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Crystal structure of new coordinated calcium-cesium benzene-1,3,5-tricarboxylate complex

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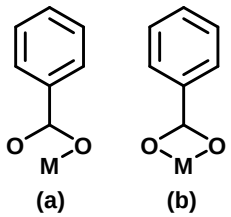
ABSTRACT

A new two dimensional coordination polymer of calcium-cesium benzene-1,3,5-tricarboxylate (BTC) was obtained from aqueous solution. Structure was composed of zigzag chains constructed with Ca^{2+} and Cs^{+} ions with BTC. $[CaCs(BTC)(OH_2)_9]$ crystallizes in monoclinic space group P 1 21/c 1 with a = 7.105(6) Å, b = 22.405(20) Å, c = 12.032(0) Å, V = 1911.9 (30) Å^3.

INTRODUCTION

Supramolecular framework structures of metal-organic coordination compounds have potential applications as absorbents, ion exchangers, protonic conductors and catalysts[1-4]. Open frame work structures of Benzene-1,3,5-tricarboxylic acid (BTC) with alkaline earth metal ions[5] were reported earlier. BTC with three fold symmetry makes it a very attractive choice for obtaining a (6,3) type structure, the frame work of a kagome lattice[6-8]. Controlled co-ordination networks of BTC with transition metal ions such as Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} etc., were synthesized through hydrothermal technique[9-11]. Some of the guest molecules such as C_6H_6, $C_{12}H_{10}$ etc., are selectively absorbed into compounds, $Cd(NH_3)_2Ni(CN)_4.G$ (G= guests), $Zn_2(BTC)NO_3.(C_2H_5OH)_5.H_2O$[12-14]. In a similar way Ca-BTC complex also allowing Cs^{+} ions into their coordination sphere as counter cations. In general carboxylate groups from Benzene-1,3,5-tricarboxylate molecules exhibits two kinds of bonding modes such as unidentate (a) and bidentate (b) (Scheme 1).



Scheme 1 : Benzene-1,3,5-tricarboxylate molecules (a) unidentate and (b) bidentate

EXPERIMENTAL

All chemicals used for synthesis were purchased from Aldrich, Fluka, Merck and Lancaster chemicals and used without further purification. 1.0mmol benzene-1,3,5-tricarboxylic acid (0.210g) and 3.0mmol $CsOH.H_2O$ (0.504g) were taken in 10 ml of distilled water and stirred for few minutes. 0.5mmol $CaCl_2.2H_2O$ (0.074g) was added to the above mixed solution and stirred again for few minutes. Needle-shaped colourless crystals of $[CaCs(BTC)(OH_2)_9]$

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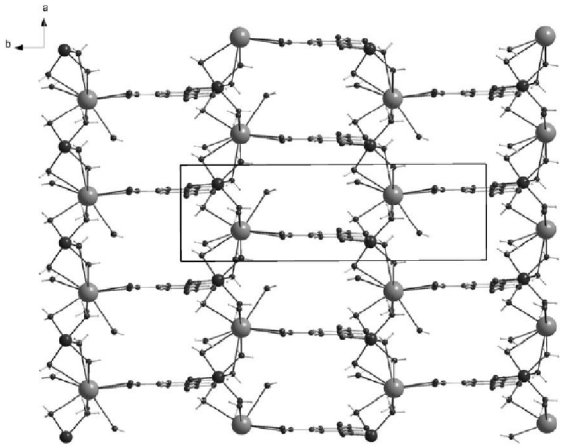

Figure 1: Complex [Ca Cs (BTC) $(OH_2)_9$] (view along with *c*-axis)

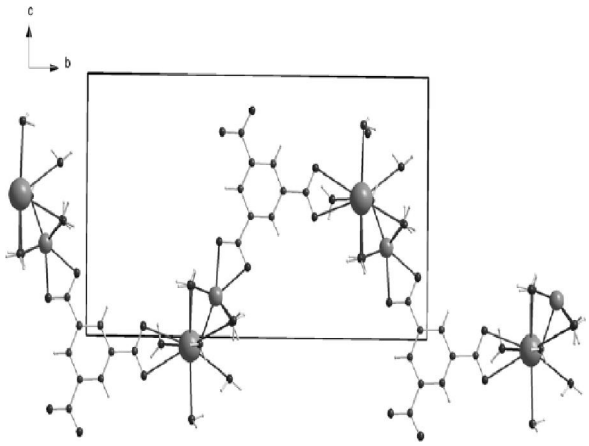

Figure 2: Complex [Ca Cs (BTC) $(OH_2)_9$] (view along with *a*-axis)

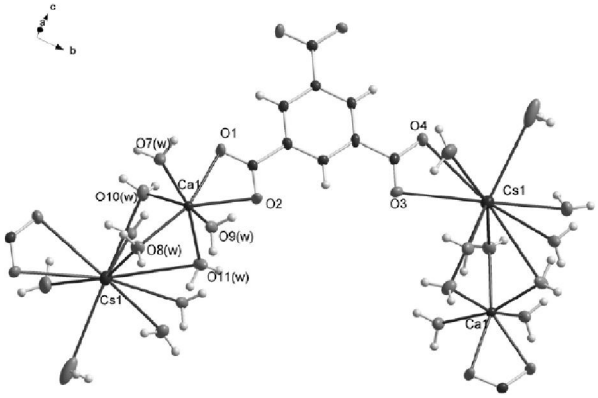

Figure 3: The coordination of Ca^{2+} and Cs^{+} by BTC carboxylate groups in bidentate fashion

were observed after one hour. After mixing the benzene-1,3,5-tricarboxylic acid and $CaCl_2.2H_2O$ in the presence of $CsOH.H_2O$ according to the above procedure, the solution was heated hydrothermally at

TABLE 1 : Crystal data for [CaCs(BTC)$(OH_2)_9$]

Formula	$C_9H_{21}CaCsO_{15}$
Formula weight	542.24
Crystal system	monoclinic
Space group	*P* 1 21/c
a (Å)	7.1045(6)
b (Å)	22.4047(20)
c (Å)	12.0314(10)
α (°)	90
β (°)	93.27(0)
γ (°)	90
Cell volume ($Å^3$)	1911.97(30)
D_{Cal} (g/cm^3)	1.877
Z	
Diffractometer	SMART Apex
μ(Mo-K_α) (mm^{-1})	
T(K)	200
Data measured	9159
Unique data	4130
R_{inst}	0.0274
wR_2	0.1816
S (all data)	1.056
Parameters/restraints	283/17
Peak/hole	+3.94/1.15

TABLE 2 : Selected bond lengths and angles for [CaCs(BTC)$(OH_2)_9$]

Distance	[Å]	Angles	[deg]
Ca1-O1	2.481(2)	Ca1-Cs1-Ca1	103.05°
Ca1-O2	2.460(2)	Cs1-Ca1-Cs1	103.05°
Ca1-O7(w)	2.378(1)	Ca1-O7-Cs1	105.22°
Ca1-O8(w)	2.422(1)	Ca1-O8-Cs1	98.46°
Ca1-O9(w)	2.390(1)	Ca1-O9-Cs1	100.66°
Ca1-O10(w)	3.340(1)	Ca1-O10-Cs1	102.03°
Ca1-O11(w)	2.362(1)	Ca1-O11-Cs1	96.53°
Cs1-O3	3.220(3)		
Cs1-O4	3.321(2)		
Cs1- O12(w)	3.172(2)		
Cs1-O13(w)	3.532(3)		
Cs1-O14(w)	3.439(2)		

180°C for 24hrs under autogenous pressure. Similar needle shaped colourless crystals of [CaCs (BTC)$(OH_2)_9$] were found in the autoclave. Yield: 0.086g, 31.72%. Elemental analysis calculated for $C_9H_{21}CaCsO_{15}$ (542.24): C 19.94, H 3.90. Found: C

20.86, H 3.42. IR, υ/cm^{-1}: 3424br, 1614s, 1554m, 1433m, 1369m, 1104s, 763s, 732m, 521s. The infrared spectra were measured using the KBr disk method on a Perkin Elmer 'spectrum one FTIR' system.

Crystal structure determination

Data were measured on SMART Apex diffractomer using graphite- monochromated Mo-Ka radiation (λ = 0.71073 A°). The structures were solved by direct methods and refined by full-matrix least-squares against F^2 for all data, using the SHELXTL software[15]. Crystal data and details of the data collection and structural refinement are summarized in TABLE 1.

RESULTS AND DISCUSSION

Figure1 shows the single X-ray crystal structure of [CaCs(BTC)$(OH_2)_9$]. The absorption bands of the asymmetric and symmetric vibrations of BTC appear at 1554 cm^{-1} and 1433 cm^{-1} in the IR spectrum of the compound. The broad band at 3424 cm^{-1} and the sharp band at 1614 cm^{-1} are an indicative of the presence of water in the metal coordination sphere. Two dimensional networks were constructed from Ca(II) with Benzene-1,3,5-tricarboxylate (BTC) in presence of CsOH. A single crystal analysis performed on the compound [CaCs(BTC)$(OH_2)_9$] shows that the structure is composed of zig-zag chains constructed with Ca^{2+} and Cs^+ ions with BTC as shown in figure 2. The carboxylate unit (O1 and O2) of BTC bind with Ca2+ ion in a bidentate fashion. Similarly, the second carboxylate unit bind with Cs^+ ion in bidentate manner (Figure 3). Third carboxylate group was not involved in the bonding. Ca^{2+} ions exhibits *7-fold* coordination and binds with five water ligands (O7, O8, O9, O10, O11) in addition to BTC carboxylate group. Selected bond lengths and angles of [CaCs(BTC)$(OH_2)_9$] are presented in TABLE 2. The layers are held together by carboxylate units in the structure to yield a tightly held 2-D solid structure.

SUMMARY

This study demonstrates that multidentate linker, BTC when polymerized with Ca^{2+}, produced two dimensional zigzag frameworks in presence of Cs^+.

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