetic interaction in L^1.

For complex **I**, the variation curve of χ_M and $\chi_M T$ vs. T is represented in Fig. 3. The value of $\chi_M T$ at

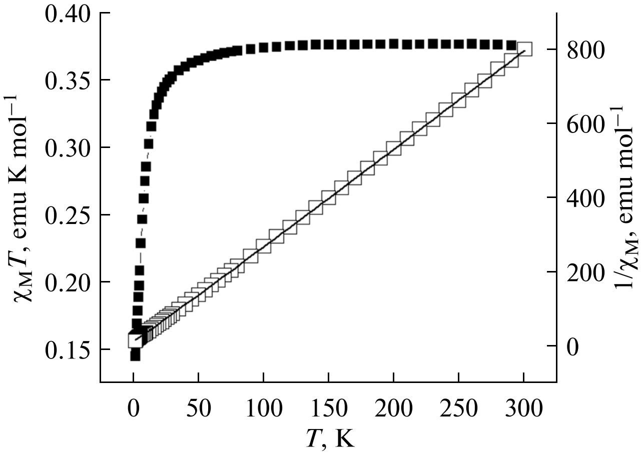

Fig. 2. Plot of L^1 in the form of $1/\chi_M$ (○) and $\chi_M T$ (□) vs. T.

300 K is 2.24 emu K mol^{-1}, close to the spin-only value (2.25 emu K mol^{-1}) expected for the uncorrelated spin system with Co^{2+} ion ($S = 3/2$) and the nitronyl nitroxide unit ($S = 1/2$). The $\chi_M T$ values decreased steadily with decreasing temperature and dropped rapidly below 50 K. These results show there exists strong antiferromagnetic coupling between the Co^{2+} ion and the directly coordinated nitroxide group. The strict analysis of the magnetic data of Co(II) complexes needs to consider the effects of spin-orbit coupling and zero-field splitting. A more elaborate model, taking into account all these factors, may be constructed but is then over-parameterized. The interaction between Co^{2+} ions ($S = 3/2$) and nitronyl nitroxide can be analyzed with Eq. (1) derived from the Hamiltonian: $\hat{H} = -2J\hat{S}_{\mathrm{Co}}\hat{S}_R - DS_Z^2$ for the two spin units with $S1 = 3/2$ and $S2 = 1/2$, where J refers to the magnetic exchange between Co^{2+} ions ($S = 3/2$) and the nitronyl nitroxides, and D is the zero-field splitting parameter for Co^{2+} ions [14].

$$\chi_{\mathrm{M}} = \frac{2Ng^2\beta^2}{kT} \times \frac{\exp A_1 + 4\exp A_3 + \exp A_5}{2\exp A_1 + \exp A_2 + 2\exp A_3 + \exp A_4 + 2\exp A_5}, \tag{1}$$

$$A_1 = [4J + 5D/4 - (4J^2 - 2DJ + D^2)^{1/2}]/kT,$$

$$A_2 = (2J + D/4)/kT,$$

$$A_3 = (6J + 9D/4)/kT,$$

$$A_4 = (6J + D/4)/kT,$$

$$A_5 = [4J + 5D/4 + (4J^2 - 2DJ + D^2)^{1/2}]/kT.$$

The best-fit parameters are $J = -158.18$ cm^{-1}, $D = -3.56$ cm^{-1}, $g = 2.84$ with $R = 1.74 \times 10^{-4}$, where R is defined as $R = \Sigma[(\chi_M T)_{\mathrm{calc}} - \chi_M T)_{\mathrm{expt}}]^2/\Sigma[(\chi_M T)_{\mathrm{expt}}]^2$. The result ($J = -158.18$ cm^{-1}) indicates that a strong aniferromagnetic interaction exists between Co(II) and NITphtrz via Co(II)···O coordination bonding. The magnitudes of the exchange integrals of Co(II)-radical complexes are basically dependent on the extent of overlap of the SOMO π^* orbital of the radical with the magnetic orbital of metal ions [15]. The temperature dependence of $1/\chi_M$ of complex **I** follows the Curie–Weiss law in the range 1.8–300 K. The values obtained for θ in this manner is –24.94 K ($C = 2.359$ emu K mol^{-1}). The negative Weiss constant (θ) indicates the strong anti-ferromagnetic interaction between the Co^{2+} ion and the directly coordinated nitroxide.

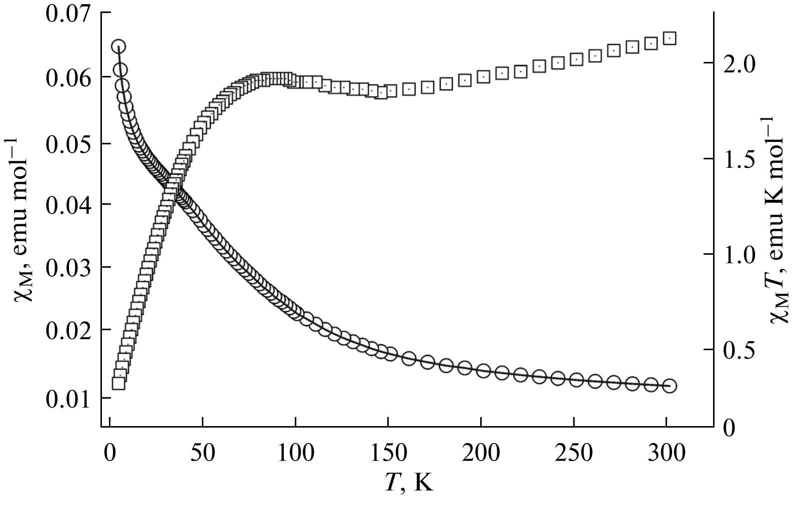

Fig. 3. Plot of temperature dependence of χ_M (○) and $\chi_M T$ (□) for complex **I**.

Due to its low-yield and difficult to repeat, the temperature dependence of the magnetic susceptibility for complex **II** has not been investigated.

ACKNOWLEDGMENTS

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