

A Co^{II/III} oxo-carboxylate cluster featuring a Lindqvist core

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ABSTRACT: A nonanuclear mixed-valent coordination cluster, isolated as [Co^{III}₃Co^{II}₆(μ₆-O)(piv)₇(thmp)₄(MeCN)₂(H₂O)]·4(MeCN) (**1**), forms in a one-pot reaction of cobalt(II) pivalate and 1,1,1-tris(hydroxymethyl)propane (H₃thmp) in acetonitrile solution. Single-crystal X-ray diffraction analysis reveals an unusual {Co₆O₁₉} Lindqvist-type core capped by three Co sites. High-resolution ESI-mass spectrometry studies confirm the integrity of this core structure in solution, exhibiting a series of peaks corresponding to the intact cluster species. Magnetic studies indicate that the magnetic behavior in **1** is dominated by six high-spin Co(II) ions in octahedral ligand fields exhibiting weak intra-cluster antiferromagnetic exchange coupling.

KEYWORDS: cluster, cobalt, magnetism, Lindqvist structure

1 Introduction

The design and (self-)assembly of transition-metal nanoclusters remain a subject of significant interest, driven not only by their distinctive structural characteristics, but also by their diverse physicochemical properties [1-4]. In this context, mixed-valent polynuclear Co(II/III) clusters are of particular interest due to their complex magnetochemical characteristics. A key strategy for altering the magnetic performance of such nanoscale systems involves the rational modification of the core to reduce distances between spin carriers, thereby promoting efficient magnetic exchange coupling [5]. For instance, the {M₄O₄} cubane-like motif, comprising four metal centers and four bridging oxido ligands at alternating vertices, ensures close proximity of spin carriers and relatively strong magnetic coupling, which can be tuned by selecting appropriate bridging ligands. For example, several Mn-oxo clusters containing one or more Mn-cubane units, such as {Mn₁₃} [6], {Mn₂₆} [7], {Mn₃₂} [8], and {Mn₈₄} [9], have been reported to exhibit intriguing magnetic behavior. High-temperature slow magnetic relaxation has been detected in decanuclear {Co₁₀} [10] and {Ni₁₀} [11] cages, both of which possess a supertetrahedral core topology, up to 12 K and 17 K, respectively. Additionally, hexanuclear clusters based on the {Co₄O₄} cubane core have been suggested as promising structural motifs for single-molecule magnets (SMMs) [12]. Note that such metal-oxo-heteroligand clusters rarely adopt the archetypal structure motifs that characterize the thermodynamically most favorable polyoxometalates. This is primarily due to the fact that the middle transition metal ions are usually in their lower valence states and rarely tend to assemble to highly condensed metal oxo structures characterized by edge- and face-sharing MO_n coordination polyhedra, which is a key aspect of polyoxometalates.

And while very few examples of such coordination clusters that resemble polyoxometalate archetypal structures exist, most of these differ from the oxometalate ideals in several details. For example, while a few Co^{II}-based coordination clusters are known that contain a core of six edge-sharing MX₆ octahedra akin to the Lindqvist-type ideal, these contain non-oxide donor sites (X) [13], heterometals [14,15] or represent substructures of much larger assemblies and extended frameworks [10,16,17].

Recently, we reported a mixed-valence heterometallic {Mn^{II}Mn^{III}₂DyO₄} cubane units [18] and a nonanuclear {Mn₇Dy₂} cluster featuring a {Mn^{III}₆Mn^{IV}Dy₂} core [19]. The latter is based on vertex-sharing {Mn^{III}₂Mn^{IV}Dy^{III}O₄} double-cubane units, which are unprecedented in Mn-4f chemistry and exhibit single-molecule magnet (SMM) behavior [19]. As a continuation of this work, we herein report a new homometallic mixed-valent Co^{II/III} coordination cluster, which crystallizes as [Co^{III}₃Co^{II}₆(μ₆-O)(piv)₇(thmp)₄(MeCN)₂(H₂O)]·4(MeCN) (**1**) (where Hpiv = pivalic acid; H₃thmp = 1,1,1-tris(hydroxymethyl)propane). Importantly, this cluster comprises a three-capped Lindqvist-type {Co₆O₁₉} structure, and **1** represents the first mixed-valent Co-based Lindqvist compound. Alternatively, the cluster structure can be rationalized to consist of {Co^{III}₃Co^{II}₆(μ₃-O)₈(μ₆-O)} core topology of three condensed Co₄O₄ cubanes, each of which incorporating one Co^{III} and three Co^{II} ions. The remaining three vertices are occupied by μ₃-oxo positions belonging to deprotonated thmp³⁻ ligands, and one common central vertex is defined by an μ₆-oxo ion. While several polynuclear nanoclusters featuring {Co₄O₄} cubane-like cores have been previously reported, including {Co₁₀} [20, 21], {Co₁₂} [22], {Co₁₄} [23], {Co₁₆} [24], {Co₁₉} [20], and {Co₁₆Co₄} [25], the nonanuclear cluster in **1** represents a distinct addition to this family. Notably, whereas the

chemistry of cobalt coordination clusters has been largely dominated by higher-nuclearity homovalent Co^{II} cubane-based motifs (ranging from $\{\text{Co}_{10}\}$ to $\{\text{Co}_{19}\}$), **1** introduces a structurally unique nonanuclear $\{\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\}$ framework. This specific 1:2 ratio of Co^{III} to Co^{II} centers within a fused tetrahedral arrangement represents a significant departure from established structural types, providing a rare example of a discrete nonanuclear assembly in stark contrast to the few known mixed-valence systems such as the afore-mentioned $\{\text{Co}^{\text{II}}_{16}\text{Co}^{\text{III}}_4\}$ cluster [25]. **1** was characterized by elemental analysis, IR spectroscopy, magnetometry and ESI mass spectrometry. Its molecular structure was determined by single-crystal X-ray diffraction, and the magnetic properties were investigated and correlated with the structural features.

2 Results and discussion

2.1 Synthesis and crystallography

The reaction of $\text{Co}(\text{II})$ pivalate with 1,1,1-tris(hydroxymethyl)propane, in a 2.55:1 molar ratio, in an acetonitrile solution under reflux and aerobic conditions afforded the title compound, $[\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\text{O}(\text{piv})_7(\text{thmp})_4(\text{MeCN})_2(\text{H}_2\text{O})] \cdot 4(\text{MeCN})$ (**1**). (We note that even minor deviations from this molar ratio do not result in the formation of crystals.) Under these reaction conditions, a portion of the Co^{II} centers undergoes in situ oxidation by atmospheric oxygen, resulting in the formation of the mixed-valence $\{\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\}$ core. To evaluate the stability and behavior of **1** in solution, electrospray ionization mass spectrometry (ESI-MS) was performed in methanol in both positive and negative ion modes (Figs. S1-S2, Table S1). The positive-ion spectrum displays a base peak at m/z 1677, which is assigned to the cation $[\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\text{O}(\text{piv})_6(\text{thmp})_4]^+$ (calcd. m/z 1677). This species corresponds to the loss of one pivalate ligand and all coordinated solvent molecules ($[\text{M}-\text{piv}-2\text{MeCN}-\text{H}_2\text{O}]^+$). In negative-ion mode, a prominent peak at m/z 1879 was observed, corresponding to the $[\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\text{O}(\text{piv})_8(\text{thmp})_4]^-$ anion (calcd. m/z 1879), which can be described as an $[\text{M}+\text{piv}-2\text{MeCN}-\text{H}_2\text{O}]^-$ adduct. The excellent match between experimental and simulated isotopic distributions confirms that the nonanuclear $\{\text{Co}_9(\mu_6\text{-O})\}$ framework remains intact in solution, highlighting the robustness of the fused-heterocubane core.

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 14.333(1)$, $b = 27.822(1)$, $c = 23.645(1)$ Å, $\beta = 98.648(4)^\circ$, $V = 9322.0(7)$ Å³ (Table S2). The asymmetric part of unit cell consists of a $[\text{Co}_9\text{O}(\text{piv})_7(\text{thmp})_4(\text{MeCN})_2(\text{H}_2\text{O})]$ cluster and four solvate MeCN molecules. The structure of the cluster in **1** is shown in Figure 1.

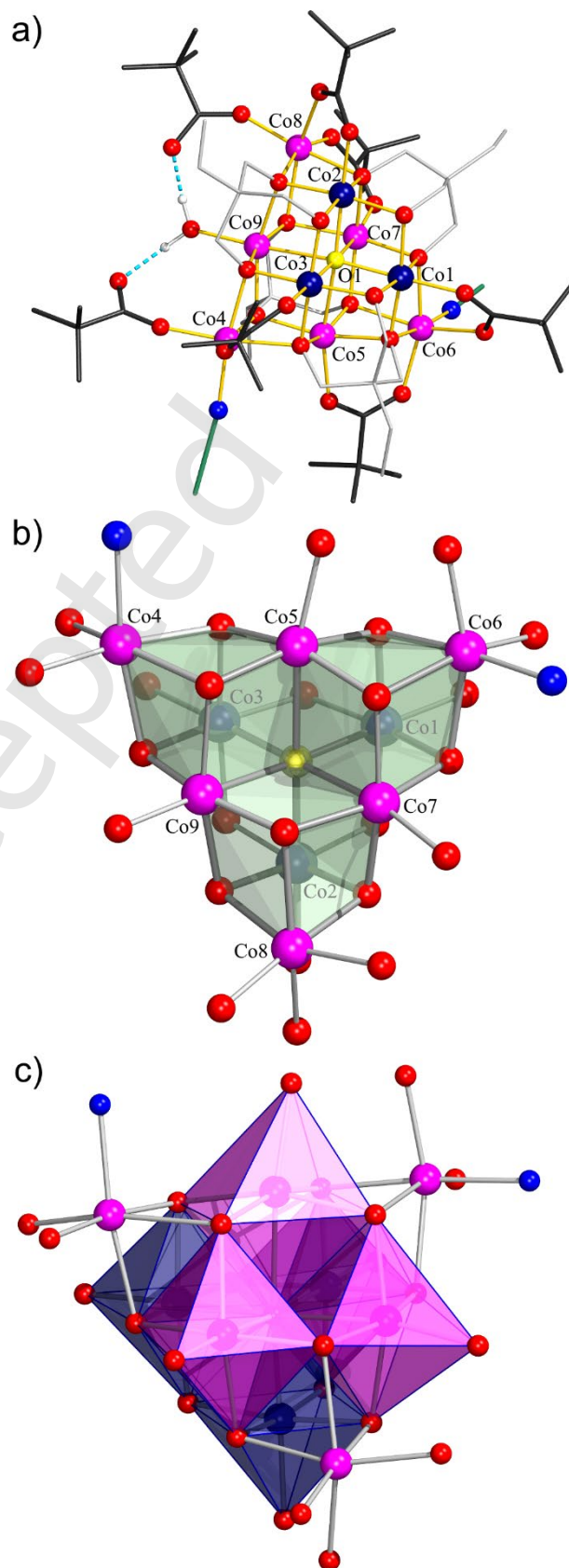


Figure 1 (a) Structure of $[\text{Co}_9\text{O}(\text{piv})_7(\text{thmp})_4(\text{MeCN})_2(\text{H}_2\text{O})]$ with partial atom numbering. Hydrogen bonds: blue dotted lines; for clarity, only the H atoms of water are shown. Co^{II} : magenta, Co^{III} : dark blue, C(MeCN): green, C(piv): dark gray, C(thmp): light gray, O: red, $\mu_6\text{-O}$: yellow, N: blue. (b) Rotated view of the mixed-valence core highlighting the three $\{\text{Co}^{\text{II}}_3\text{Co}^{\text{III}}_4\}$ cubane-like units; organic constituents omitted for clarity. (c) Polyhedral representation of the Lindqvist-type $\{\text{Co}_6\text{O}_{19}\}$ substructure and the three

adjoined Co sites.

The cluster core comprises six Co^{II} and three Co^{III} atoms interconnected by a μ_6 -oxido ion, four thmp³⁻ ligands, and five bridging piv⁻ moieties. The coordination spheres of the peripheral Co^{II} centers are completed by various ligands: Co4 by one MeCN and a monodentate piv⁻ ligand; Co6 by one MeCN molecule; Co8 by one monodentate piv⁻ ligand. Additionally, the coordination sphere of the core Co9 atom is completed by a coordinated water molecule. The core can be described as three fused {Co^{II}₃Co^{III}O₄} cubane units, connected by a common μ_6 -oxido ion (O1) at a common vertex. Moreover, each cubane has two common μ_6 -O-Co^{II} edges (O1-Co5, O1-Co7, and O1-Co9) with two neighboring cubanes. Within each cubane unit, it is defined by one μ_6 -oxido ion and three μ_3 -alkoxido oxygen atoms from three thmp³⁻ ligands, which locally bridge three Co^{II} and one Co^{III} centers (Fig. 1b).

All cobalt atoms are six-coordinate but possess distinct coordination environments. To quantify the deviation of the coordination polyhedra from ideal geometries, SHAPE analysis [26] was performed (Table S4). The Co^{III} atoms (Co1, Co2, and Co3) and Co^{II} atoms (Co5 and Co7) exhibit O₆ coordination spheres, each formed by the central μ_6 -oxido ion, four O atoms from two thmp³⁻ ligands, and one O atom from a piv⁻ moiety. According to the SHAPE calculations, these atoms reside in a slightly distorted octahedral geometry (*O_h*) with Continuous Shape Measure (CShM) values of 0.228–0.234 for Co^{III} atoms and 1.142 and 1.111 for Co^{II} atoms, respectively. The significantly lower CShM values for Co1–Co3 reflect the more rigid and symmetric environment of the Co^{III} centers compared to the Co^{II} ions. The remaining Co^{II} ions exhibit more diverse environments. The Co4 and Co6 atoms feature an O₅N geometry, formed by three O atoms from three thmp³⁻ ligands, two O atoms from different carboxylate moieties, and one N atom from a MeCN molecule; the CShM values for these atoms are 0.973 and 1.071, respectively. The Co8 atom adopts an O₆ octahedral geometry (CShM = 1.722), coordinated by three O atoms from three piv⁻ and three O atoms from three thmp³⁻ ligands. Finally, the Co9 atom is coordinated by two O atoms from two thmp³⁻, two O atoms from two piv⁻, and one O atom from a water molecule (CShM = 0.802). The observed variations in CShM values (0.2–1.7) are consistent with the diverse nature of the terminal ligands and the inherent differences in Co–O/N bond distances between the Co^{II} and Co^{III} oxidation states. For Co^{III} atoms the Co–O bond distances are in the range of 1.897–1.946 Å, whereas for Co^{II} the Co–O bond distances are longer (1.938–2.445 Å), and the Co–N bond distances are 2.084 and 2.053 Å (Table S3).

The assigned oxidation states for the cobalt centers were further confirmed by Bond Valence Sum (BVS) calculations [27, 28] (Table S5), which yielded values in the ranges of 2.99–3.00 for Co^{III} (Co1–Co3) and 1.86–2.02 for Co^{II} (Co4–Co9). These results, together with the observed variations in CShM values and bond distances (1.897–1.946 Å for Co^{III} vs. 1.938–2.445 Å for Co^{II}), are fully consistent with the nonanuclear mixed-valence nature of cluster 1. The water molecule coordinated to Co9 atom forms two strong hydrogen bonds (O...O distances are 2.565(9) and 2.573(8) Å) with oxygen atoms of monodentate piv⁻ ligands coordinated to

Co4 and Co8 atoms stabilizing their orientation.

The comparison of the experimental powder X-ray diffraction (PXRD) patterns for cluster 1 with the simulated patterns derived from single-crystal X-ray data (see Fig. S3) confirms the phase purity and homogeneity of the as-synthesized bulk material.

2.2 Magnetic properties

The data of the magnetic SQUID measurements are shown in Figure 2. At 300 K, the $\chi_m T$ values are 19.42 cm³ K mol⁻¹ at 0.1 T and slightly smaller at 1.0 T (19.30 cm³ K mol⁻¹). These values are within (although closer to the upper limit of) the range 13.9–20.3 cm³ K mol⁻¹ expected [29] for six non-interacting high-spin Co^{II} centers. Note that the three low spin Co^{III} centers show temperature-independent paramagnetism (TIP) that has been accounted for in the data correction. Upon cooling the compound, both curves show similar behavior down to about 20 K: the $\chi_m T$ values are continuously decreasing with a distinctly higher rate at $T < 100$ K. However, the $\chi_m T$ curves diverge below 20 K. While $\chi_m T$ continues to decrease with a similar slope at 0.1 T down to 7 K, and subsequently drops off to 8.90 cm³ K mol⁻¹ at 2.0 K, such a noticeable slope change occurs at 1.0 T already at 16 K, yielding 5.41 cm³ K mol⁻¹ at 2.0 K. Note that the curve at 0.1 T also potentially indicates a rather barely visible plateau in the range from 14 to 20 K.

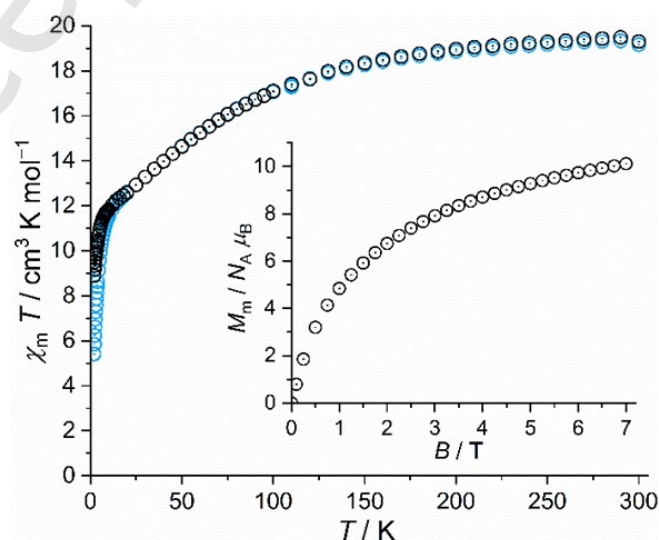


Figure 2 Magnetic measurements data of 1 shown as $\chi_m T$ vs. T curves at 0.1 T (black symbols) and 1.0 T (blue symbols); inset: molar magnetization M_m vs. applied magnetic field B at 2.0 K.

Such a behavior of $\chi_m T$, in particular between 20 and 300 K, differs from the spin-only behavior of six non-interacting $S = 3/2$ centers. However, this is well known for octahedral high-spin Co^{II} centers, where contributions from the orbital momentum are not quenched. Thus, the combined effects of electron-electron interrepulsion, ligand field and spin-orbit coupling yield such temperature-dependent instead of (almost) constant $\chi_m T$ curves at $T > 20$ K. In addition, the curves indicate the presence of exchange interactions between the Co^{II} centers, analyzing the data at $T < 20$ K. The pronounced drop offs at lower temperatures reveal weak antiferromagnetic exchange interactions, since contributions due to the Zeeman effect are, in particular, at 0.1 T

distinctly smaller. At 2.0 K, the notable difference of the $\chi_m T$ values at both applied fields is, however, due to the Zeeman effect. Finally, the potential plateau between 14 and 20 K at 0.1 T could possibly be caused by very weak ferromagnetic intramolecular exchange interactions.

At 2.0 K, the molar magnetization M_m rapidly increases at fields smaller than 2 T, and subsequently increases with a smaller slope to $10.1 N_A \mu_B$ without being saturated at 7.0 T. Not being saturated even at 7.0 T is commonly found analyzing octahedrally coordinated high-spin Co^{II} centers. Such behavior is partially due to the magnetic anisotropy of such Co^{II} centers, but mainly due to pronounced superposition of energy states characterized by different magnetic moments. However, non-interacting Co^{II} centers reach about $2.4 N_A \mu_B$ per center (about half to two thirds of the saturation value) at 7.0 T. Therefore, the lower value of $10.1 N_A \mu_B$ indicates the presence of weak antiferromagnetic exchange interactions between the Co^{II} centers within the compound.

3 Conclusions

In summary, we have synthesized the new mixed-valence nanocluster $[\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\text{O}(\text{piv})_7(\text{thmp})_4(\text{MeCN})_2(\text{H}_2\text{O})]$ via reaction cobalt pivalate with 1,1,1-tris(hydroxymethyl)propane in acetonitrile under reflux. The cluster consists of three Co_4O_4 cubane subunits fused around a central μ_6 -oxide ion, which results in a $\{\text{Co}_6\text{O}_{19}\}$ Lindqvist-type core capped by three additional Co sites. The cluster stands out from the well-known family of cobalt coordination nanoclusters based on $\{\text{Co}_4\text{O}_4\}$ cubane-like motifs by introducing a distinct 1:2 ratio of Co^{III} to Co^{II} centers within a fused heterocubane framework. SHAPE analysis further confirmed that the six-coordinate cobalt centers reside in distorted octahedral environments, with Co^{III} ions exhibiting more rigid and symmetric coordination spheres compared to their Co^{II} counterparts. Furthermore, ESI-MS studies demonstrated that the highly condensed nonanuclear framework remains intact in solution, highlighting its structural robustness.

The investigation of the magnetic properties provides an insight into the magnetochemistry of mixed-valence cobalt clusters and underscores the complex interplay between single-ion effects and exchange interactions in this compact architecture. The observed magnetic behavior is due to the well-known larger contributions of the non-quenched orbital momentum of high-spin Co^{II} centers combined with predominately antiferromagnetic exchange interactions, over the whole observed temperature range. In particular, excited energy states of the same symmetry as the ground term are energetically close so that they affect the composition of the ground state, and thus the associated magnetic moment.

This work not only highlights the effectiveness of the cubane-based strategy in constructing stable, high-nuclearity molecular architectures with intriguing structural and electronic properties, but also indicates that highly condensed, archetypal polyoxometalate structures can be realized based on the middle transition metals. Beyond structural interest, the stable mixed-valence $\{\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_6\}$ core of cluster **1** provides an attractive platform for exploring redox-active transformations, where the

coexistence of different oxidation states can be beneficial, as demonstrated by examples of related mixed-valence cobalt catalyst systems [30–32]. Moreover, the structured arrangement of anisotropic Co^{II} ions within this platform suggests its potential as a molecular precursor for the design of multimetallic magnetic materials, particularly through the incorporation of highly anisotropic 4f ions such as Dy^{III} and Tb^{III} , or as a building block for higher-order supramolecular assemblies. Future studies will focus on exploring its utility as a rigid, oxo-rich scaffold for the assembly of heterometallic Co-Ln ($\text{Ln} = \text{Dy}, \text{Tb}$) systems. The peripheral oxygen atoms of the core provide ideal coordination sites for oxophilic Ln^{III} ions, while the anisotropic Co^{II} centers offer a pathway to establish 3d–4f magnetic exchange coupling, a possible strategy for suppressing quantum tunneling of magnetization to gain pronounced single-molecule magnet (SMM) characteristics.

4 Experimental

4.1 Materials and methods

All procedures were conducted under aerobic conditions using reagents and solvents as received without further purification. Cobalt(II) pivalate was synthesized as reported elsewhere [33]. IR transmission spectrum was recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer in the range $400\text{--}4000\text{ cm}^{-1}$ (Fig. S4). Electrospray ionization mass spectrometry (ESI-MS) was performed in both positive and negative ion modes using a ThermoFisher Scientific LTQ-Orbitrap XL mass spectrometer. Samples were prepared by dissolving the cluster in MeOH containing 0.1% acetic acid. Powder X-ray diffraction (PXRD) data for a freshly prepared sample of **1** were collected on a RIGAKU MiniFlex 600 diffractometer. Magnetic properties measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. A microcrystalline sample of **1** was compacted and immobilized into a cylindrical PTFE sample holder. Magnetic dc data were recorded at 0.1 and 1.0 T in the temperature range 2.0–300 K, and at 2.0 K in the field range 0.1–7.0 T. All data were corrected for the diamagnetic contributions of the sample holder and the compound ($\chi_{m,\text{dia}} = -9.40 \times 10^{-4}\text{ cm}^3\text{ mol}^{-1}$), as well as for TIP contributions of the three low-spin Co^{III} centers ($1.48 \times 10^{-4}\text{ cm}^3\text{ mol}^{-1}$ per Co^{III} center).

4.2 X-ray crystallography

Single-crystal X-ray diffraction data for **1** were collected on an Oxford Xcalibur diffractometer equipped with a CCD detector and graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by direct methods and refined by full-matrix least-squares on weighted F^2 values for all reflections using the SHELX suite of programs [34]. All non-H atoms in the compound were refined with anisotropic displacement parameters. Several methyl groups of the pivalate ligands were found to be disordered over two positions. Therefore, SIMU, DELU, SADI, and ISOR restraints were used to deal with the disordered moieties in the structures and to obtain reasonable geometric parameters and thermal displacement coefficients. The positions of the hydrogen atoms in the structure were either located from difference Fourier maps or calculated geometrically and refined isotropically. Crystallographic data and structure

refinements of **1** are summarized in Table S2, and selected bond distances are given in Table S3. All figures were prepared using Diamond software [34]. One MeCN solvent molecule per formula unit was localized. The contribution of additional highly disordered solvent molecules occupying the lattice voids was accounted for using the PLATON SQUEEZE tool [35]. A total of 60 electrons per formula unit was found, corresponding to approximately three MeCN molecules. The CCDC reference number for the structure is 2538845.

4.3 Synthesis

A mixture of Co(II) pivalate (0.050 g, 0.191 mmol) and 1,1,1-tris(hydroxymethyl)propane (0.010 g, 0.075 mmol) in 10 mL of MeCN was refluxed for 30 min. The resulting brown solution was filtered and the filtrate was allowed to evaporate slowly in a vial covered with a perforated plastic cap. After 20 days, green crystals of **1**, suitable for single-crystal X-ray analysis, were filtered off, washed with 10 mL of MeCN and air-dried. Yield: 0.030 g, (79% based on H₃thmp). Anal. Calcd. for **1** without solvate acetonitrile, C₆₃H₁₁₅Co₉N₂O₂₈: C, 40.27; H, 6.17; N, 1.49%. Found: C, 39.86; H, 6.27; N, 1.01%. FT-IR (cm⁻¹): 3404 (w, br), 2958 (m), 2926 (m), 2868 (m), 1557 (s), 1538 (sh), 1481 (s), 1467(sh), 1402 (vs), 1367 (sh), 1352 (s), 1218 (s), 1116 (m), 1106 (sh), 1053 (s), 1013 (m), 946 (s), 890 (m), 787 (m), 770 (sh), 640 (sh), 580 (vs), 527 (m), 466 (sh), 420 (m).

Electronic Supplementary Material: Supplementary material (Spectroscopic and mass spectrometric measurements, powder X-ray diffraction (PXRD) patterns, crystal data and structure refinement details, selected bond distances, continuous shape measures (CShM), and bond valence sum (BVS) calculations) is available in the online version of this article at <https://doi.org/10.26599/POM.2026.9140163>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

D.S.: Experimental design, data collection, writing manuscript. J.v.L.: Analysis of magnetic data, writing manuscript. V.Ch.K.: Single-crystal data collections and refinement, writing manuscript. Y.C.: Data collections. P.K.: Conceptualization, writing-review manuscript, figures. S.G.B.: Conceptualization, writing-review manuscript. All the authors have approved the final manuscript.

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