Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 45–46

New chain polymer $[Yb(tpa)(H_2O)_2Co(CN)_6]_n\cdot 7nH_2O$: synthesis, structure and magnetic characteristics

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S1. X-ray data collection

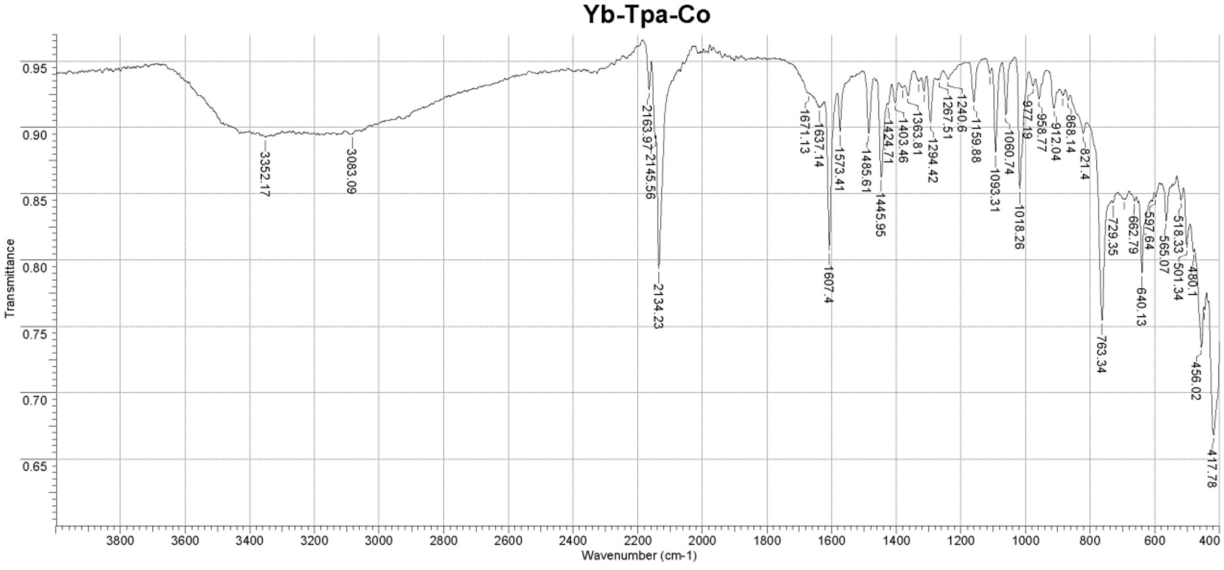
Experimental single crystal XRD data for **1** were collected on a Bruker SMART APEX2 instrument[S1] (Table S1). The habit of crystals of **1** was thin filaments, which determined the low quality of the X-ray diffraction experiment: high errors in bond lengths and unrealistic atomic displacement parameters (ADP) for a number of non-hydrogen atoms. When refined, 205 restraints were imposed on the ADP. Because of the lack of well-faceted crystals, absorption was taken into account by a semiempirical method based on equivalents using SADABS.[S2] The structures were determined using a combination of the direct method and Fourier syntheses. The structures were refined by the full-matrix anisotropic least squares method. All the calculations were carried out using SHELXS and SHELXL software.[S3]

S1 Bruker, APEX2 and SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
S2 G. M. Sheldrick, SADABS. University of Göttingen, Germany, 2014.
S3 G. M. Sheldrick, Acta Crystallogr. Sect. C, 2015, 71, 3.

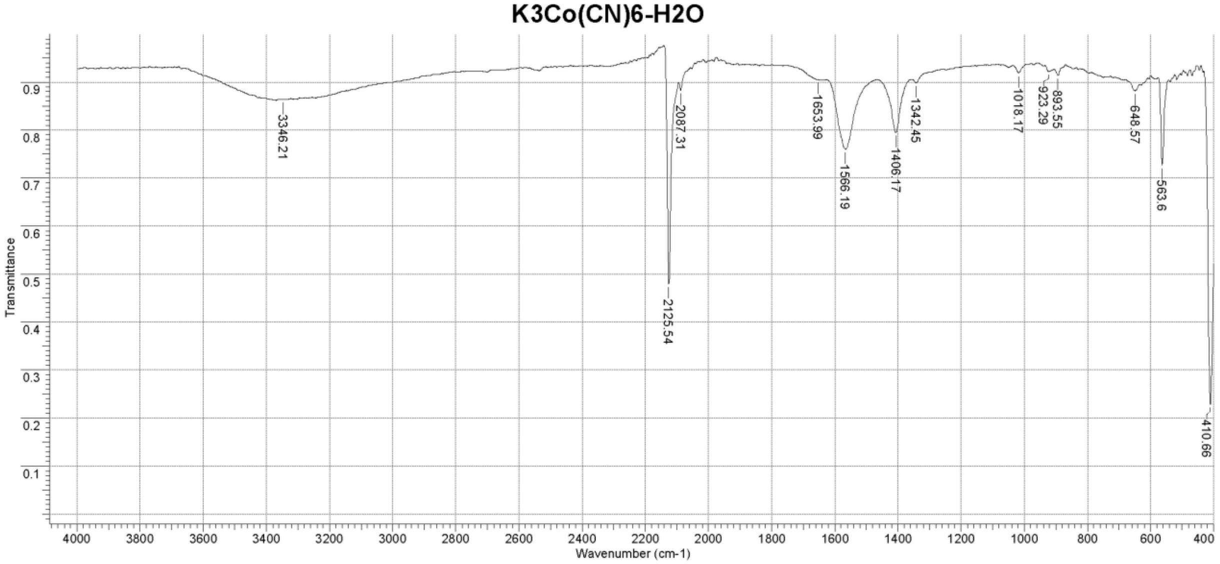
Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	$C_{24}H_{36}CoN_{10}O_9Yb$
Formula weight	840.60
Temperature, K	100(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$
a, Å	13.9826(8)
b, Å	17.9074(9)
c, Å	13.0559(7)
Volume, Å3	3269.1(3)
Z	4
D (calc), Mg/m3	1.708
μ, mm-1	3.413
F(000)	1676
Crystal size, mm	0.50 x 0.01 x 0.01
θ range, °	2.418, 25.022
Index ranges	-16<=h<=16 -21<=k<=21 -14<=l<=15
Reflections collected	21606
Independent reflections, Rint	5608, 0.0679
Completeness to θ = 25.022°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max, min transmission	0.0955, 0.0639
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5608 / 205 / 400
Goodness-of-fit	0.732
R1, wR2 [I>2sigma(I)]	0.0533, 0.1336
R1, wR2 (all data)	0.0727, 0.1543
Absolute structure parameter	-0.018(16)

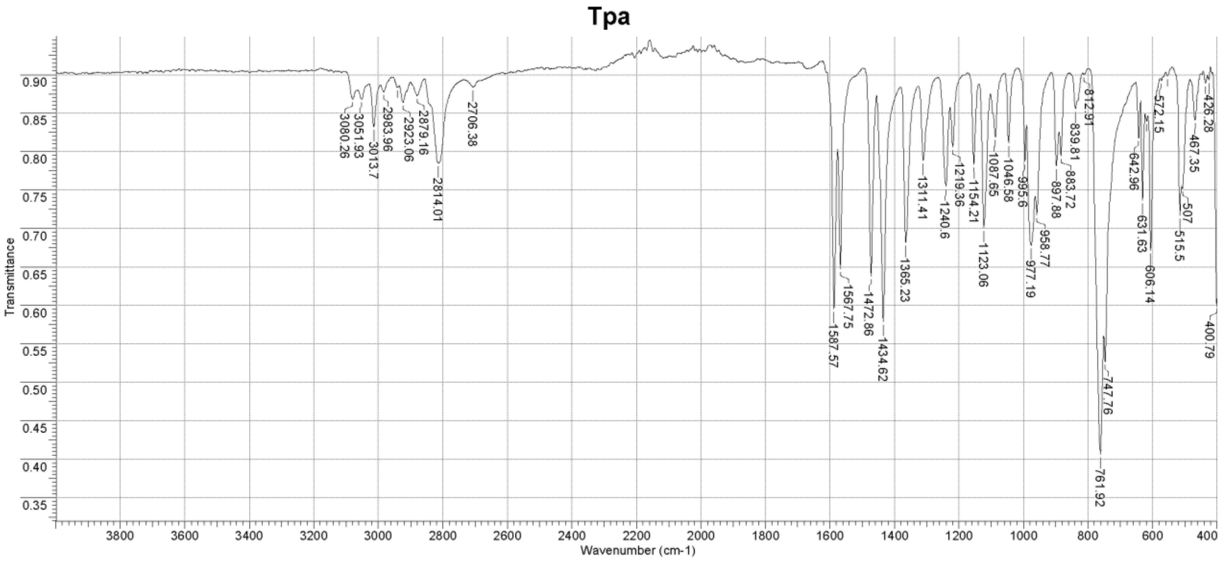
Largest diff. peak and hole, e.Å-3	1.377, -1.379



a



b



c

Figure S1. IR spectra of complex **1** (a), $K_3[Co(CN)_6]$ (b), and tpa ligand (c).

S2. Magnetic studies

Magnetic susceptibility measurements for **1** were performed with a Quantum Design susceptometer PPMS-9 in the range of 2 – 300 K. For ac susceptibility measurements, oscillating ac fields with an amplitude of 5-1 Oe within 10 - 10000 Hz frequency ranges, respectively, were used. These settings allowed both to avoid sample heating at low temperatures (which may occur at high modulation amplitudes) and to obtain the best signal-to-noise ratio. Measurements were performed on a polycrystalline sample sealed in polyethylene bag and covered with mineral oil in order to prevent field-induced orientation of the crystallites. The paramagnetic components of the magnetic susceptibility χ were determined taking into account the diamagnetic contribution evaluated from Pascal's constants as well as the contributions of the sample holder and mineral oil.

The magnetic properties of compound **1** in the static mode were studied in the range of 2–300 K in a constant magnetic field of 5000 Oe (Figure S2). The χT value at 300 K is 2.14 cm^3Kmol^{-1} which satisfactorily agrees with the theoretical value of 2.57 cm^3Kmol^{-1} for one non-interacting Yb^{3+} ion. The value of χT decreases insignificantly with temperature lowering down to 200 K, then more and more noticeable with further cooling to reach the minimum value of 1.27 cm^3K/mol at 2 K. Such behavior of $\chi T(T)$ dependence is typical of Yb^{3+} complexes. Taking into account the closeness of the theoretical and experimental values of χT (300 K), we can conclude that the magnetic behavior of complex **1** under the conditions described is determined almost exclusively by the nature of Yb^{3+} ion.

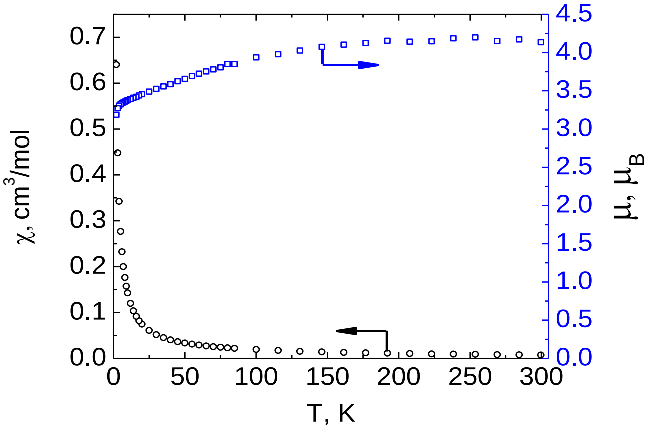


Figure S2. Temperature dependences of the magnetic susceptibility (o) and effective magnetic moment (□) for complex **1** (H = 5 kOe).

In order to determine the presence of SMM properties in complex **1**, we studied its magnetic behavior in the dynamic mode, i.e., under the fields of various intensity. No slow magnetic relaxation was found for complex **1** in a zero magnetic field. As it is known, the application of an external magnetic field reduces the probability of quantum tunneling, which can lead to a decrease in the relaxation rate. Measurements of the ac-magnetic susceptibility in nonzero magnetic field revealed the appearance of a significant signal of imaginary component of ac-magnetic susceptibility. Varying the strength of the external magnetic field H_{dc} made it possible to determine the optimal field under which the maxima in the corresponding dependences $\chi''(\nu)$ are located at the lowest frequencies, which corresponds to the longest relaxation times. The optimal magnetic field value found was 1000 Oe (Figure S3).

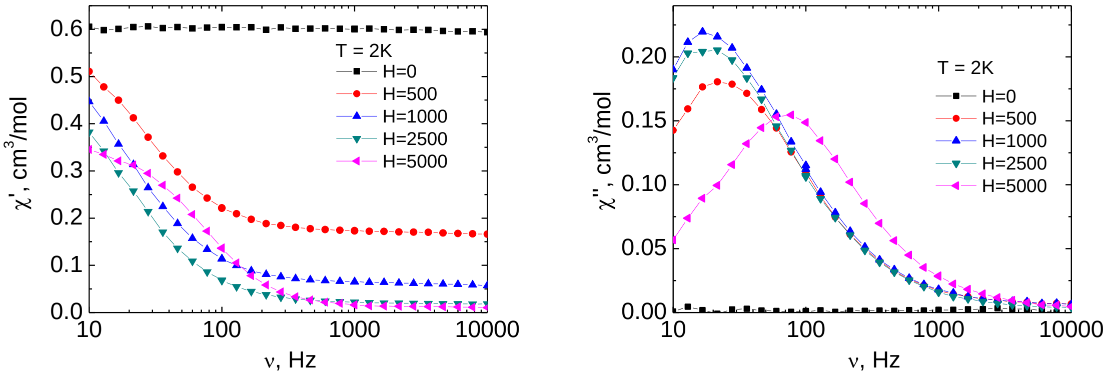


Figure S3. Frequency dependences of the real (left) and imaginary (right) components of the ac-magnetic susceptibility for complex **1** at various dc-magnetic field (T = 2 K).

In order to determine the temperature dependences of the relaxation times in the optimal dc-field, we measured the isotherms of the frequency dependences of the ac-magnetic susceptibility in the range of 2–7 K (Figure S4) for complex **1**. The relaxation times were determined from the positions of the maxima in the frequency dependences.

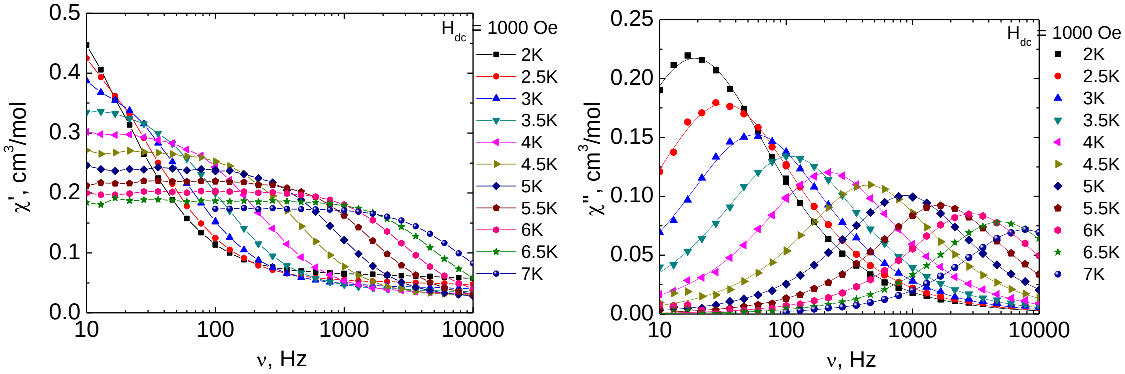


Figure S4. Frequency dependences of the real (left) and imaginary (right) components of the ac-magnetic susceptibility for complex **1** at various temperatures under 1000 Oe field.

Based on these data, the dependences of the relaxation time on the reciprocal temperature τ(1/T) for complex **1** were calculated (Figure S5). To determine the parameters of relaxation processes in the complex, the high-temperature (6–7 K) part of the τ(1/T) dependence was approximated by Arrhenius equation $\tau = \tau_0 \cdot \exp(\Delta E/k_B T)$, which describes the Orbach relaxation process. The best approximation of the theoretical dependence to the experimental data was obtained with the value of the pre-exponential factor $\tau_0 = 6.5 \cdot 10^{-8}$ s and the remagnetization barrier $\Delta E/k_B = 40$ K. The deviation of the lnτ(1/T) dependence from linearity with temperature increasing indicates the presence of additional relaxation mechanisms. To identify additional relaxation pathways and to determine their parameters, an approximation was carried out using the sum of several mechanisms. The best approximation of the experimental data by the theoretical curve was obtained for the sum of the direct, Raman and Orbach relaxation mechanisms according to the following equation:

$$\tau^{-1} = A_{direct} \cdot H_{dc}{}^{n} \cdot T + C_{Raman} \cdot T^{n\_Raman} + \tau_0{}^{-1} \cdot \exp(-\Delta E/k_B T),$$

where A_{direct} and n are the parameters of the direct relaxation mechanism, $C_{\_Raman}$ and $n_{\_Raman}$ are the parameters of the Raman relaxation mechanism; T is temperature; τ_0 is the time of the fastest relaxation; $\Delta E/k_B$ is the height of the energy barrier of the molecule magnetization reversal; k_B is

Boltzmann constant. The values of the parameters obtained as a result of approximation in the entire temperature range under study (2–7 K) turned out to be as following: $A_{direct} = 4.2\cdot10^{-11}$ s K^{-1} Oe^{-4}; n = 4.0 (fixed for Kramers' ions); $C_{Raman} = 1.48$ $K^{-4.6}\cdot c^{-1}$; $n_{Raman} = 4.6$, $\tau_0 = 7.5\cdot10^{-8}$ s; $\Delta E/k_B = 42$ K.

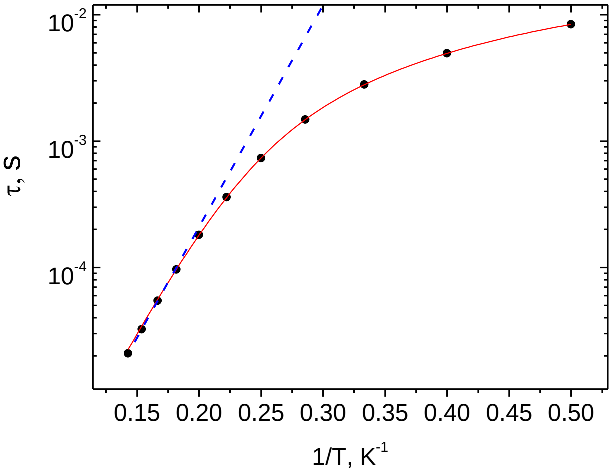


Figure S5. – Dependence of the relaxation time τ on the reciprocal temperature for complex **1** under 1000 Oe field. The data were obtained by the χ''(ν) approximation using the generalized Debye model. The blue dotted line is the approximation of high-temperature data by Arrhenius equation. The red line is the data approximation by the sum of Orbach, Raman, and direct relaxation mechanisms.

It can be concluded that the $\Delta E/k_B$ value obtained using the sum of the direct, Orbach and Raman relaxation mechanisms is in good agreement with the analogous value obtained by approximation of the high-temperature region using the Arrhenius equation. This fact indicates that, even at temperatures above 6 K, it is the Orbach mechanism that makes the main contribution to the magnetic relaxation of complex **1**.