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Novel Example of a Chain Structure Formed by 1,4-Dioxane and Cobalt(II) Links. Chain $[Co_3(\mu\text{-}OOCCF_3)_4(\mu\text{-}H_2O)_2(OOCCF_3)_2(H_2O)_2(C_4H_8O_2)]\cdot 2C_4H_8O_2$

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The trimer $[Co_3(\mu\text{-}OOCCF_3)_4(\mu\text{-}H_2O)_2(OOCCF_3)_2(H_2O)_2(C_4H_8O_2)]\cdot 2C_4H_8O_2$ (**1**) is composed of three tetragonally distorted Co^{II} centers bridged by four trifluoroacetates and two bridging water molecules. 1,4-Dioxane is coordinated at a distance of 2.120(3) Å from the terminal cobalt Co2; the remaining oxygen of this 1,4-dioxane links the terminal cobalt to a neighbor trimer, forming a one-dimensional chain. The crystal structure displays a network of hydrogen bonds between four noncoordinated 1,4-dioxane molecules and the coordinated terminal water molecules. The magnetic properties of **1** were analyzed with the use of the Hamiltonian including isotropic exchange interactions between real spins of a high-spin Co^{II}, spin–orbit coupling and a low-symmetry crystal field acting within the $^4T_{1g}$ ground manifold of each cobalt ion. A weak antiferromagnetic exchange interaction between cobalt ions in **1** was found. The results of the magnetic model are in good agreement with the experimental observations.

Introduction

Cobalt(II) dimers[1] and trimers[2a] with antiferromagnetic behavior have been reported when bases are present during the reaction. The carboxylate bridge seems to be the exchange path in these polynuclear cobalt(II) compounds. The use of quaternary ammonium (or arsonium) carboxylate usually leads to cobaltates(II) with tetrahedral symmetry and the $^4A_2$ ground state. The tetrahedral species of trifluoroacetate cobaltate(II), $[Co(OOCCF_3)_4]^-$,[2] displays a magnetic moment typical of $S = ^3/_2$.[3] In our laboratory, we found that a tetrahedral cobalt(II) is favored when using basic conditions to assemble cluster carboxylatocobaltate(II) dimers.[4] On the other hand, the structure of a chain of octahedral cobalt(II) aquo acetate was reported, which apparently formed because of the acidic conditions employed during the synthesis.[5] Furthermore, structurally related trimers of cobalt(II) acetates have been reported, but no magnetic characterization is available,[6,9] precluding a magnetostructural comparison with the current compound. The synthesis and crystal structure of a related aquo-bridged Co trimer were reported recently by Brown and colleagues.[7a]

Most of these bridging carboxylates arise from weak carboxylic acids,[8] with the trichloroacetato one of the few weak bases being able to form bridges.[2a,b] Trifluoroacetato

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(1) (a) Boyd, P. D. W.; Gerloch, M.; Harding, J. H.; Woolley, R. G. *Proc. R. Soc.* London A **1978**, *360*, 161. (b) Turpeinen, U.; Hämäläinen, R. *Polyhedron* **1987**, *6*, 1603. (c) Hagen, K. S; Lachicotte, R.; Kitaygorodskiy, A.; Elbouadili, A. *Angew.* Chem., Intl. Ed. Engl. **1993**, *32*, 1321.

(2) (a) Shova, S. G.; Novitskii, G. V.; Marzus, M. D.; Gulya, A. P. *Proc. Natl. Acad.* Sci. *U.S.*A. **1994**, *337*, 348. (b) Chaudhuri, P.; Querbach, J.; Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1990**, 271.

(3) Bergman, J. G.; Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1420.

(4) Calvo-Perez, V.; Spodine, E. *Inorg. Chim. Acta* **2000**, *310*, 133.

(5) Jiao, X. D.; Guzei, I. A.; Espenson, J. H. *Z. Kristallogr.* **2000**, *215*, 173.

(6) (a) Estienne, J. *Acta Crystallogr.*, Sect. C: Cryst. Struct. Commun. **1985**, *41*, 338. (b) Estienne, J.; Ewiss, R. *J. Chem. Soc., Chem. Commun.* **1972**, 862.

(7) (a) Brown, D. A..; Clarkson, G. J.; Fritzpatrick, N. J.; Glass, W. K.; Hussein, A. J.; Kemp, T. J.; Muller-Bunz., H. *Inorg. Chem. Commun.* **2004**, *7*, 495. (b) Brown, D. A.; Ostrovsky, S.; Tomkovics, Z.; Haase, W., personal communication

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displays a poorer basic character; therefore, it is relatively uncommon to find oligomers of cobalt(II) μ-aquo μ-trifluoroacetato.[6] However, a magnetostructural correlation has been established for hydroxy and aqua bridges based on NMR and X-ray diffraction analysis for a couple of dicobalt(II) (μ-hydroxo)bis(μ-trifluoroacetato) dimers as models for hemerythrin.[10] In this case the hydroxo bridge plays an important role in the dimer formation.

In our laboratory, we have reported a copper(II) trifluoroacetato chain where hydrogen bonds to the neighbor water ligand help to stabilize a one-dimensional chain within a 1,4-dioxane network.[11] The chain of copper(II) bis(trifluoroacetato) displays a very weak ferromagnetic coupling as observed by electron paramagnetic resonance ($J \approx 10\ \mathrm{cm}^{-1}$) and magnetic susceptibility, but no trifluoroacetato bridge was found between the cupric centers. A similar behavior was described for a isostructural one-dimensional copper(II) bromine benzoate chain, displaying ferromagnetic coupling with $\theta = +9$ K.[12]

Extending our investigation to the assembly of cobalt(II) trifluoroacetato in anhydrous conditions, we found a new cobalt(II) trimer with interesting structural and magnetic properties starting from a cobalt trifluoroacetato monomer. Our interest is actually to assemble large arrays of covalently bonded cobalt(II) centers, using the less explored chemistry of cobalt(II) in acidic conditions and to correlate the geometric parameters of the bridging water and the cobalt−cobalt distance with the magnetic properties. The angle of the water bridge and therefore its hybridization may also be important to the proposal of a route to magnetic exchange. We also aim to describe the role of the trifluoroacetato group on the cobalt trimer magnetic properties.

Experimental Section

Synthesis. Preparation of $Co(OOCCF_3)_2(H_2O)_4$. Large blocks of cobalt(II) trifluoroacetato were obtained from the reaction of CoO dissolved in hot concentrated (5 M) trifluoroacetic acid (Aldrich). The resulting purple solution was refluxed for 1 h, concentrated under reduced pressure, and allowed to stand at room temperature. Upon cooling, red blocks of the compound $Co(OOCCF_3)_2(H_2O)_4$ were obtained. The crystals were characterized by FTIR and elemental analysis. Anal. Calcd: C, 13.46; H, 2.26. Found: C, 14.1; H, 2.7. FTIR (KBr pellet, cm^{-1}): 3263(b), 1672(s), 1447(m), 1196(s) 1147(s).

Preparation of $[Co_3(\mu\text{-}OOCCF_3)_4(\mu\text{-}H_2O)_2(OOCCF_3)_2(H_2O)_2(C_4H_8O_2)]\cdot 2C_4H_8O_2$ (1). Compound **1** was prepared by refluxing $Co(OOCCF_3)_2(H_2O)_4$ in a 10:1 mixture of trifluoroacetic acid and trifluoroacetic acetic anhydride in 1,4-dioxane. Toluene vapors were allowed to diffuse into the 1,4-dioxane solution. Red crystals of compound **1** were obtained after 2 weeks. Anal. Calcd: C, 24.18; H, 2.78. Found: C, 24.65; H, 3.3. FTIR (KBr pellet, cm^{-1}): 2934(w), 1710(s), 1462(m), 1195(s).

Table 1. Crystallographic Data for **1**

chemical formula	$C_{28}H_{40}Co_3F_{18}O_{24}$
fw	1279.4
cryst color and habit	pale pink, parallelepiped
cryst size (mm)	0.80 × 0.40 × 0.40
cryst syst and space group	triclinic, $P\bar{1}$
cell dimens	
a (Å)	10.135(1)
b (Å)	10.240(1)
c (Å)	12.907(2)
α (deg)	93.968(2)
β (deg)	106.912(2)
γ (deg)	103.709(2)
cell volume (Å^3)	1231.3(3)
Z (formula units/cell)	1
d_{calcd} (g/mL)	1.725
absorption coefficient (μ, mm^{-1})	1.144
F(000)	643
diffractometer	Siemens SMART CCD area detector
radiation source and wavelength (Å), Mo Kα, λ	0.7107
data collection temp (K)	
2θ range (deg)	293(2)
index ranges	4.14−50.18
	$-12 < h < 11$; $-12 < k < 12$; $-15 < l < 15$
reflection collected	4299
reflections obsd	3438
abs corrn method	empirical
max and min transmission factors	0.633−0.583
no. of least-square param	347
residuals (obsd data)	
R (F)	0.0563
wR (F^2)	0.1473
residuals (all data)	
R (F)	0.0697
wR (F^2)	0.1575
GOF (all data)	
S (F^2)	1.0750
largest, mean least-square shifts (δ/σ)	0.000, 0.000
largest e^- density peak and hole (e/A^3)	0.844, −0.565

Structure Determination. X-ray diffraction data for the structure determination at room temperature were collected with a Siemens diffractometer equipped with a graphite monochromator and a Siemens SMART-APEX CCD area detector system, using 0.3° between frames. Data collection parameters and refinement results are given in the Supporting Information. Structure solutions by direct methods and least-squares refinement were obtained using the *SHELX97* package.[18] All hydrogen atoms were found in the difference Fourier synthesis and were not refined in the subsequent cycles. Crystal data are summarized in Table 1. Atomic coordinates, anisotropic displacement parameters, hydrogen coordinates, and equivalent isotropic displacement parameters are also included in the Supporting Information.

Magnetic Measurements. The magnetic properties of the investigated compound are in the temperature range of 2−300 K. Variable-temperature susceptibility measurements were carried out at a magnetic field of 0.1 T on a ground polycrystalline sample of **1** with a SQUID magnetometer Quantum Design MPMS. The susceptibility data were corrected for the diamagnetic contributions as deduced by using Pascal's constant tables. The corrected magnetic moment at room temperature is 7.96 μ_B per trimer, which is consistent with three pseudo-octahedral Co^{II} centers with significant spin−orbit coupling.[13] The magnetic moment decreases as the temperature drops near 2 K.

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(8) Yen-Hsiang, L.; Hui-Lien, T.; Lu, Y.; Wen, Y.; Wang, J.; Lu, K. *Inorg. Chem.* **2001**, *40*, 6426.

(9) Reynolds, R. A., III; Dunham, W. R.; Coucouvanis, D. *Inorg. Chem.* **2000**, *39*, 3915.

(10) Lachicotte, R.; Kitaygorodskiy, A.; Hagen, K. S. *J. Am. Chem. Soc.* **1993**, *115*, 8883.

(11) Calvo-Perez, V.; Cortes, P.; Moreno, Y.; Vega, A.; Spodine, E. *J. Chil. Chem. Soc.* **2000**, *45*, 259.

(12) Del Sesto, R. E.; Arif, A. M.; Miller, J. S. *Inorg. Chem.* **2000**, *39*, 4894.

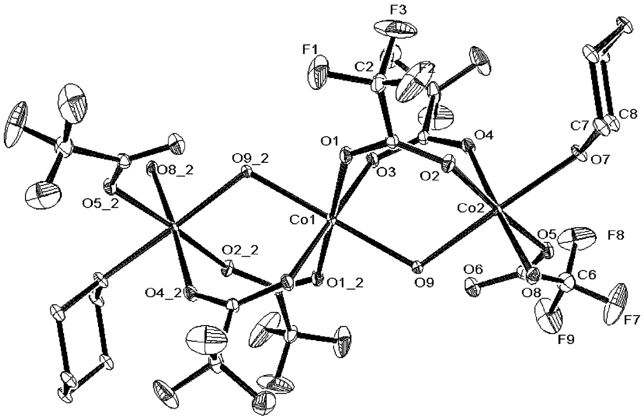

Figure 1. Illustration of trimer $Co_3(\mu\text{-}OOCCF_3)_4(\mu\text{-}H_2O)_2(OOCCF_3)_2(H_2O)_2(C_4H_8O_2)$ at 20% thermal ellipsoids with atom numbering. Hydrogen atoms are not shown for clarity.

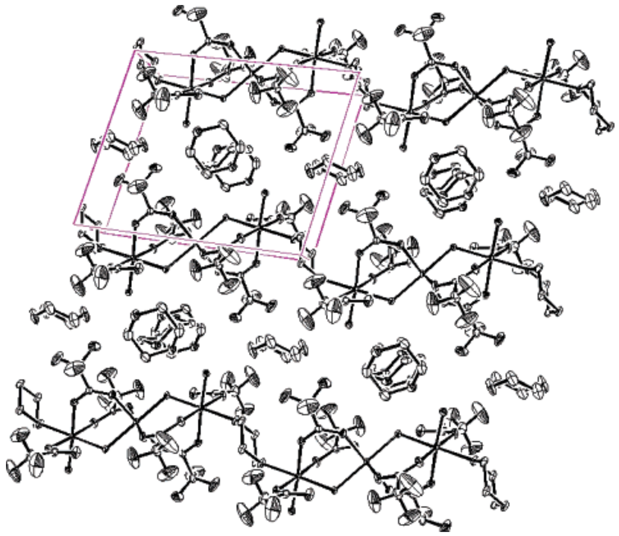

Figure 2. Illustration of the one-dimensional chain of trimers between a 1,4-dioxane scaffold. The hydrogen-bonding network is not shown for clarity. An alternative view along the one-dimensional chain is included in the Supporting Information.

Table 2. Selected Bond Distances (Å), Angles (deg), and Dihedral Angles (deg) for Trimer **1**[a]

Co1−O1	2.067(3)	Co1−O3	2.076(3)
Co1−O9	2.143(3)	Co2−O2	2.053(3)
Co2−O4	2.055(3)	Co2−O5	2.072(3)
Co2−O7	2.044(3)	Co2−O9	2.160(3)
Co2−O8	2.120(3)	Co1···Co2	3.632(3)
Co1−O9−Co2	115.1(1)	Co2a−Co1−Co2	180.000(1)
O1−Co1−O3	89.8(2)	O1−Co1−O3a	90.2(2)
O3−Co1−O9	90.4(1)	O1−Co1−O9	94.6(1)
O8−Co2−O4	176.6(1)	O2−Co2−O5	176.4(1)
O8−Co2−O7	87.5(1)	O7−Co2−O9	176.8(1)
O2−Co2−O9	93.0(1)	O8−Co2−O5	90.8(1)
O4−Co2−O5	87.9(1)	O2−Co2−O4	92.3(1)
Co1−O1−O2−Co2	19.19(3)	Co1−O3−O4−Co2	13.54(3)

[a] a: *x*, *y*, *z*.

Results and Discussion

Structural Details. The trimer **1,** which includes four trifluoroacetato bridges, two terminal trifluoroacetato groups, two bridging waters (O9), and two terminal water ligands (O8), is centrosymmetric, with an inversion center on Co1, as shown in Figure 1. The crystal structure shows the cobalt(II) trimers forming a one-dimensional chain connected through 1,4-dioxane molecules (O7); see Figure 2. A list of selected distances and angles is presented in Table 2; a full list of noncoordinated atoms is included in the Supporting Information. The terminal cobalt centers (Co2) display a tetragonal distortion. The equatorial Co2−O4, Co2−O2, and Co2−O8 distances to the Co2−trifluoroacetate is an average of 2.06 Å. The equatorial Co2−O8 distance to the non-bridged water is 2.044 Å, while the axial distance to the dioxane, Co2−O7, is 2.120(3) Å, and the axial distance to the bridging water, Co2−O9, is 2.160(3) Å, defining a tetragonally distorted octahedron. The central cobalt also displays a tetragonal elongation of the $H_2O-Co1-OH_2$ axis [Co1−O9 = 2.143(3) Å] over the trifluoroacetato axial oxygens (Co1−O1 and Co1−O3 = 2.071 Å average). Both the Co2−O9 and nonbonding Co1···Co2 distance [3.632(3) Å] and the Co2−O9−Co1 angle are relevant to explain the observed magnetic properties.

For comparison, some relevant structural data for an isolated cobalt(II) trimer is reported by Brown and colleagues.[7a] This molecule is built up from four trifluoroacetato bridging groups, two hydroxamato (oxygen) bridged groups, and two terminal TMEN groups, where the Co1···Co2 distance is 3.550(5) Å, the $Co1-O_{bridge}-Co2$ angle is 119.31(6)°, the $Co1-O_{bridge}$ distance is 2.048(13) Å, and the $Co2-O_{bridge}$ distance is 2.065(12) Å, and the magnetic properties are analyzed.[7b]

The bridging water $Co-OH_2-Co$ angle found in **1** is 115.1(1)°, a little bit larger than the angle found in the related cobalt(II) (μ-aquo)nicotinato (113.67°)[8] but smaller than that in the cobalt(II) (μ-aquo)trichloroacetato dimer (116.161°).[2a] A structural comparison between the above-mentioned cobalt(II) trichloroacetato and nicotinato dimers indicates that in the current structure **1** the Co1···Co2 distance 3.632(3) Å is even shorter (3.696 Å) than that found in antiferromagnetic dimers of Co^{II}.[2a] Interestingly, in the nicotinato-related structure,[8] the cobalt centers are organized as dimers bridged by water that are not collinear with their neighbor; this material displays an antiferromagnetic coupling, while in the cobalt (μ-hydroxo)succinate ring, the coupling is ferromagnetic.[9] Because the cobalt−(μ-trifluoroacetato) distance in **1** is rather short (2.06 Å) compared to those of the other carboxylates referenced (2.09−2.07 Å) and the angle discussed before is small in **1**, we conclude that the bridging trifluoroacetato and the bridging water together force the cobalt centers into a tetragonal distortion that is significant for the explanation of the observed magnetic properties (vide infra). In addition, the orientation of the two tetragonal axes is perpendicular, as discussed later in our model. As shown in Table 2, the Co−trifluoroacetato−Co atoms are not coplanar [torsion angle = 19.19(3)°]; therefore, we believe that this is not a feasible exchange path. As already mentioned, each trimer **1** displays two 1,4-dioxane molecules coordinated (O7) to the terminal cobalt centers Co2, and because of this, a neighbor trimer ($Co2^a$) is coordinated to

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(13) Cotton F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988.

this 1,4-dioxane (O7^{a}), forming a one-dimensional chain. The one-dimensional arrangement is a unique example of a chain linked by a weak and hindered base such as 1,4-dioxane (see Figure 2). One chain is separated from the neighbor chains [10.240(1) Å] by a network of 1,4-dioxane molecules held by a network of hydrogen bonds. The large distance between parallel chains precludes magnetic interactions between them.

Model of Magnetism. Let us consider a linear cobalt trimer; each high-spin Co^{II} ion is octahedral coordinated, but the site symmetry of each cobalt position is axial because of some distortions of the surroundings. From the structure analysis of the studied compound, one can see that C$_4$ axes of terminal ions are parallel to each other and not parallel to the C$_4$ one of the central ion (Co1), with the angle between them being $\alpha = 115°$. We assign these C$_4$ axes as local z_i ones. The local y_i axes are parallel to each other and perpendicular to all of the local z_i axes. The local x_i axis for each Co ion is perpendicular to the z_iy_i plane.

The calculations are performed in the molecular coordinate system that coincides with the local ones of the terminal ions.

The Hamiltonian of the regarded system can be presented as

$$\mathbf{H} = \mathbf{H}_{SO} + \mathbf{H}_{Cr} + \mathbf{H}_{ex} \tag{1}$$

The first term in the full Hamiltonian represents the spin−orbit coupling. The ground state of each cobalt ion is orbitally degenerate ($^4T_{1g}$ triplet in the cubic crystal field). When we focus on the $^4T_{1g}$ ground state, only, the Co^{II} can be described as an ion with the spin value $S = {}^3/_2$ and fictitious angular momentum $L = 1$. The spin−orbit interaction within the $^4T_{1g}$ triplet can be written as follows:

$$\mathbf{H}^i_{SO} = -\frac{3}{2}\kappa_i\lambda\mathbf{S}_i\mathbf{L}_i \quad (i = 1-3) \tag{2}$$

Subscript 1 refers to the central Co^{II} ion, and subscripts 2 and 3 refer to the terminal ones. In eq 2, λ is the spin−orbit coupling parameter for the Co^{II} ion, and according to ref 14, $\lambda = -170$ cm^{-1}. The orbital reduction factor κ takes into account both the covalence of the cobalt−ligand bonds and the mixture of both $^4T_{1g}$ states of each Co^{II} ion. When the covalence is neglected, κ varies between 1 (weak field limit) and $^2/_3$ (strong field limit). The factor $(-^3/_2)$ appears because of the fact that the matrix elements of **L** within the $^4T_{1g}$ states are exactly the same as the matrix elements of $-3\mathbf{L}/2$ within the p basis.

The second term in eq 1 represents the low-symmetry (noncubic) crystal field that takes into account the distortions of the local surroundings. For the real complex under consideration, these distortions are tetragonal, and in the local coordinate systems, the crystal field operator for each cobalt ion can be written as

$$\mathbf{H}^i_{Cr} = \Delta_i[L_{iZ}{}^2 - \mathbf{L}_i(\mathbf{L}_i + 1)/3] \tag{3}$$

To obtain the low-symmetry part of the Hamiltonian for the central ion in the molecular coordinate system, the unitary transformation (rotation around the Y axis by the angle α) should be performed:

$$\mathbf{H}^1_{Cr} = \Delta_1[L_{1Z}{}^2\cos^2\alpha + L_{1X}{}^2\sin^2\alpha - (L_{1Z}L_{1X} + L_{1X}L_{1Z})\cos\alpha\sin\alpha - \mathbf{L}_1(\mathbf{L}_1 + 1)/3] \tag{4}$$

In the following consideration, we take into account that the investigated complex is centrosymmetric, so the corresponding symmetry holds for all parameters (for example, $\kappa_2 = \kappa_3$, $\Delta_2 = \Delta_3$, etc.).

The last term in eq 1 represents the magnetic exchange between the central Co^{II} ion and the terminal ones. Because the ground state of each cobalt ion is orbitally degenerate, the exchange interaction should contain, in general, both orbital and spin contributions. However, following the idea of Lines,[15] we assume that the exchange coupling contains only isotropic contributions operating with the real spins of Co^{II}:

$$\mathbf{H}_{ex} = -2J\mathbf{S}_1\mathbf{S}_2 - 2J\mathbf{S}_1\mathbf{S}_3 \tag{5}$$

where J is the exchange-coupling parameter.

To calculate the magnetic properties of the investigated trimer, the Zeeman interaction should be added to the Hamiltonian (1):

$$\mathbf{H}_{Ze} = \sum_i \beta(-3/2\kappa_i\mathbf{L}_i + g\mathbf{S}_i)\mathbf{H} \tag{6}$$

All matrix elements of the general Hamiltonian equations (1)−(6) can be calculated with the use of the irreducible tensor operator technique.[16] The tensor of the magnetic susceptibility calculated in the molecular coordinate system contains both the diagonal and off-diagonal components. The value of the magnetic susceptibility for an arbitrary direction of the applied magnetic field can be calculated as

$$\chi(\vartheta,\varphi) = Nk_BT\frac{\partial^2}{\partial H^2(\vartheta,\varphi)}\{\ln\sum_g \exp\{-E_g[H(\vartheta,\varphi)]/k_BT\}\} \tag{7}$$

where $E_g(\vartheta,\varphi)$ are the energy levels of the system in the external magnetic field. In eq 7, N and k_B are Avogadro's number and Boltzmann's constant, respectively. The powder-average magnetic susceptibility is given by the integration of eq 7 over ϑ and φ. It can be shown that after this integration the contribution of the off-diagonal components of the χ tensor disappears and the powder-average magnetic susceptibility is

$$\chi_{av} = \frac{1}{3}(\chi_{XX} + \chi_{YY} + \chi_{ZZ}) \tag{8}$$

The presented approach fully describes the magnetic properties of the studied complex in the whole temperature interval. Unfortunately, the best-fit procedure to the experimental data is time-consuming because of the large size of

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(14) Kahn, O. *Molecular Magnetism;* VCH Publishers: New York, 1993.

(15) Lines, M. E. *J. Chem. Phys.* **1971**, *55*, 2977.

(16) Varshalovich, D. A.; Moskalev, A. N.; Khersonskii, V. K. *Quantum Theory of Angular Momentum*; World Scientific: Singapore, 1988.

the matrices to be diagonalized (1728 × 1728 matrices), so some simplifications are required.

(a) Low-Temperature Region. The relatively strong spin−orbit coupling results in the ground doublet on each cobalt ion. This Kramers doublet is well separated from the excited levels. The effect of the low-symmetry tetragonal field does not change this conclusion (we neglect the case of strong positive Δ, where the orbital angular momentum is completely quenched). As a result, at temperatures lower than 50 K only these ground Kramers doublets of each cobalt ion are thermally populated. Both the exchange coupling and the Zeeman interaction are much smaller than the energy separation between the ground doublet and the excited levels and can be regarded as a perturbation operating within the restricted space of the direct product of the Kramers doublets. The effect of the excited levels on the magnetic properties can be taken into account by the second-order perturbation theory.

The magnetic exchange between two $\mathrm{Co^{II}}$ ions in the slightly distorted octahedral surroundings was regarded in ref 17. The analytical expressions for parameters of the effective pseudo-spin-$^1/_2$ Hamiltonian were found. In the present consideration, we do not restrict ourselves to the situation of small distortion. The low-symmetry component of the crystal field can have an arbitrary value and is included in the zeroth-order terms. Under this condition, the full Hamiltonian of the cobalt trimer can be split into the nonperturbed part $\mathbf{H}_0$ involving spin−orbit coupling and a low-symmetry field (eqs 2−4) and the perturbation $\mathbf{V}$ that includes exchange and Zeeman interactions (eqs 5 and 6). As was already mentioned, the action of $\mathbf{H}_0$ results in the ground doublet on each cobalt ion. The corresponding wave functions can be easily calculated (12 × 12 matrices) and are denoted as Φ_i^k. The superscript $k = 1-3$ indicates the cobalt ion in trimer, and the subscript $i = 1$ and 2 labels the two different functions on each ion. The restricted space for the Co trimer is constructed as the direct product of these wave functions:

$$\Psi(i,j,k) \equiv \Phi_i^1\,\Phi_j^2\,\Phi_k^3 \tag{9}$$

The first- and second-order terms are calculated as

$$\langle\Psi(i,j,k)\,|\mathbf{H}^{(1)}|\Psi(i',j',k')\rangle = \langle\Psi(i,j,k)\,|\mathbf{H}_{\mathrm{ex}} + \mathbf{H}_{\mathrm{Ze}}|\Psi(i',j',k')\rangle \tag{10}$$

$$\langle\Psi(i,j,k)\,|\mathbf{H}^{(2)}|\Psi(i',j',k')\rangle = -\sum_{\mathrm{ex}}\frac{1}{\Delta_{\mathrm{ex}}}\langle\Psi(i,j,k)\,|\mathbf{H}_{\mathrm{ex}} + \mathbf{H}_{\mathrm{Ze}}|\Psi_{\mathrm{ex}}\rangle\langle\Psi(i',j',k')\,|\mathbf{H}_{\mathrm{ex}} + \mathbf{H}_{\mathrm{Ze}}|\Psi_{\mathrm{ex}}\rangle^* \tag{11}$$

In eq 11, the summation is performed over all of the excited states, with Δ_{ex} being the energy gap between the corresponding excited state and the ground one (eq 9).

Let us examine briefly the second-order terms (eq 11). They consist of terms that are independent of the applied magnetic field, linear and quadratic in H. The terms independent of H contain contributions to the exchange interaction. The exchange interaction operating on the basis of eq 9 is strongly anisotropic. Moreover, terms such as $\langle\Psi(i,j,k)||\Psi(i,j',k')\rangle$ appear that can be assigned as the exchange coupling between terminal cobalt ions. This coupling is the result of the second-order perturbation theory and takes place via the excited levels of the central cobalt ion. The terms linear in H contribute to the g factor of the system. This g factor is strongly anisotropic and depends both on the magnetic properties of the interacting ions and on the strength of the exchange interaction. Finally, the terms quadratic in H result in strong temperature-independent paramagnetism.

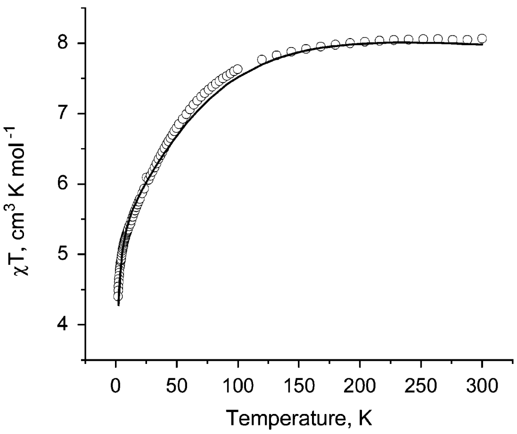

Figure 3. Temperature dependences of χT. Circles: experimental data. Solid line: theoretical curve calculated with the best-fit parameters $\kappa_1 = 0.77$, $\kappa_2 = 0.72$, $\Delta_1 = -970$ cm^{-1}, $\Delta_2 = -1160$ cm^{-1}, and $J = -0.4$ cm^{-1}.

Because of the account of the low-symmetry field in the zeroth-order terms, it is not possible to derive simple analytical expressions such as those in ref 17. The calculations can be performed numerically, and the calculation procedure is as follows:

(i) The wave functions of the lowest Kramers doublet for all cobalt ions are found at some values of the Δ_i and κ_i parameters by means of diagonalization of 12 × 12 matrices.

(ii) The energy matrix of the exchange and Zeeman interactions (eqs 5 and 6) is constructed within the direct product of the lowest Kramers doublets (eq 9).

(iii) The magnetic behavior of the cobalt trimer is calculated using eqs 7 and 8.

(b) High-Temperature Region. The typical value of the exchange-coupling parameter in the regarded cobalt complexes is approximately several reciprocal centimeters. This means that at temperatures higher than 50K this exchange interaction can be neglected and the cobalt trimer can be regarded as a paramagnetic mixture of three noninteracting $\mathrm{Co^{II}}$ ions. The magnetic properties of each cobalt ion can be easily calculated using eqs 2−4 and 6−8.

Analysis. The χT value is about 8 cm^3 K mol^{-1} at room temperature and goes down with the temperature decrease, as presented in Figure 3. This magnetic behavior is typical of pseudo-octahedrally coordinated $\mathrm{Co^{II}}$ ions. For the analysis of the properties of the studied trimer, we split the

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(17) Palii, A. V.; Tsukerblat, B. S.; Coronado, E.; Clemente-Juan, J. M.; Borras-Almenar, J. J. *Inorg. Chem.* **2003**, *42*, 2455.

(18) *SHELXTL*, version 5.1; Brüker AXS: Madison, WI, 1998.

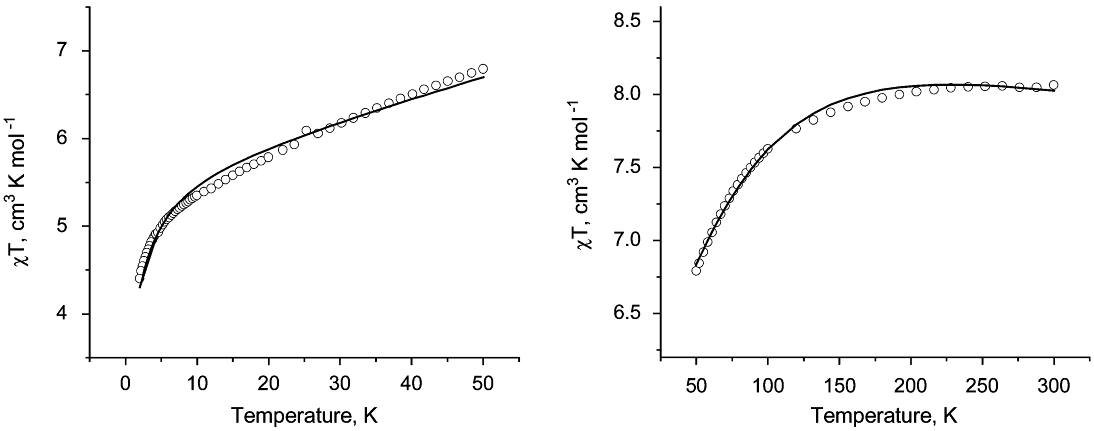

Figure 4. (a, left) Temperature dependences of χT in the low-temperature region. (b, right) Temperature dependences of χT in the high-temperature region. Circles: experimental data. Solid line: theoretical curve.

experimental data into two subsets: for temperatures lower and higher than 50 K. The former subset was fitted with the use of the model for the low-temperature region and second-order perturbation theory. The latter one was fitted by neglecting any exchange interaction with the use of the model for the high-temperature region. Both fitting procedures were performed simultaneously. The results of these fitting procedures are shown in Figure 4a,b. One can see very good agreement between the theoretical simulations and the experimental results. The best-fit parameters are $\kappa_1 = 0.77$, $\kappa_2 = 0.72$, $\Delta_1 = -970$ cm^{-1}, $\Delta_2 = -1160$ cm^{-1}, and $J = -0.4$ cm^{-1}. The values of the orbital reduction factor are in the middle between the weak and strong field limits. Best-fit values of the low-symmetry component of the crystal field indicate that for the terminal ions the distortions from the octahedral surroundings are stronger than those for the central one. This conclusion is in good agreement with the structural data. The small obtained value of the exchange parameter is explained by the relatively large distances between the cobalt ions and the bridging oxygen atoms from the water molecules.

To control the correctness of the application of the low-temperature model to the data up to 50 K, we calculated the energy gap between the lowest Kramers doublets and the first excited levels for each Co^{II} ion using the best-fit parameters obtained in the fitting procedure. For the central Co^{II} ion, this gap is about 200 cm^{-1}, while for the terminal ions, this value is 186 cm^{-1}. The thermal populations of the excited levels at 50 K are 0.30% and 0.48% for the central and terminal cobalt ions, respectively. One can see that even at 50 K the magnetic behavior is mainly determined by the interactions within the lowest Kramers doublets on each cobalt ion. The contributions from the excited levels can be accounted for using the perturbation theory.

At the final step of our investigations, we used the obtained best-fit parameter to calculate the magnetic behavior of the trimer in the framework of the general model (1728 × 1728 matrices) in the whole temperature range. The theoretical curve is presented in Figure 3 as a solid line. There exist good agreement between this theoretical curve and both experimental data and curves obtained in the simplified models. This demonstrates the validity of the proposed approach for the analysis of the magnetic behavior of the cobalt compounds in the whole temperature interval and allows one to simulate the properties of the complexes with a large number of interacting ions.

Concluding Remarks

In this paper, we report the synthesis and magnetic behavior of a new cobalt(II) trifluoroacetato trimer bridged by two water molecules within and linked by 1,4-dioxane into a one-dimensional chain. The unprecedented ability of 1,4-dioxane to link the trimers is attributed to the anhydrous conditions employed during the synthesis. The structure of the trimer of cobalt(II) in **1** shows that all cobalt centers are tetragonally distorted with their axes near perpendicular. A good fit of the calculated magnetic behavior of the investigated trimer to the experimental data was obtained. The key parameters of the interacting cobalt ions were found. The magnetic properties of the investigated compound are mainly determined by the spin−orbit coupling and low-symmetry crystal field. A weak antiferromagnetic exchange interaction between Co^{II} ions manifests itself at low temperature only. It should be mentioned that during the fitting procedure several sets of the best-fit parameters were obtained. However, in all cases, the exchange interaction was antiferromagnetic and very weak. The structural and magnetic data indicate that isolated trimer units are responsible for the magnetism and the trifluoroacetate bridge is a rather poor exchange path.

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Supporting Information Available: An alternative view of the one-dimensional chain of trimers along the longitudinal axis, together with a full list of distances and angles plus hydrogen positions found by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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