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Three-dimensional 3d–4f heterometallic polymers containing both azide and carboxylate as co-ligands

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ABSTRACT

The hydrothermal reaction of $Ln(NO_3)_3$, $Ni(NO_3)_2$, NaN_3, and isonicotinic acid (**L**) yielded two novel 3-D coordination frameworks (**1** and **2**) of general formula $[Ni_2Ln(L)_5(N_3)_2\,(H_2O)_3]\cdot 2H_2O$ (Ln = Pr(III) for **1** and Nd(III) for **2**), containing Ni–Pr or Ni–Nd hybrid extended three-dimensional networks containing both azido and carboxylate as co-ligands. Both the compounds are found to be isostructural and crystallize in monoclinic system having $P2_1/n$ space group. Here the lanthanide ions are found to be nonacoordinated. Both bidentate and monodentate modes of binding of the carboxylate with the lanthanides have been observed in the above complexes. Variable temperature magnetic studies of the above two complexes have been investigated in the temperature range 2–300 K which showed dominant antiferromagnetic interaction in both the cases and these experimental results are analyzed with the theoretical models.

1. Introduction

The design and synthesis of higher-dimensional metal–organic hybrid extended networks are currently of great interest [1]. The intense interest in this field is justified not only by the fascinating structural diversity of the architectures but also by the potential applications of these compounds as important functional materials in magnetism, molecular adsorption, catalysis and nonlinear optics [1]. However, most of the works have been focused on the homometallic assemblies of 3d series transition metals [2]. Surprisingly, the analogous system and synthetic strategy of 3d–4f heterometallic hybrid extended assemblies is still less developed, though several discrete 3d–4f heterometallic assemblies have been reported in last few years [3]. The competitive reaction of a mixture of 3d–4f metal ions in conjunction with a mixture of ligands often result in a mixture of homometallic assemblies instead of heterometallic analogous. It has been well established that lanthanide ions behave as hard acids and they prefer to bind hard donor carboxylate oxygen. On the other hand, d-block metal ions are borderline acceptors when the oxidation state is not very high, as in the present case, and they have a strong tendency to coordinate to N-donor ligands. Hence, an appropriate approach towards the construction of 3d–4f heterometallic frameworks would be the reaction of a mixture of 3d and 4f metal ions with ligand or mixture of ligands containing both oxygen and nitrogen donors. Here we report the utilization of an ambidentate ligand L (L = isonicotinate) and azide in combination with a mixture of Ni(II) and Ln(III) for the synthesis of two new hybrid polymers, $[Ni_2Pr(L)_5(N_3)_2\,(H_2O)_3]\cdot 2H_2O$ (**1**) and $[Ni_2Nd(L)_5(N_3)_2(H_2O)_3]\cdot 2H_2O$ (**2**).

2. Experimental

2.1. Materials and measurements

A Perkin–Elmer spectrometer was used for recording FT-IR spectrum in the range 4000–400 cm^{-1} using KBr pellets. Elemental analysis was carried out using Perkin–Elmer analyzer 2400 CHN. Magnetic measurements of crystalline sample were carried out with Quantum Design SQUID magnetometer. The crystal data for **1** and **2** were collected on Bruker SMART APEX CCD diffractometer using the SMART/SAINT software [4]. The measurements were recorded at a magnetic field of 0.2 T in the temperature range 2–300 K. All the chemicals were obtained commercially and used as received without further purification.

2.2. X-ray crystallographic studies

X-ray quality crystals were mounted on a glass fibre with traces of viscous oil. Intensity data were collected using graphite-monochromated Mo Kα radiation (0.7107 Å) at 293 K. The structures

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Table 1
Crystal data and structure refinement parameters for **1** and **2**

Compound	1	2
Empirical formula	$C_{29}H_{24}N_{11}Ni_2O_{16}Pr$	$C_{30}H_{25}N_{10}Ni_2O_{16}Nd$
Fw	1040.88	1043.22
T (K)	150(2)	150(2)
Space group	$P2_1/n$	$P2_1/n$
a (Å)	8.2206(16)	8.207(3)
b (Å)	26.939(5)	26.902(11)
c (Å)	17.017(3)	16.964(7)
α (°)	90.00(0)	90.00
β (°)	95.952(4)	95.759(7)
γ (°)	90.00(0)	90.00
V (Å^3)	3748.2(12)	3726.2(3)
Z	4	4
μ(Mo Kα) (mm^{-1})	0.857	0.857
λ (Å)	0.71073	0.71073
R_w	0.1172	0.0906
R	0.0706	0.0484
D_{calc} (Mg m^{-3})	1.841	1.860

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

were solved by direct methods using the SHELX-97 [5] incorporated in WINGX [6]. Empirical absorption corrections were applied with SADABS [7]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, $U(H) = 1.2U(C)$ or $1.5U$ (C-methyl), and their coordinates were allowed to ride on their respective carbons. Structures were drawn using either ORTEP-3 for Windows[8] or PLUTON [9]. Cambridge Crystallographic Data Center (CCDC) reference numbers for the complexes **1** and **2** are CCDC 683424 and CCDC 683425, respectively. Crystallographic data and structure refinement parameters are assembled in Table 1.

2.3. Synthesis of the complexes

The hydrothermal reaction of a mixture of $Ln(NO_3)_3$ (Ln = Pr(III) for **1** and Nd(III) for **2**), $Ni(NO_3)_2 \cdot 6H_2O$, NaN_3, isonicotinic acid, and H_2O in the ratio of 1:1:2:3:2000 in a Teflon-lined autoclave at 165 °C for 24 h followed by slow cooling (15 °C/h) to room temperature yielded crystalline complexes (**1** and **2**) in pure form. The crystals were obtained in ca. 30% yield based on Ni. Calc. for Compound **1**: C, 34.52; H, 3.35; N, 14.77. Found: C, 34.80; H, 3.43; N, 14.59%. IR: $\nu(COO^-)$, 1582, 1651 cm-1; ν (N3-), 2055.6, 2094.5 cm^{-1}. Calc. for Compound **2**: C, 34.43; H, 3.34; N, 14.72. Found: C, 34.71; H, 3.48; N, 14.47%. IR: $\nu(COO^-)$, 1583, 1651 cm^{-1}; $\nu(N_3^-)$, 2055.9, 2095.5 cm^{-1}.

Caution: Azide complexes are potentially explosive in presence of organic ligands. Only a small amount of the material should be prepared and handled with care.

3. Results and discussion

The IR spectra of the complexes **1** and **2** displayed characteristic bands of azide (N_3^-) and carboxylate (COO^-). As expected from $\nu_{as}(N_3^-)$ absorption, both the compounds **1** and **2** exhibit bands at 2055.6, 2094.5 cm^{-1} and 2055.9, 2095.5 cm^{-1}, respectively. This shows the presence of both end-on (EO) and end-to-end (EE) bridging modes of the azide in the above complexes while the peaks at 1582 and 1583 cm^{-1} in the IR spectra of complexes **1** and **2** are due to the carboxylate moiety.

3.1. Description of structures

The structure (Fig. 1) of complex **1** displays a complicated three-dimensional network, containing one Pr(III) ion, two unique Ni(II) (Ni1 and Ni2) ions, two unique azide ligands, and five different isonicotinate anions, two of which are tridentate and three are bidentate.

The structure contains one water molecule coordinated to the Pr(III) ions and a pair of water molecules coordinated to the Ni2 ion, and also uncoordinated water molecules trapped within the lattice. The hard acceptor Pr(III) ions are coordinated to nine oxygen atoms, two doubly coordinated carboxylates and four singly coordinated carboxylates and a water molecule coordinates the 9th position. The tridentate isonicotinate anions bridge the Pr(III) ions into one-dimensional zig-zag chain via the carboxylate groups. These tridentate isonicotinate anions also coordinate to Ni1 via the N atoms. Two alternating end-on (EO) and end-to-end (EE) types of double azide bridges in turn, connect the Ni1 ions into chain (Fig. 2).

The Ni(II) chain connects the neighboring Pr(III) chains via μ-O,O,N isonicotinate linkers. This result in two-dimensional sheet of alternating Pr-isonicotinate and $Ni1/N_3$ chains linked by the isonicotinate N–Ni1 bond (Fig. 3). Relatively harder donor oxygens link the hard acceptor Pr(III) and borderline acceptor Ni(II) ions are coordinated to nitrogens of azide and isonicotinate. This nature of coordination in the formation of the 2D sheets in this molecule is a nice example of symbiosis.

Meanwhile, the three different bidentate isonicotinate ions coordinate to the Ni2 ions in an equatorial arrangement. One type of bidentate isonicotinate bridges the Ni1 ions into linear chains, coordinating via its pyridyl N to one Ni1 and via a carboxylate O to another. Thus, each Ni2 coordinates to one of these ligands via the N, and to another, trans from the first, via an O atom. The remaining two types of bidentate isonicotinate anions occupy the other two equatorial positions. These anions are N-bound and connect the Ni2 cations to the Pr(III) ions: one to a Pr/Ni1 sheet below and one to a Pr/Ni1 sheet above. Thus, the Pr/Ni1 sheets are connected via the Ni2 ions into a single three-dimensional network (Fig. 4). In the complicated overall topology, the Pr(III) ions act as

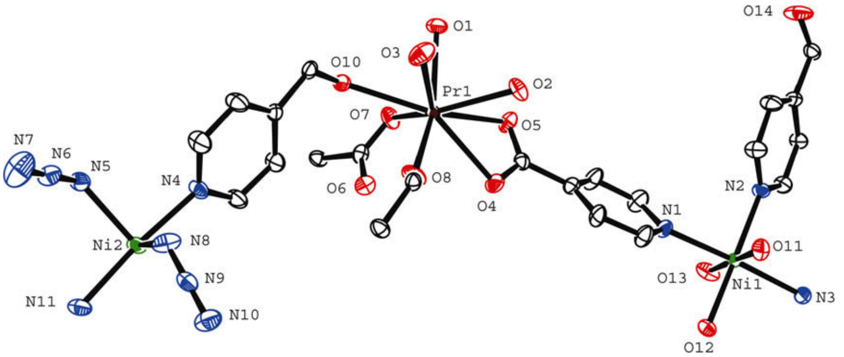

Fig. 1. ORTEP view of the basic coordination geometry around the metal ions in complex-**1** with atom numbering scheme.