Unique Magnetic Behavior in a One-Dimensional Coordination Polymer $[Co(tmpyim)_2(tp)]$

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A one dimensional cobalt(II)–radical complex $[Co(tmpyim)_2(tp)]$ [tmpyim = 4,4,5,5-tetramethyl-2-(3′-pyridyl)-imidazoline-1-oxyl 3-oxide and tp = terephthalate dianion] has been synthesized and characterized by X-ray crystallography. The crystal structure consists of infinite chains of $Co(tmpyim)_2$ units cross-linked by terephthalate ligands. The magnetic behavior of the complex is unique and is discussed in connection with the crystal structure.

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In the field of molecular-based magnetic materials, it is fundamentally important to understand the interactions between organic or inorganic spin-carriers and the structure-function relationships of the magnetic systems.[1−2] The so-called "crystal engineering" approach has been used extensively to control material structure and dimensionality in which extended inorganic structures with organic bridges are synthesized to give coordination polymers or networks.[3−4]

Metal complexes based on pyridyl-substituted nitronyl nitroxides have attracted considerable attention in recent years due to the ability of these radicals to coordinate metal ions and act as magnetic couplers, giving rise to new functional materials with a variety of structural topologies.[5−12] The terephthalate ligand is a versatile ligand with good binding ability, as exemplified by the formation of polymeric structures.[13−15] In this paper we report the crystal structure and magnetic properties of a one-dimensional Co^{II}−radical complex with a terephthalate bridge, $[Co(tmpyim)_2(tp)]$ (**1**) [tmpyim = 4,4,5,5-tetramethyl-2-(3′-pyridyl)imidazoline-1-oxyl 3-oxide and tp = terephthalate dianion).

The structure of **1** (Figure 1) shows that each terephthalate dianion binds to two Co^{II} ions in a bis-bidentate mode, leading to a 1-D chain structure. Two tmpyim radical ligands coordinate to the Co^{II} ion through the nitrogen atoms of their pyridyl rings. The Co^{II} ion has a distorted octahedral coordination environment, which is centrosymmetric. Four carboxylato oxygen atoms from two tp ligands form the equatorial plane. The Co−O bond lengths in the basal plane are 2.117(2) and 2.122(2) Å for Co(1)−O(3) and Co(1)−O(4), respectively. The axial positions, occupied by nitrogen atoms from the tmpyim ligands, have a Co−N bond length of 2.144(3) Å. The dihedral angle between the pyridyl ring and the nitroxide group [O(1)−N(1)−C(3)−N(2)−O(2)] is 31.6°. The shortest contact between nitroxide groups is 3.860 Å. However, it should be noted that the closest contact is observed between the oxygen atom [O(1)] of the nitroxide group and the carbon atom [C′(5)] belonging to the adjacent chain [O(1)−C′(5) = 3.156 Å; Figure 2]. The intrachain Co^{II}−Co^{II} distance is 10.633 Å and the shortest interchain Co^{II}−Co^{II} separation is 7.119 Å, which corresponds to the unit cell length (*b*).

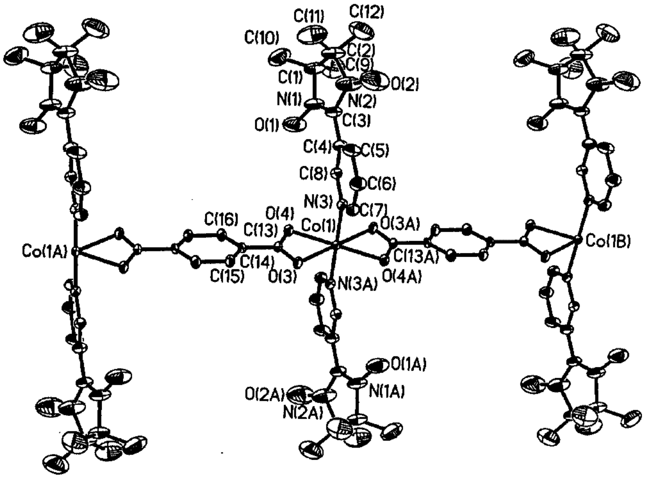

Figure 1. View of the molecular structure of $[Co(tmpyim)_2(tp)]$ with atom labeling and 30% thermal ellipsoids

The magnetic susceptibility of complex **1** was measured in the temperature range 2−300 K, with an applied field of

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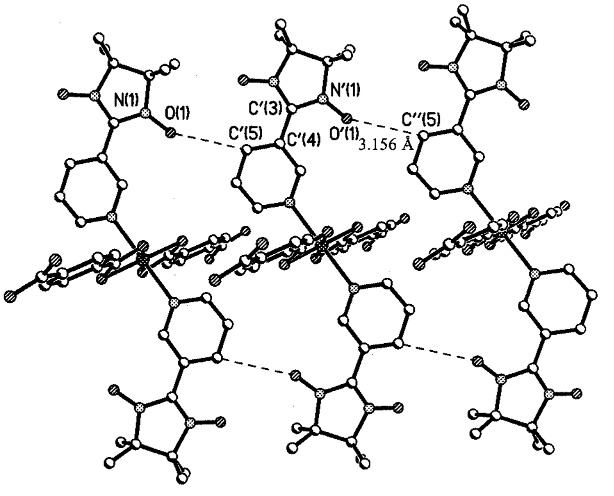

Figure 2. The closest contact in [Co(tmpyim)$_2$(tp)] showing exchange coupling through NO···C interactions

1000 G. The plot of effective magnetic moment μ_{eff} versus T is shown in Figure 3.

At room temperature, μ_{eff} is equal to 6.13 μ_B, which is much higher than that expected for noninteracting S_{Co} = 3/2 and S_{rad} =1/2 spins, indicating that an important orbital contribution is involved. The plot of μ_{eff} versus T reveals four domains: (i) from 300 K to 55.1 K, μ_{eff} increases continuously from 6.13 μ_B to a value of 6.46 μ_B; (ii) between 55.1 K and 25 K μ_{eff} decreases gradually with decreasing temperature; (iii) from 25 K to 2 K, μ_{eff} increases rapidly to reach a maximum of 6.84 μ_B at 3 K; (iv) below 2 K, μ_{eff} decreases again on cooling. This magnetic behavior is unique. In complex **1**, there are four kinds of magnetic interactions, namely: (i) Co^{II} interacting with the coordinated tmpyim radical, (ii) a Co^{II}−Co^{II} interaction *via* the terephthalate bridge, (iii) a magnetic coupling between neighboring tmpyim radicals through the NO···C pathway (3.156 Å), and (iv) a through-space interaction between neighboring NO groups of tmpyim radicals (3.860 Å). The magnetic interaction between the cobalt(II) ions should be very weakly antiferromagnetic and can be neglected since the tp bridge is long.[16] The extent of magnetic coupling of the two adjacent NO groups depends on their separation and the relative orientation of the π* orbitals.[17] In complex **1**, the shortest O−O separation between the nitroxide groups is rather large (3.860 Å) and the planes of the π systems of the nitroxide radicals form an angle of 26.8° with the plane defined by the two adjacent NO groups. These geometrical parameters are not disposed favorably for strong overlap and lead to weakly antiferromagnetic interactions.[17−19] The last kind of magnetic coupling is also weak and should be dominant only at low temperatures. Therefore the magnetic behavior of the complex between 300 K and 55.1 K must correspond to that of Co^{II} interacting with the coordinated tmpyim radical, which implies that the magnetic interaction between cobalt(II) and tmpyim radical is ferromagnetic. The decrease of μ_{eff} between 55.1 K an 25 K is attributed to the spin-orbit coupling of the cobalt(II) ion. Regarding the interaction between radicals, the crystal structure shows that the closest contact involves the oxygen atom [O(1)] of the uncoordinated NO group, which carries a large, positive spin density, and the carbon atom [C′(5)] of the adjacent tmpyim radical, which carries a small, negative spin density [O(1)···C′(5) = 3.156 Å]. These two atoms carrying opposite signs of the spin density alternate, leading to ↑N(1)−O(1)↑···↓C′(5)−↑C′(4)−↓C′(3)−↑N′(1)−↑O′(1)···↓C′′(5), which matches McConnell's criteria.[20] Thus, the exchange coupling between neighboring tmpyim radicals through an NO···C pathway should be ferromagnetic and so results in the increase in μ_{eff} between 25 K and 2 K. The μ_{eff} value decreases below 2 K due to the weak antiferromagnetic interaction between neighboring NO groups of the tmpyim

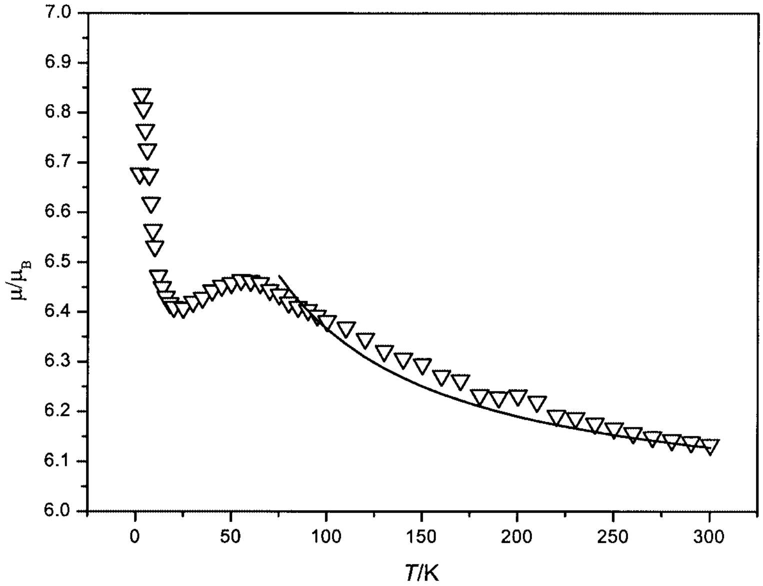

Figure 3. A plot of μ_{eff} (▽) versus T for [Co(tmpyim)$_2$(tp)]

radicals, spin-orbital coupling and zero-field splitting. It would be very difficult to incorporate all of these into a model to fit the magnetic data at the lower temperature. However, according to Sinn,[21] the higher temperature magnetic data above 70 K may be approximately interpreted by the isotropic spin Hamiltonian. For the Co(tmpyim)$_2$ unit, the spin Hamiltonian can be expressed as

$$\hat{H} = -2J\sum(\hat{S}_{Co}\hat{S}_R + \hat{S}_{Co}\hat{S}_R)$$

where J represents the magnetic interaction between the Co^{II} ion and the coordinated tmpyim radical. The expression of the magnetic susceptibility is given below:

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

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

The best fit (line in Figure 3) for the magnetic data (70−300 K) leads to $g_{Co} = 2.86$, $g_{rad} = 2.00$, $J = 7.62$ cm^{-1}, $R = 7.67 \times 10^{-5}$ (the residual value R is defined as $[(\chi_M)_{obsd} - (\chi_M)_{calcd.}]^2/[(\chi_M)_{obsd.}]^2$). The fitting results show that the exchange coupling between the Co^{II} ion and the tmpyim radical is weakly ferromagnetic. In complex **1**, the magnetic orbital of the tmpyim radical is a π* orbital and the spin density can delocalized on the pyridyl ring by spin polarization. The cobalt ion has two magnetic orbitals with σ symmetry ($d_{x^2-y^2}$, d_{z^2}),which are orthogonal to the magnetic orbital of the nitroxide, leading to a ferromagnetic interaction, and one magnetic orbital with π symmetry (either of d_{xy}, d_{xz}, d_{yz}) that will able to overlap with the magnetic orbital of the nitroxide, leading to antiferromagnetic coupling. The magnetic coupling constant J can be expressed as $J = 1/3(J_{x^2-y^2,\pi^*}, + J_{z^2,\pi^*} + J_{xy,\pi^*})$.[22] The first two terms are ferromagnetic and are capable of overcoming the third antiferromagnetic term, leading to a ferromagnetic interaction being observed between the cobalt(II) ion and the tmpyim ligand. Since the nitroxide moiety has a large dihedral angle of 31.6° to the plane of the tmpyim pyridyl ring, which reduces the possibility of delocalizing the spin density of the NO group, the exchange coupling between the cobalt(II) ion and tmpyim is weak. The obtained g_{Co} value is considered to be acceptable in view of the corresponding value of other high-spin octahedral Co^{II} complexes.[23,24]

Experimental Section

General: Elemental analysis was carried out on a Perkin−Elmer elemental analyzer model 240. Infrared spectra were recorded on a Shimadzu IR spectrophotometer model 408, as KBr pellets. Variable temperature magnetic susceptibilities on polycrystalline samples in a gelatin capsule were measured on a Quantum Design MPMS-7 SQUID magnetometer.

Preparation of 1: An aqueous solution (10 mL) of dipotassium terephthalate (0.121 g, 0.5 mmol) was added to a solution of $[Co(ClO_4)_2]\cdot 6H_2O$ (0.183 g, 0.5 mmol) and tmpyim (0.234 g, 1 mmol) in H_2O (10 mL). The reaction mixture was then stirred for 1 h. Dark blue single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature after three weeks. $C_{32}H_{36}CoN_6O_8$ (691.60): calcd. C 55.57, H 5.25, N 12.15; found C 55.46, H 5.51, N 12.50. Important IR absorptions (KBr): $\tilde{\nu}$ = 1550 (s) cm^{-1}, 1400 (s) cm^{-1}, 1370 (br) cm^{-1}.

X-ray Crystallographic Analysis of 1: A dark blue crystal (0.30 × 0.25 × 0.20 mm) was selected and mounted on a glass fiber. All measurements were made on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A total of 6654 reflections including 2897 independent reflections (R_{int} = 0.0559) were collected in the 2.13 < θ < 25.03° range at room temperature. A summary of the crystallographic data is given in Table 1. The absorption correction was performed empirically.[25] The structure was solved by direct methods using the SHELXS-97 program[26] and refined with SHELXL 97[27] by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically.

CCDC-192270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for complex **1**

Empirical formula	$C_{32}H_{36}CoN_6O_8$
Molecular weight	691.60
Crystal system	Monoclinic
Space group	C_2/c
a [Å]	20.040(5)
b [Å]	7.119(2)
c [Å]	24.717(7)
β [°]	107.652(5)
V [Å^3]	3360.1(16)
Z	4
ρ (calcd.) [g/cm^3]	1.367
μ [mm^{-1}]	0.569
F(000)	1444
θ range [°]	2.13- 25.03
Limiting indices	$-23 \leq h \leq 23$, $-8 \leq k \leq 8$, $-13 \leq l \leq 29$
Reflections collected	6554
Independent reflections	2897 [R_{int} = 0.0559]
Observed reflections [$I > 2\sigma(I)$]	1802
Data/restraints/parameters	2897/ 0/214
Goodness-of-fit on F^2	0.977
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0556$, $wR_2 = 0.1300$
R indices (all data)	$R_1 = 0.1005$, $wR_2 = 0.1481$
Largest diff. peak and hole[e·Å^{-3}]	0.564 and −0.366

Acknowledgments

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