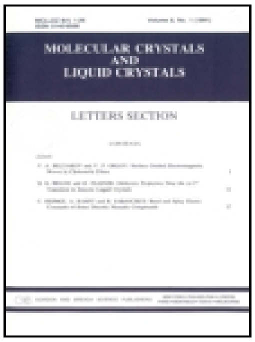

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Synthesis and X-Ray Crystal Structure Determination of Pyridine-2,6-Dicarboxylate Ligand-Based 2D Complex with Heterometallic Ions

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This title compound, $[C_{14}H_{20}N_2NaO_{15}Sm]_n$, is synthesized by reacting $Sm(NO_3)_3$ and 2,6-pdca in the presence of 1M NaOH. The 2D sheet-based complex is formed, where Sm(III) ion occupied nine coordinating sites and Na (I) ion occupied six coordination sites. The Sm(III) atom is coordinated by two pyridine N atoms and four carboxylate O atoms from two doubly deprotonated pyridine-2,6-dicarboxylate ligands in a distorted octahedral geometry. There are three water molecules coordinated with Sm(III) ions. One Na(I) cation is coordinated by three carboxylate O atoms and two water molecules and the other is coordinated by five carboxylate O atoms and two water molecules in an irregular geometry. In this complex, Na(I) cations are connected with Sm(III) ions through bridging coordinated water molecules O1W and O3W. Topologically, structure consists of layers (1 0 0) with point symbol for Na(I) ion is $(3^2.4.5.6^2.7^4)$ and for net is $(3.4.5)(3^2.4.5.6^2.7^4)$ and 3,5-c 2-nodal net with topological type is gek1.

Keywords Coordination; deprotonated; octahedral geometry; point symbol; topology

1. Introduction

The rational design and synthesis of coordination polymers (CPs) with predictable structures has acquired great interest in fields of catalysis, chromatographic media, magnets, and nonlinear optics [1,2]. They have intrinsic structural aspects and variety of coordination system with interesting compositions, geometries, nature of ligands (neutral and charged organic ligands) as well as coordinating organic and inorganic anions [3,4]. In the past, most of the work regarding CPs has been focused on CPs containing transition-metal ions [5,6] and few lanthanide ions [7]. This is because of predictability of the coordination geometry of the transition metals compared to the lanthanide ions. Most of times lanthanide metal ions containing CPs acquire flexibility as compare to transition metal ions [8,9]. The flexibility of the lanthanides based CPs combined with the rigidity of the transition metal ions based CPs can be beneficial to give variety of structures These CPs are dictated by the different size of the lanthanide ions and can result in fascinating and interesting structures with specific properties. More recently, fascinating coordination networks have been achieved by the using of pyridine carboxylate based ligands and followed and lately

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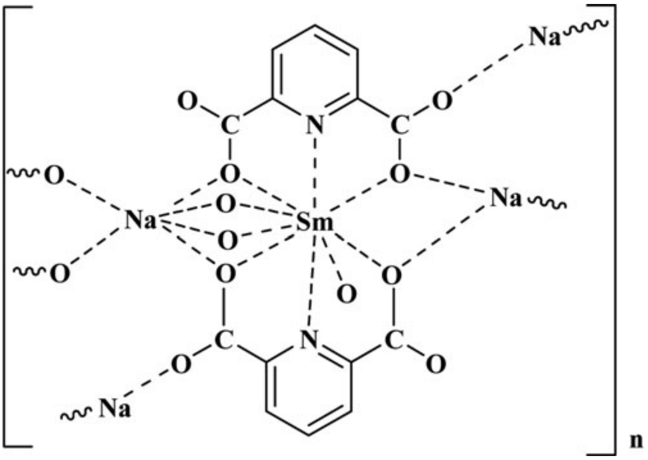

Figure 1. Structure of complex (**I**) showing coordination modes of isonicotinic acid with Sm^{3+} and Na^{+} metal ions.

by choosing isonicotinate *N*-oxide, where both carboxylate and *N*-oxide units can bind to construct lanthanide CPs. Our original aim was to combine lanthanide ions and alkali metals to construct specifically stable CPs where alkali metals can play the role of bridging units as well as increase the dimensionality. The CPs can be denoted as heterometallic CP where it can have properties of both lanthanides as well as alkali metal ions. It is evident that alkali metal ions, incorporated as bridging component, do not act simply as a

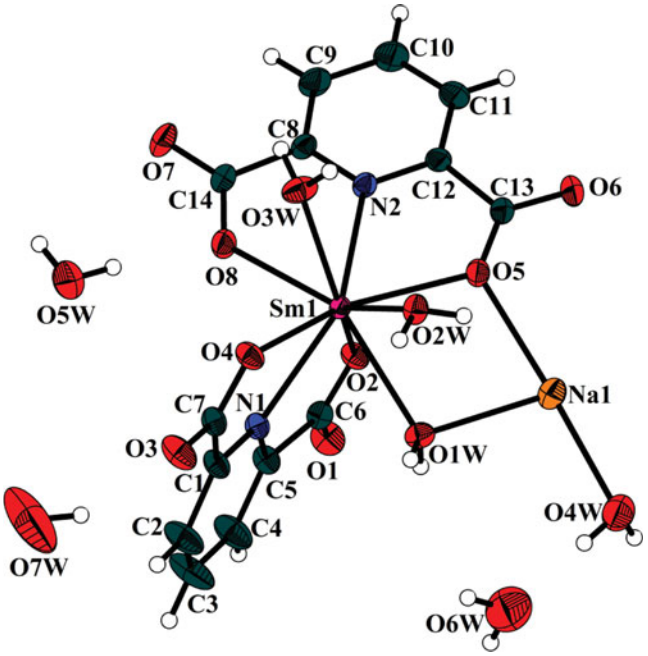

Figure 2. ORTEP diagram of (**I**), showing the atom-labeling scheme (with 50% probability).

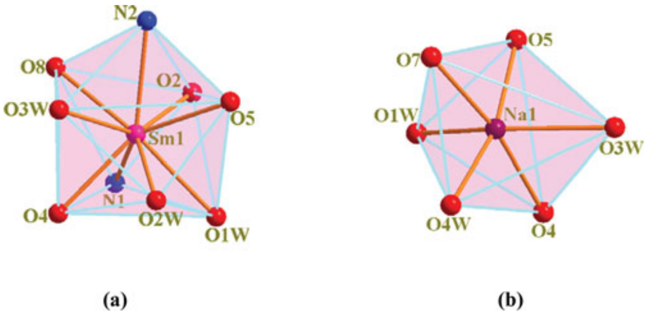

Figure 3. (a) Coordination environment around Sm(III) metal ion and, (b) and around Na(I) ion occupied octahedral geometry.

passive constituent but rather contribute to the increased complexity and hence functionality. Hydrogen-bonding involving water molecules play an important role in self-assembly processes for building metal organic framework (MOF) architectures. The structure of the title compound has already been reported [10,11], role of lattice solvent molecules was not fully understood. We here report the X-ray crystal structure analysis of the compound, and demonstrate a unique hydrogen-bonding cluster of water molecules located in interlayer spaces. It has been investigated from single-crystal data that the coordinated and bridging water molecules play important role to generate higher topological structures. There are similar structures present in literature with Co(II) metal ions by Liu et al. [12] and Alexander et al. [13] and with Ni(II) metal based ions by Xiang et al. [14]. Complex (**I**) has been solved afresh and included for the sake of explanation of its crystal structure which is different from previously discussed structures.

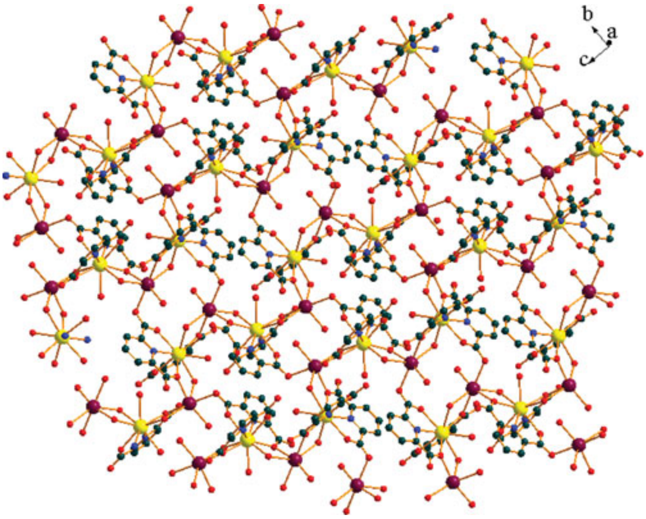

Figure 4. 2-D sheet like structure of complex (**I**) in *bc* plane.

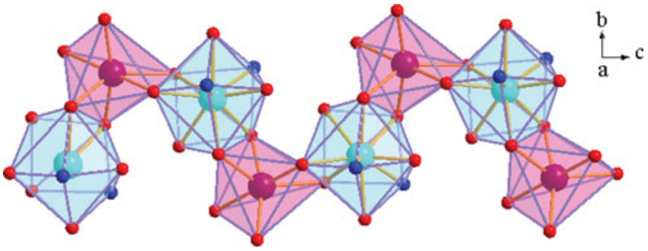

Figure 5. 1D chain is formed along *c* axis, where Sm(III) and Na(I) ions are present alternatively.

2. Experimental

2.1. Materials and Physical Measurements

All the starting reagents of analytical grade were used without further purification. The melting points were determined with an electrically heated apparatus. C, H, N elemental analyses were obtained with a CHNS-O analyzer flesh-EA-1112 series. Single-crystal structural X-ray diffraction was carried out on a Bruker's Apex-II CCD diffractometer using Mo $K\alpha$ ($\lambda = 0.71069$) at room temperature.

2.2. Synthesis of Complex (I)

$Sm(NO_3)_3$ (0.338 g, 1.0 mmol) and 2,6-pdca (0.167 g. 1.0 mmol) were dissolved in 10 mL mixture of distilled water and methanol (1:1) and stirred well at room temperature and then to obtain clear solution, solution sodium hydroxide (1 M, 1 mL) was added dropwise. The mixture was stirred for 30 min, filtered and set aside for crystallization by slow evaporation. The light pink crystals formed within one week. Yield: 76%, M.P. > 300°C. Anal. Calcd for (**I**), $\mathbf{C_{14}H_{20}N_2O_{15}NaSm}$ (%): C, 26.70; H, 3.20; N, 4.45; Found: C, 26.67; H, 3.18; N, 4.54.

2.3. X-Ray Crystallography

The crystals were grown by slow evaporation at room temperature and recrystallized in de-ionized water (Fig. 1). X-ray data of all these complexes were collected on a Bruker's Apex-II CCD diffractometer using Mo $K\alpha$ ($\lambda = 0.71069$) at room temperature. The data collected by CCD diffractometer were processed by SAINT. Lorentz and polarization

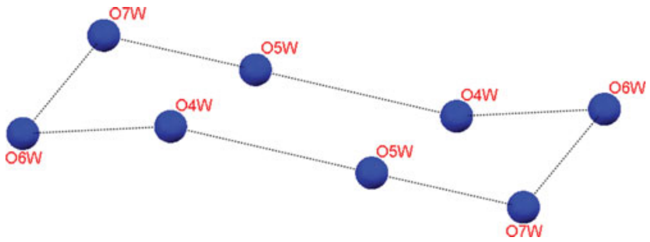

Figure 6. Showing formation of H-bonded chair like structure by oxygen atoms of coordinated and lattice water molecules with carboxylate oxygen atoms of ligands.

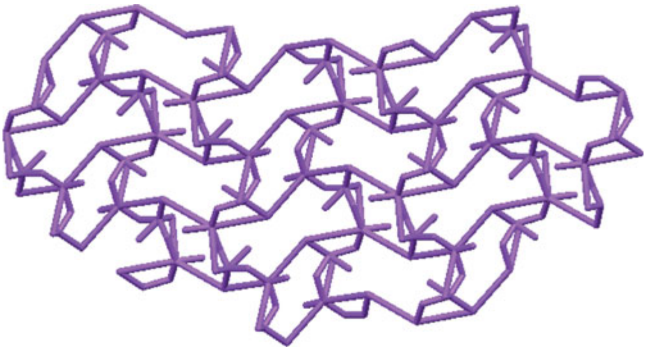

Figure 7. Showing gek1 topology of complex (**I**) with 3,5-c 2-nodal net.

Table 1. Crystal data and structure refinement for complex (**I**)

Identification code	Complex (**I**)	
Empirical formula	C14 H20 N2 Na O15 Sm	
Formula weight	629.67	
Temperature	296 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	$a = 11.166(3)$ Å	$a = 90^\circ$
	$b = 17.432(4)$ Å	$b = 98.3280(15)^\circ$
	$c = 11.357(3)$ Å	$g = 90^\circ$
Volume	2187.3(10) Å^3	
Z	4	
Density (calculated)	1.912 Mg/m^3	
Absorption coefficient	2.783 mm^{-1}	
F(000)	1244	
Crystal size	$0.12 \times 0.09 \times 0.06$ mm^3	
Theta range for data collection	2.16 to 34.10°.	
Index ranges	$-17 <= h <= 16, -26 <= k <= 27, -17 <= l <= 17$	
Reflections collected	33,434	
Independent reflections	8,802 [R(int) = 0.0437]	
Completeness to theta = 34.10°	98.0%	
Absorption correction	Semiempirical from equivalents	
Max. and min. transmission	0.7466 and 0.4840	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8,802/14/340	
Goodness-of-fit on F^2	0.894	
Final R indices [I>2sigma(I)]	$R1 = 0.0247$, $wR2 = 0.0588$	
R indices (all data)	$R1 = 0.0360$, $wR2 = 0.0653$	
Largest diff. peak and hole	1.100 and −0.721 e.Å-3	
CCDC number	**1010192**	

Table 2. Showing important H-bonding interactions in compound (**I**)

X-H… Y	X… .Y	H… Y	∠X-H… Y
O4W-H42W… O6W	2.78	1.97 (2)	171
O5W-H52W… O7	3.25	2.63 (3)	132
O5W-H52W… O8	2.77	1.94 (3)	170
O7W-H71W… O3	2.77	1.98 (5)	153
C2-H2… O6^1	3.31	2.69(2)	125
C3-H3… O6^1	3.38	2.82 (2)	120
C2-H2… O5W^2	3.52	2.93 (2)	123
O7W-H72W… O5W^2	2.85	2.43 (7)	111
C9-H9… O2^3	3.37	2.54 (2)	149
C9-H9… O1^3	3.31	2.61 (2)	132
C10-H10… O7W^4	3.34	2.69 (4)	128
C11-H11… O7W^4	3.44	2.91 (4)	118
O3W-H32W… O6^5	2.75	1.93 (3)	168
O2W-H22W… O5^5	3.19	2.89 (2)	104
O1W-H11W… O1^5	2.78	1.97 (2)	172
O2W-H22W… O1^5	3.56	2.98 (2)	131
O6W-H61W… O1^5	2.98	2.22 (4)	154
O2W-H22W… O2^5	2.71	1.90 (2)	177
O3W-H32W… O5^5	3.33	2.84 (3)	119
O1W-H12W… O4^6	3.25	2.74 (2)	124
O6W-H62W… O7W^6	2.75	1.93 (5)	162
O1W-H12W… O3^6	2.72	1.93 (3)	172
O4W-H41W… O5W^6	2.78	2.00 (3)	165
O2W-H21W… O7^7	2.85	2.05 (2)	169
O3W-H31W… O4W^8	2.79	1.98 (2)	170
O5W-H51W… O6^8	2.91	2.15 (2)	155

(1) *x*-1,-*y*+1/2,+*z*-1/2 (2) -*x*,-*y*,-*z* (3) -*x*+1,-*y*,-*z*+1 (4) *x*+1,+*y*,+*z*+1.
(5) *x*,-*y*+1/2,+*z*-1/2 (6) *x*,-*y*+1/2,+*z*+1/2 (7) -*x*+1,+*y*+1/2,-*z*+1/2 (8) -*x*+1,+*y*-1/2,-*z*+1/2.

effects and empirical absorption corrections were applied using SADABS from Bruker. The structure was solved by direct methods, using SIR-92 [15] and refined by full-matrix least squares refinement methods [16] based on F^{-2}, using SHELX-97. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were located from the difference Fourier synthesis and were refined isotropically with U_{iso} values 1.2 times that of their carrier oxygen atoms, with their distances fixed as 0.82 (2) Å. All other hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of methylene carbons. Geometry of this complex and hydrogen bonding interactions were calculated using PARST programme [17]. All the drawings of complexes were made using ORTEP [18] and MERCURY [19] programs. All calculations were performed using Wingx package [20].

3. Results

3.1. X-Ray Crystal Structure

The X-ray crystal structure revealed that this complex is solved in monoclinic space group P2$_1$/n. The asymmetric unit of this complex is having one Sm(III) ion, one Na(I) ion, two completely deprotonated 2,6-pdca ligands, four coordinated and three lattice water molecules (Fig. 2). The Sm(III) metal is having nine-coordination sites (Fig. 3a) surrounded by two 2,6-pdc ligands through four oxygen atoms of carboxylate groups and two pyridine nitrogen atoms with Sm-O distances are in the range of 2.4099 (17)–2.5451(16) Å and average Sm-N distances are 2.5265(16) Å, occupied distorted octahedral geometry. Three coordinated water molecules are coordinated to complete its other three coordination places. The Na(I) ion is six-coordinated with distorted octahedral geometry (Fig. 3b), where three coordinated water molecules O1W, O3W, O4W, and three carboxylate oxygen atoms O4, O5 and O7 have coordinated with Na-O distances are in the range of 2.388 (2)–2.4537(17) Å. There are two coordinated water molecules O1W, O3W, and carboxylate oxygen atoms O4 and O5 are bridging between Sm(III) and Na(I) ions. Due presence of bridging water molecules in this bimetallic complex 2D-polymeric sheet is formed (Fig. 4). The 2D sheets or layers are formed in this complex from six-coordinated $\mathbf{NaO_6}$ polyhedra and nine-coordinated $\mathbf{SmN_2O_7}$ polyhedra. These two polyhedra share edges with each other along the *c*-axis by bridging O atoms of water and carboxylate groups forming 1D chain (Fig. 5). The octameric chair shaped H-bonded rings (Fig. 6) are formed from oxygen atoms of lattice and coordinated water molecules in the interlayer spaces. All the bond distances for Sm-O, Sm-N, and Na-O are comparable to those reported previously and there is little bit difference in them. The presence of three water molecules in lattice of crystal structure, extensive H-bonding interactions are present. Topologically, structure consists of layers (1 0 0) with point symbol for Na ion is ($3^2.4.5.6^2.7^4$) and for net is (3.4.5) ($3^2.4.5.6^2.7^4$) and 3,5-c 2-nodal net with topological type is gek1 (Fig. 7). The structure refinement data and H-bonding interactions are present in Tables 1 and 2.

4. Conclusion

In summary, we have synthesized a 2D sheet-based complex, where Sm(III) ion-occupied nine coordinating sites and Na(I) ion-occupied six coordination sites. The Sm(III) atom is coordinated by two pyridine N atoms and four carboxylate O atoms from two doubly deprotonated pyridine-2,6-dicarboxylate ligands in a distorted octahedral geometry. There are three water molecules coordinated with Sm(III) ions. One Na(I) cation is coordinated by three carboxylate O atoms and two water molecules and the other is coordinated by five carboxylate O atoms and two water molecules in an irregular geometry. In this complex, Na(I) cations are connected with Sm(III) ions through bridging coordinated water molecules O1W and O3W. Topologically, structure consists of layers (1 0 0) with point symbol for Na(I) ion is ($3^2.4.5.6^2.7^4$) and for net is (3.4.5)($3^2.4.5.6^2.7^4$) and 3,5-c 2-nodal net with topological type is gek1.

Supporting Information

Tables of selected bond distances, bond angles, and torsion angles; The *cif* and structure factor data are available from Cambridge structure data base, free of cost, CCDC number = **1010192**

Acknowledgments

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