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p-Toluenesulfonate를 가진 새로운 코발트(II) 층상 화합물의 합성과 구조 분석

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Synthesis and Structural Analysis of a New Layered Cobalt (II) Compound with *p*-Toluenesulfonic Acid : $[\text{Co}(\text{H}_2\text{O})_6] (\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$

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Abstract: The title compound, $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$, has been prepared and characterized by X-ray crystallography. The crystal structure of the compound demonstrates a layered material constituted by hexaaquacobalt (II) cations and *p*-toluenesulfonate anions. Geometrical environment of the cobalt atom is octahedrally coordinated by water molecules. The *p*-toluenesulfonate anions are arranged with the sulfonate groups turned toward opposite side of the layer, alternately. The layered structure is stabilized by the hydrogen bondings between the ligated water molecules and the anionic sulfonate oxygen atoms.

Key words: cobalt compound, *p*-toluenesulfonic acid, layered material, structure analysis

1. Introduction

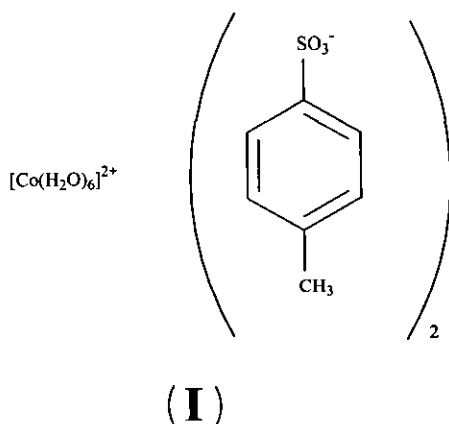
Layered materials have been of the great interest in both academic research and industrial applications because of the plausible candidates as ion exchangers, molecular sieves, size- and shape-selective catalysts.^{1,2} Particularly, zirconium-, titanium-phosphates and phosphonates have been extensively studied for the application as a new family of layered and zeolitic materials.³⁻⁵ Most commonly, these mixed inorganic-organic two- or three-dimensional compounds contain covalent

metal-oxygen-phosphorus frameworks. Recently, Squattrito and co-workers⁶⁻¹¹ have studied the metal sulfonate compounds, and reported two- or three-dimensional materials with layered and zeolitic structures analogous to recently reported metal phosphonates. These metal sulfonate compounds are quite different in structure and properties from recently reported metal phosphonates of similar composition. Therefore, we have investigated the preparations, structures and properties of the sulfonate compounds with alkali-, alkali earth-, transition- and lanthanide metals. Here, we report the preparation and crystal structure of a new layered cobalt (II) compound with *p*-toluenesulfonic acid, (I).

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2. Experimental

2.1. Preparation and Analysis of $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$

Into 50 ml of distilled water, a 10 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and a 10 mmol of p-toluenesulfonic acid were introduced successively under stirring. After the mixture was stirred for about 10 min and the small amount of precipitate was filtered off. The resulting solution was kept standing in a refrigerator at ca. 5°C for a few days to obtain the pale red block crystals.

IR spectrum of the obtained crystal was recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using KBr disk methods. The assignment of the relevant absorption bands confirmed the presence of p-toluenesulfonic acid and water molecules.¹² EDS spectrum performed on a Jeol 840A scanning electron microscope/Link AN10000 energy dispersive X-ray spectrometer unit revealed the presence of Co and S elements. The quantitative analysis of Co^{2+} ion was conducted on a Perkin-Elmer 2380 atomic absorption spectrometer and the analyses of the total organic carbon, hydrogen and sulfur were made on a CE EA-1110 elemental analyzer. The composition of the crystal compound (I) was deduced from the elemental analyses; the formula of $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ is consistent with the results of single crystal X-ray diffraction analysis. *Anal. Found:* C, 32.45; H, 5.11; S, 12.38; Co, 11.3%. *Calc.* for $\text{C}_{14}\text{H}_{26}\text{O}_{12}\text{S}_2\text{Co}$: C, 33.01; H, 5.14; S,

12.59; Co, 11.57%.

2.2. X-ray Crystallography

A pale red block crystal of the title compound was coated with epoxy glue in order to prevent spontaneous liberation of water molecules from the specimen under ambient conditions. The intensity data were collected at room temperature on a Siemens P4 four-circle X-ray diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Accurate unit cell dimensions were refined using 54 reflections with 2θ ranges 8.72–24.96°. Three standard reflections were measured every 97 reflections; no remarkable decays were observed throughout data collection. The reflections used with the intensities $|I| > 2\sigma(I)$ were Lorentz and polarization corrected; a semi-empirical absorption correction based on the psi-scans was applied. A total of 3696 reflections was collected in the 2θ range 6.0–55.0° using θ - 2θ scan mode.¹³

All calculations in the structural solution and refine-

Table 1. Crystallographic data for $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$

Formula	$\text{C}_{14}\text{H}_{26}\text{O}_{12}\text{S}_2\text{Co}$
Formula weight	509.40
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	6.9814(9)
b (Å)	6.300(1)
c (Å)	25.211(4)
β (°)	91.76(1)
V (Å ³)	1108.3(3)
Z	2
D_o, D_m (g/cm ³)	1.526, 1.52(1)
$F(000)$	530
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	1.018
2θ range for data (°)	6–55
Limiting indices	$-9 \leq h \leq 1, -8 \leq k \leq 1, -32 \leq l \leq 32$
Reflections collected	3696
Independent reflections	2533 [$R_{\text{int}} = 0.0256$]
Parameters	157
Goodness-of-fit on F^2	1.18
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.048, wR_2 = 0.136$

ment were performed using the Siemens SHELXTL crystallographic software package¹⁴ on a PC system. The space group was assigned based on the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method¹⁵ and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at the calculated positions with the isotropic thermal parameters were included in the final structure factor calculations. Final difference of electron density maps contained no significant features. The crystallographic and experimental data are summarized in Table 1.

3. Results and Discussion

Fig. 1 and 2 show a molecular structure and a perspective view of the $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$, respectively. The selected bond lengths and bond angles are listed in Table 2. As shown in Fig. 1 and 2, the cobalt metal ion lies on an inversion center and is six-coordinated by water molecules with no direct bonding to

the sulfonate groups. Its structural coordination feature can be described as a regular octahedral arrangement. As listed in Table 2, the $\text{Co}-\text{O}_{\text{water}}$ bond lengths range

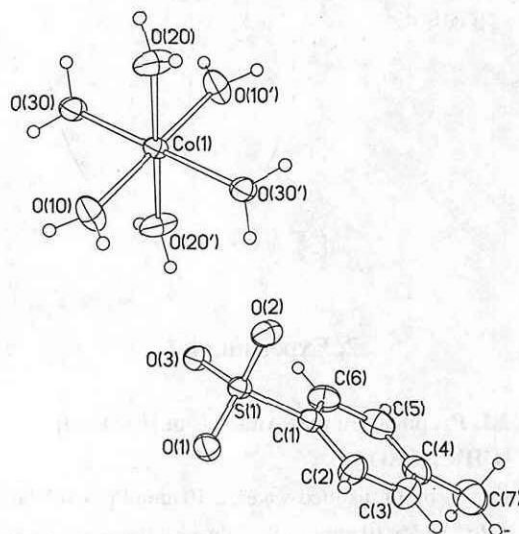


Fig. 1. The molecular structure of $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ showing the atomic numbering scheme and 30% probability thermal ellipsoids except for the hydrogen atoms.

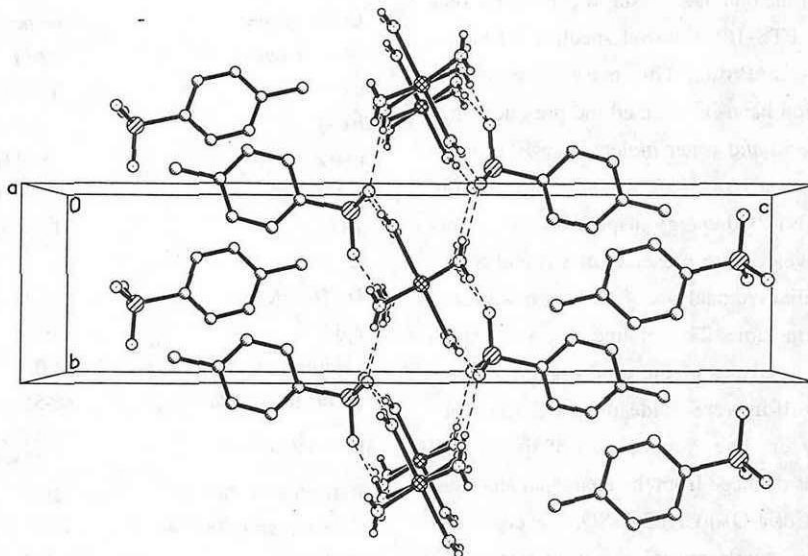


Fig. 2. A perspective view of the unit cell of $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ along the α -axis; hydrogen bonds are shown by broken lines; H atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for [Co(H₂O)₆](CH₃C₆H₄SO₃)₂

Co(1)-O(10)	2.077(3)	Co(1)-O(20)	2.078(3)
Co(1)-O(30)	2.051(2)	S(1)-O(1)	1.456(3)
S(1)-O(2)	1.456(3)	S(1)-O(3)	1.456(2)
S(1)-C(1)	1.767(4)	C(1)-C(2)	1.389(5)
C(1)-C(6)	1.375(5)	C(2)-C(3)	1.378(6)
C(3)-C(4)	1.375(7)	C(4)-C(5)	1.368(7)
C(4)-C(7)	1.509(7)	C(5)-C(6)	1.398(7)
O(10)-Co(1)-O(20)	92.6(1)	O(10)-Co(1)-O(30)	91.0(1)
O(20)-Co(1)-O(30)	91.1(1)	O(10)-Co(1)-O(10)* ¹	180.0(2)
O(20)-Co(1)-O(20)* ¹	180.0(1)	O(30)-Co(1)-O(30)* ¹	180.0(2)
O(1)-S(1)-O(2)	112.2(2)	O(1)-S(1)-O(3)	112.4(2)
O(2)-S(1)-O(3)	112.3(2)	O(1)-S(1)-C(1)	106.2(2)
O(2)-S(1)-C(1)	106.6(2)	O(3)-S(1)-C(1)	106.7(2)
S(1)-C(1)-C(2)	119.0(3)	S(1)-C(1)-C(6)	121.3(3)
C(1)-C(2)-C(3)	119.5(4)	C(1)-C(6)-C(5)	119.4(4)
C(2)-C(3)-C(4)	121.6(5)	C(2)-C(1)-C(6)	119.7(4)
C(3)-C(4)-C(5)	118.5(4)	C(3)-C(4)-C(7)	121.2(5)
C(4)-C(5)-C(6)	121.3(4)	C(5)-C(4)-C(7)	120.3(5)

Symmetry transformations used to generate equivalent atoms: *¹: -x, -y+1, -z+1.

from 2.051(2) to 2.078(3) Å, and the O_{water}-Co-O_{water} bond angles from 91.0(1) to 92.6(1)° and 180°. Bond lengths and angles within the hexaaquacobalt cation are unexceptional, similar to previous reported results.⁶ The S-O_{sulfonate} bond lengths in the *p*-toluenesulfonate anion range from 1.456(2) to 1.456(3) Å and the O_{sulfonate}-S-O_{sulfonate} bond angles from 112.2(2) to 112.4(2)°. The geometry, bond lengths, and angles of the *p*-toluenesulfonate ring are similar to those of the previously reported results.^{16, 17}

As shown in Fig. 2, the title compound [Co(H₂O)₆](CH₃C₆H₄SO₃)₂ is a layered material constituted by positively charged metal-aqua complex cation layers and negatively charged *p*-toluenesulfonate anion layers. The hexaaquacobalt complex cations and *p*-toluenesulfonate anions are linked together in chains along the *c* direction by the O_{water}-H...O_{sulfonate} hydrogen bond, and the chains are inter-linked in the *ab* plane by the hydrogen bonds. Therefore, the crystal structure of the title compound is constructed a two dimensional networks and furthermore stabilize by the crystal packing

through hydrogen bonds. The detailed hydrogen bonding interactions between the sulfonate oxygen atoms and coordinated water molecules are described in follows: O(1)...H(10a)-O(10), 2.760(4) Å, 166(6)°; O(1)...H(30b)-O(30), 2.757(4) Å, 173(6)°; O(2)...H(20a)-O(20), 2.764(4) Å, 174(6)°; O(2)...H(30a)-O(30), 2.742(4) Å, 174(7)°; O(3)...H(10b)-O(10), 2.813(4) Å, 174(5)°; O(3)...H(20b)-O(20), 2.794(4) Å, 177(5)°.

Although the layer structure of compound (I) and hexaaquatitanium (III) tris (*p*-toluenesulfonate) trihydrate¹⁸ are essentially the same, the types of water molecules and hydrogen bonding are significantly different. Hexaaquatitanium (III) tris (*p*-toluenesulfonate) trihydrate compound have a coordinated and uncoordinated water molecules. All the water molecules and two of the oxygen atoms of the *p*-toluenesulfonate anions are involved in hydrogen bonding. In contrast, compound (I) has only coordinated water molecules. All the water molecules and oxygen atoms of the *p*-toluenesulfonate anions are involved in hydrogen bonding. These obser-

vations indicate that the introduction of di- or tri-valent metal ions can be used to change host composition and hydrogen bond linkage.

Supporting Information Available

Tables of crystallographic details, atomic coordinates, interatomic distances and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for title compound are available from C.H. Kim.

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