

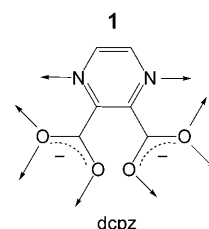
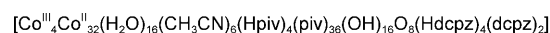
A Co₃₆ Cluster Assembled from the Reaction of Cobalt Pivalate with 2,3-Dicarboxypyrazine**

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High-nuclearity transition-metal clusters are of remarkable interest in chemistry and physics because their dimensions and physical properties play a central role linking the microscopic and macroscopic world, and quantum and classical systems. The smallest classical nanoparticles fabricated today are on the same order of size as the largest metal clusters synthesized by bottom-up methods.^[1] Transition-metal clusters can exhibit single-molecule magnetism at low temperatures,^[2] that is, they show magnetic bistability as classical macroscopic magnets, but at the same time they also may exhibit quantum tunneling of magnetization (QTM),^[3] which is clearly not a classical physical property. For these reasons transition-metal clusters are of great relevance from the viewpoint of basic research, and applications have been proposed relating to memory devices^[4] and quantum computing.^[5]

Although reports on new polynuclear 3d metal complexes continue to appear, the size limit has not definitely been reached and new records can still be established. For example, considering only homonuclear clusters, the largest iron compound, Fe₆₄, has recently been reported,^[6] whereas for nickel the record compound Ni₃₄ was reported more than twenty years ago.^[7] Of the 3d metal ions, cobalt is particularly attractive with regard to high-nuclearity clusters because of its enormous flexibility in adopting different coordination environments, both, in terms of coordination number and geometry. To date, the largest homonuclear cobalt cluster reported is a Co₂₄ unit whose structure is based on [Co₃(OH)₄]²⁺ cubes with all the cobalt ions in the +II oxidation state.^[8] We report herein a new record holder, the mixed-valent Co₃₆ cluster **1** (scheme 1).^[9]

One possible strategy for building up clusters of higher dimensionality is the use of polydentate ligands which have the capability to coordinate to several metal centers. Among the extensive library of this type of ligand, 2,3-dicarboxypyrazine (H₂dcpz; Scheme 1) appears to be largely unexplored



Scheme 1. Formula of **1** and possible coordination sites of the ligand 2,3-dicarboxypyrazine. The dcpz dianion species is shown; piv = pivalate = trimethylacetate.

with only a few examples of 1D and 2D systems reported^[10] and no examples of discrete polynuclear compounds, even dinuclear ones. In addition to the bridging N-donor pyrazine functionality, the dcpz dianion has two carboxylate groups which make the ligand polydentate and thus suitable for the design of high-nuclearity clusters.

We investigated the reaction of this ligand in acetonitrile with the cobalt(II) pivalate complex, [Co₂(OH)₂(piv₄)-(Hpiv)₄] (piv = trimethylacetate). This species has proven extremely versatile in the preparation of several cobalt clusters^[11] and also recently as the repetitive unit of a 1D system.^[12] Independently of the dcpz:Co ratio, after some days a unique product crystallizes in low yield as thin purple plates.^[13] Even though not of high quality, suitable single crystals for X-ray diffraction experiments were collected. The results showed a record size Co₃₆ cluster, **1**.^[14] It crystallizes in the space group *P2₁/n* with the asymmetric unit containing half of the molecule and approximately 24 water molecules, which are severely disordered, seven acetonitrile and one pivalic acid solvent molecules of crystallization. The cluster is almost rhombohedral, but distortion arises from the capping of two additional faces (Figure 1). A space-filling plot is shown in the Supporting Information. Because of the capped faces, the overall shape is a distorted, axially compressed octahedron, with equatorial edges lengths of about 3 and 2 nm and axial edges of about 2 and 2.5 nm. These dimensions are of the same order of magnitude as those of the smallest nanoparticles,^[1] thus making perfect a meeting of both quantum and classical “worlds”.

A closer inspection of the structural coordination features allows a hierarchical arrangement within the Co₃₆ cluster to be distinguished. The oxygen-bridged Co₁₂ inner core has four fused heterocubane-type units with two of these edge-shared cubanes further connected through two vertices (Figure 2). Attached to this inner heterocubane core, are two Co₁₁ boomerang-like wings related by an inversion center, each wing has a pendant arm containing a single Co center

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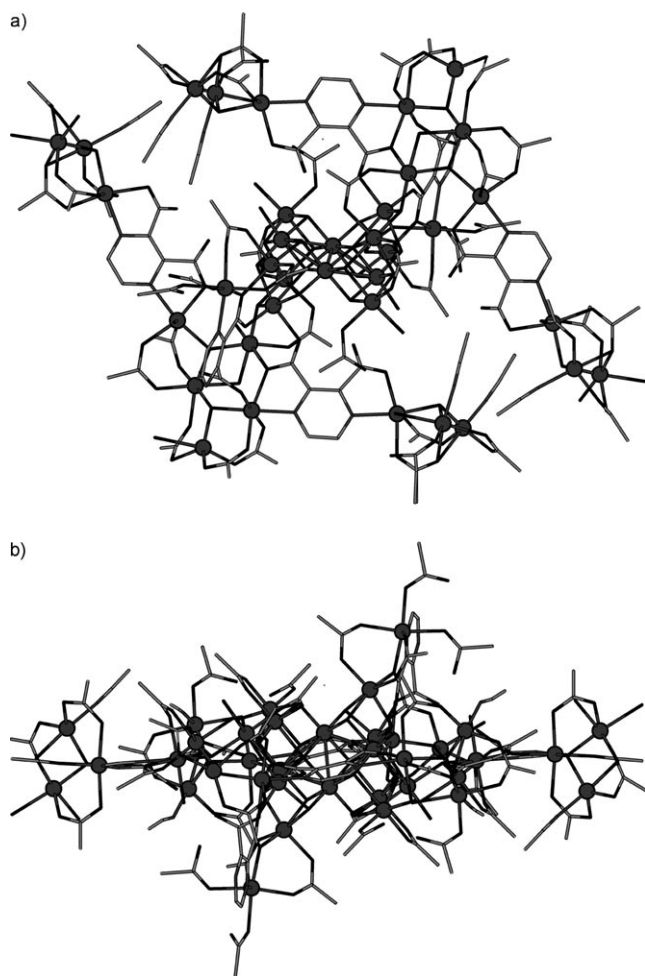


Figure 1. Molecular structure of **1**, mutually orthogonal views. For clarity, all labels as well as *tert*-butyl groups and hydrogen atoms have been omitted. Cobalt ions are shown as spheres.

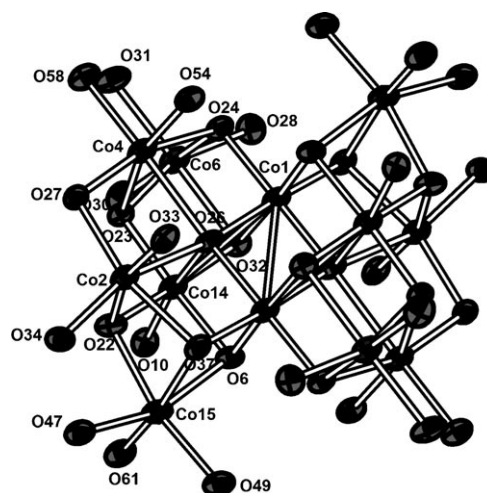


Figure 2. ORTEP representation (thermal ellipsoids set at 30% probability) of the Co_{12} inner core. For clarity, only Co and O atoms are shown.

(Figure 3 and Supporting Information). Thus, the overall arrangement can be understood as a Co_{12} multiple heterocubane core, clamped by two identical Co_{12} wings resulting in the Co_{36} cluster.

Noticeably, a similar Co_{12} core was also observed in a related pivalate-based Co_{14} cluster.^[11] In this Co_{14} cluster, the formula seems to be $\{\text{Co}^{\text{III}}_6\text{Co}^{\text{II}}_8\}$ with the oxidation states inferred from the Co–O bond lengths from all the cobalt coordination spheres. The Co_{14} structure seems to be present in complex **1**. The bond lengths in **1** suggest four Co^{III} sites, with bonds between 1.873(8) and 1.959(9) Å, and ten Co^{II} sites, with bonds ranging from 1.998(9) to 2.456(9) Å (see Supporting Information). Consequently, in complex **1**, the inner Co_{12} core has a formula $\{\text{Co}^{\text{III}}_4\text{Co}^{\text{II}}_8\}$, in which Co1 and

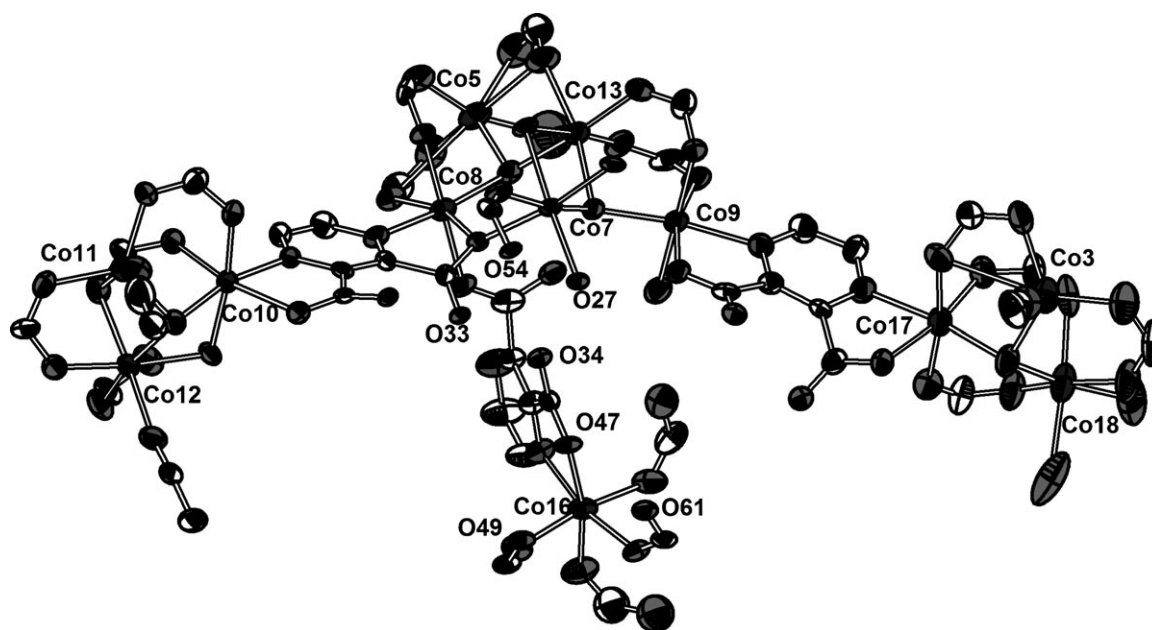


Figure 3. ORTEP representation (thermal ellipsoids set at 30% probability) of one of the symmetry-related Co_{12} wings. For clarity, *tert*-butyl groups and hydrogen atoms are omitted. All the Co atoms are labeled, but only the O atoms attached to the inner Co_{12} multiple heterocubane.

Co14 (and their symmetry-related sites) are Co^{III} sites (BVS calculations support this assignment). By assigning Co7 (and the symmetry related partner) as Co^{II}, the Co₁₄ core is completed.

A closer inspection of the coordination features of the two equivalent Co₁₂ wings reveals a supramolecular arrangement comprising one central Co₅ moiety linked to two Co₃ cores by the dcpz ligand to afford the bent Co₁₁ fragment, which additionally has a pendant arm also connected through the dcpz ligand (O-N,O' mode) with a single octahedrally coordinated cobalt moiety (see Supporting Information). From the Co–O bond lengths which range between 1.945(12) and 2.233(11) Å, it is suggested that all the cobalt sites in the Co₁₂ wings are in the +II oxidation state (BVS calculations again support this assignment). Remarkably, Co5 and Co11 have tetrahedral coordination environment.

Obtaining a precise overall formula for the Co₃₆ cluster is hard because none of the acidic protons of the ligands are found in the crystal-structure refinement. The extremely complex intracluster hydrogen-bonding network involving coordinated ligands (pivalate, hydroxy, oxo, aqua, and dcpz) as well as crystallization solvents (see Supporting Information), makes this task even more difficult. For this purpose the overall cluster must be analyzed in smaller cluster units.

For the central Co₁₂ core, one possible formulation is [Co^{III}₄Co^{II}₈(piv)₄(H₂O)₄(OH)₆O₈]²⁺ (see Supporting Information), in which eight oxygen atoms not involved in hydrogen bonds are assigned as μ-oxo ligands. These eight ligands complete the Co^{III} coordination sites as μ₅ and μ₃ oxo bridges. The remaining μ₃-bridging single oxygen atoms are assigned to hydroxo ligands (all involved in hydrogen bonding), whereas terminal single oxygen atoms are assigned to aqua ligands (also involved in hydrogen bonding). Bridging μ₂ pivalate ligands can be safely assigned to deprotonated species. The nonbridging pivalate ligands are also assigned as deprotonated because they form strong hydrogen-bonding interactions with the terminal aqua ligands.

For the Co₅ moiety in the Co₁₂ wing, a reasonable formulation is [Co^{II}₅(piv)₆(OH)₃(H₂O)₂(dcpz)]⁻ (see Supporting Information). In this case, the dcpz ligand seems to be fully deprotonated, bridging four cobalt centers. The pendant arm cobalt moiety has a [Co^{II}(piv)₂(Hpiv)₂] formula with two μ₂ bridging pivalate ligands and two nonbridging pivalic acids, the latter being involved in hydrogen bonding (see Supporting Information). The remaining backbone of the Co₅ moiety corresponds to two [Co₃(μ₃-OH)] triangles sharing one vertex. One of them is further held together through three additional μ₂-pivalate bridges. The other one has an additional μ₂-aqua bridge and two μ₂-pivalate bridges. Terminal aqua ligands complete the coordination spheres.

The remaining two Co₃ substructures of the Co₁₂ wings are closely related. Most suitable formulations for them are: [Co^{II}₃(piv)₄(OH)(Hdcpz)(H₂O)(CH₃CN)₂] and [Co^{II}₃(piv)₄(OH)(Hdcpz)(H₂O)₂(CH₃CN)] (see Supporting Information). The first is a [Co₃(μ₃-OH)(μ₂-H₂O)] core with three additional μ₂-pivalate bridges. The second is a [Co₃(μ₃-OH)] moiety with three additional μ₂-pivalate and one further pivalate bridging in a κ²O,O' μ₃ mode. In this core, the μ₂-H₂O bridge is replaced by the O25 atom (see Supporting Informa-

tion) of the κ²O,O' μ₃ bridging pivalate. In both Co₃ cores the dcpz ligand is protonated once and links these cores with the Co₅ in a κ⁴N,O,N',O' μ₂ mode in [Co₃(μ₃-OH)]; and with the Co₅ and the Co₁₂ inner core in a κ⁵N,O,N',O',O' μ₄ mode in [Co₃(μ₃-OH)(μ₂-H₂O)]. The protonated carboxylic group of the Hdcpz ligand is strongly involved in hydrogen-bonding interactions. A few examples of Co^{II}₃ single μ₃-OH complexes are reported^[15] none of them showing the {Co^{II}₃(μ₃-OH)(μ₂-H₂O)} or {Co^{II}₃(μ₃-OH)(κ²O,O' μ₃-OOCR)} motifs, found in the Co₃ cores of complex **1**.

Adding all the subcores of the inner Co₁₂ moiety and the symmetry equivalent Co₁₂ wings to give the neutral Co₃₆ cluster **1**, and including the modeled solvents of crystallization, the following overall formula is obtained: [Co^{III}₄Co^{II}₃₂(H₂O)₁₆(CH₃CN)₆(Hpiv)₄(piv)₃₆(OH)₁₆O₈(Hdcpz)₄(dcpz)₂]·24H₂O·7CH₃CN·Hpiv. Chemical analysis over the dried crystals agrees with this formulation after removal of all acetonitrile molecules, supposed to be volatile.

The record number of cobalt centers in complex **1**, including 32 Co^{II} ions (the four octahedrally coordinated Co^{III} ions are clearly closed-shell) undoubtedly makes its magnetic properties worthy of investigation. Variable-temperature (2–300 K) preliminary magnetic susceptibility data at 0.1 T, and magnetization data at different applied external fields (10–70 kOe) in the temperature range 2–5 K were recorded (Figure 4). The χ_mT product at 300 K of 96.0 cm³ mol⁻¹ K is significantly higher than the spin-only value (g = 2.0) expected for 32 non-interacting ions with S = 3/2 (59.9 cm³ mol⁻¹ K). This result is attributed to the orbital contribution of Co^{II} ions, which is known to be significant in an octahedral field.^[16] A more realistic g value is in the range 2.4–2.6 which corresponds to χ_mT values ranging from 86.4–101.4 cm³ mol⁻¹ K in close agreement with the experimental data. The continuous decrease in χ_mT with decreasing temperature is indicative of dominant antiferromagnetic interactions, however orbital contributions cannot be discarded and will also influence the overall profile.^[16] Below 5 K, χ_mT reaches a plateau with a value of 30.8 cm³ mol⁻¹ K for 2 K. This nonzero value and the continuous increase in χ_m on cooling indicate the existence of a magnetic ground state, or eventually a diamagnetic ground state with low-lying magnetic excited states which are populated even at 2 K.

The reduced magnetization data in the range 2–5 K provide more information (Figure 4b). Above 40 kOe, saturation of the magnetization is observed but without superposition of the isofield plots, indicating zero-field splitting components or mixing of the spin multiplets. At the maximum applied field of 70 kOe, the saturation value of 40 Nβ suggests a S = 16 ground state with a g value close to 2.5, under the assumption of a spin-only model. This saturation value disagrees with the observed one for χ_mT at 2 K (30.8 cm³ mol⁻¹ K) which suggests an S = 6 ground state. To clarify this situation, and to test possible slow relaxation behavior of **1**, zero-field alternating current (AC) susceptibility measurements between 2 and 10 K were carried out at frequencies of 10, 400, 750, 1100, and 1500 Hz (see Supporting Information). The extrapolation of χ' T at 0 K gives a value of 32 cm³ mol⁻¹ K, confirming a magnetic S = 6 ground state in agreement with direct current (DC) susceptibility data. No

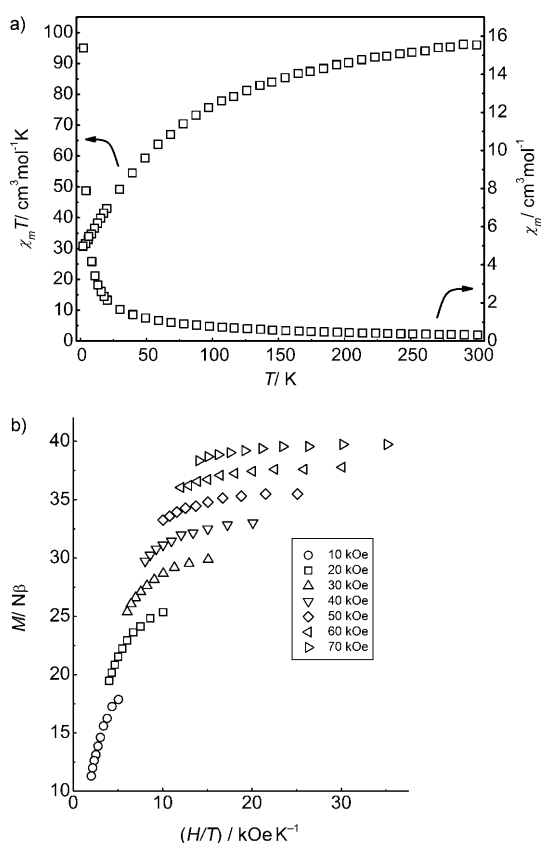


Figure 4. a) χ_m and $\chi_m T$ data as a function of T of complex **1** (constrained powder sample) measured at 0.1 T external field. b) M versus H/T data of the same sample in the range 2–5 K and at 10–70 kOe applied external fields.

out of phase signal is observed down to 2 K, hence above this temperature limit slow relaxation processes are not operative. The most suitable explanation for the non-superimposed reduced magnetization data relies in the presence of low-lying spin-excited states of higher S values that become populated at increasing magnetic field strengths. The lack of saturation of the magnetization at 2 K at increasing field strengths supports this hypothesis (see Supporting Information).

What can be said about the suggested $S=6$ state in terms of the molecular architecture of complex **1**? In terms of exchange interactions, because of the diamagnetic Co^{III} ions present in the central $\{\text{Co}_4\}$ core, the whole structure can be understood as two covalently attached, but magnetically isolated, Co_{16} wings (see Supporting Information). Independent of the coupling scheme within these cobalt units, it appears clear that the magnetic properties of the Co_{36} cluster must be analyzed in terms of a Co_{16} – Co_{16} supramolecular dimer without exchange interaction (or at least a negligible one). Thus after taking account of this, a ground state of two identical non-interacting $S=4$ systems is recognized ($\chi_m T$ data at low T also correspond to a unique $S=6$ spin system). To gain more insight into the origin of the $S=4$ ground state of the Co_{16} cores and the presence or not of anisotropic components, further studies are needed, however because of the size and complexity of the molecule this is not a simple task.

In summary, we have synthesized and characterized a record breaking Co_{36} cluster thereby showing that a definite final limit for the size of high-nuclearity transition-metal clusters is not yet established. Moreover, **1** is the first example of a discrete polynuclear coordination compound bearing the multidentate 2, 3-dicarboxypyrazine ligand, and highlights its unique properties regarding the design and assembly of high-nuclearity systems within transition-metal chemistry.

Experimental Section

$[\text{Co}_2(\text{OH}_2)(\text{piv}_4)(\text{Hpiv})_4]$ (1 g, 1.05 mmols) was dissolved in acetonitrile (150 mL). To the resulting dark violet solution solid 2,3-dicarboxypyrazine (0.057 g, 0.34 mmols) was added and the mixture was vigorously stirred at room temperature overnight. A white residue was then removed by filtration and the pale violet solution was left slowly evaporating at room temperature. After about one week large purple plates suitable for X-ray diffraction had formed from the solution. One of them was picked up for the measurement and the remaining ones were collected by filtration, washed with acetonitrile and dried under vacuum. Yield: 0.053 g. (ca. 10%). The same reaction conditions but employing different ratios of $\text{Co}:\text{dcpz}$ afforded similar yields. The dried solid analyzed as **1** ($-\text{C}_6\text{H}_3\text{CN}$)·1 (CH_3)₂CCOOH·16H₂O. Elemental analysis (%) calcd for $\text{C}_{241}\text{H}_{470}\text{Co}_{36}\text{N}_{12}\text{O}_{162}$ C 35.09, H 5.74, N 2.04; found: C 35.10, H 5.35, N 1.92.

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