Crystal structure of hexaaquacobalt(II) piperazinium hexafluorogallate(III) chloride, $[\text{Co}(\text{H}_2\text{O})_6][\text{C}_4\text{H}_{12}\text{N}_2][\text{GaF}_6]\text{Cl}$

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Abstract

$\text{C}_4\text{H}_{24}\text{ClCoF}_6\text{GaN}_2\text{O}_6$, monoclinic, $P2_1/m$ (no. 11), $a = 5.757(2)$ Å, $b = 15.028(4)$ Å, $c = 9.697(3)$ Å, $\beta = 100.439(3)^\circ$, $V = 825.1$ Å³, $Z = 2$, $R_{\text{int}}(F) = 0.041$, $wR_{\text{ref}}(F^2) = 0.108$, $T = 298$ K.

Source of material

Single crystals of the title compound were obtained by mild solvothermal reaction as follows: 0.041 g of H_3BO_3 , 0.254 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.696 g of triethylenediamine were dissolved in a mixture solution of 2 ml of H_2O and 0.1 ml of hydrofluoric acid under constant stirring. After ten minutes, 0.097 g of Ga_2O_3 was added to this mixture and stirred for 6 h at room temperature. The resulting mixture with pH 4.0 was sealed in a 20 ml Teflon-lined stainless steel vessel, heated at 443 K for about 6 days under autogenous pressure and then cooled to room temperature. The resulting pink prism-like crystals were separated by filtration, washed with deionized water, alcohol, and dried in a dryer to a constant mass at room temperature. Elemental analysis — found: N, 5.56 %; C, 10.61 %; H, 4.78 %; calculated for $\text{C}_4\text{H}_{24}\text{ClCoF}_6\text{GaN}_2\text{O}_6$: N, 5.90 %; C, 10.12 %; H, 5.06 %. All the experimental results are consistent with the calculated values based on the formula given crystal structure determination. FT-IR and Raman data are available in the CIF.

Discussion

Microporous materials have attracted considerable attention on the basis of their fundamental properties and practical applications, such as catalysis, ion exchange, and adsorption [1]. The discovery of aluminophosphate analogues of zeolites [2] has greatly stimulated the interest in designing and looking for other novel inorganic microporous materials with different topological structure. Recently, our research interests have been focused on the synthesis of borogallate microporous materials [3]. In the course of preparing borogallates, we obtained a novel organic-inorganic hybrid hexafluorogallate, $[\text{Co}(\text{H}_2\text{O})_6][\text{C}_4\text{H}_{12}\text{N}_2][\text{GaF}_6]\text{Cl}$.

The crystal structure of the title compound consists of two kinds of cations, an organic cation $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+}$ and a hydrated transition-metal cation $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, and two kinds of anions, an isolated $[\text{GaF}_6]^{3-}$ and a Cl^- (figure, top). The organic piperazinium comes from the decomposition of triethylenediamine material under hydrothermal condition. The $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ octahedron is quite regular with Co—O distances from 2.065(7) Å to 2.086(5) Å (mean 2.075 Å) and the O—Co—O angles between $89.1(2)^\circ$ and $178.7(3)^\circ$. The $[\text{GaF}_6]^{3-}$ octahedron is almost regular with Ga—F distances from 1.873(4) Å to 1.901(3) Å (mean 1.890 Å) and the F—Ga—F angles between $89.0(2)^\circ$ and $179.4(1)^\circ$, which are consistent with those observed in other gallium fluorides [4,5]. The cations and anions are held together through both electrostatic interactions and the N—H...F, O—H...F and O—H...Cl hydrogen bonds. In this crystal, extensive hydrogen bondings play a very important role in stabilizing the structure (figure, bottom).

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Table 1. Data collection and handling.

Crystal:	pink block, size 0.15 × 0.25 × 0.29 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	28.82 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\max}$:	50.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5996, 1595
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1228
$N(\text{param})_{\text{refined}}$:	106
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1W)	2e	0.0388	¼	-0.1099	0.097
H(2W)	2e	0.1663	¼	-0.2162	0.097
H(3W)	2e	0.7800	¼	0.2517	0.120
H(4W)	2e	0.9166	¼	0.1493	0.120
H(5W)	4f	0.1973	0.3466	0.1354	0.137
H(6W)	4f	0.4189	0.3708	0.1978	0.137
H(7W)	4f	0.6369	0.3396	-0.1831	0.162
H(8W)	4f	0.7104	0.3873	-0.0629	0.162
H(1A)	4f	0.8063	0.3735	0.5281	0.046
H(1B)	4f	1.0278	0.3803	0.4767	0.046
H(1C)	4f	0.6688	0.5035	0.4227	0.049
H(1D)	4f	0.7407	0.4390	0.3098	0.049
H(2A)	4f	1.0987	0.4178	0.7062	0.050
H(2B)	4f	0.8992	0.4901	0.6757	0.050

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga(1)	2e	0.4157(1)	¼	0.50877(8)	0.0294(4)	0.0249(4)	0.0222(4)	0	0.0091(3)	0
Co(1)	2e	0.4794(2)	¼	0.0149(1)	0.0474(7)	0.0385(6)	0.0220(5)	0	0.0105(4)	0
Cl(1)	2c	0	½	0	0.075(2)	0.044(1)	0.055(1)	0.004(1)	-0.005(1)	-0.001(1)
F(1)	2e	0.6708(7)	¼	0.4123(4)	0.035(2)	0.039(2)	0.034(2)	0	0.014(2)	0
F(2)	2e	0.1588(7)	¼	0.6029(4)	0.032(2)	0.037(2)	0.030(2)	0	0.013(2)	0
F(3)	4f	0.2665(6)	0.3399(2)	0.3857(3)	0.055(2)	0.047(2)	0.038(2)	0.022(2)	0.022(2)	0.016(2)
F(4)	4f	0.5651(6)	0.3402(2)	0.6296(3)	0.053(2)	0.044(2)	0.034(2)	-0.020(2)	0.016(1)	-0.011(1)
O(1)	2e	0.171(1)	¼	-0.1325(6)	0.057(4)	0.109(5)	0.029(3)	0	0.013(3)	0
O(2)	2e	0.782(1)	¼	0.1668(6)	0.060(4)	0.149(7)	0.032(3)	0	0.013(3)	0
O(3)	4f	0.339(1)	0.3473(4)	0.1272(5)	0.157(5)	0.083(4)	0.036(2)	0.063(4)	0.022(3)	0.002(2)
O(4)	4f	0.626(1)	0.3458(4)	-0.0995(5)	0.175(6)	0.113(5)	0.037(3)	-0.095(4)	0.019(3)	-0.002(3)
N(1)	4f	0.9150(8)	0.4120(3)	0.5077(5)	0.040(3)	0.024(2)	0.053(3)	-0.002(2)	0.015(2)	0.001(2)
C(1)	4f	0.801(1)	0.4731(4)	0.3937(6)	0.038(3)	0.032(3)	0.053(4)	0.001(2)	0.005(3)	-0.001(3)
C(2)	4f	1.022(1)	0.4600(4)	0.6370(6)	0.056(4)	0.028(3)	0.044(3)	0.003(3)	0.016(3)	0.003(3)

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