Cobalt Complexes of the Chelating Dicarboxylate Ligand "esp": A Paddlewheel-Type Dimer and a Heptanuclear Coordination Cluster

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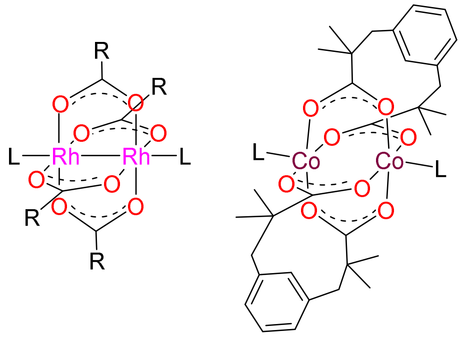
The coordination chemistry of Co(II) with the chelating dicarboxylate ligand esp (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate) is explored. We report here the bimetallic paddlewheel-type dimer, $Co_2(esp)_2(EtOH)_2$ (**1**), and a bowl-shaped, heptanuclear coordination cluster, $Co_7(OH)_4(Hesp)_2(esp)_4(MeCN)_2 \cdot 4MeCN$ (**2**). Crystal structures of both complexes are reported as well as their magnetic properties, which indicate antiferromagnetic interactions among the Co(II) ions.

Introduction

The bimetallic paddlewheel-type structure (**I**, Chart 1) is a ubiquitous structural motif for Rh_2(II,II) carboxylates (with over 5,000 entries in SciFinder!).[1] In comparison, relatively few bimetallic Co(II) carboxylate compounds adopt this structure type; molecular examples have been known since the 1970s,[2] as well as more recent examples of metal-organic frameworks (MOF) built upon the Co_2-paddlewheel unit.[3] The molecular examples that are known are generally supported by a limited set of bulky *N*-donor heterocycles, such as quinoline, that serve as ligands in the axial sites, whereas the MOF examples can contain smaller axial ligands. Based on these examples, we hypothesized that we could use the chelate effect to generate Co_2 paddlewheel-type complexes that could potentially bind and activate small molecules at the axial sites. A similar idea has been used in the chemistry of Rh_2 carboxylates, where the chelating dicarboxylate ligand "esp" (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate) has been found to be critical for the expansion of intermolecular C–H amination catalyzed by Rh_2 complexes.[4] Furthermore, the esp ligand has been shown to support more stable and typically more soluble systems than monodentate carboxylates.[5]

In line with these goals, we report here our preparation of the first Co_2 paddlewheel-type structure supported by the esp ligand (**II**) and also a surprising and topologically unique heptanuclear Co_7 cluster.



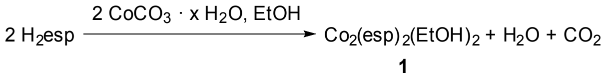
I **II** (L = EtOH)

Chart 1 Comparison of the dirhodium tetracarboxylate structure (**I**) with the $Co_2(esp)_2$ structure (**II**).

Results and Discussion

Synthesis and Structural Studies

The $Co_2(esp)_2$ paddlewheel unit was successfully prepared as its ethanol adduct, $Co_2(esp)_2(EtOH)_2$ (**1**), in the reaction between $CoCO_3$ and H_2esp in refluxing EtOH (Eq. 1):



$$2\,H_2esp \xrightarrow{2\,CoCO_3 \cdot x\,H_2O,\ EtOH} \underset{\mathbf{1}}{Co_2(esp)_2(EtOH)_2} + H_2O + CO_2$$

Eq. 1

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Electronic Supplementary Information (ESI) available: ESI includes additional synthetic details and crystallographic information. See DOI: 10.1039/x0xx00000x

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Black crystals suitable for X-ray diffraction are formed directly from the reaction mixture; under polarized light, the black solid is revealed to show every color of the rainbow, depending on the angle of the crystals. The crystals grow in the triclinic space group $\boldsymbol{P\bar{1}}$ as twins with a 180° rotation about *b**. There are two unconnected half units of the $Co_2(esp)_2$ structure per asymmetric unit, with an inversion center bisecting each Co–Co vector. The Co–Co distances are 2.7245(6) and 2.7595(7) Å, quite long in comparison to compounds containing genuine Co–Co bonds. Co–Co distances in neutral, Co-Co bonded compounds range from 2.27 – 2.39 Å;[1a] however, longer Co–Co bonds of 2.80 and 2.74 Å are known for the $[Co_2(CN)_{10}]^{6-}$ and $[Co_2(CNCH_3)_{10}]^{4+}$ ions, respectively.[6] If anything, we may at most anticipate only σ-type Co–Co interactions to be possible in the compound. Notable is the "squished" appearance of the dimer (Fig. 1). Lacking a strong Co–Co bonding interaction, the two cobalt square pyramids in **1** are not coaxial (the Co-Co-O_{EtOH} angles are 162, 163, and 170°), in contrast to the near-linear angles seen in $Rh_2(O_2CR)_4(L)_2$ species. One of the two paddlewheel units has ordered ethanol axial ligands while the other has ethanol ligands that are disordered over two positions. The ethanol molecules in both cases engage in hydrogen bonding to a carboxylate oxygen on a neighboring $Co_2(esp)_2$ unit, with O···O distances ranging from 2.72 – 2.76 Å.

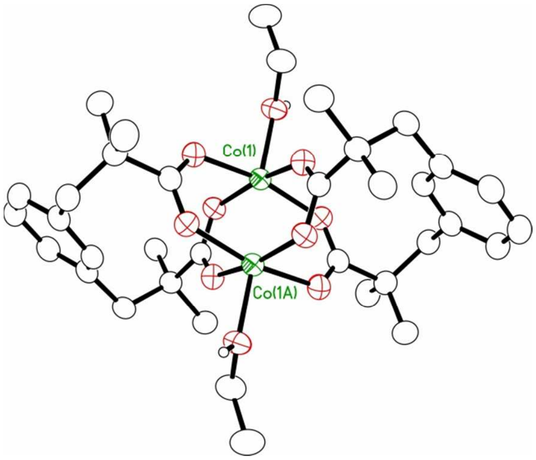

Fig. 1 Crystal structure of **1** with displacement ellipsoids drawn at the 50% probability level. The non-alcoholic hydrogen atoms have been omitted for clarity. Co1–Co1A: 2.7245(6) Å, Co1–O(EtOH): 2.022(2) Å, Co1–O(esp): 2.008(2)–2.106(2) Å. Distances for the other symmetry independent molecule are given in the supporting information.

Interestingly, incomplete reaction of $CoCO_3$ and H_2esp followed by recrystallization from acetonitrile in air yielded crystals of a structurally complex heptanuclear Co_7 cluster with the formula $Co_7(OH)_4(Hesp)_2(esp)_4(MeCN)_2 \cdot 4$ MeCN (**2**) (Fig. 2). The structure of **2** consists of a central, six-coordinate Co(II) ion bound to four μ_3-OH ligands and two neutral MeCN ligands in a *cis*-CoO_4N_2 geometry. Each of the four μ_3-OH ligands bridges an additional two Co(II) ions to the central Co(II) ion, and the six $[esp]^{2-}$/$[Hesp]^{-}$ ligands chelate and bridge the six Co(II) ions around the periphery of the molecule. Four of the six peripheral Co(II) ions are six-coordinate, and two are four-coordinate. The result is a bowl-shaped molecule with a single Co(II) ion at the center of the bowl with six Co(esp) units around the rim. All of the six-coordinate Co ions are easily identified as having a +2 oxidation state in this structure due to charge balance considerations, reflected in the Co–L bond distances in Table S3. Additionally, the protonation states of the esp ligands are clear: all the dianionic esp^{2-} ligands are either bridging or chelating, while the monoanionic $Hesp^{-}$ ligands form hydrogen bonding interactions to a neighboring carboxylate group with O···O distances of 2.57 – 2.60 Å. The bowl shape of the structure is further supported by weak intramolecular hydrogen bonds between two of the μ_3-OH groups and bridging esp ligands (the O···O separations are 3.10 – 3.19 Å).

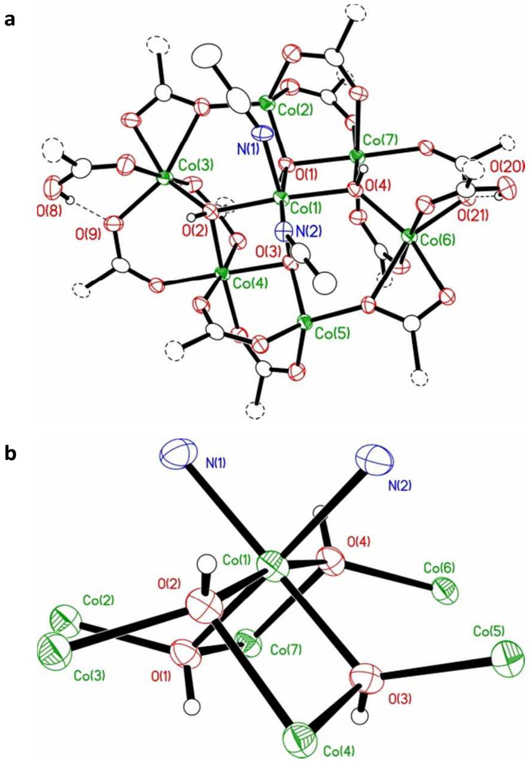

Fig. 2 X-ray structure of **2**, with thermal ellipsoids drawn at the 50% probability level. In (a), for clarity, the hydrogen atoms have been omitted, except those on the carboxylate and hydroxide groups. Additionally, the esp ligands have been truncated to only include the carboxylate and α carbon atoms, the latter of which are represented as dashed ellipsoids. A further truncated representation is shown in (b), highlighting the $Co_7(OH)_4$ core, plus the acetonitrile nitrogen atoms.

Compound **2** belongs to a fairly extensive class of Co_7 coordination cluster compounds, mostly containing Co(II) ions,[7] though some are Co(II)/Co(III) mixed-valent species.[8] The known Co_7 cluster compounds are exclusively supported by mixed *N*,*O*-donor ligands at the molecular periphery, and they typically support a central $[Co(OH)_6]^{4-}$ unit; **2** is the only Co_7

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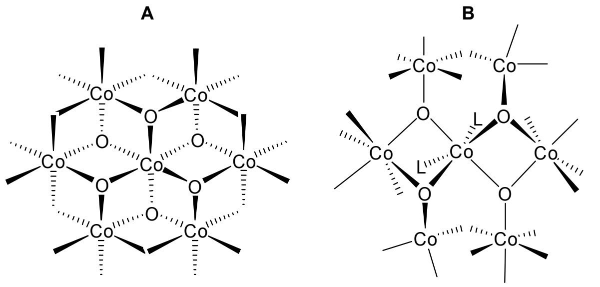
cluster supported exclusively by carboxylates, and it possesses a central $[Co(OH)_4(CH_3CN)_2]^{2-}$ unit. Moreover, all previously reported Co_7 clusters have a D_{3d} symmetrical, planar, disc-like topology in which the central Co ion is coordinated in a *trans* geometry (Chart 2A); the *cis* geometry of the central Co atom in **2** gives rise to its unique C_2-symmetric bowl-like structure (Chart 2B).



Central *trans* geometry
Symmetric disc-like structure

Central *cis* geometry
Unsymmetric bowl-like structure

Chart 2 Comparison of *trans* and *cis* geometries for heptacobalt clusters.

Magnetic Studies

Magnetic properties of molecular Co compounds are of significant interest.[9] Magnetic susceptibility data for **1** were measured from 2 to 300 K, and a plot of χ·T vs T is given in Fig. 3. The room temperature χ·T value of ~4.4 emu·K·mol^{-1} is slightly larger than expected for two non-interacting high-spin Co(II) centers (spin only χ·T = 3.75 emu·K·mol^{-1}), suggesting average g values greater than 2, as expected for d^7 Co(II) centers. The value of χ·T decreases monotonically with decreasing temperature, approaching a value of 0 emu·K·mol^{-1} at 2 K. There is a small bump in the data below 20 K that could not be modeled, and we suggest it is due to an impurity in the sample. As shown in Fig. 3, the data between 15 and 300 K were fitted to a model taking into account both the zero-field splitting (D) of the two Co(II) ions and the antiferromagnetic exchange interaction (J) between them. This model yields $g_{avg} = 2.57$, $D = -55$ cm^{-1}, and $J = -13.2$ cm^{-1}, indicating a large zero-field splitting and antiferromagnetic coupling. Notably, we do not find an acceptable fit of the data with $D > 0$, suggesting that D is negative. The D value is similar to that reported by Boča and coworkers for $Co_2(benzoate)_4(quinoline)_2$ ($g_{avg} = 2.39$, $|D| = 55$ cm^{-1}), who used a similar model to fit their magnetic data.[2g] We find an order of magnitude larger intramolecular exchange coupling (J) in **1** than in the benzoate analog (–13.2 cm^{-1} vs –1.5 cm^{-1}), in agreement with the fact that our data tend towards 0 emu·K·mol^{-1} at low temperatures and the benzoate data remain at ~0.25 emu·K·mol^{-1} at the lowest recorded temperature. It is currently unclear why exchange coupling in $Co_2(esp)_2(EtOH)_2$ is so much larger than that in the benzoate analog, though we note that the Co–Co distance in the esp compound is shorter by 0.05 – 0.1 Å, perhaps enabling a direct orbital overlap mechanism for spin coupling.

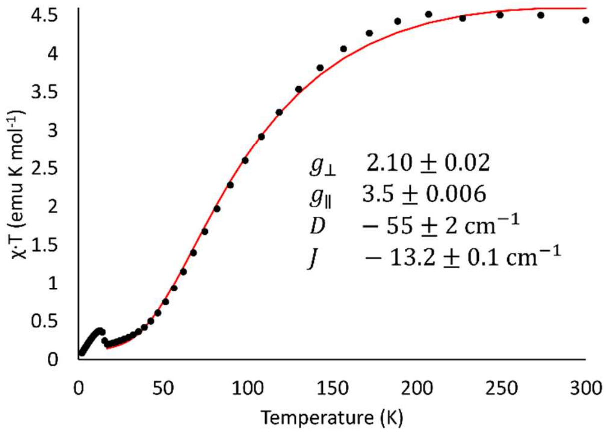


Fig. 3 Plot of χ·T vs T for **1**; the red line is a best fit to the data using the model described in the text.

Magnetic susceptibility data were also measured from 2 to 300 K for the heptacobalt complex **2**, and a plot of χ·T vs T is given in Fig. 4. At room temperature, χ·T approaches a value of 21 emu·K·mol^{-1}, well above the expected spin-only value for seven non-interacting Co(II) ions (13.125 emu·K·mol^{-1}). The χ·T value drops precipitously as the temperature is lowered below 100 K, consistent with an overall antiferromagnetic interaction within the cluster. For a system this complicated, it is impossible to attempt to model the χ·T data taking into account all of the spin centers, their (anisotropic) g tensors, their zero-field splitting, and their exchange couplings without grossly overparameterizing the model. We have therefore adopted a simplified model in order to obtain a phenomenological fit to the data that yields chemically useful information.

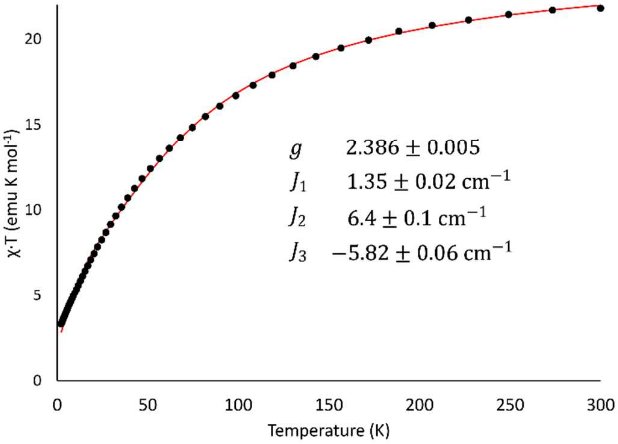


Fig. 4 Plot of χ·T vs T for **2**. The solid line is a theoretical fit to the data based on the model described in the text.

This model takes into consideration the unusual geometry of the complex and makes a number of simplifying assumptions. First, anisotropy of the Co(II) ions is ignored, and all Co(II) ions are assigned to the same (isotropic) *g* parameter. Second, considering the closer distance between the central Co atom and two pairs of outer Co atoms, we assume that the spin of the central Co sets the spins of the outer pairs such that each pair aligns as an effective *S* = 3 unit. Thus, we have effectively a central *S* = 3/2 Co(II) unit (Co1) with two outer identical *S* = 3/2 Co(II) units (Co2 and Co3) and two identical *S* = 3 Co_2(II,II) units (sites 4 and 5, Chart 3). Treating this as a system of five spins is a much more tractable problem than attempting to treat seven separate spins.

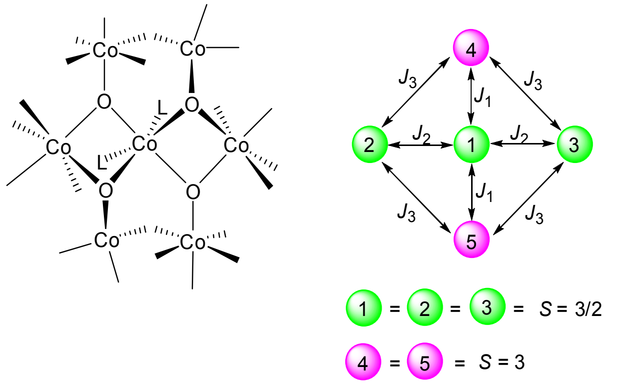


Chart 3 Simplified model for the magnetic data of **2**, highlighting the antiferromagnetic interaction between the purple spin centers (modeled as Co_2 units with *S* = 3) and the green spin centers (each corresponding to an individual *S* = 3/2 Co(II) ion).

At 2 K, the value of χ·T for **2** drops to ~3.3 emu·K·mol^{-1}, which allows us to make an educated guess about the nature of the ground spin state. If all seven Co(II) ions were ferromagnetically coupled, the resulting *S* = 21/2 ground state would have a spin-only low-temperature limit of χ·T = ½*S*(*S*+1) = 60.375 emu·K·mol^{-1}, which is much larger than the observed value. If we have a single central Co(II) ion antiferromagnetically coupled to the outer six Co(II) ions, the resulting *S* = 15/2 ground state yields a spin-only low-temperature limit of χ·T = 35.625 emu·K·mol^{-1}, which is also too large. The most reasonable spin coupling model is one in which three Co(II) ions align together ferromagnetically and couple against the other four Co(II) ions antiferromagnetically, yielding a ground state of *S* = 3/2 (χ·T = 1.875 emu·K·mol^{-1} at the low-temperature limit). This value compares best with the observed value of 3.3 emu·K·mol^{-1}. We therefore propose that the three individual Co(II) ions in our model (spins 1, 2, and 3 in Chart 3) couple ferromagnetically with each other and antiferromagnetically with spins 4 and 5, the *S* = 3 Co_2 units. Thus, of the three distinct *J* values describing the exchange coupling in the complex outlined in Chart 2, we expect J_1 and J_3 to be negative (antiferromagnetic) and J_2 to be positive (ferromagnetic). The best fit of this model to the experimental data (Fig. 4) yields *g* = 2.34, J_1 = +1.4 cm^{-1}, J_2 = +6.4 cm^{-1}, and J_3 = –5.8 cm^{-1}. With this model, the anticipated signs of *J* are correct, except for that of J_1, but this value is considerably smaller than the other two *J* values, which will dominate the magnetic properties.

Electronic Structure Calculations

The electronic structure of **1** was examined using the geometry of the crystal structure. Consistent with the magnetometry data, we find the compound to be best modeled as containing a pair of antiferromagnetically-coupled high-spin Co(II) ions. The magnetic orbitals are shown in Figure 4, and there are three types of interactions observed. The bottom set of orbitals is of π symmetry with respect to the Co–Co vector, whereas the middle set of orbitals resembles canted d_{z^2} orbitals pointed in such a way as to only yield a π-type Co–Co interaction. The top set of orbitals is of δ symmetry and, as expected, has the weakest interaction. The antiferromagnetic interactions within the complexes yield calculated *J* values ranging from –16 cm^{-1} to –22 cm^{-1}, which are quite comparable to the experimentally determined value of –13 cm^{-1}.

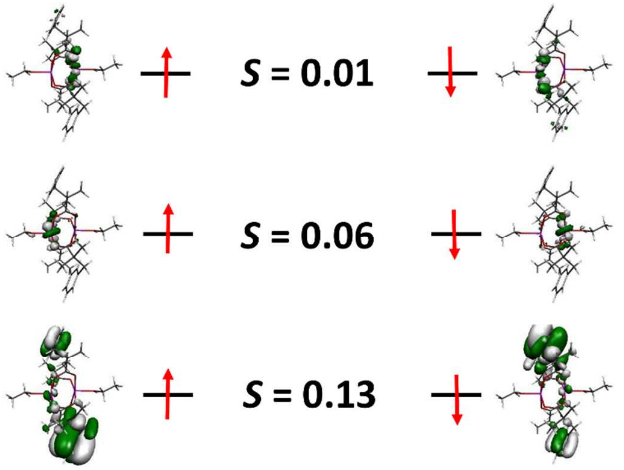


Fig 4 Calculated corresponding magnetic orbitals of **1** of both α (left) and β (right) spin. The numbers in the middle are the calculated overlap integral values, *S*.

Conclusions

The chelating dicarboxylate ligand esp is used to support a dimeric Co_2(II,II) paddlewheel-type structure bearing axial ethanol ligands and a heptanuclear complex $Co_7(OH)_4(Hesp)_2(esp)_4(MeCN)_2$. In the dimer, the relatively short Co–Co distances of 2.72 – 2.76 Å support an intramolecular magnetic exchange interaction with *J* = –13 cm^{-1}, which is an order of magnitude larger than in the corresponding benzoate complex that has longer Co–Co distances. In the Co_7 complex, the magnetic properties suggest an *S* = 3/2 ground state due to antiferromagnetic alignment of four of the Co(II) ions against the other three. We propose a possible model for the spin alignment within the structure.

Experimental

General Procedures

All reagents were obtained from commercial sources and used as received, except as noted. All work was performed with oven-dried glassware under a dry, nitrogen atmosphere using standard Schlenk technique or an inert-atmosphere glovebox, except as noted. Ethanol was dried over $Mg(OEt)_2$ and distilled under nitrogen immediately prior to use.

The dinitrile precursor to H_2esp ("esp-diCN") and the dicarboxylic acid H_2esp were synthesized as originally reported by DuBois and coworkers[4] but with important modifications previously described,[10] and with additional modifications described in the supporting information to improve yield and purity.

Synthetic Procedures

$Co_2(esp)_2(EtOH)_2$ (1): A 25 mL Schlenk flask was charged with a stirbar, $CoCO_3 \cdot x\ H_2O$ (0.07 g, 43-47% Co by weight), and H_2esp (0.14 g). The flask was evacuated and backfilled with nitrogen three times. Freshly distilled EtOH (25 mL) was added, and the flask was fitted with a condenser. The suspension was heated with gentle stirring at 90 °C for 24 hours. Within the first ten minutes, a purple mother liquor quickly formed, and the solid slowly converted from a pink powder to black crystals over the 24 hour period. The reaction mixture was cooled to room temperature and filtered, and the solid was washed with room temperature EtOH. After air-drying, shiny black crystals were collected (0.15 g, 79%, assuming 47% Co by weight in $CoCO_3 \cdot x\ H_2O$). The crystals are polychromatic under polarized light, displaying pink, yellow, blue, and orange among other less prominent colors. Analysis calc'd for $Co_2C_{36}H_{52}O_{10}$: C, 56.69 %; H, 6.87 %. Found: C, 56.03(5) %; H, 6.77(2) %. MS (MALDI-TOF) *m/z* calc'd for $Co_2C_{36}H_{52}O_{10}$ $[M\text{-}2(EtOH)]^+$: 670.1; found 670.4. IR (ATR, cm^{-1}): 1592.2 s, 1480.5 m, 1416.3 s, 1375.9 m, 1358.2 m, 1046.5 m, 925.9 m, 907.2 m, 879.2 m, 707.9 s, 613.7 m. ^1H NMR (CD_3OD): δ = 14.05 (br s), 7.59 (br s), 4.75 (br s), 2.34 (d), -0.24 (t), -20.68 (br s).

$Co_7(OH)_4(Hesp)_2(esp)_4(MeCN)_2 \cdot 4$ MeCN (2): A 100 mL Schlenk flask was charged with a stirbar, $CoCO_3 \cdot x\ H_2O$ (0.62 g, 43-47% Co by weight), and H_2esp (1.39 g). The flask was evacuated and backfilled with nitrogen three times. Freshly distilled EtOH (50 mL) was added and the flask was fitted with a condenser. The suspension was heated with gentle stirring at 90 °C for 4 hours, during which time a purple mother liquor quickly formed and a black solid formed, though some purple solid remained. The reaction mixture was cooled to room temperature and filtered, and the solid was washed with room temperature EtOH. After air-drying, the shiny black solid was dissolved in MeCN, the resulting mixture was filtered, and the purple filtrate was allowed to concentrate in air to yield purple plate-shaped crystals suitable for X-ray diffraction (0.37 g, 22%, assuming 47% Co by weight in $CoCO_3 \cdot x\ H_2O$). Analysis calc'd for $Co_7C_{96}H_{126}O_{28}$: C, 53.87 %; H, 5.93 %. Found: 53.51(3) %; H, 5.88(5) %. IR (ATR, cm^{-1}): 2961 w, 2923 w, 2872 w, 1680 w, 1583 s, 1476 m, 1413 m, 1375 m, 1361 m, 1265 w, 749 w, 707 m, 648 w, 614 m.

Instrumentation

Mass spectral data were collected using a Bruker ULTRAFLEX III MALDI-TOF mass spectrometer equipped with a SmartBeam laser. IR spectra were collected on a Bruker Tensor 27 FTIR spectrometer using the ATR technique. Elemental analyses were measured at Midwest Microlab, LLC in Indianapolis, Indiana, USA.

Crystallography

Crystallographic data were measured at the Molecular Structure Laboratory of the Chemistry Department of the University of Wisconsin–Madison. Crystals were selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount. Each crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEX-II diffractometer with Cu K_α (λ = 1.54178 Å) radiation for **1** or Mo K_α (λ = 0.71073 Å) radiation for **2**. The data were collected using a routine to survey an entire sphere of reciprocal space and indexed by the SMART program.[11] The structures were solved using the Olex2 program[12] via direct methods or charge flipping and refined by iterative cycles of least-squares refinement on F^2 followed by difference Fourier synthesis.[13] All H atoms were included in the final structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients, except as noted.

Crystals of **1** and **2** were both found to be twinned. For the resulting data sets, all possible combinations of domains and inclusion or exclusion of overlapping reflections were used to generate .hkl files using either HKLF4 or HKLF5 format. The HKLF4 or HKLF5 file that yielded the smallest uncertainties in bond distances was used for the final refinement.

When selecting a crystal of **1** for diffraction, only crystals having non-merohedral twinning could be found; the two twin domains are related by a 180° rotation about *b**. The HKLF5 file generated based on component one and excluding overlapping reflections was used for the final refinement. During refinement, there was positional disorder in the ethanol molecule on one of the two half-dimers in the asymmetric unit, the two components of which refined to a 64:36 occupancy ratio. Additionally, the DFIX restraint was used to set the O-H distances to ~0.87 Å, and the DANG restraint was used, on C···H and Co···H distances, to set the angles to those typically adopted by ethanol molecules.

When selecting a crystal of **2** for diffraction, only crystals having non-merohedral twinning could be found; the two twin domains are related by a 180° rotation about *c**. The HKLF5 file generated based on component one and excluding overlapping reflections was used for the final refinement.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center under CCDC 1857930-1857931.

Magnetic Susceptibility Measurements

Samples were only handled with glass and plastic tools to avoid contamination from metallic materials. Crystalline samples were placed in a glass vial with a glass ball bearing and ground into powders using a vortex mixer. The powdered samples were weighed and placed inside of plastic capsules in plastic drinking straws. Variable-temperature DC magnetization was measured using a Quantum Design MPMS 3 SQUID magnetometer over a temperature range of 2 – 300 K at an applied magnetic field of 1000 G (0.1 T). Magnetization data were converted to magnetic susceptibility via $\chi \approx M/H$. The data were fitted using the PHI software program.[14] Variable-frequency, variable-field AC magnetic susceptibility measurements were also made on **2** at 1.8 K at frequencies from 10 to 1000 Hz and applied fields ranging from 0 to 1 T. An out-of-phase signal is detected at modest applied fields (maximum signal at ~2300 G), but no maxima were observed in the plots of χ″ vs log(freq.). Diamagnetic corrections[15] for each sample were calculated using the equation

$$\chi_{dia} \approx -\frac{MW}{2} \times 10^{-6} emu/mol$$

and were applied to the experimental data along with a correction for the intrinsic diamagnetism of the sample holder. Magnetic susceptibility data were additionally corrected for temperature independent paramagnetism.

Electronic Structure Calculations

Calculations were performed using the ORCA program, version 4.0.0.2.[16] The B3LYP functional[17] was used with Def2-TZVP bases on all atoms.[18] The broken symmetry formalism was used to model the electronic structure of **1** with 3 α and 3 β weakly interacting electrons. The interactions were analyzed using the corresponding orbital transformation.[19] Three methods were used for the prediction of *J*: The method of Ginsburg[20] and Noodleman[21] yields *J* = –22 cm^{-1}, as does the method of Yamaguchi,[22] while the method from Bencini and Gatteschi[23] yields *J* = –16 cm^{-1}.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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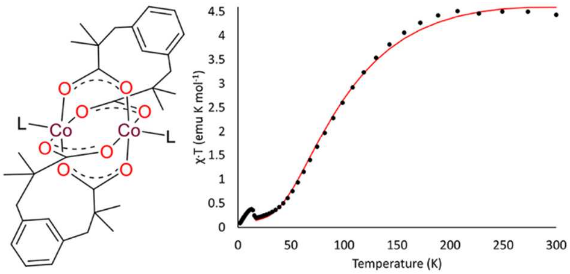

Table of Contents Entry:

Reaction of cobalt carbonate with α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid (H2esp) in ethanol forms the paddlewheel-type dimer Co2(esp)2(EtOH)2, which hydrolyzes in acetonitrile solution to give a bowl-shaped heptacobalt coordination cluster complex; both compounds display antiferromagnetic interactions between high-spin Co(II) ions.