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A Coordination Polymer of Cobalt(II)–Glutarate: Two-Dimensional Interlocking Structure by Dicarboxylate Ligands with Two Different Conformations

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A novel Co–glutarate, Co[$O_2C(CH_2)_3CO_2$] (**1**), was synthesized as single crystals by the hydrothermal reaction of $CoCl_2$ with glutaric acid in the presence of KOH and characterized by single-crystal X-ray diffraction analysis, TGA, IR, UV–vis reflectance spectrometry, and SQUID measurements. The dark purple Co–glutarate crystallizes in the monoclinic system in the space group *P*2/*c*, with $a = 14.002(3)$ Å, $b = 4.8064(10)$ Å, $c = 9.274(3)$ Å, $\beta = 90.5(2)°$, and $Z = 4$. The Co^{2+} centers are tetrahedrally coordinated to four oxygen atoms from the dicarboxylate ligands. The anhydrous-pillared three-dimensional structure consists of infinite Co–CO_2–Co inorganic layers, which are stacked by the coordinated glutarate alkyl chain along the *a*-axis. There are two different conformations for glutarate ligands, i.e., the gauche- and the anti-forms. These ligands reside between the inorganic layers alternatively to separate each layer by 7.01 Å (gauche) and 6.99 Å (anti). Magnetic measurement reveals that the predominant magnetic interactions are antiferromagnetic below 14 K.

Introduction

There has been considerable interest in inorganic−organic hybrid materials whose crystal structures present various types of metal−ligand coordination and their dimensionality.[1] The studies on inorganic−organic hybrid pillared structures are also focused on materials science as well as structural chemistry, for potential applications such as catalysis,[2] sorption,[3] photochemistry,[4] or magnetism.[5] "Crystal engineering" through connection of transition-metal centers has proven to be a reasonable approach to building three-dimensional structures based on layered structural motifs, controlling the packing of layers by organic pillars of variable lengths and types.[6] The terminal bifunctional groups such as diphosphonate, carboxyphosphonate, and dicarboxylate allow a variety of crystal structures of the coordination complex depending on the synthetic conditions, metal cations, and characteristics and flexibility of the ligands used.[7] The structures and physical properties of transition-metal-containing complexes with various carboxylato ligands

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such as α,ω-dicarboxylate,[8] phthalate,[9] and biphenyldicarboxylate (bpdc)[10] and other ligands[11] have been reported.

Recently, we have reported the syntheses and X-ray crystal structural analyses of a series of Mn(II)−dicarboxylates, $Mn_2(H_2O)[_2OC(CH_2)_nCO_2]_2$ ($n = 3-12$, denoted as MnDC-*n*), prepared by the hydrothermal method.[12] The topology of MnDC-*n* presents a structure constituted by the stacking along one direction of MnO_6 layers interweaved with alkyl chains. The alkyl chains are well aligned with only the anti-form (i.e., trans-form) and closed-packed between the inorganic layers. The interlayer spacings of the Mn compounds were varied by varying the number of carbon atoms in the alkyl chain. Interestingly the crystal structures of MnDC-*n* (n = even) differ from those of MnDC-*n* (n = odd). All the prepared manganese dicarboxylate compounds involve the replication of the local crystal structure in the Mn−O monolayer to present an antiferromagnetic interaction. It should be noted that Co−pimelate, reported by Livage et al.,[8a] also consists of only the anti-form of two independent pimelate ions. All the anti-form alkyl chains between two terminal functional groups may have a strong tendency to self-assemble to induce a three-dimensional network of the previous MnDC-*n* and Co−pimelate. However, this argument provokes the question of whether other conformations of alkyl chains are possible, since simultaneous rotations of alkyl chains due to their conformational freedom could construct organic layers of alkyl chains possessing gauche conformations.

In this paper we report the synthesis, single-crystal X-ray diffraction analyses, and physical characterizations of Co−glutarate, $Co[O_2C(CH_2)_3CO_2]$ (**1**). The title compound, **1**, exhibits two-dimensional arrangements of cobalt(II) cations interconnected by dicarboxylate anions. Conformational freedom of α,ω-dicarboxylate ligands in transition-metal-containing coordination polymers was observed in the crystal structure of compound **1**. Two distinct conformations (anti and gauche) in compound **1** are presented in the alkyl chains of the glutarate ligands. As far as we know, this is the first example of inorganic−organic hybrid layered structures consisting of gauche- and anti-form dicarboxylate layers stacked alternatively between the inorganic layers along the same direction. A construction of a three-dimensional network using ligands with conformational freedom to engender supramolecular isomerism has been reported for $[Co(NO_3)_2(1,2\text{-bis}(4\text{-pyridyl})\text{ethane})_{1.5}]_n$.[13] However, the latter coordination polymer involves nitrate ligands, which give rather flexible coordination environments, and also does not possess the close packing of alkyl chains as demonstrated in compound **1**.

Experimental Section

Synthesis. All chemicals used were of reagent grade and were used without further purification. $Co[O_2C(CH_2)_3CO_2]$ was prepared by the following procedure: glutaric acid (5 mmol) was dissolved in 5 mL of 1.5 M KOH solution. To this solution (pH ≈ 4) was added $CoCl_2 \cdot 6H_2O$ (5 mmol) to attain a pH of ca. 3.5 after homogenization. The solution was heated under hydrothermal conditions in a 23 mL Teflon vessel at 180 °C for 24 h. Then the heated autoclave was quenched with cold water. Platelike dark purple crystals of $Co[O_2C(CH_2)_3CO_2]$ were obtained with a small amount of glutaric acid by filtration. The product was dried in air after off the residual glutaric acid was washed with ethyl alcohol, and the yield was ca. 70% based on the utilized cobalt.

Physical Measurements. IR spectra were obtained in the 4000−400 cm^{-1} range using a Nicolet 1700 FT-IR spectrometer. The sample was ground with dry KBr and pressed into a transparent disk. The Inter-University Center of Natural Science Research Facilities at Seoul National University performed the elemental analyses. Thermogravimetric analyses were performed using a TA Instruments SDT 2960. The samples were placed in platinum containers, and the data were recorded under a nitrogen atmosphere (heating rate of 5 °C/min from room temperature to 200 °C and 10 °C/min to 1000 °C). Magnetic susceptibility measurements were taken at 5000 Oe from 2 to 300 K, using a Quantum Design SQUID MPMS7S magnetometer. UV−vis diffuse reflectance spectra were recorded between 400 and 1500 nm on a Shimadzu UV-3101PC spectrophotometer at room temperature.

Single-Crystal X-ray Diffraction. Single-crystal X-ray data were collected on a Siemens P4 automated four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71079$ Å). A crystal of dimensions $0.40 \times 0.36 \times 0.32$ mm^3 was glued to a glass fiber and mounted onto the goniometer. Initial random search on the crystal resulted in 25 peaks ($10.0° \leq 2\theta \leq 20.0°$) that could be indexed with the monoclinic unit cell similar to the final crystallographic results. Data collections were performed with the ω mode on an octant ($2.91° \leq 2\theta \leq 24.98°$). Three check reflections were measured every 100 reflections throughout data collection and showed no significant variation in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. An absorption correction was applied on the basis of the ϕ-scan data of six averaged reflections. Compound **1** crystallizes in the monoclinic crystal system. The pattern of systematic absences observed in the data was consistent with either the space group $P2/c$ or the space group Pc. The centric space group $P2/c$ was assumed and confirmed by the successful solution and refinement of the structure. The structure of **1** is solved by direct methods (SHELX-86) and standard difference Fourier

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Table 1. Crystal Data and Structure Refinement Parameters for **1**

empirial formula	$CoC_5H_6O_4$	vol (Å^3)	624.1(3)
fw	189.03	Z	4
temp (K)	296(2)	D_{calcd} (mg/m^3)	2.012
wavelength (Å)	0.71073	μ (cm^{-1})	26.93
space group	$P2/c$ (no.13)	goodness-of-fit on F^2	1.078
a (Å)	14.002(3)	final R indices [$I > 2\sigma(I)$]	R1^a = 0.0480, wR2^b = 0.1316
b (Å)	4.8064(10)		
c (Å)	9.274(3)	R indices (all data)	R1^a = 0.0566, wR2^b = 0.1601
α (deg)	90		
β (deg)	90.50(2)		
γ (deg)	90		

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2]/\sum w(|F_o|^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Co(1)−O(4)	1.969(3)	C(4)−C(5)−C(6)	115.6(3)
Co(1)−O(3)	1.981(2)	C(5)−C(6)−C(5)^f	115.6(5)
Co(1)−O(1)	1.984(3)	O(4)−Co(1)−O(3)	106.51(11)
Co(1)−O(2)	1.988(3)	O(4)−Co(1)−O(1)	99.03(11)
O(1)−C(4)	1.276(4)	O(3)−Co(1)−O(1)	116.37(11)
O(2)−C(4)^a	1.262(4)	O(4)−Co(1)−O(2)	121.44(12)
O(3)−C(1)	1.261(4)	O(3)−Co(1)−O(2)	110.28(11)
O(4)−C(1)^b	1.274(4)	O(1)−Co(1)−O(2)	103.28(11)
C(1)−O(4)^c	1.274(4)	C(4)−O(1)−Co(1)	126.3(2)
C(1)−C(2)	1.514(5)	C(4)^a−O(2)−Co(1)	112.2(2)
C(2)−C(3)	1.525(5)	C(1)−O(3)−Co(1)	117.8(2)
C(3)−C(2)^d	1.525(5)	C(1)^b−O(4)−Co(1)	133.7(2)
C(4)−O(2)^e	1.262(4)	O(3)−C(1)−O(4)^c	120.8(3)
C(4)−C(5)	1.512(5)	O(3)−C(1)−C(2)	118.7(3)
C(5)−C(6)	1.533(5)	O(4)^c−C(1)−C(2)	120.4(3)
C(6)−C(5)^f	1.533(5)	C(1)−C(2)−C(3)	115.2(3)
		C(2)^d−C(3)−C(2)	109.8(5)
		O(2)^e−C(4)−O(1)	120.0(3)
		O(2)^e−C(4)−C(5)	120.7(3)
		O(1)−C(4)−C(5)	119.3(3)

[a] Symmetry transformations used to generate equivalent atoms: (a) $x, -y, z - 1/2$; (b) $x, y + 1, z$; (c) $x, y - 1, z$; (d) $-x, y, -z - 1/2$; (e) $x, -y, z + 1/2$; (f) $-x + 1, y, -z + 1/2$.

techniques (SHELX-97).[14] A summary of crystal data is represented in Table 1, and the selected bond distances and angles are given in Table 2.

Cobalt and oxygen atoms were first located, and then the carbon atoms were found by difference Fourier maps. Absorption corrections were applied using the SHELX-86 program. Refinements for 117 parameters were performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms and with isotropic ones for all hydrogen atoms. Hydrogen positions were separately included in the refinements using the electron density map, which defines clearly both the anti and gauche conformations of the glutarate ligands. The final reliability factors converged to $R1(F_0) = 0.0480$ and $wR2(F_0^2) = 0.1316$.

Result and Discussion

Synthesis. The hydrothermal reaction of cobalt chloride in the presence of KOH gives **1** as dark purple crystals in an aqueous solution. Anal. Calcd: C, 31.8; H, 3.2; Co, 31.2. Found: C, 31.6; H, 3.2; Co, 29.7. FT-IR data (KBr, ν(C−H)) are observed at 2957 and 2921 cm^{-1}. The asymmetric and symmetric vibrations of carboxylate are observed at 1580, 1534, 1449, and 1405 cm^{-1}. The aqueous solution of the starting materials appeared to be thermochromic, being violet-pink in color at room temperature and changing to dark purple when heated over 60 °C, which may be ascribed to transformation of the coordination environments of cobalt ions from octahedral to tetrahedral sites. The pH and concentration of the starting solution, heat treatments, and washing procedures are critical to obtain crystal samples of high purity. Lower concentrations of the starting solution gave glutaric acid, and higher pH values resulted in cobalt hydroxide. Starting with a low concentration solution gave no solid product after hydrothermal treatments. Compound **1** (dark purple crystals) transforms slowly to an unknown pink compound in distilled water, and then produces a transparent aqueous solution pink in color.

Thermogravimetric analyses were conducted under a nitrogen atmosphere. Only one distinct mass loss region is seen in TGA of the title compound. The 43% mass loss (300−450 °C) corresponds to the decomposition of the organic chains through the pyrolysis reaction. The weight loss curve was not observed around 200 °C, indicating that **1** has no hydrate water in the lattice, corresponding to the absence of bands at above 3000 cm^{-1} in the IR spectroscopic data.

The UV−vis reflectance spectra of compound **1** show a sharp d−d absorption corresponding to Co(II) in tetrahedral coordination geometry. The observed band of 7680 cm^{-1} is assigned to $^4T_1(F) \leftarrow {}^4A_2(F)$, and those of 12107, 17483, and 19011 cm^{-1} are assigned to $^4T_1(P) \leftarrow {}^4A_2(F)$. The crystal field strength value ($\Delta_t = 3612$ cm^{-1}) and the Racah parameter ($B = 860$ cm^{-1}) were calculated using the above values, which are comparable with those given in the literature ($\Delta_t = 4090$ cm^{-1}, which is calculated as $4/9\Delta_o$, and $B = 825$ cm^{-1} for the free ion Co^{2+}).[15]

Structure Determination of $Co[O_2C(CH_2)_3CO_2]$ (1). The structure of **1** is an inorganic−organic hybrid layered system, consisting of inorganic layers of cobalt ions and organic layers of glutarate ligands. A unique Co atom site is coordinated to four oxygen atoms, all belonging to different glutarate ligands, and the Co atom is centered in the tetrahedron among the four carboxylates (Figure 1). The glutarate ligands are located roughly along the *a*-axis. The replication of this basic unit involves the formation of two-dimensional cobalt networks with glutarate ligands being interlocked as pillars, leading to a complex three-dimensional layered structure as shown in Figure 2.

Two different conformations of glutarate ligands, i.e., anti- and gauche-forms, are observed in the same ratio (Figure 3). The dihedral angle of the gauche-form in compound **1** is observed to be 65.5°. It is surprising that the conformation of the ligands of Co−pimelate reported by Livage et al.[8a] consists of only anti-forms though both compound **1** and Co−pimelate have similar three-dimensional networks. The alkyl chains between two terminal carboxyl groups may have an enhanced preference to self-assemble all anti conformations in some 3D network solids such as the previous MnDC-*n*[12] and Co−pimelate.[8a] These closely related structures of alkyl chains belong to one of the categories of supramolecular isomerism.[6g]

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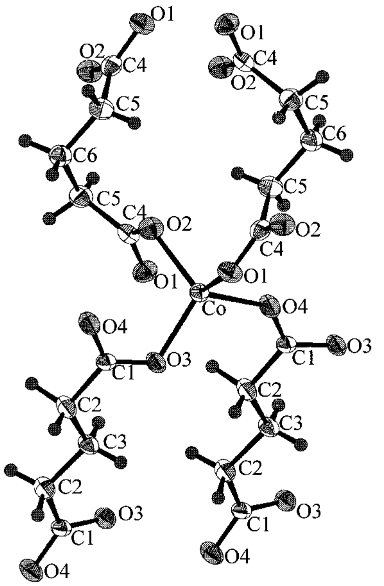

Figure 1. Coordination of **1**. The Co(II) atom is coordinated to four glutarate alkyl chains, in a tetrahedral geometry. (Thermal ellipsoids are given at 50% probability.)

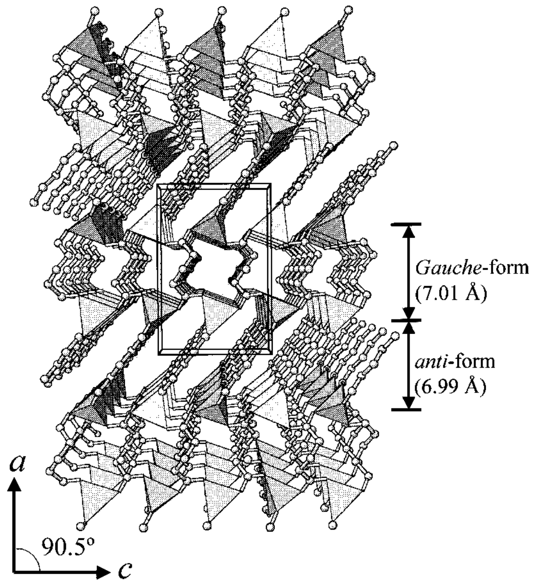

Figure 2. Polyhedral structure view of **1** along [010]. The hydrogen atoms of the carboxylate molecules are not shown for clarity.

The “gauche effect” in conformational analysis occurs when the gauche rotamer is more stable than the anti rotamer.[16,17] The gauche conformation of compound **1** can be compared with simultaneous rotation of alkyl chains in a well-known self-assembled monolayer on metal substrates. In compound **1**, the coexistence of both forms in the same layer may cause disorder or disruption of the metal−carboxylate coordination in the next layer, which results in the strained self-assembly of alkyl chains with the same conformation exclusively in a layer. This type of “conformational assembly” or “assembled gauche effect” is rarely found in inorganic−organic hybrid compounds. The strain

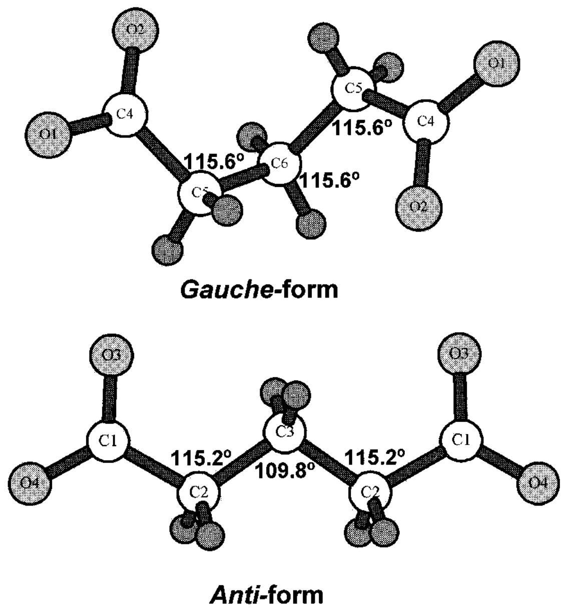

Figure 3. Two different conformations of glutarate alkyl chains with C−C−C bond angles in the (a) gauche-form and (b) anti-form.

may result not only from the coordination environment of CoO_4 but also from the short distance between two terminal carboxylate groups bound to the cobalt ions. For butane, the energy of the gauche conformation is ∼1 kcal/mol higher than that of the anti conformation, although the energy minimum may change to construct a three-dimensional network by the applied strain. These criteria suggest that the adoption of the gauche conformation may be explained by reasonable low-energy alternatives as observed in the organodisulfonate system.[18]

The 2-fold axis, parallel to the *b*-axis in **1**, stands on the middle of the alkyl chain ligands in both conformations (C(3) and C(6)), and the rest of the carbon atoms in the alkyl chains are represented by symmetric operations. The bond angles of alkyl chains in **1** happen to vary with the conformations as shown in Figure 3. For the gauche-form, the C(4)−C(5)−C(6) and C(5)−C(6)−C(5) bond angles are both 115.6°. However, in the anti-form, the bond angle of C(1)−C(2)−C(3) is 115.2° and that of C(2)−C(3)−C(2), the middle chain, is 109.8°. Those of the anti-form in **1** give values close to the experimental data of the free glutaric acid in the solid state (115.0° and 109.0°, respectively).[19] Terminal groups of the carboxylate (OCO) in both forms link the cobalt atoms in (100) through the syn−anti mode, leading to an infinite two-dimensional inorganic layer (Figure 4).

Compound **1** presents an exclusive tetrahedral coordination of CoO_4, without sharing edges or corners among the polyhedra, although most cobalt coordination compounds with oxygen ligands have a strong tendency to form Co−O−Co linkages to adopt trigonal bipyramidal[20] or octahedral[21] coordinations. The O−Co−O bond angles in the

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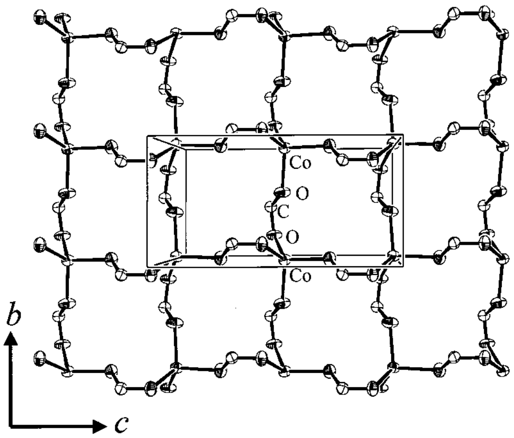

Figure 4. ORTEP view of the inorganic layer of Co[$O_2C(CH_2)_3CO_2$] in (100). The connectivity of Co−CO_2−Co is shown. (Thermal ellipsoids are given at 50% probability.)

distorted CoO_4 tetrahedral site range from 99.0° to 121.4° (av 110.8°). Bonds connecting oxygen atoms in the anti bridging mode (O(1)−Co−O(4)) happen to bring the minimum bond angle value (99.0°), and the rest of the angles, O_{syn}−Co−O_{syn} and O_{anti}−Co−O_{syn}, show no specific tendency toward the bridging modes. The bond distances of Co−O range from 1.969 to 1.988 Å with an average bond distance of 1.981 Å, which is slightly larger than that of cobalt phosphate compounds in tetrahedral coordination [Co−O = 1.96 Å on average].[22] The bond valence sum calculations,[23] depending on the Co−O distances, support the oxidation state (+2) of the cobalt of **1**.

Each Co atom is located in a pseudo-two-dimensional square network between glutarate layers. The Co···Co distances are 4.81 and 4.64 Å along the *b*- and *c*-axes, respectively. The carboxylate (OCO^-) linkages on the end of the anti-form ligand are found to connect the Co atoms along the *b*-axis, and those of the gauche-form ligand to connect along the *c*-axis from the other side of the inorganic plane. Therefore, the planes of the two terminal functional groups $(OCO^-)_{anti}$ and $(OCO^-)_{gauche}$ are nearly perpendicular to each other. These two carboxylate groups extending in opposite directions lead each ligand to reside between the inorganic layers alternatively. In addition, they separate each inorganic layer by 7.01 Å (gauche) and 6.99 Å (anti) along the *a*-axis. The bond angle of the syn bridge in the anti-form, C(1)−O(3)−Co, is 117.8°, and that in the gauche-form, C(4)−O(2)−Co, is 112.2°. That of the anti bridge in the anti-form, C(1)−O(4)−Co, is 133.7°, and that in the gauche-form, C(4)−O(1)−Co, is 126.3°. The glutarate ligands stack one inorganic layer on top of another that is an identical inorganic layer represented by the symmetry operations.

The anti-form ligands are tilted over ~52° with respect to the inorganic layer when projected onto the (010) plane (Figure 2), and bridge each Co atom diagonally to the next inorganic layer. The gauche-form is also tilted over ~52° at the end of the alkyl chain, when projected onto the (001) plane (Figure 5). However, the gauche-form alkyl chains are twisted, rotating up in left- or right-handed direction as a coil, which also build perpendicular pillars between the inorganic layers (Figure 6). The gauche-form ligands are arranged along the *b*-axis in a row with the glutarate helices of the same handedness. The left-handed and right-handed gauche-forms are located in a row alternatively in one layer. Both anti- and gauche-form ligands occupy the space in the middle of the metal grid, surrounded by the six nearest alkyl chains in a hexagonal shape. The chain···chain distance is about 4.7 Å, which implies the framework of compound **1** is less compact than those of MnDC-*n* compounds, which have 4.1 Å with all anti conformations.

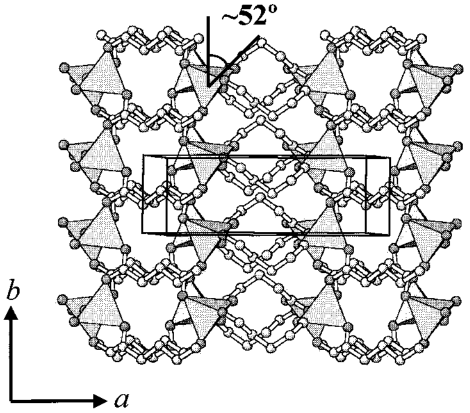

Figure 5. Polyhedral structure view of **1** projected along [001]. The carboxylate alkyl chains are tilted over the inorganic layer. The hydrogen atom molecules are not shown for clarity.

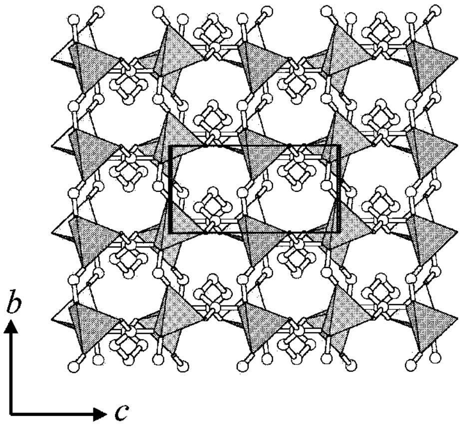

Figure 6. Structure view of interlocking alkyl chains of the gauche-form between two inorganic CoO_4 layers along [100]. The alkyl chains of the anti-form and hydrogen atoms of the gauche-form are not shown for clarity.

Magnetic Measurements. The temperature dependence of the molar susceptibility for **1** is shown in Figure 7. The compound shows simple Curie−Weiss antiferromagnetism above 14 K, with the best linear fit yielding $C = 2.71$ cm^3 K/mol and $\Theta = -25.75$ K. A small increase of the magnetic susceptibility is observed below 9 K, and a very small amount of paramagnetic impurity was assumed to have a Curie behavior in this temperature region. The value of $\chi_M T$ at room temperature is 2.52 cm^3 mol^{-1} K, and the effective magnetic moment μ_{eff} is 4.49 μ_B/mol of cobalt. They are common values for high-spin complexes in tetrahedral Co^{2+}

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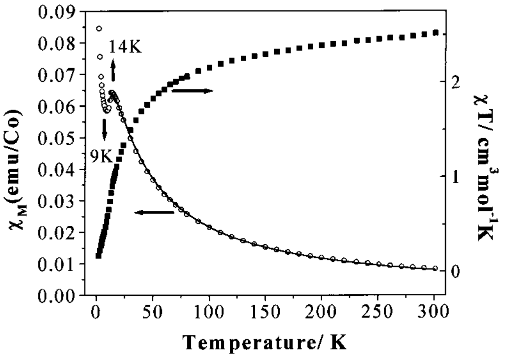

Figure 7. Magnetic susceptibility (open circles) of **1** plotted as χ_M with the fit to eq 1 (solid line) and $\chi_M T$ (black squares), plotted as a function of temperature.

centers (4.30−5.20 μ_B).[24] The susceptibility curve of compound **1** is similar to that of Co−pimelate, presumably because two different cobalt dicarboxylate compounds have identical Co^{2+} inorganic layers separated by organic ligands.[8a] This implies that the exchange pathways for magnetic coupling mainly correspond to the Co−O−C−O−Co linkages within the (100) plane and little interaction via the alkyl chains. The negative Θ value is consistent with antiferromagnetic interactions between the cobalt atoms ($S = 3/2$). According to the Lines model,[25] the high-temperature susceptibility data (11−300 K) can be fit by the expansion series

$$\frac{Ng^2\mu_B^{\ 2}}{2\chi_M|J|} = 3\Theta + \sum_{n=1}^{6}\frac{C_n}{\Theta^{n-1}} \qquad (1)$$

where $\Theta = kT/2|J|S(S+1)$, g is the Landé g-factor, μ_B is the Bohr magneton, N is the number of spins in the lattice, $S = 3/2$, and the coefficients $C_1 = 4$, $C_2 = 1.600$, $C_3 = 0.304$, $C_4 = 0.249$, $C_5 = 0.132$ and $C_6 = 0.013$. The values for the intraplanar exchange J and the Landé g-factor, obtained from this formula, are $-2.42(1)$ cm^{-1} and 2.34(1), respectively. The cobalt(II) ions residing in a tetrahedral geometry have a $^4A_2$ ground state, and the g values are slightly anisotropic and lie in the range of 2.2−2.4.[24]

Conclusion

A novel layered cobalt(II)−glutarate containing dicarboxylate ligands with conformational assembly of two different conformations has been synthesized by the hydrothermal method. A single-crystal X-ray diffraction study of **1** shows the presence of both anti and gauche conformations of the glutarate alkyl chain layers interlocking the inorganic layer of $Co(II)O_4$. The exclusive assembly of ligands with this type of conformation gives one of the most important structural aspects in supramolecular isomerism in coordination polymers; that is, conformational freedom of the ligands could be limited by geometrical conditions. This could be denoted as an example of the coordination gauche effect in self-assembly. Syntheses of the other transition-metal-containing complexes applicable to the gauche effect are under investigation.

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Supporting Information Available: X-ray crystallographic file, in CIF format, for **1**. This material is available via the Internet at http://pubs.acs.org.

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