

Synthesis, Structure, and Spectral and Magnetic Properties of a Three-dimensional Cobalt(II)-Neodymium(III) Heterometal-Organic Framework Based on Oxydiacetic Acid

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A new 3d-4f heteronuclear coordination polymer containing cobalt and neodymium, $[\text{Nd}_2\text{Co}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$ (**1**) (H_2oda = oxydiacetic acid), has been synthesized and structurally characterized. In **1**, the oxydiacetate dianions (oda^{2-}) act as pentadentate ligands, and each of them chelates one Nd^{3+} ion and bridges two Co^{2+} ions. The infinite connection of metal ions and ligands results in a highly ordered 3D hexagonal channel framework. The photoluminescent, EPR and magnetic properties of the complex were also investigated.

Key words: Oxydiacetic Acid, Cobalt-Neodymium Complex, Fluorescence, EPR, Magnetic Properties

Introduction

The studies of lanthanide/transition-metal (*Ln/TM*) heterometallic frameworks with the metal centers bridged by carboxylate groups have aroused much attention recently, not only because of their relevance in solid-state technology [1, 2], but also as appropriate models to investigate the nature of magnetic exchange interactions between lanthanide and *d*-transition metal ions [3, 4]. However, the preparation of 3d-4f organic frameworks is still difficult owing to the variable and versatile coordination behavior of 4f metal ions. One of the major methodologies to prepare these heteronuclear coordination polymers is to link suitable building blocks together by a chemical bridge.

Among the potential carboxylate bridges, the oxydiacetate dianion (oda^{2-} , H_2oda = oxydiacetic acid), in possession of five potential oxygen donor atoms, has been proved to be a satisfactory bridging ligand in the assembly of Ln^{III} and Cu^{II} ions in a series of 3D *Ln*-Cu-oda complexes formulated as $\{[\text{Ln}_2\text{Cu}_3(\mu_2\text{-H}_2\text{O})(\text{oda})_6(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{La}, \text{Ce}$) [5] and $\{[\text{Ln}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{Nd}, \text{Y}, \text{Eu}, \text{Pr}, \text{Gd}, \text{Sm}, \text{La}, \text{Er}, \text{Tb}, \text{Yb}, \text{Dy}, \text{Ho}$) [6–12]. All of them are three-dimensional frameworks with hexagonal channels.

Surprisingly, other transition metal ions, such as Co^{II} , have seldom been involved in this series. There are only few *Ln*-Co-oda compounds reported so far, including the 3D compounds $\{[\text{Ln}_2\text{Co}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{Sm}, \text{La}$) with hexagonal aperture structures [7, 13], and $[\text{Sm}_2(\text{oda})_6\text{Co}_2][\text{Co}(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$ with topological NaCl nets [14]. Because the radius of the Co^{II} ion is larger than that of the Cu^{II} ion, the Ln^{III} - Co^{II} -oda complexes probably can not be easily obtained through the same synthetic strategies. In our recent studies, we have successfully prepared and published one 3D Dy^{III} - Co^{II} -oda [15] and one 2D Eu^{III} - Ni^{II} -oda-dpds complex [16]. Here, we describe the synthesis and crystal structure of $[\text{Nd}_2\text{Co}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$ (**1**). The solid-state fluorescence and EPR spectra and the magnetism of **1** are discussed in detail.

Experimental Section

All reagents were commercially available and used without further purification. Elemental analyses for C, H were carried out on an Elementar Vario EL elemental analyzer. The photoluminescence spectra were recorded on an F-4500 FL fluorescence spectrophotometer. The wavelength was scanned from 200 to 400 nm at $20 \text{ nm} \cdot \text{s}^{-1}$. The solid samples of complex **1** were locked between two glass slides and

Table 1. Crystal structure data for **1**.

Formula	C ₂₄ H ₄₂ Co ₃ Nd ₂ O ₃₉
<i>M_r</i>	1419.85
Temperature, K	296(2)
Crystal size, mm ³	0.21 × 0.11 × 0.08
Crystal system	hexagonal
Space group	<i>P</i> 6/ <i>mcc</i> (no. 192)
<i>a</i> , Å	15.0841(7)
<i>c</i> , Å	15.4276(13)
<i>V</i> , Å ³	3040.0(3)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ^{−3}	1.55
<i>μ</i> (MoK _α), cm ^{−1}	2.6
<i>F</i> (000), e	1398
<i>hkl</i> range	±18, ±18, ±18
((sin <i>θ</i>)/ <i>λ</i>) _{max} , Å ^{−1}	0.6055
Refl. measured / unique / <i>R</i> _{int}	17533 / 995 / 0.0263
Param. refined	60
<i>R</i> (<i>F</i>) / <i>wR</i> (<i>F</i> ²) ^a (all refl.)	0.0497 / 0.1476
GoF (<i>F</i> ²) ^b	1.128
Δ <i>p</i> _{fin} (max / min), e Å ^{−3}	0.894 / −0.551

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0787P)^2 + 20.1091P]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^b GoF = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1**.

Nd(1)–O(1)	2.460(4)	Nd(1)–O(3)	2.542(6)
Co(1)–O(2)	2.061(4)	Co(1)–O(4)	2.156(6)
O(1)–Nd(1)–O(3)	62.07(10)	O(1) ^a –Nd(1)–O(1)	124.1(2)
O(1)–Nd(1)–O(1) ^b	80.32(16)	O(1)–Nd(1)–O(1) ^c	85.30(2)
O(1) ^d –Nd(1)–O(3)	137.36(11)	O(3)–Nd(1)–O(3) ^e	120
O(1)–Nd(1)–O(1) ^d	149.0(2)	O(1) ^j –Nd(1)–O(3) ^e	74.50(11)
O(2)–Co(1)–O(4)	86.86(17)	O(4)–Co(1)–O(4) ^f	180
O(2) ^f –Co(1)–O(2) ^g	90.4(3)	O(2)–Co(1)–O(2) ^h	90.4(3)

Symmetry codes: ^a $-y+1, -x+1, -z+1/2$; ^b $-y+1, x-y, z$; ^c $-x+y+1, y, -z+1/2$; ^d $x, x-y, -z+1/2$; ^e $-x+y+1, -x+1, z$; ^f $-x+1, -y, -z$; ^g $x, y, -z$; ^h $-x+1, -y, z$.

then measured. The EPR spectra were measured on a Bruker EMX-6/1 EPR spectrometer. The used microwave frequency was 9.853 GHz. Temperature-dependent magnetic susceptibilities of solid samples were recorded on a MPMS Multivu magnetometer in the temperature range from 2 to 300 K with an applied field of 10 kOe ($7.96 \times 10^5 \text{ A m}^{-1}$). Pascal's constants were used to estimate the correction for the underlying diamagnetism of the sample. All data except for magnetic data were collected at r. t.

*Preparation of catena-(hexakis(μ₃-oxydiacetato)-hexa-aqua-tri-cobalt(II)-di-neodymium(III) trihydrate), [Nd₂Co₃(oda)₆(H₂O)₆·3H₂O]_n (**1**)*

An aqueous solution (15 mL) containing oxydiacetic acid (0.067 g, 0.5 mmol) and Co(CH₃COO)₂·4H₂O (1.245 g, 0.5 mmol) was added to a stirred solution of Nd₂O₃ (0.084 g, 0.25 mmol) in 4 mL of HCl–H₂O (v/v, 1 : 1). Then the pH of

Table 3. Hydrogen bond geometries (Å, deg) for **1**.

Donor–H...Acceptor	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O(4)–H(1W)...O(1) ^a	0.85	1.90	2.752(6)	179.1(3)

Symmetry code: ^a $-x+1, -y, -z$.

the obtained mixture was adjusted with KOH (0.5 mol·L^{−1}) to pH = 6.0. After that, the mixture was sealed in a 25 mL Teflon reactor and kept under autogeneous pressure at 403 K for 4 d. After cooling to r. t. at a rate of 279 K·h^{−1}, red club-shaped crystals suitable for X-ray diffraction were obtained and collected. Yield: 163 mg (46 % based on Nd). – Anal. for C₂₄H₄₂Co₃Nd₂O₃₉: calcd. C 20.28, H 2.96; found C 20.33, H 2.88.

Crystal structure determination

A red club-shaped single crystal with dimensions of 0.21 × 0.11 × 0.08 mm³ was selected for all subsequent measurements. Diffraction data of **1** were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ Å}$). A total of 17533 reflections were collected in the range of $2.64 \leq \theta \leq 25.49^\circ$ by using the ω -2 θ scan mode. 955 reflections were unique with *R*_{int} = 0.0263. The structure was solved by Direct Methods [17] and refined by full-matrix least-squares on *F*² using the SHELXL-97 software [18]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The crystal data and collection parameters for **1** are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2. Hydrogen bond parameters are listed in Table 3.

CCDC 736958 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis

Compound **1** has been prepared by hydrothermal reaction of Nd₂O₃, Co(CH₃COO)₂ and oxydiacetic acid in HCl–H₂O, subsequently neutralized by KOH (pH = 6). Other Ln₂O₃ oxides such as Dy₂O₃, Ce₂O₃, Eu₂O₃, and Pr₂O₃ and cobalt(II) salts including CoCl₂, Co(NO₃)₂ and CoSO₄ were also tried in similar experiments. Unfortunately, all of them have failed in obtaining the desired heterometallic Ln^{III}–Co^{II}–oda compounds, expect for the complex {[DyCo(oda)₃]₄–[Co(H₂O)₆]₂·6H₂O}_n [15]. From these facts it can be seen that subtle changes in the synthesis conditions

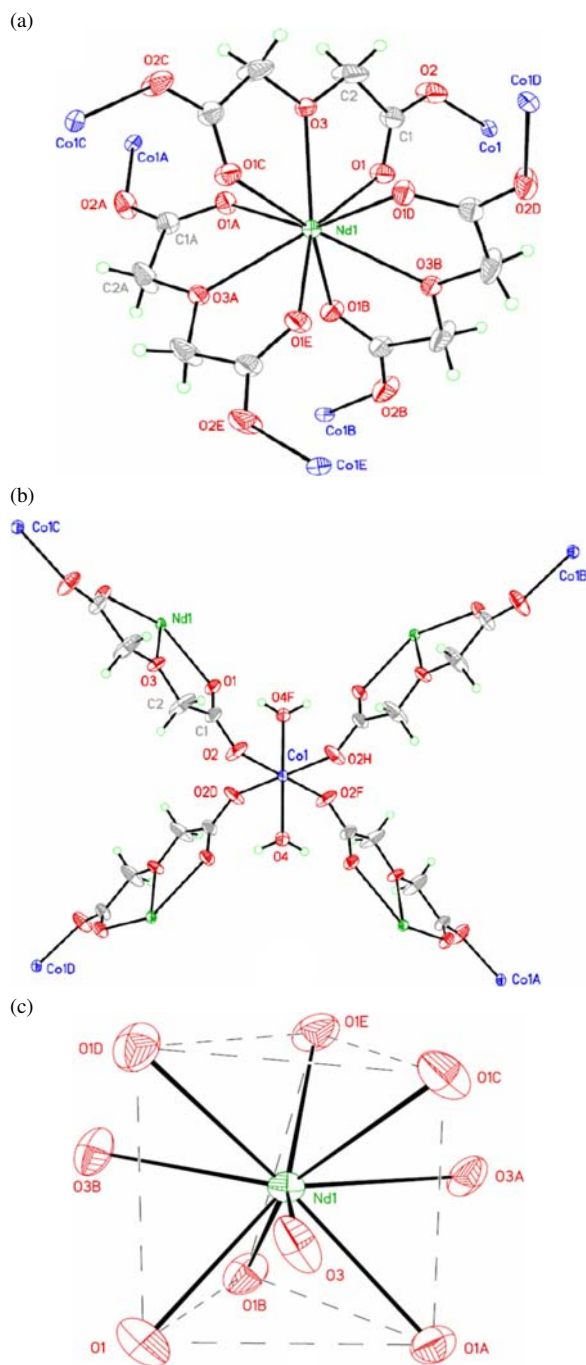


Fig. 1 (color online). Diagrams (30 % ellipsoids) showing the building units of **1** with the atom numbering scheme adopted. (a) NdO₉; (b) CoO₆; (c) the coordination polyhedron of the Nd³⁺ ion.

sometimes have a great influence on forming new target complexes.

Structure description

Compound **1** crystallizes in the hexagonal crystal system, space group $P6/mcc$ (Table 1). It is constructed by two small and simple building blocks, NdO₉ and CoO₆, shown in Fig. 1. These come together to build the three-dimensional framework with hexagonal channels in the (001) plane (Fig. 3). **1** is a new member of the isostructural series of 3D coordination polymers formulated as $\{[Ln_2M_3(oda)_6(H_2O)_6] \cdot xH_2O\}_n$ ($Ln = Nd, Y, Eu, Pr, Gd, Sm, La, Er, Tb, Yb, Dy, Ho, M = Cu$ [6–12]; $Ln = Sm, M = Zn, Ni, Mn, Co, Ca, Mg$ [7, 14]; $Ln = La, M = Zn, Ni, Co, Ca$ [13, 19]).

In detail, the Nd³⁺ ion is nine-coordinated by three ether O (O3) atoms and six carboxylato O (O1) atoms

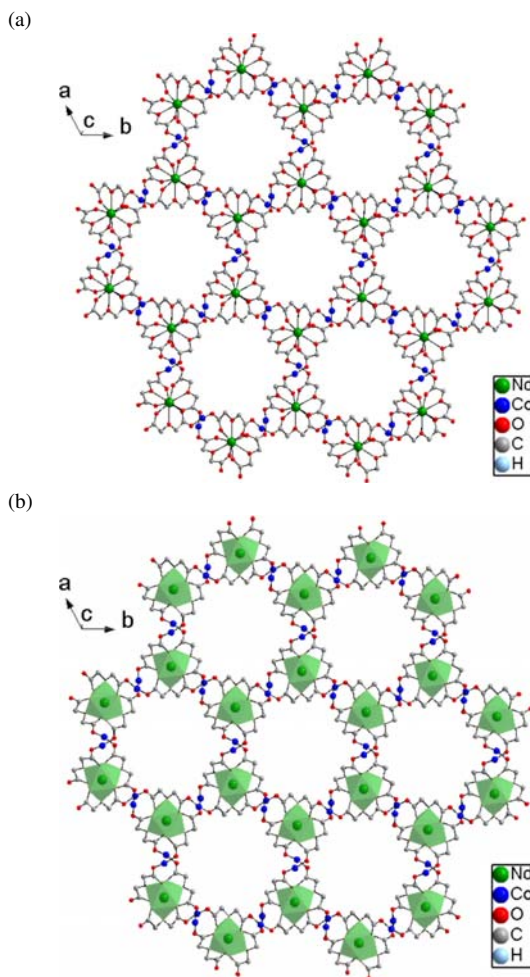


Fig. 2 (color online). Layer structure of **1** in the (001) plane. (a) Ball and stick; (b) Nd³⁺ ions in polyhedra.

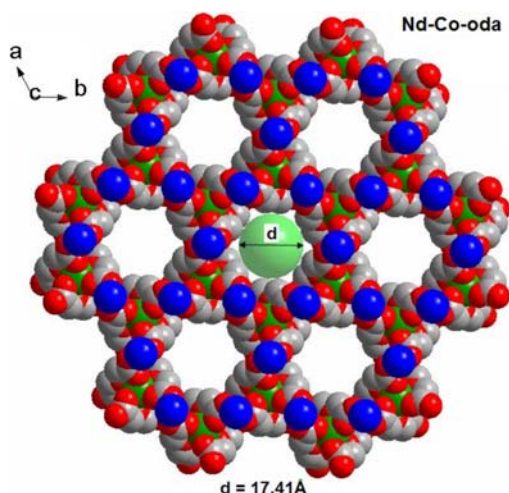


Fig. 3 (color online). 3D network structure with hexagonal channels of **1**.

from three equivalent oda²⁻ ligands. The Nd–O (ether) and Nd–O (COO) distances are 2.542(6) and 2.460(4) Å, respectively (Table 2). From these bond lengths we can see that the coordination ability of the carboxylato O atom is stronger than that of the ether O atom. The coordination geometry around the Nd³⁺ ion conforms closely to tricapped trigonal prismatic (TCTP); the six carboxylato O atoms compose the trigonal prism and three ether O atoms occupy the cap positions. The dihedral angle between the triangular bases (planes O1,O1A,O1B and O1C,O1D,O1E) is also 0°.

In turn, the Co²⁺ ion, which lies on the intersection of two twofold axis, is six-coordinated by the remaining outer bridging carboxylato O (O2) atoms of four oda²⁻ anions in the equatorial plane and two H₂O ligands in the axial positions. The bond length Co–O (COO) is 2.061(4) Å while that for Co–OH₂ is 2.156(6) Å, resulting in a slightly elongated octahedron. The fact that each oda²⁻ anion tridentately chelates one Nd³⁺ ion and its two remaining outer carboxylato O atoms link two Co²⁺ ions determines that each Nd³⁺ ion is surrounded by six Co²⁺ ions as the nearest neighbors, while each Co²⁺ ion has four Nd³⁺ ions in its vicinity, as expected for the Co/Nd molar ratio of 3/2.

As a result of this connectivity pattern, a 2D planar honeycomb structure parallel to the (001) plane is formed with NdO₉ polyhedra (Fig. 2). The layers are connected *via* Co²⁺ ions, each of which bonds to four outer carboxylato O atoms (two from above

and two from below), and thereby the 2D structure is extended into a 3D network with columnar channels (Fig. 3). The cross section of the channel is formed by six NdO₉ and six CoO₆ polyhedra in which the Nd³⁺ and Co²⁺ ions are arrayed alternately and linked by O–C–O bridges. The diameters of the hexagonal channels (defined as the distance between two diagonal Nd³⁺ ions) are 17.41 Å. This value agrees well with that of the reported compound {[Nd₂(PDA)₆Co₃-(H₂O)₆]·7H₂O}_n (17.82 Å) [H₂PDA = pyridine-2,6-dicarboxylic acid] [20]. The channels are partially filled by the H atoms of the methylene groups and crystal water molecules. The Co···Nd distances across the carboxylate bridges are 5.823(3) Å; the shortest Nd···Nd and Co···Co separations are 7.734(8) and 7.541(9) Å, respectively.

The coordinated H₂O ligands and carboxylate O atoms take part in intermolecular hydrogen bonding (Table 3). The extended structure of **1** is thus stabilized by these O–H···O hydrogen bonds.

Fluorescence spectral studies

Fig. 4 shows the photoluminescence spectra of complex **1** in a solid glass state at r. t. It can be seen that **1** displays a weak emission at about 228 nm and a broad emission centered at 364 nm ($\lambda_{\text{ex}} = 449$ nm). The overall spectral features of **1** are nearly the same as that of the free H₂oda ligand (centers 224 nm and 359 nm, $\lambda_{\text{ex}} = 442$ nm) [17]. The emissions of **1** can be similarly assigned to intraligand π – π^* transitions of the oda²⁻ ligand just as observed in the Dy^{III}–Co^{II}–oda compound [15].

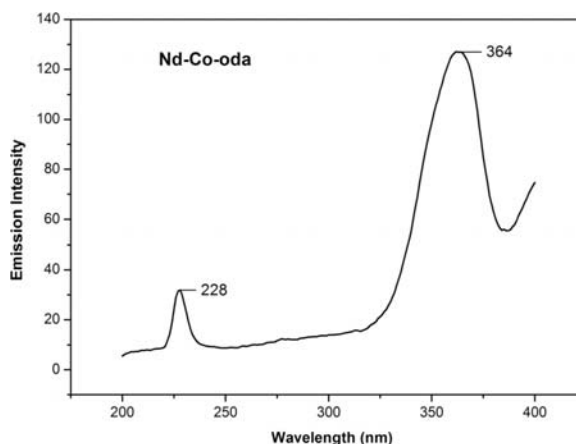
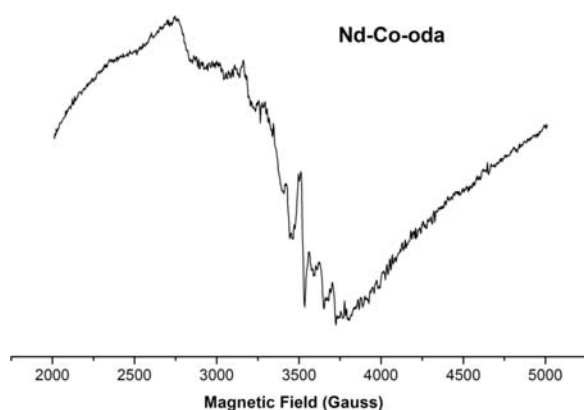


Fig. 4. The emission spectrum of **1** in the solid state at r. t.

Fig. 5. X-Band EPR spectrum of **1** at r. t.

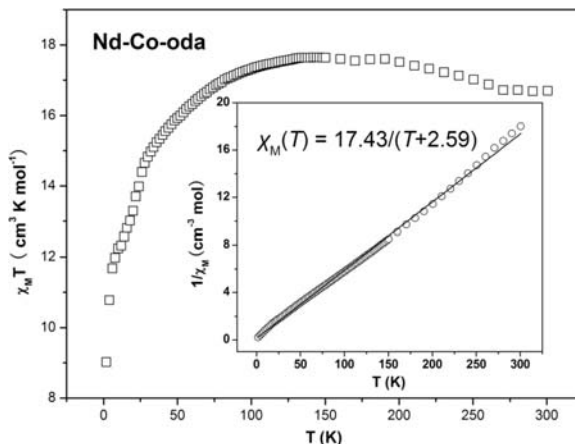
EPR spectra

The EPR spectra of the polycrystalline powder of **1** were recorded at r. t., as shown in Fig. 5. The spectrum of **1** shows a hyperfine splitting pattern which may result from the coupling of Nd^{3+} and Co^{2+} ions. The orbital angular momentums of Nd^{3+} and Co^{2+} ions are complicated, and thus it is impossible to have a simple and explicit analysis [21]. A similar example that can be found is $\{[\text{Nd}_2(\text{PDA})_6\text{Co}_3(\text{H}_2\text{O})_6] \cdot 7\text{H}_2\text{O}\}_n$ [21].

Magnetic properties

The temperature dependence of the magnetic susceptibility of **1** was measured in the temperature range of 2–300 K. The plots of $\chi_{\text{M}}T$ versus T and $1/\chi_{\text{M}}$ versus T are shown in Fig. 6 with χ_{M} being the molar magnetic susceptibility and T the temperature.

For **1**, the $\chi_{\text{M}}T$ value is $16.69 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K and then increases gradually from 300 to 150 K. As the temperature is further lowered, the $\chi_{\text{M}}T$ values are sharply reduced to $9.02 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The experimental effective magnetic moment (μ_{eff}) is $11.55 \mu_{\text{B}}$ at r. t., which is much higher than the theoretical value $8.44 \mu_{\text{B}}$ for three isolated spin-only Co^{2+} and two Nd^{3+} ions in the ground state ($^4I_{9/2}$, $g=8/11$),

Fig. 6. Experimental $\chi_{\text{M}}T$ versus T curves for **1**.

indicative of a typical contribution of the orbital momentum for the $^4T_{1g}$ ground state of Co^{2+} ions [21]. The coupling interactions between Nd^{3+} and Co^{2+} are not explicitly characterized because of the strong spin-orbit coupling of Nd^{3+} and Co^{2+} ions. In the $1/\chi_{\text{M}}$ versus T plot (inset in Fig. 6), the molar susceptibility basically obeys the Curie-Weiss law ($1/\chi_{\text{M}} = (T - \theta)/C_{\text{M}}$) in the 2–250 K temperature range. The Curie and Curie-Weiss constants are $\theta = -2.59 \text{ K}$ and $C_{\text{M}} = 17.43 \text{ cm}^3 \text{ K mol}^{-1}$, respectively.

Conclusions

In summary, we have shown that the reaction of Nd_2O_3 , $\text{Co}(\text{CH}_3\text{COO})_2$, H_2oda , and KOH under hydrothermal conditions results in the formation of complex **1**. Compound **1** is a new member of the isostructural series of the 3D $3d$ - $4f$ organic frameworks with the formula $\{[\text{Ln}_2\text{M}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}\}_n$ in possession of special hexagonal channels. The solid-state fluorescence, EPR and magnetic properties of **1** were studied. Our work may be a useful reference for designing other $3d$ - $4f$ model complexes for magnetic materials.

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