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A cobalt (II)-based semiconductor complex with two-channel slow magnetic relaxation

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ABSTRACT

The hydrothermal reaction of 2-methylimidazole (hereafter abbreviated as 2-mim) with cobalt (II) sulfate heptahydrate in methanol affords a novel sulfate cobalt (II) complex with formula $[Co(C_4H_6N_2)_4](SO_4) \cdot (H_2O)$ (1). Its crystal structure was refined from X-ray diffraction data, complemented with the structural information derived from spectroscopic (IR and UV–Vis), thermal data and magnetic measurements. The crystal structure of **1** is made up of isolated $[Co(2-mim)_4]^{2+}$ cations, $(SO_4)^{2-}$ anions and lattice water molecules. An extensive network of hydrogen bonds ensures the interconnection of the different entities. Greater knowledge on these interactions has been provided based on the Hirshfeld surface analysis and 2D fingerprint plots. Heating of **1** above 97 °C initiates gradual decomposition stages, which lead to the metal oxide as a final product at 710 °C, as proven by TGA/DSC analysis. A UV–Vis spectroscopy study confirms the tetrahedral environment around the metal. The determined bandgap energy $E_g = 2.6$ eV from the UV–Vis spectra indicate the interesting semiconducting behavior of our compound. Static magnetic measurements and EPR study revealed the presence of the easy-axis anisotropy with axial term D = -5.45 cm⁻¹ and very small rhombicity, confirmed by the first-principle calculations. Complex **1** behaves as a field-induced single-ion magnet with two relaxation channels. The highfrequency relaxation can be described by the interplay of the two-phonon Orbach and Raman process, the relaxation barrier $U_{eff} = 11.4$ cm⁻¹ agrees well with the difference between the two lowest Kramer's doublets.

1. Introduction

The design and synthesis of novel metal-containing complexes are one of the most prospering areas of research in solid-state chemistry. The recent decades have witnessed an inexorable upswing in the development of new crystals. The major reasons for this leap stem from their intriguing structural diversities and potential relevance to a variety of fields, including catalysis [1,2], luminescence [3,4], magnetism [5–7], and biomedicine [8,9]. Nevertheless, constructing new materials with multifunctional properties is still one of the most significant challenges faced by scientists nowadays due to many factors such as metal ion, coordination nature of ligand structure, counter ion, solvent, pH value, temperature, reaction time, and so forth. Contemporary research has shown that the intercalation of N-donor heterocyclic ligands produces a plethora of structurally diverse multifunctional materials. Among the Ndonor heterocyclic ligands, imidazole and its derivatives have been demonstrated to be prominent structural constructors, due to their

amphoteric character, hydrogen bond donor-acceptor capability as well as high affinity for metals [10]. A significant number of metal coordination complexes with imidazole and its derivatives have authenticated their potency in several biological and pharmacological procedures, as already pointed out in several works, viz. antifungal [11], antioxidant [12], antimicrobial [13], and antitumor activities. Apart from being biologically active, imidazole compounds have been broadly used in various catalytic processes such as hydroamination [14,15], hydrosilvlation [16], Heck reaction [17,18], and Henry reaction [19]. Furthermore, they have been reported as effective corrosion inhibitors [20], chromophores for non-linear optic (NLO) systems [21], and a proton carrier in proton exchange membrane fuel cell (PEMFC) [22]. A literature survey reveals that imidazole-containing complexes were the focus of magnetic studies due to their capacity to foster long-range indirect magnetic exchange interactions when forming a covalent bridge between magnetic ions [23].

As part of our ongoing efforts in the design and development of

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Research articles





functional materials, we herein report on the synthesis of a novel complex through the combination of 2-methylimidazole and cobalt sulfate heptahydrate, which was expected to possess a peculiar structure. The design of Co(II)-based coordination complexes is lately closely connected to the search for single-ion magnets (SIM) with one paramagnetic metal ion of high anisotropy. The tuning of the local symmetry of the Co (II) center imposed by the ligand field yielded many examples of Co(II) SIMs with exceptionally high relaxation barriers for spin flipping, e.g. [24–27]. While on average the magnetic anisotropy in tetragonally distorted octahedral Co(II) complexes is larger than in tetrahedrally coordinated Co(II) complexes, tetrahedral complexes with a higher degree of distortion of the metal polyhedron can also yield exceptionally high anisotropy and spin relaxation barrier [26–32].

A meaningful structural characterization to achieve a complete and accurate structural picture followed by a Hirshfeld surface analysis, spectroscopic, thermal, optical, and magnetic measurements supplemented by *ab initio* and DFT calculations are reported hereunder.

2. Experimental section

2.1. Materials and physical measurements

All the employed chemicals were used as received without further purification. Cobalt (II) sulfate heptahydrate and 2-methylimidazole, were purchased from Sigma Aldrich.

Infrared measurements were recorded at room temperature using KBr pellets in the range 400–4000 $\rm cm^{-1}$ on a Bruker Optics, Vertex 70 FT-IR spectrophotometer.

TGA coupled to DSC analysis was carried out using a simultaneous TGA/DSC thermal analyzer Mettler Toledo 1100 system with a UMX1 balance, using a platinum crucible. TG/DSC measurement was recorded in the air on a 6.75 mg sample within the 25–800 °C temperature range at a 10 K/min heating rate.

To determine the optical properties of our complex, the crystals were first dissolved in dimethyl sulfoxide (hereafter abbreviated as DMSO) solution and optical absorption spectra of the diluted solution were measured at room temperature using a conventional UV–visible absorption spectrometer (Hitachi, U-3300).

2.2. X-Ray data collection

Single crystal X-ray diffraction data of complex 1 were obtained at 120 K, using an Oxford Gemini S diffractometer equipped with a graphite monochromatic Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation source. The molecular solid-state structure was solved by direct methods and refined by full-square methods on F^2 using SHELXS/SHELXL-2013 [33] in the WinGX [34] interface. Direct methods located the positions of all non-H atoms. C-bonded hydrogen atoms were introduced at calculated positions and treated as riding on their parent atoms. A riding model was utilized in the treatment of the hydrogen atom positions. The NH hydrogen atoms were found from the difference Fourier maps and constrained using DFIX 0.870 0.010. A summary of the crystal data, experimental details, and refinement results can be found in Table S1. The molecular drawings were designed using the DIAMOND [35] and OLEX [36] programs. Crystallographic data for the herein reported structure can be found in the Supporting Information of this paper and deposited at the Cambridge Crystallographic Data Centre under CCDC No. 1897588.

2.3. Hirshfeld surface analysis

To provide further insight into the packing and the intermolecular contacts in our compound, scrutiny of the Hirshfeld surface (HS) has been undertaken, using CrystalExplorer software (Version 3.1) [37] on the structure of the CIF file. The associated 2D fingerprint plots were generated to quantify those contacts' relative contribution to the crystal

stability. The HS is calculated using the normalized contact distance (d_{norm}) based on both d_e and d_i as given by this formula:

$$d_{norm} = rac{d_i - r_i^{vdw}}{r_i^{vdw}} + rac{d_e - r_e^{vdw}}{r_e^{vdw}}$$

Where d_i is the distance of the nearest nucleus internal to the surface, d_e is the distance from the point to the closest nucleus external to the surface and r_i^{vdw} , r_e^{vdw} are the *Van der Waals* radii of the atoms. Identifying the particularly relevant areas in the d_{norm} map is illustrated using a redwhite-blue colour scheme, where bright red spots highlight shorter contacts, white regions correspond to the contacts around the van der Waals separation and blue areas indicate the more extended contacts.

2.4. Magnetic measurements and EPR

Static and alternating-current (AC) magnetic measurements were performed in a commercial Quantum Design MPMS®3 magnetometer in the temperature range from 1.8 to 300 K in magnetic fields up to 70 kOe. The static susceptibility was estimated as the ratio of the magnetic moment and applied magnetic field of 1 kOe. The AC susceptibility measurements covered the excitation frequency range from 0.1 Hz to 1 kHz in MPMS®3. Additional measurements were performed using ACMS option in Quantum Design PPMS to cover the frequency range up to 10 kHz. A nascent polycrystalline specimen was fixed in a VSM polypropylene capsule held by a brass holder for static measurements. For AC measurements in PPMS the sample was placed in the gelatine capsule held by a clear plastic straw. The diamagnetic contribution of the sample was subtracted using Pascal's constants [38]. The spectra of electron paramagnetic resonance (EPR) were studied using Bruker ELEXSYS II E500 X-band spectrometer with an operating frequency of 9.4 GHz equipped with ESR910 helium flow-type cryostat. The measurements were performed in the temperature range from 2 K to 50 K. A nascent powder was mixed with Apiezon N grease and attached to the Suprasil sample holder.

2.5. Computational details

Ab initio calculations were performed using the ORCA 4.0.1 computational package [39]. The calculations of single-ion anisotropy parameters were based on the state-averaged complete-active-space selfconsistent field (SA-CASSCF) wave functions followed by N-electron valence second-order perturbation theory (NEVPT2) [40-44]. The active space of the CASSCF calculations on metal-based d-orbitals was defined at the beginning as CAS(7,5). The state averaged approach was used with all 10 quartets and 40 doublet states equally weighted. The ZFS parameters were calculated through the quasi-degenerate perturbation theory (QDPT) [45] in which an approximation to the Breit-Pauli form of the spin-orbit coupling operator (SOMF) [46], and the effective Hamiltonian theory [47] was utilized. Relativistic effects were taken into account by using the zeroth-order regular approximation (ZORA) [48,49] and the second-order Douglas-Kroll-Hess Hamiltonian (DKH) [50] together with the corresponding segmented all-electron relativistic contracted (SARC) version of the triple-ζ basis set Def2-TZVP [51,52] for all atoms. Since no significant difference in the obtained parameters was observed between ZORA and DKH approach, the results are presented from the calculations using DKH.

The BS DFT calculation [53] was done using the B3LYP, BPE0, and TPSSh exchange–correlation functionals [54–56]. The exchange coupling was obtained using the Yamaguchi formalism [57] $J_{BS} = -\frac{E_{HS}-E_{BS}}{\langle S^2 \rangle_{HS}-\langle S^2 \rangle_{BS}}$ from single-point approach (using X-ray determined structure), with a spin Hamiltonian in the form $\widehat{\mathscr{H}} = -2J_{BS}\widehat{S}_1\widehat{S}_2$ (intermolecular interactions $J = 2J_{BS}$ in the analysis of the experimental data).

All calculations utilized the RI approximation and the chain-ofspheres (RIJCOSX) approximation to exact exchange [58] with appropriate decontracted auxiliary basis sets SARC/J and Def2-TZVP/C [59,60]. Increased integration grids (Grid4 for DFT and Grid4X for RIJCOSX) and tight SCF convergence criteria were used. The SARC def2-SVP basis sets were used for the hydrogen and carbon atoms while the SARC def2-TZVP basis set was used for all other atoms in BS DFT calculations.

3. Synthesis process, results, and discussion

3.1. Synthesis process

Pale red block crystals of **1** have been afforded through a hydrothermal reaction between the complex precursor cobalt (II) sulfate heptahydrate and 2-methylimidazole in methanol. The resulting solution was transferred to a sealed Teflon-coated stainless-steel autoclave and placed in a programmable stove. After heating for 24 h at 140 °C (heating rate 5 °C/min), the autoclave was cooled at the same speed to 100 °C and held for another 24 h before being cooled down to room temperature at 2 °C/min. The resulting crystals were filtered off, washed with distilled water, then air-dried.

3.2. Results and discussion

3.2.1. Infrared spectroscopy

The IR spectrum of **1** (Fig. 1) displays broadband at 3154 cm⁻¹, which can be attributed to the ν (C–H) stretching modes of the 2-mim ring. The relatively weak bands in the [2800–3000 cm⁻¹] spectral range corresponding to the methyl group of 2-mim. ν (C = N) of 2-mim appeared as a strong band at 1420 cm⁻¹. Bands from 1413 to 1635 cm⁻¹ correspond to the C–C and C–N stretches vibration of the organic ligand [61]. Stretching vibration modes of 2-mim ring can be observed at 1059–1400 cm⁻¹ regions for this complex, while deformation vibration modes can be detected in the wavenumber range 678–865 cm⁻¹ [62]. The bands noticed at 601, 928 and 1011 cm⁻¹; correspond to ν_1 , ν_3 and ν_4 stretching and bending mode of the free sulfate groups, respectively [63]. The presence of crystal water molecules was evidenced by the appearance of the broad absorption bands at 3473 cm⁻¹ [64].

3.2.2. Thermal behaviour

The thermal stability of the studied crystal was established by a simultaneous TGA/DSC analysis under air while increasing the temperature at a rate of 10 K/min from ambient temperature up to 800 °C. As shown in Fig. 2, the weight loss is steady over a large temperature range. The compound is stable up to 97 °C, after which decomposition starts until 150 °C with a weight loss of about 3.52%, corresponding to



Fig. 1. The Infrared spectra of [Co(2-mim)₄]SO₄·H₂O (KBr pellet).



Fig. 2. Simultaneous TG-DTA curves for the decomposition of $[Co(2-mim)_4]$ SO₄·H₂O under air at a rate of 10 K/min.

the removal of one water molecule per formula unit (3.58% theoretical). Upon further heating, an abrupt weight loss of 65.3% is observed between 250 and 350 °C, due to the loss of four coordinated molecules of 2methylimidazole (65.48% theoretical). This coincides with endothermic peaks on the DSC curve. A further weight loss of 18.91% observed in the temperature range 350–650 °C corresponds to the loss of one sulfate group (19.15% theoretical), associated with an exothermic peak on the DSC curve. The remainder complex of the last step is expected to be the cobalt oxide (CoO) as a final product.

3.2.3. Crystal structure determination

The molecular structure of **1** in the solid-state has been determined by single-crystal X-ray diffraction analysis. The ORTEP diagram is shown in Fig. 3 and selected bond lengths (Å), bond angles (°), and torsion angles (°) are gathered in Table 1.

The title compound crystallizes in the monoclinic crystal system with the space group P_{2_1}/c . The asymmetric unit (Fig. 3) consists of one [Co (2-mim)₄]²⁺ cation, one sulfate anion and half a molecule of water. The cobalt complex reveals a tetrahedral coordination sphere, occupied by nitrogen atoms of four distinct 2-mim ligands, with a τ_4^{-1} value [64] of 0.97, indicating a small degree of distortion. The N–Co–N angles are varying from 107.42(6)° to 112.21(7)° and the Co – N bond lengths span from 1.990(16) to 2.008(15) Å (Table 1). Those values agree with those found in other cobalt imidazole analogue [65]. The packing of the different molecular entities is displayed in Fig. 4; the projection along the a-axis reveals a supramolecular layered structure built of an alternate stacking of [Co(2-mim)₄]²⁺ cations, between which are intercalated the water molecules and the sulfate anions.

An intricate network of hydrogen bonds ensures the interconnection of the different components in the crystal (Fig. 5, Table 2). Two molecules of each water and sulfate form a crown-shaped macromolecular hydrogen bond pattern including 12 atoms. Each of the therein-involved oxygen atoms (O2, O3) also interacts with the NH functionality of a 2mim entity (N6, N4). O1 acts as a trifurcated acceptor with N2, N4, and N8. The remaining O4 atom is not involved in intermolecular interactions. The number of hydrogen bonds is reflected in the S–O bond distance, which decreases via O1 > O2 \approx O3 > O4, in turn showing that the S1–O4 bond possesses the highest degree of double bond character.

¹ $\tau_4 = [360-(\alpha + \beta)]/141$, where α and β are the two largest ligand-metal-ligand angles of the coordination sphere. For a perfect square planar geometry, τ_4 is equal to zero, while it becomes unity for ideal tetrahedral geometry.



Fig. 3. ORTEP (50% probability level) of the asymmetric unit of the molecular structure of 1 together with the atom numbering scheme. H atoms labels have been omitted for clarity.

Table 1			
Selected bond	geometries	(Å/°)	of 1

S101	1.4943 (13)	N3-Co1-N5	109.92 (7)
S1-O2	1.4755 (14)	N3-Co1-N7	112.21 (7)
S1-O3	1.4706 (15)	N5-Co1-N7	108.27 (6)
S104	1.4504 (14)	N3-Co1-N1	110.40 (7)
Co1–N3	1.9906 (16)	N5-Co1-N1	107.42 (6)
Co1–N5	1.9970 (16)	N7-Co1-N1	108.48 (6)
Co1–N7	2.0075 (16)		
Co1–N1	2.0081 (15)		
05–H10	0.87 (4)	H10-05-H20	106 (3)
O5–H2O	0.92 (4)		
O3-S1-O2	109.70 (9)	N2-C3-N1-Co1	172.56 (13)
04-S1-01	109.72 (8)	N4-C7-N3-Co1	174.10 (14)
03-S1-01	107.16 (8)	C10-C9-N5-Co1	179.60 (13)
O2–S1–O1	108.11 (8)	N8-C15-N7-Co1	176.72 (13)

3.2.4. Hirshfeld surface analysis

Fig. 6 shows a view of the three-dimensional HS of 1 plotted with the normalized contact distance (d_{norm}) over electrostatic potential energy in the range -0.7097 to 1.3566 a.u. The water molecule and the sulfate group are involved in a strong O–H…O hydrogen bond interaction highlighted in the d_{norm} surface as deep red circular spots near the hydrogen atoms of the 2-mim ligand.

The associated 2D fingerprint plots (Fig. 7) point out that the $H \cdots H$ interactions, depicted as a central spike, comprise the major contribution in the crystal stability comprising 51.6% of the total HS. The second important intermolecular contact for our complex corresponds to the $O \cdots H$ interactions, with 20.2% of the whole surface. The $C \cdots C$ contacts appear as a pair of wings in the fingerprint plot, while $C \cdots N$ contacts are depicted in the shape of a butterfly, showing a contribution of 18 and 8.7%, respectively. Furthermore, some other interactions with a minor quantitative contribution to the crystal packing sustainability are noticed, such as $C \cdots N$ (0.5%), $O \cdots N$ (0.5%), and $C \cdots C$ (0.3%) contacts.

3.2.5. UV-vis absorption analysis

The UV–Vis absorption spectra of the compound **1** (Fig. 8) displays two well-resolved bands, with one at 561 nm characteristic for d–dtransitions within tetra-coordinated Co(II) complexes, and at 266 showing the $\pi \cdots \pi^*$ transition within the aromatic ligand entities [66].

Based on the Tanabe-Sugano diagram for tetrahedral Co(II), three spin-allowed bands are expected in tetrahedral cobalt(II) complexes, that is, ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(F)$, ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$ and ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$. Generally, in such complexes and taking into consideration that in the tetrahedral coordination, the crystal field strength D_{q} is remarkably lowered, the two bands associated with the transition of the two first excited levels (${}^{4}T_{2}(F)$ and ${}^{4}T_{1}(F)$), should be shifted to the infrared region [67]. Whereas the third band arising from the transition ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$ is usually observed as a well-defined shoulder at about 550 nm [68], which is, in our case, located at 561 nm.

Apart from *d*-*d* transitions, the complex shows a strong band centered at 266 nm are ascribed to the $\pi \cdots \pi^*$ transition within the aromatic ligand entities.

To determine the bandgap energy of our complex, an accurate spectrophotometric method has been applied based on the combination between the commonly used Tauc relationship Eq. (1) [69] and the so-called Kubelka-Munk function F(R) Eq. (2) [70,71] given by those formulas:

$$\alpha h\nu = A \left(h\nu - E_{op} \right)^n \tag{1}$$

Where α , h, A, ν , E_g are the absorption coefficient, the Planck's constant, the absorption constant, the light frequency, and the optical band gap energy, respectively.

The exponent *n* in Eq. (1) is a constant related to the type of the optical transitions (n equals to 2 for an indirect allowed transition, 3 for an indirect forbidden transition, 1/2 for a direct allowed transition, and 3/2 for a direct forbidden transition).

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{s}$$
(2)

Where *R* is the absolute reflectance of the sample, α is the absorption coefficient and *s* is the scattering coefficient.

The plot F(R) versus $h\nu$, depicted in Fig. 9, permits the calculation of the intermediate optical band gap E_{op} by fitting the flat section of the curve. E_{op} can be defined as the onset of photon absorption. This value is slightly lower than the value of the electronic bandgap as given in this expression: $E_g = E_{op} - E_B$, where E_B is the excitonic binding energy. The



Fig. 4. Packing of 1 along the crystallographic a-axis.



Fig. 5. Packing of 1 showing hydrogen bonds interaction network with the view along with the crystallographic c-axis.

Table 2	
Hydrogen bonds	properties (Å/°) for 1.

D–H···A	<i>d</i> (D–H)	<i>d</i> (H…A)	<i>d</i> (D…A)	∠D–H…A
N2-H2N-01	0.88(2)	1.91(2)	2.758(2)	164(3)
N4-H4N…O1	0.87(3)	2.43(3)	3.056(2)	129(3)
N8-H8N…O1	0.87(3)	1.87(3)	2.733(2)	173(3)
N6–H6N…O2	0.87(3)	1.84(3)	2.695(2)	173(3)
05–H10…02	0.87(3)	2.11(3)	2.959(3)	168(3)
N4–H4N…O3	0.87(3)	1.99(3)	2.826(2)	160(3)
O5-H20O3	0.92(4)	2.06(4)	2.979(3)	173(3)

scheme in Fig. 9 illustrates this difference.

The obtained E_{op} value is equal to 2.48 eV and it will be exploited to determine the n in the Tauc relationship Eq. (1) as follow:

$$n = \frac{Ln(\alpha h\nu)}{Ln(h\nu - E_{op})}$$
(3)

Where the absorption coefficient α can be replaced by F(R) [72]. At the point when the material disperses in a completely diffuse way, the scattering coefficient *s* in Eq. (2) is constant regarding wavelength [73].

The slope of the plot $\ln(F(R)h\nu)$ versus $\ln(h\nu - E_{op})$ gives a value of n equal to 0.53, indicating a direct allowed transition.



Fig. 6. Hirshfeld surface mapped with *d_{norm}* around the asymmetrical unit of 1.

Considering the *n* value previously obtained, the electronic bandgap energy is extracted from the plot $(F(R)h\nu)^{1/n}$ versus $h\nu$ (Fig. 10), by extrapolating the values of the y-axis to zero: $E_g = 2.6$ eV, suggesting a semi-conductor behaviour of our compound.

3.2.6. Magnetic properties and theoretical calculations

The temperature dependence of the χT product (Fig. 11) and field dependence of magnetization at several temperatures (plotted against the reduced field in Fig. 12) was studied to estimate the crystal-field parameters of Co(II) ion and exchange interactions in **1**. The room--temperature value of the effective magnetic moment of **1**, $\mu_{eff} = 4.34\mu_B$ (μ_B is Bohr magneton) corresponds to $\chi T = 2.36$ emuK/mol. It is higher than the spin-only value $\mu_{eff} = 3.9\mu_B$ for high-spin Co(II) (3d⁷ ion with S = 3/2) calculated for g = 2.0, which indicates some influence of the spin-orbit coupling. The χT product gradually decreases at lowest temperatures reaching only 1.72 emuK/mol at 1.8 K. No difference between zero-field cooled (ZFC) and field-cooled (FC) magnetic response was observed ruling out magnetic ordering or the presence of the blocking temperature at low temperatures. The deviation between the magnetization curves plotted against the reduced field between 1.8 K and 15 K show the presence of the sizable anisotropy.

The ground electronic state of Co(II) ions in an ideal tetrahedral environment represents the crystal-field term ${}^{4}A_{2}$ with zero-field splitting (ZFS) parameter D = 0. The ground term is well separated from the first excited terms with the excitation energy to the ${}^{4}T_{2}$ in the order of 5000 cm⁻¹. The distortion to a flattened or elongated bisphenoid leads to the ground state ${}^{4}B_{1}$ with D_{2d} symmetry. Upon both distortions, it is possible to describe two Kramers doublets of ${}^{4}B_{1}$ state by the effective spin Hamiltonian with non-zero ZFS parameters (negative or positive D) [74]. The D-values usually span the typical range from –15 to 11 cm⁻¹ [75], but some extreme |D| > 50 cm⁻¹ values were reported in the literature [26–31]. For the analysis of the magnetic response, the effective spin Hamiltonian taking into account ZFS parameters D and E including a Zeeman term was used in the form

$$\widehat{\mathscr{H}}_{ZFS} = D\left[\widehat{S}_z^2 - S(S+1)/3\right] + E\left[\widehat{S}_x^2 - \widehat{S}_y^2\right] + \mu_B \widehat{S}\overline{g}\widehat{H}.$$
(4)



Fig. 8. Optical absorption spectra of [Co(2-mim)₄]SO₄·H₂O dissolved in DMSO.



Fig. 7. 2D fingerprint plots of the title complex showing the areas of different intermolecular contacts.



Fig. 9. Plot of F(R) versus $h\nu$ for [Co(2-mim)₄]SO₄·H₂O, and a scheme illustrating the difference between the intermediate optical bandgap and electronic bandgap.



Fig. 10. Plot of $[F(R)h\nu]^2$ versus $h\nu$ for a direct gap.



Fig. 11. Experimental χ T product measured in the applied field of 1 kOe (open symbols) compared with fit using Eq. (4) employing spin-Hamiltonian formalism (simultaneous fit of χ T vs. T and M vs. H, red and χ T vs. T only fit, blue line) and simulation result obtained from SA-CASSCF/NEVPT2 calculations (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. Experimental magnetization *vs.* reduced field measured up to 70 kOe (open symbols) compared with the result of the simultaneous fit of χT *vs.* T and M *vs.* H using spin Hamiltonian (blue and red solid line) and with the result of the simulation obtained from SA-CASSCF/NEVPT2 calculations (blue and red dashed lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The resulting temperature dependence of the susceptibility including the intermolecular interactions introduced in the frame of the meanfield theory [76] can be written in the form

$$\chi = \chi_S \bigg/ \bigg(1 - \frac{zJ}{N_A g^2 \mu_B^2} \chi_S \bigg), \tag{5}$$

where χ_S is the susceptibility of isolated ions, N_A is Avogadro constant, g is average g-factor, and exchange interaction J with neighboring z molecules. The χ_S represents the sum of the ZFS contribution, χ_{ZFS} , based on effective spin Hamiltonian Eq. (4) and underlying temperatureindependent paramagnetism, χ_{TIP} (which eventually can include the possible correction to the estimation of diamagnetic contribution using Pascal's constants). The calculation of susceptibility and magnetization based on Eqs. (4) and (5) was performed using EasySpin [77] toolbox in MATLAB environment. The average magnetic response was calculated from the distribution of the magnetic-field vector over the triangular orientational grid to account for the polycrystalline characteristics of the sample. A simultaneous fit of the temperature dependence of χT vs. T and M vs. H (measured at 1.8 K) was performed neglecting intermolecular interactions since the inclusion of both rhombic ZFS term E and intermolecular interactions in the frame of the mean-field theory for powder magnetization is not trivial. The fit shown in Figs. 11 and 12 yielded D = -5.45(2) cm⁻¹, E/D = 0.011(5) and g-factor components g_x $= g_y = 2.154(5)$, and $g_z = 2.297(5)$ (g_x , $g_y < g_z$ relation agrees with the expectations for easy-axis anisotropy, constraints on g-factor components $g_x = g_y$ were applied in the fitting procedure according to *ab initio* calculations, vide infra) with $\chi_{TIP} = 2.97(3) \times 10^{-4}$ emu/mol that would be the result of the flattening of the coordination tetrahedron. A separate fit the χT vs. T using Eq. (5) was performed to estimate the magnitude of the intermolecular interactions yielding $D = -5.43(2) \text{ cm}^{-1}$, E/D = 0.04(1), zJ = 0.11(2) cm⁻¹ and g-factor components $g_x = g_y = 2.195(5)$, and $g_z = 2.222(5)$ with $\chi_{TIP} = 2.86(3) \times 10^{-4}$ emu/mol (see Fig. 11). Some deviations from the first set of the parameters are not surprising since the susceptibility of the powder sample is quite insensitive to the change of the rhombic parameter E when intermolecular interactions are also included. Nevertheless, the resulting ferromagnetic intermolecular interaction and rhombic parameters are very small and can be neglected in the analysis of the magnetic properties. Obtained ZFS parameters allow the calculation of the energy difference between the two lowest Kramers doublets as $\Delta = 10.9 \text{ cm}^{-1}$ (using formula $\Delta = 2\sqrt{D^2 + 3E^2}$) that could be expected as an energy barrier for the spin reversal in the case of easy-axis anisotropy.

To be able to apply some constraints on the spin Hamiltonian

parameters in the analysis of magnetic properties and to verify their plausibility, ab initio calculations were performed in ORCA on isolated $[Co(2-mim)_4]^{2+}$ cations of the compound **1**. As was shown recently [78], the inclusion of the second coordination sphere including the anions close to cation can significantly affect the resulting values of the ZFS parameters in Co(II) and Fe(II) complexes. For the comparison, the calculations were performed also on a molecular unit comprising [Co(2- \min_{4}^{2+} cation and four nearest SO₄²⁻ anions as shown in Fig. S1a, ESI. The results of the SA-CASSCF/NEVPT2 calculations using the approach of the SOC contribution to the effective spin Hamiltonian using the atom positions estimated from the X-ray diffraction are summarized in Table 3). Both ZORA and DKH Hamiltonians were used to account for relativistic effects but the obtained differences were negligible, so only the results within DKH formalism are presented. As one can see, an enhancement of the axial parameter D was obtained when the second coordination sphere is included. The predicted values of ZFS parameters are in very good agreement with the experimental results showing the importance of anions surrounding the molecule with the active metal center. The resulting energy gap between the ground Kramers doublet and the first of the doublets in the excited ${}^{4}T_{2}$ term is predicted to be of a typical value of 5207 cm⁻¹, which means that the two lowest Kramers levels are well separated from higher excited states, justifying the use of the effective spin Hamiltonian in the case of tetrahedral Co(II) ions. The χT vs. T and M vs. H dependences calculated directly by ORCA using the obtained set of parameters for the second coordination sphere shown in Figs. 11 and 12 agree perfectly with the experimental data.

In addition to SA-CASSCF/NEVPT2 calculations, the BS DFT calculations were performed on a selected pair of $[Co(2-mim)_4]^{2+}$ cations as shown in Fig. S1b, ESI. For the comparison, popular B3LYP, TPSSh, and PBE0 exchange–correlation functionals were used in BS DFT calculations to estimate the magnitude of the intermolecular interactions. The resulting exchange interactions obtained using different exchange–correlation functionals are $J_{BS} = -0.25 \text{ cm}^{-1}$ (B3LYP), $J_{BS} = 0.12 \text{ cm}^{-1}$ (TPSSh), and $J_{BS} = 0.25 \text{ cm}^{-1}$ (PBE0). These fluctuations might suggest that the exchange interaction is indeed very small, perhaps within the accuracy of the method, but in comparison with the analysis of the experimental data ($zJ = 0.11 \text{ cm}^{-1}$, using the mean-field theory for the intermolecular interactions) it seems to be ferromagnetic.

Another tool to determine the parameters of the effective spin Hamiltonian is EPR. As discussed above, Co(II) ions in a tetrahedral environment can be described by the effective spin Hamiltonian Eq. (4) for spin S = 3/2 with ZFS parameters D and E. For the easy-axis anisotropy (D < 0) two Kramers doublets separated by the energy gap $\Delta = 2\sqrt{D^2 + 3E^2}$ are present in the energy spectra. While for E = 0 only transitions between the levels of the excited doublet with $M_S = \pm 1/2$ are allowed, a non-zero rhombic term allows also transitions between the ground-state doublet with $M_S = \pm 3/2$. In the X-band frequency range, no EPR transitions can be observed between the levels of the groundstate and excited doublet in our field range up to 10 kOe, the energy gap only affects the thermal population of doublets and the temperature dependence of the intensity of EPR spectra components. The X-band EPR spectra of complex 1 were measured in the temperature range from 2 K to 30 K (Fig. S2, ESI), the peak-to-peak signal intensity is clearly decreasing with increasing temperature above 10 K. An anisotropic broadening and eventual change of thermal population of energy levels lead to a slight change of the spectra obtained below 5 K. The spin

Hamiltonian formalism using Eq. (4) was applied for the analysis of the EPR spectra using the EasySpin simulation package [77]. The simulation attempts have shown that for the values of D parameter close to the one obtained from the analysis of the magnetic properties and ab initio calculations the shape of the spectra mainly depends on E/D ratio and weakly on g-factors. We were able to simulate spectra similar to the experimental ones for D < 0 only and for very small values of 0.04 < E/D < 0.08. The evolution of the X-band EPR spectra depending on the ratio *E/D*, with fixed *D* and *g*-values according to the previous analysis, are shown as a colormap plot in Fig. S3 ESI. The high-field components of the spectra important for the estimation of E/D originate from the transition between the levels of ground-state doublet and they vanish at sufficiently high temperature. The strongest component at 1.5 kOe originates from transitions between the levels of the excited doublet, its integral intensity should increase below about 5 K then gradually decrease with the increasing temperature (a small increase of the intensity might not be obvious from the derivative of the absorption spectra at low temperatures due to its anisotropic broadening). In the following, the axial ZFS parameter was fixed to D = -5.4 cm⁻¹, and the g-factors were adjusted close to the values as predicted from ab initio calculations. The best agreement with the experimental EPR spectra was obtained for E/D = 0.045, $g_x = g_y = 2.19$, and $g_z = 2.4$ (Fig. 13, comparison with the spectra measured at 10 K is shown). An anisotropic convolutional broadening of $\Delta H_x = 700$ Oe, $\Delta H_y = 350$ Oe, and $\Delta H_z =$ 550 Oe was used in the simulation. Although the obtained g_z is higher as expected and a small low-field peak cannot be satisfactorily described, the limitation of the *E/D* ratio given by the EPR spectra confirms its very low value, resulting in a negligible rhombic ZFS parameter. Once the hyperfine interaction is included in the model one can reduce g_z value more and shift low-field peak close to the experimental position, but that could lead to overparameterization of the model.

Following examples of Co(II)-based SIMs displaying a slow magnetic relaxation, the investigation of the dynamic response of **1**, AC susceptibility measurements, at low temperatures and in different applied static (DC) magnetic fields were performed. A signature of high-frequency relaxation above 10 kHz was observed in the zero-magnetic field at 2 K. The application of the DC magnetic field slows down the



Fig. 13. X-band EPR spectrum of **1** measured at 10 K (black line) including a simulation (red line) using spin Hamiltonian using the parameter set as described in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Comparison of the spin Hamiltonian parameters for 1 derived from SA-CASSCF/NEVPT2 calculations with active space CAS(7,5) using DKH Hamiltonian done in ORCA and from experimental data.

	$D ({\rm cm}^{-1})$	E/D	g 1	g 2	g 3	g _{avg}	Δ (cm ⁻¹)
$[Co(2-mim)_4]^{2+}$	-4.92	0.034	2.188	2.196	2.244	2.209	9.9
[Co(2-mim) ₄](SO ₄) ₄] ⁶⁻	-5.29	0.010	2.188	2.196	2.247	2.210	10.6
Experiment, $zJ = 0$	-5.45	0.011	2.154	2.154	2.297	2.203	10.9
Experiment, $zJ \neq 0$	-5.43	0.04	2.195	2.195	2.222	2.204	10.9

high-frequency (HF) relaxation channel and slows it down below 10 kHz. At higher magnetic fields another relaxation channel appears in the low-frequency (LF) region close to 1 Hz, which is also slowed down by the magnetic field (Fig. S4). The presence of the zero-field relaxation is expected for Co(II) SIMs with easy-axis anisotropy confirmed for compound **1**. The existence of multiple relaxation channels in SIMs has been predicted theoretically [79–81] and also observed experimentally in tetrahedral Co(II) SIMs [82–86]. The field dependence of the relaxation time of both, LF and HF relaxation channels, estimated at 2 K, was extracted from AC susceptibility data by fitting the modified Debye function with two relaxation channels described by the formula Eq. E1 ESI (corresponding Cole-Cole plots for selected field values are shown in Fig. 14a).

First, we analyzed the behavior of the HF relaxation channel (Fig. 14b). The relaxation slows down with the increasing DC field up 0.2 kOe and then accelerates again upon further increase of the DC magnetic field. The field dependence of the relaxation time reminds the behavior observed in e.g. [32,83,87,88]. The maximum in the field dependence of the relaxation time is the result of the competition between two field-dependent relaxation processes. The high-field decrease of the relaxation time is assigned to the field-supported one-phonon direct relaxation process between the levels of the ground Kramers doublet with $\tau_{\rm D}^{-1} = ATH^4$. The magnetic field in this case increases the energy separation of the two spin states, so the phonon density with an energy corresponding to this difference is higher. The low-field increase is often assigned to the quantum-tunneling of magnetization (QTM), but in our case, QTM seems not to be present in compound 1 since the temperature dependence of the relaxation time measured in a small applied DC field does not tend to saturate at low-temperatures (vide infra) and our attempt to include the field dependence of QTM in the form $\tau_{OTM}^{-1} = \frac{D_1}{1 + D_2 H^2}$ did not yield a correct description of the field dependence of $\tau_{\rm HF}$. Another possibility is to include the field-dependent Raman process described by Brons-Van Vleck formula $\tau_{BVV}^{-1} = \tau_{ZF}^{-1} \frac{1+dH^2}{1+eH}$ promoted by spin-spin and spin-nuclei interactions that are suppressed by increasing the DC field [89-92]. A good agreement of the experimental $\tau_{HF}(H)$ dependence was obtained using a combination of $\tau^{-1} =$ $\tau_{BVV}^{-1} + \tau_D^{-1}$ with parameters $A = 13.26 \times 10^{-12} \text{ s}^{-1} \text{Oe}^{-4} \text{K}^{-1}$, $\tau_{ZF} = 3.37 \times 10^{-6} \text{ s}$, $d = 4.51 \times 10^{-6} \text{ Oe}^{-2}$, and $e = 55.26 \times 10^{-6} \text{ Oe}^{-2}$.

Next, one DC magnetic field was selected (close to maximum relaxation time and signal magnitude of the imaginary component of AC susceptibility) to study the temperature dependence of the relaxation time $\tau_{\rm HF}$. The corresponding frequency-dependent AC susceptibility at different temperatures in the applied DC field of 1.5 kOe is shown in Fig. S5 showing the gradual acceleration of the relaxation time upon warming up, the corresponding Cole-Cole plots analyzed using the modified Debye model (Fig. 15a) yielded the temperature dependence of the relaxation time presented in Fig. 16. Since there is no saturation of the relaxation time in the low-temperature region (the analysis of the

field dependence of $\tau_{\rm HF}$ excluded OTM), the OTM process was neglected. The direct relaxation process represents also a small contribution at low magnetic fields (it dominates high-field regime as shown from the analysis of the field dependence of the relaxation time). Therefore, for the easy-axis anisotropy present in 1 it is expected that a contribution of the two-phonon Orbach and Raman relaxation process governs the spin reversal with $\tau_{ORB}^{-1} = \tau_0^{-1} e^{-\frac{U_{eff}}{k_B T}}$ and $\tau_R^{-1} = CT^n$, where U_{eff} is the energy barrier for thermally activated relaxation within the Orbach process. The exponent *n* describing the Raman process has a value n = 9 for Kramers ions with an insulated ground doublet [93], but in SIMs often takes lower values due to the involvement of both acoustic and optical phonons [94]. Since the Orbach process requires exact thermal energy of participating phonons comparable to the energy barrier it is more effective at higher temperatures than the Raman process. In the Arrhenius type plot in Fig. 16, one can see a small change of the slope between the low-temperature and high-temperature regimes. The simple fit of the τ_{OBB}^{-1} in the high-temperature region yields attempt time $\tau_0 = 6.1 \times 10^{-8}$ s and energy barrier $U_{eff} = 9.8 \text{ cm}^{-1}$ (or $U_{eff}/k_{\rm B} = 14.1 \text{ K}$) close to the expected value $U_{eff} = \Delta = 10.9 \text{ cm}^{-1}$ as obtained from the analysis of static magnetic response. To describe the temperature dependence of the relaxation time in the full temperature range influence of the Raman process was included $\tau_{HF}^{-1} = \tau_{ORB}^{-1} + \tau_R^{-1}$ and the fit shown in Fig. 16 resulted in $\tau_0 = 5 \times 10^{-8}$ s, $U_{eff} = 11.4 \text{ cm}^{-1}$ (16.4 K), $C = 1106.9 \text{ K}^{-n}$, and n = 3.67. Since there is no significant change of the slope in $\ln \tau_{HF} \propto$ 1/T dependence one cannot say which of the relaxation mechanisms is dominant in most of the temperature range but clearly, Orbach process typical for the spin reversal in SIMs with easy-axis anisotropy was identified with the energy barrier predicted by the analysis of the static magnetic response, EPR and SA-CASSCF/NEVPT2 calculations.

The relaxation time $\tau_{\rm LF}$ of the LF relaxation channel is increasing in the DC magnetic field up to much higher values (11 kOe) in comparison to the HF relaxation channel (Fig. 14b). Such behavior was observed also in the low-frequency relaxation channels of other SIMs, see e.g. [95–101], and is also attributed to the influence of the intermolecular interactions. Its temperature dependence was further studied in a higher magnetic field of 5 kOe to increase the magnitude of the imaginary component of the AC susceptibility. The frequency-dependent AC susceptibility in the temperature range from 1.9 K up to 3 K (where the imaginary component magnitude becomes negligible) is shown in Fig. S6. The temperature dependence of the relaxation rate was obtained from the analysis of Cole-Cole diagrams using the modified Debye model (a second modified Debye component was included in the fit to account for the shoulder of the HF relaxation mode that is still not suppressed at 5 kOe) as shown in Fig. 15b. An interesting behaviour was observed, relaxation time τ_{LF} is decreasing when increasing the temperature up to 2.5 K followed by the subsequent increase of $\tau_{\rm LF}$. This was reported also in several Co(II)- or Mn(III)-based systems, or even in Gd(III)-, Mn(II)-, Cu(II)-based magnets with negligible or no ZFS [83,97,98,101-104]



Fig. 14. a) Cole-Cole plots of 1 at different applied DC fields measured at 2 K including the fits of the modified Debye model with two relaxation channels. b) Field dependence of the relaxation time of HF and LF relaxation channel.



Fig. 15. a) Cole-Cole plots of **1** obtained at 1.5 kOe in the temperature range 1.8–3.5 K in the high-frequency region including the fits of the modified Debye model. b) Cole-Cole plots of **1** obtained at 5 kOe in the temperature range 1.9–3 K in the low-frequency region including the fits of the modified Debye model.



Fig. 16. Temperature dependence of the relaxation time in reduced coordinates in applied DC field 1.5 kOe (HF channel, blue symbols) and 5 kOe (LF channel, green symbols). Models to describe the behaviour of the relaxation time are shown by the corresponding lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

usually for low-frequency field-induced relaxation channels. Unfortunately, this behavior is not widely discussed and its origin remains unclear. In the work of Rajnák and Boča [105], a reciprocating relaxation mechanism is proposed to explain the unusual behavior of the HF relaxation channel at low temperatures, which results from the second solution of the phonon-bottleneck effect [106] with the temperature dependence of the relaxation time $\tau^{-1} \propto T^{-1}$ that defines the rate of the change in the so-called hot-phonon excitation number. While the suggestion of the reciprocating relaxation behaviour for the high-frequency relaxation is plausible, it is questionable if this could apply to the lowfrequency relaxation, which is several orders of magnitude slower as expected for the second solution of phonon-bottleneck effect. We have tried to include the reciprocating contribution and power law in the fitting of $\tau_{LF}^{-1} = FT^{-1} + CT^n$, but no reasonable agreement was obtained. Therefore, only the fit of power dependence $\tau^{-1} = CT^n$ in the lowtemperature region below 2.5 K (Fig. 16) was performed yielding exponent n = 1.44 suggesting that LF relaxation channel is related to direct relaxation process influenced by the presence of the phononbottleneck effect [98,107,108] renormalizing the temperature dependence of the relaxation time towards $\tau \propto T^{-2}$. In summary, the HF relaxation channel in 1 is characterized by the over-barrier relaxation with $U_{eff} = 11.4 \text{ cm}^{-1}$ typical for molecular magnets with the easy-axis of magnetization. The LF relaxation channel displays an unusual temperature dependence, at low temperatures a direct relaxation process is present affected by the phonon-bottleneck effect, the high temperature slowing down of the relaxation time requires further experimental and

theoretical studies.

4. Conclusion

To sum up, a new imidazole-based complex has been successfully synthesized. Its crystal structure shows that the Co(II) metal ion is tetrahedrally coordinated with four nitrogen atoms from four distinct 2mim ligands and free sulfate anions balance the formed cationic unit. The crystal packing is governed by the formation of a significant number of O-H-O, N-H-O hydrogen bonds established between the lattice water molecules, the free sulfate anions and the $[Co(2-mim)_4]^{2+}$ cations. Further insight into these interactions was provided based on the Hirshfeld surface analysis and 2D fingerprint plots. The thermal study of our complex shows that it remains stable up to 97% then decomposes gradually to end up by the formation of the metal oxide at 710 °C. The optical band gap determined for the title compound is 2.6 eV, suggesting a semi-conductor behaviour of our compound. The presence of the characteristic bands of the functional groups of our complex was confirmed by FTIR spectroscopy. The presence of the easy-axis anisotropy with axial term D = -5.45 cm⁻¹ in **1** was confirmed by the analysis of the static magnetic response, EPR spectroscopy, and predicted by ab initio calculations. A very small rhombic term of E/D = 0.045 was revealed from the analysis of EPR spectra. Furthermore, the ab initio calculations show the importance of a large coordination sphere in the correct estimation of magnetic anisotropy. Complex 1 behaves as a fieldinduced single-ion magnet with two relaxation channels. The analysis of the high-frequency relaxation channel revealed thermally activated relaxation described by the Orbach model with energy barrier $U_{eff} =$ 11.4 cm⁻¹. The low-frequency relaxation channel appears to be affected by the phonon-bottleneck effect.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmmm.2021.168140.

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