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Mendeleev Commun., 2023, **33**, 45–46

Mendeleev Communications

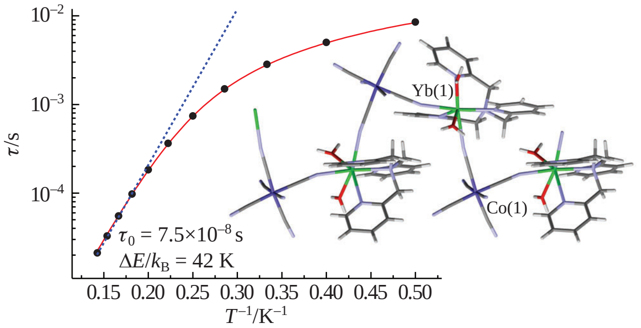
New chain polymer $[Yb(tpa)(H_2O)_2Co(CN)_6]_n \cdot 7n\,H_2O$: synthesis, structure, and magnetic characteristics

Svetlana P. Petrosyants, Andrey B. Ilyukhin, Konstantin A. Babeshkin, Nikolay N. Efimov and Pavel S. Koroteev*

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: pskoroteev@list.ru

DOI: 10.1016/j.mencom.2023.01.013

The 3*d*–4*f* heterometallic polymeric complex, namely $[Yb(tpa)(H_2O)_2Co(CN)_6]_n \cdot 7nH_2O$ [tpa = tris(2-pyridylmethyl)amine], was synthesized and characterized. Its polymer structure is formed of $[Yb(tpa)(H_2O)_2Co(CN)_6]$ chains and crystallization water molecules with a two-capped trigonal prism Yb^{3+} coordination polyhedron; the Yb^{3+} coordination number is 8, and the coordination site is YbN_6O_2. Magnetic characteristics indicate that the complex exhibits the properties of a single-chain magnet with a magnetization reversal barrier ($\Delta E/k_B$) of 42 K.



Keywords: ytterbium, heterometallic complexes, cyanometallate chains, coordination polymers, single-molecule magnets.

Promising types of magnetic nanomaterials vary from transition metal complexes[1] and stable organic radicals[2] to stabilized ferromagnetic oxide nanoparticles.[3] Among them, single-molecule magnets (SMMs) are of particular interest. Like usual magnets, the SMMs are able to maintain magnetization in the absence of an outer magnetic field, and they can retain their magnetization for hundreds of seconds. The presence of an energy barrier, which allows the magnetic moments of a system to be in an ordered state for a certain time, makes it promising to use SMMs in devices for storing high-density information, in quantum computers, and in circuits for miniature spintronics.[4] Today, much attention is drawn to a subclass of SMMs such as single-chain magnets (SCMs), the most promising of which are coordination-polymer 3*d*–4*f* chains, whose magnetic characteristics depend on the nature of the lanthanide cation. Among the chain structures, the polymer chains based on cyanometallate bridging complexes belong to the most interesting types.[5–8] For the construction of chain structures, the well-known 'complex as a ligand' approach is used; the polycyanide anions $[M(CN)_6]^{3-}$ (M = Cr, Mn, Co, Fe, *etc.*), which are potential N donors, are often used as such ligands. The formation of chain structures is controlled by introducing blocking mono- or polydentate molecular or ionic N or N,O ligands into the reaction media.[9–18]

In this work, as a part of our research of SCMs,[12,13] we synthesized the coordination polymer $[Yb(tpa)(H_2O)_2Co(CN)_6]_n \cdot 7nH_2O$ [tpa = tris(2-pyridylmethyl)amine] and studied its physical and chemical properties, structure, and magnetic characteristics in static and dynamic modes.

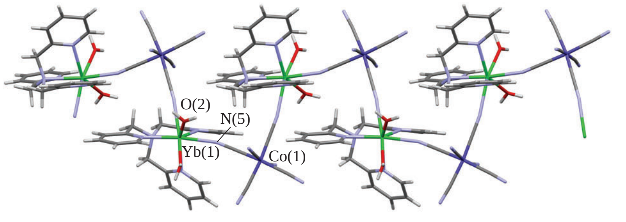


Figure 1 Polymeric chain pattern of $[Yb(tpa)(H_2O)_2Co(CN)_6]_n$ in compound **1**.

The compound $[Yb(tpa)(H_2O)_2Co(CN)_6]_n \cdot 7nH_2O$ **1** was obtained by the slow diffusion of an ethanolic solution of $YbCl_3 \cdot 6H_2O$ and tpa into a solution of $K_3[Co(CN)_6]$ in a mixture of H_2O and EtOH with the molar ratio Yb : Co : tpa = 1 : 1 : 1.[†] Comparison of the IR spectra of $K_3[Co(CN)_6]$ and compound **1** showed that the characteristic ν(C≡N) band in the synthesized compound was split to unambiguously indicate the presence of terminal (2134 cm^{-1}) and bridging (2164 cm^{-1}) cyanide ligands [Figure S1(*a*), see Online Supplementary Materials]. There was no splitting of the corresponding band (2126 cm^{-1}) in the spectrum of $K_3[Co(CN)_6]$ [Figure S1(*b*)]. According to X-ray diffraction data,[‡] the structure of complex **1** is built of 1D polymeric chains $[Yb(tpa)(H_2O)_2Co(CN)_6]_n$ (Figure 1) and crystallization water molecules. The coordination

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[†] A solution of $YbCl_3 \cdot 6H_2O$ (0.109 mmol, 0.0422 g) in EtOH (2.5 ml) was added in small portions to a solution of tpa (0.109 mmol, 0.0317 g) in EtOH (2 ml), and the mixture was stirred for about 30 min. The resulting solution was overlaid onto a solution of $K_3[Co(CN)_6]$ (0.109 mmol, 0.0363 g) in a mixture of H_2O (2 ml) and EtOH (2 ml) obtained by dissolving the salt in water followed by the addition of the alcohol. The system was left at room temperature until the complete isolation of solid phase (for about a week). The solid phase was separated on a paper filter, washed with a mixture of solvents, and dried in air.

[‡] *Crystal data for* **1**. $C_{24}H_{36}CoN_{10}O_9Yb$ (M = 840.60), orthorhombic, space group $Pna2_1$, T = 100(2) K, a = 13.9826(8), b = 17.9074(9) and c = 13.0559(7) Å, V = 3269.1(3) $Å^3$, Z = 4, d_{calc} = 1.708 g cm^{-3}; crystal size, 0.50 × 0.01 × 0.01 mm. Total of 23798 reflections were collected (2.28° < θ < 25.02°), μ = 3.413 mm^{-1}, 5608 independent reflections (R_{int} = 0.068). Data / restraints / parameters: 5608 / 205 / 400. The final refinement parameters were: R_1 = 0.0533, wR_2 = 0.1336 for reflections with $I > 2\sigma(I)$; R_1 = 0.0729, wR_2 = 0.1543 for all reflections; absolute structure parameter −0.018(16); largest diff. peak/hole: 1.377/–1.379 $eÅ^{-3}$, GOF = 0.732. X-ray diffraction data for **1** were collected on a SMART APEX2 area-detector diffractometer (graphite monochromator, ω-scan technique) using MoKα radiation (0.71073 Å).

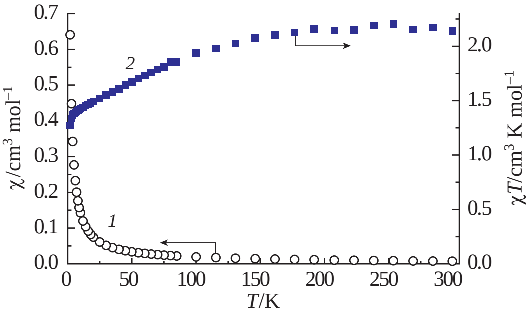

Figure 2 Temperature dependences of (*1*) the magnetic susceptibility and (*2*) χT for complex **1** (H = 5 kOe).

number of Yb is 8, and the polyhedron is a two-capped trigonal prism. The bridging CN ligands of the $Co(CN)_6$ fragment are in the *cis* position to each other, which determines the zigzag structure of the polymer chain. A branched system of hydrogen bonds with crystallization H_2O molecules combines structural units into a framework.

The studies of magnetic susceptibility[§] have shown that the value of χT at 300 K is 2.14 cm^3 K mol^{-1}, which is close to the theoretical one for a single isolated Yb^{3+} ion (C = 2.57 cm^3 K mol^{-1}). The value of χT decreased insignificantly with lowering temperature down to 200 K, and more noticeably with further cooling to reach a minimum value of 1.27 cm^3 K mol^{-1} at 2 K (Figure 2). This behavior is typical for Yb complexes.[19–23]

No slow magnetic relaxation was detected for complex **1** in a zero magnetic field. Measurements of the ac-magnetic susceptibility in non-zero fields revealed a significant signal of imaginary component of the ac-magnetic susceptibility χ'' for **1** (Figures S3, S4). Varying the strength of the external dc-magnetic field allowed us to determine an optimal dc field under which the maximums of $\chi''(\nu)$ were located at lowest frequencies corresponding to the longest relaxation times. The optimal dc-magnetic field was 1000 Oe. The value of $\Delta E/k_B$ = 42 K obtained using the sum of the Orbach, Raman, and direct relaxation mechanisms was close to an analogous value of 40 K found by the Arrhenius approximation in the high-temperature region (Figure 3). This fact indicates that, even at temperatures above 6 K, the Orbach mechanism makes the main contribution to the molecular relaxation. The results showed that the Kramers ion Yb^{3+} can be the basis for the development of single-molecule magnets with promising characteristics.

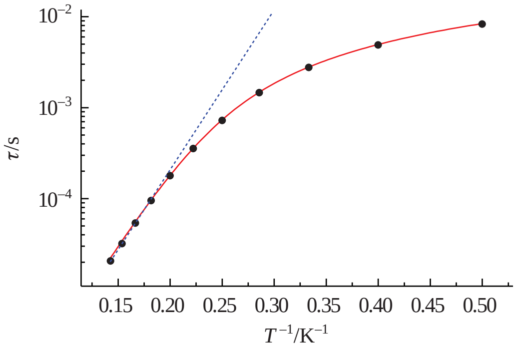

Figure 3 Dependence of the relaxation time τ on the reciprocal temperature for complex **1** under a 1000 Oe field. The data were obtained by the $\chi''(\nu)$ approximation using the generalized Debye model. The blue dashed and solid red lines refer to the Arrhenius approximation of high-temperature data and an approximation by the sum of the Orbach, Raman, and direct relaxation mechanisms, respectively.

In summary, using an exchange reaction in an aqueous organic medium, we obtained the coordination polymer $[Yb(tpa)(H_2O)_2Co(CN)_6]_n \cdot 7nH_2O$ built of 3*d*- and 4*f*-containing units connected with each other *via* bridging cyanide ligands. The complex exhibits the properties of a single-chain magnet under an external field of 1000 Oe with the magnetization reversal barrier $\Delta E/k_B$ = 42 K, which is a promising value for Yb^{3+} derivatives.

The study was carried out using the research equipment of the Center for Collective Use of Physical Investigation Methods of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

This work was supported by the Russian Science Foundation (grant no. 22-23-00574).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.013.

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Received: 27th June 2022; Com. 22/6942

CCDC 2181280 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] For details of the magnetic study, see Online Supplementary Materials.