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# Synthesis and characterization of cobalt(II)–salicylate complexes derived from N<sub>4</sub>-donor ligands: Stabilization of a hexameric water cluster in the lattice host of a cobalt(III)–salicylate complex

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#### ABSTRACT

The syntheses and structural characterization of four cobalt(II)-salicylate complexes, [(TPA)Co<sup>II</sup>(HSA)] (ClO<sub>4</sub>) (1), [(isoBPMEN)Co<sup>II</sup>(HSA)](BPh<sub>4</sub>) (2), [(TPzA)Co<sup>II</sup>(HSA)](ClO<sub>4</sub>) (3) and [(6Me<sub>3</sub>TPA)Co<sup>II</sup>(HSA)](BPh<sub>4</sub>) (4) [TPA = tris(2-pyridylmethyl)amine, isoBPMEN =  $N^1$ , $N^1$ -dimethyl- $N^2$ , $N^2$ -bis(2-pyridylmethyl)ethane-1,2-diamine, TPzA = tris((3,5-dimethyl-1H-pyrazole-1-yl)methyl)amine and 6Me<sub>3</sub>TPA = tris(6-methyl-2pyridylmethyl)amine] are described. While **2**, **3** and **4** are unreactive towards dioxygen, **1** reacts slowly with molecular oxygen to a cobalt(III)-salicylate complex, [(TPA)Co<sup>III</sup>(SA)](ClO<sub>4</sub>) (**1**a). Two different crystalline forms, **1a** and **1a**-**4H**<sub>2</sub>**0** were isolated depending upon the condition of oxidation and crystallization. The solid-state structures of cobalt(III)-salicylate unit in both **1a** and **1a**-**4H**<sub>2</sub>**0** show a six-coordinate distorted octahedral coordination geometry at the cobalt(III) center ligated by the tetradentate ligand (TPA) where the dianionic salicylate (SA) binds in a bidentate fashion through one carboxylate and one phenolate oxygen. The hydrated form **1a**-**4H**<sub>2</sub>**0** reveals a hexameric water cluster formation in the inorganic lattice host. The complex cation and the perchlorate counterion are involved in stabilizing the (H<sub>2</sub>O)<sub>6</sub> cluster in a rare 'pentamer planar+1' conformation. A one-dimensional water tape consisting of edge-shared water hexamers is observed. The water tape represents a subunit of ice structure.

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#### 1. Introduction

Water plays an important role in the structure and function of biological macromolecules. The unusual properties and importance of water in life have fueled the interest to understand the structure of water in solid and liquid state [1-6]. The structures of different hydrogen bonded networks in various environments help in understanding the structure and behavior of water [7]. In synthetic chemistry, one approach is to stabilize water cluster in organic and/or inorganic lattice host. The host molecules stabilize the guest water cluster through hydrogen bonding interaction giving rise to one-dimensional chains [8-13], tapes [13-17], two-dimensional layers [13,18-26] and three-dimensional networks [27-30]. The structure of water cluster depends on various non-covalent interactions that the host molecule can render in a lattice. A large number of water clusters stabilized in various crystal lattice hosts have been structurally characterized [23,31–76]. The crystalline  $I_{\rm h}$  and  $I_{\rm c}$ structures of ice show chair and boat conformation of hexameric

water [1]. A cyclic hexamer structure in liquid helium has been proposed to be the building block of  $I_h$  structure of ice [77]. The hexameric water cluster has been proposed to be the smallest unit in bulk water [1]. Water co-crystallized as a self-assembled cluster with chair, boat and cyclic planar hexameric conformation in inorganic lattice host has also been reported [47–49,61,65–67,78–85]. Very recently, it has been shown theoretically that 24 different conformations are possible for hexameric water cluster [86]. However the structure of hexameric water cluster with high energy conformations like pentamer planar+1, twisted boat, pentamer+1, closed chair down, tetramer+2, triple trimer and trimer/trimer+1 are rare.

In this paper, we report the synthesis and structural characterization of four cobalt(II)–salicylate complexes of different tripodal N<sub>4</sub>-donor ligands (Scheme 1). A hexameric water cluster is stabilized in the lattice host of [(TPA)Co<sup>III</sup>(SA)](ClO<sub>4</sub>) (**1a**) formed upon oxidation of the corresponding cobalt(II)–salicylate complex, [(TPA)Co<sup>II</sup>(HSA)](ClO<sub>4</sub>) (**1**) in the presence of dioxygen in moist solvent. The water hexamer shows a rare 'pentamer planar+1' type structure and forms an infinite one-dimensional water tape. The controlled crystallization of hydrated cobalt(III)–salicylate complex and the role of anion in stabilizing the hexameric water cluster are described.





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Scheme 1. Ligands.

#### 2. Experimental

#### 2.1. General considerations and physical methods

Commercial grade chemicals were used for the synthetic purposes and solvents were distilled and dried before use. Although no problem was encountered during the synthesis of the ligand and the complex, perchlorate salts are potentially explosive and should be handled with care [87]. The air sensitive complexes were prepared and stored in an inert-atmosphere glove box. Ligands were prepared according to the reported procedures [88,89].

Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin–Elmer 2400 series II CHN analyzer. Electro-spray ionization mass spectra were recorded with a Waters QTOF Micro YA263. <sup>1</sup>H NMR spectra were measured at room temperature using Bruker DPX-300 spectrometer. Solution electronic spectra were measured on an Agilent 8453 diode array spectrophotometer. Room temperature magnetic data were collected on a Gouy balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contributions were estimated for each compound by using Pascal's constants. TGA measurements were carried out on a TA instruments SDT Q 600 thermal analyzer. Powder XRD measurements were carried out on a Bruker D8 Advance Powder (CuK $\alpha_1$  radiation,  $\lambda = 1.5406$  Å) instrument.

#### 2.2. Syntheses

#### 2.2.1. [(TPA)Co<sup>II</sup>(HSA)](ClO<sub>4</sub>) (**1**)

Cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) was added to a methanolic (5 mL) solution of the ligand (0.29 g, 1 mmol). The resulting orange solution turned to green immediately upon addition of a mixture of salicylic acid (0.14 g, 1 mmol) and 1 eq. of Et<sub>3</sub>N (140  $\mu$ L, 1 mmol) in 1 mL methanol. The solution was allowed to stir at room temperature for 3 h whereupon a green crystalline solid was precipitated. The solid was isolated by filtration and dried. Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether into a THF–MeOH solution of the complex. Yield: 0.34 g (58%). *Anal.* Calc. for C<sub>25</sub>H<sub>23</sub>ClCoN<sub>4</sub>O<sub>7</sub> (585.86 g/mol): C, 51.25; H, 3.96; N, 9.56. Found: C, 50.9; H, 3.8; N, 9.4%. IR (KBr, cm<sup>-1</sup>): 3425 (m), 1610 (s), 1566 (m), 1483 (s), 1442 (m), 1389 (s), 1253 (m), 1144 (m), 1107 (s), 1088 (s), 764 (m). ESI-MS (in positive ion mode, CH<sub>3</sub>CN): m/z = 486.06 (100%, [(TPA)Co(HSA)]<sup>+</sup>). UV–Vis (in CH<sub>3</sub>CN): 465 nm (200 M<sup>-1</sup> cm<sup>-1</sup>), 605 nm (160 M<sup>-1</sup> cm<sup>-1</sup>), 622 nm (140 M<sup>-1</sup> cm<sup>-1</sup>).  $\mu_{eff}$  (298 K): 3.96 BM.

#### 2.2.2. [(isoBPMEN)Co<sup>II</sup>(HSA)](BPh<sub>4</sub>) (**2**)

Complex **2** was synthesized according to the procedure described for **1** except that isoBPMEN ligand was used instead of TPA. The resulting green solution was stirred for 2 h and then treated with sodium tetraphenylborate (0.34 g, 1 mmol). After 1 h a green solid was precipitated which was isolated by filtration and dried. X-ray quality single crystals were obtained by vapor diffusion of diethylether into a THF–MeOH solution of the complex. Yield: 0.60 g (76%). Anal. Calc. for  $C_{47}H_{47}BCON_4O_3$  (785.63 g/mol): C, 71.85; H, 6.03; N, 7.13. Found: C, 71.6; H, 5.9; N, 6.9%. IR (KBr, cm<sup>-1</sup>): 3408 (br), 3051 (m), 2988 (m), 2926 (m), 1605 (s), 1571 (m), 1481 (s), 1443 (m), 1391 (s), 1257 (m), 762 (s), 739 (m), 706 (m). ESI-MS (in positive ion mode, CH<sub>3</sub>CN): *m/z* = 465.80 (100%, [(isoBPMEN)Co(HSA)]<sup>+</sup>). UV–Vis (in CH<sub>3</sub>CN): 472 nm (110 M<sup>-1</sup> cm<sup>-1</sup>), 601 nm (100 M<sup>-1</sup> cm<sup>-1</sup>).  $\mu_{eff}$  (298 K): 4.21 BM.

#### 2.2.3. $[(TPzA)Co^{II}(HSA)](ClO_4)$ (3)

Complex **3** was synthesized according to the procedure described for **1** except that TPzA ligand was used instead of TPA. X-ray quality pink crystals were obtained by ether diffusion into a THF–MeOH solution of the complex. Yield: 0.43 g (68%). *Anal.* Calc. for  $C_{25}H_{32}CICON_7O_7$  (636.95 g/mol): C, 47.14; H, 5.06; N, 15.39. Found: C, 47.3; H, 4.9; N, 15.2%. IR (KBr, cm<sup>-1</sup>): 3437 (m), 2928 (m), 1626 (m), 1559 (s), 1483 (s), 1468 (s), 1404 (s), 1365 (s), 1254 (m), 1109 (s), 1092 (s), 768 (m). ESI-MS (in positive ion mode, CH<sub>3</sub>CN): *m/z* = 537.09 (100%, [(TPzA)Co(HSA)]<sup>+</sup>). UV–Vis (in CH<sub>3</sub>CN): 497 nm (150 M<sup>-1</sup> cm<sup>-1</sup>), 577 nm (164 M<sup>-1</sup> cm<sup>-1</sup>).  $\mu_{eff}$  (298 K): 4.29 BM.

#### 2.2.4. $[(6Me_3TPA)Co^{II}(HSA)](BPh_4)$ (4)

Complex **4** was synthesized according to the procedure described for **2** except that 6Me<sub>3</sub>TPA ligand was used instead of isoBPMEN. Single crystals were obtained from a solvent mixture of dichloromethane and methanol. Yield: 0.55 g (65%). *Anal.* Calc. for C<sub>52</sub>H<sub>49</sub>BCoN<sub>4</sub>O<sub>3</sub> (847.71 g/mol): C, 73.68; H, 5.83; N, 6.61. Found: C, 72.7; H, 5.6; N, 6.3%. IR (KBr, cm<sup>-1</sup>): 3053–2926 (br), 1603 (s), 1580 (m), 1464 (s), 1440 (m), 1252 (m), 787–737 (m), 706 (m). ESI-MS (in positive ion mode, CH<sub>3</sub>CN): *m/z* = 528.24 (100%, [(6Me<sub>3</sub>TPA)Co(HSA)]<sup>+</sup>). UV–Vis (in CH<sub>3</sub>CN): 476 nm (50 M<sup>-1</sup> cm<sup>-1</sup>), 515 nm (40 M<sup>-1</sup> cm<sup>-1</sup>), 557 nm (50 M<sup>-1</sup> cm<sup>-1</sup>).  $\mu_{eff}$  (298 K): 4.60 BM.

#### 2.2.5. [(TPA)Co<sup>III</sup>(SA)](ClO<sub>4</sub>) (**1a**)

Complex **1** (15 mg, 0.025 mmol) was dissolved in dry acetonitrile and dioxygen was bubbled through the solution. The solution was kept under oxygen environment for 2 weeks whereupon the green solution changed to purple. A deep purple crystalline compound was obtained from the reaction solution upon slow evaporation of the solvent. Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethylether into a THF–MeOH solution of the purple solid. Yield: 13.9 mg (95%). *Anal.* Calc. for C<sub>25</sub>H<sub>22</sub>ClCoN<sub>4</sub>O<sub>7</sub> (584.85 g/mol): C, 51.34; H, 3.79; N, 9.58. Found: C, 52.2; H, 3.9; N, 9.2%. IR (KBr, cm<sup>-1</sup>): 3398 (br), 3110–2924 (m), 1606 (s), 1574 (m), 1468 (s), 1454 (s) 1359 (s), 1248 (m), 1142 (m), 1090 (s), 767 (m), 625 (m). ESI-MS (in positive ion mode, CH<sub>3</sub>CN): *m/z* = 485.23 (100%, [(TPA)Co(SA)]<sup>+</sup>). UV–Vis (in CH<sub>3</sub>CN): 405 nm (330 M<sup>-1</sup> cm<sup>-1</sup>), 561 (275 M<sup>-1</sup> cm<sup>-1</sup>).

#### 2.2.6. [(TPA)Co<sup>III</sup>(SA)](ClO<sub>4</sub>)·4H<sub>2</sub>O (**1a**·**4H<sub>2</sub>O**)

Complex **1** (15 mg, 0.025 mmol) was dissolved in moist acetonitrile and the solution was saturated with dioxygen. The solution was kept under air for 2 weeks whereupon the color of the solution was changed from green to purple. A purple crystalline solid of **1a**-**4H**<sub>2</sub>**0** was isolated from the purple solution by slow evaporation of solvent. Yield: 14.7 mg (89%). *Anal.* Calc. for C<sub>25</sub>H<sub>30</sub>ClCoN<sub>4</sub>O<sub>11</sub> (656.91 g/mol): C, 45.71; H, 4.60; N, 8.53. Found: C, 45.8; H, 4.3; N, 8.3%. IR (KBr, cm<sup>-1</sup>): 3410 (br), 3074 (m), 2930 (m), 1605 (s), 1576 (m), 1462 (s), 1356 (s), 1248 (m), 1142 (m), 1090 (s), 770 (m), 629 (m).

## 2.3. X-ray crystallographic data collection and refinement of the structures

Diffraction data were collected at 120(2) K for **1**, **1a**, **1a**, **4H**<sub>2</sub>**0**, **2** and **3** and at 298(2) K for **4** on a Bruker Smart APEX II (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). Crystallographic data are summarized in Table 1. Cell refinement, indexing and scaling of the data set were carried out using the APEX2 v2.1-0 software [90]. The structures were solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on  $F^2$  with all observed reflections [91]. One solvent molecule crystallizes with the asymmetric unit of complex **1a** but due to structural disorder that could not be modeled well and squeezed it out.

#### 3. Results and discussion

The cobalt(II)–salicylate complexes (1-4) were isolated either as perchlorate or tetraphenylborate salt by reacting the ligands with equimolar amounts of cobalt(II) perchlorate, salicylic acid (H<sub>2</sub>SA) and triethylamine in methanol (Scheme 2). All the cobalt(II) complexes were characterized by different spectroscopic and analytical tools (see Section 2). All the cobalt(II)–salicylate complexes show d–d transition in the visible region of the optical spectra and exhibit room temperature magnetic moment value between 3.96 and 4.60 BM indicative of high-spin cobalt(II) species.

Table 1

Crystallographic information for 1, 2, 3, 4, 1a and 1a 4H<sub>2</sub>O.



Scheme 2. Syntheses of cobalt(II)-salicylate complexes.

The complexes were further characterized by X-ray single crystal diffraction studies. The cobalt(II)–salicylate complexes **1**, **2** and **3** show a five-coordinate distorted trigonal bipyramidal coordination geometry at the metal center. The metal ion is coordinated by four nitrogen donors from the ligand and one carboxylate oxygen (O1) of monoanionic salicylate (Figs. 1 and 2a). The nitrogen donors (N1, N3, N4) from ligand occupy the equatorial plane while the amine nitrogen (N2) from ligand and the carboxylate oxygen (O1) of salicylate occupy the axial positions. This arrangement of the ligand forces the metal ion to adopt a distorted trigonal bipyramidal coordination geometry. The average M–N bond distance (Å) in the equatorial plane is shorter compared to that in the axial position (Table 2). The noncoordinated phenolic oxygen (O3) forms a strong intramolecular hydrogen bond with carboxylate oxygen (O2).

The solid-state structure of **4** reveals one asymmetric unit containing one mononuclear complex cation and tetraphenylborate counterion. The metal ion in the complex cation is coordinated by four nitrogen donors from ligand and two carboxylate oxygen atoms of monoanionic salicylate forming a distorted octahedral coordination geometry (Fig. 2b). The Co–N<sub>py</sub> bond distances in **4** are in the range of 2.129(3)–2.226(4) Å, longer than Co–N<sub>py</sub> distances in **1**, **2** and **3**. Steric interactions among three methyl groups on the ligand give rise to longer M–N<sub>py</sub> distances in **4**. However, the Co–N<sub>amine</sub> distance at 2.112(3) Å in **4** is close comparable to that observed in **1**, **2** and **3** (Table 3). The phenolic OH group of the

	1	2	3	4	1a	1a-4H <sub>2</sub> 0
Empirical formula	C25H23ClCoN4O7	C47H47BCoN4O3	C25H32ClCoN7O7	C53H51BCl2CoN4O3	C25H22ClCoN4O7	C25H30ClCoN4O11
Formula weight	585.85	785.63	636.96	932.62	584.85	656.91
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	P2(1)/c	ΡĪ	P2(1)/c	P2(1)/c	ΡĪ	P2(1)/c
a (Å)	18.9021(19)	10.160(3)	17.3907(16)	17.152(4)	8.3643(9)	17.7339(16)
b (Å)	9.4210(10)	10.584(3)	12.3850(12)	9.653(2)	11.8532(12)	8.3365(8)
c (Å)	14.4765(14)	19.416(5)	13.9826(13)	29.646(7)	14.8614(14)	22.5448(17)
α(°)	90.00	76.312(5)	90.00	90.00	69.416(2)	90.00
β (°)	93.816(3)	77.442(5)	104.180(2)	98.233(5)	84.133(3)	123.177(5)
γ (°)	90.00	79.518(5)	90.00	90.00	73.622(3)	90.00
$V(Å^3)$	2572.2(5)	1961.3(8)	2919.9(5)	4858(2)	1323.4(2)	2789.7(4)
Ζ	4	2	4	4	2	4
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.513	1.330	1.449	1.275	1.468	1.564
$\mu$ MoK $lpha$ (mm <sup>-1</sup> )	0.824	0.486	0.734	0.510	0.800	0.779
F(000)	1204	826	1324	1948	600	1360
$\theta$ range (°)	2.16-24.53	1.10-25.00	1.21-25.00	1.20-24.39	1.46-25.00	1.37-25.31
Reflections collected	22613	18095	26778	41630	12493	25909
Reflections unique	4273 (0.0392)	6883 (0.0622)	5150 (0.0309)	7810 (0.0477)	4639 (0.0274)	5060 (0.0446)
$(R_{\rm int})$						
Data $[I > 2\sigma(I)]$	3285	5883	4548	5865	3837	4087
Parameters refined	338	508	377	581	343	387
Goodness-of-fit (GOF) on $F^2$	1.268	1.034	1.221	1.441	0.976	1.013
$[I > 2\sigma(I)]$	$R_1 = 0.0545$	$R_1 = 0.0526$	$R_1 = 0.0396$	$R_1 = 0.0682$	$R_1 = 0.0486$	$R_1 = 0.0452$
[0(.)]	$wR_2 = 0.1688$	$wR_2 = 0.1496$	$wR_2 = 0.1394$	$wR_2 = 0.2041$	$wR_2 = 0.1441$	$wR_2 = 0.1098$
Residuals (e Å <sup>-3</sup> )	-0.522, 1.243	-1.513, 1.132	-0.428, 1.447	-0.690, 1.352	-0.572, 0.807	-0.553, 1.095



Fig. 1. Crystal structures of the cationic part of 1 (a) and 2 (b). All H atoms except that attached to O3 are omitted for clarity.



Fig. 2. Molecular structures of the cationic part of 3 (a) and 4 (b). All H atoms except that attached to O3 are omitted for clarity.

Table 2	
Selected bond lengths $(\text{\AA})$ and bond angle	es (°) for complexes <b>1</b> , <b>2</b> and <b>3</b> .

Distance (Å)/angle (°)	1	2	3
Co(1)-O(1)	1.970(3)	1.9712(17)	1.9766(18)
Co(1)-N(1)	2.048(3)	2.073(2)	2.059(2)
Co(1)-N(2)	2.189(3)	2.217(2)	2.327(2)
Co(1)-N(3)	2.070(4)	2.100(2)	2.053(2)
Co(1)-N(4)	2.076(3)	2.070(2)	2.050(2)
O(1)-Co(1)-N(1)	111.29(14)	110.33(8)	105.61(8)
O(1)-Co(1)-N(3)	100.91(13)	98.69(8)	104.40(8)
O(1)-Co(1)-N(2)	170.59(13)	170.08(7)	176.76(7)
O(1)-Co(1)-N(4)	95.33(14)	93.46(8)	101.01(8)
N(1)-Co(1)-N(2)	77.43(12)	77.87(8)	75.42(7)
N(1)-Co(1)-N(3)	115.35(14)	112.17(8)	125.27(8)
N(1)-Co(1)-N(4)	117.66(13)	116.19(8)	111.97(8)
N(2)-Co(1)-N(3)	77.56(13)	82.73(8)	77.16(7)
N(2)-Co(1)-N(4)	76.99(12)	77.59(8)	75.79(7)
N(3)-Co(1)-N(4)	112.95(14)	121.67(8)	105.73(8)

salicylate is in intramolecular hydrogen bonding interaction with the metal bound carboxylate oxygen O1 at a distance of 2.587 Å. The asymmetric binding of carboxylate group in **4** is comparable to that in iron(II)–benzoate complex of the same ligand [92].

The cobalt(II)–salicylate complexes, **2**, **3** and **4** are unreactive towards dioxygen, while complex **1** slowly reacts with aerial oxygen. The reaction was monitored by optical spectroscopy. The optical spectrum of **1** in acetonitrile exhibits bands at 465, 605 and 622 nm due to d–d transition. The d–d bands slowly vanish upon reaction of the cobalt–salicylate complex with dioxygen and a new charge transfer transition band appears at 560 nm. The latter band is attributable to the phenolate-to-cobalt(III) charge-transfer transition. The reaction of **1** with dioxygen is slow and takes place over a period of 2 weeks (Fig. 3). However, the reaction takes about 4 days when the same is carried out in the presence of a base, triethylamine. The ESI-MS of the purple oxidized solution shows peak at m/z = 485.23 with expected isotope distribution pattern calculated for [(TPA)Co(SA)]<sup>+</sup> ion. The formation of a mononuclear

 Table 3

 Selected bond lengths (Å) and bond angles (°) for complexes 4, 1a and 1a.4H20.

Distance (Å)/angle (°)	4	1a	1a-4H <sub>2</sub> 0
$\begin{array}{c} \text{Distance }(\text{\AA})/\text{angle }(^{\circ})\\ \hline \text{Co}(1)-\text{O}(1)\\ \text{Co}(1)-\text{O}(2)\\ \text{Co}(1)-\text{N}(1)\\ \text{Co}(1)-\text{N}(2)\\ \text{Co}(1)-\text{N}(2)\\ \text{Co}(1)-\text{N}(3)\\ \text{Co}(1)-\text{N}(4)\\ \text{O}(1)-\text{Co}(1)-\text{O}(2)\\ \hline \text{O}(1)-\text{O}(2)\\ \hline \text{O}(1)-\text{O}(1)-\text{O}(2)\\ \hline \text{O}(1)-\text{O}(1)-\text{O}(2)\\ \hline \text{O}(1)-\text{O}(1)-\text{O}(2)\\ \hline \text{O}(1)-$	<b>4</b> 2.246(3) 2.068(3) 2.226(4) 2.112(3) 2.159(4) 2.129(3) 60.78(11)	1a           1.882(2)           1.848(2)           1.918(3)           1.953(3)           1.930(3)           1.929(3)           95.93(10)	1a-4H <sub>2</sub> O 1.889(2) 1.860(2) 1.922(3) 1.927(2) 1.926(3) 1.925(3) 96.12(9) 96.12(9)
$\begin{array}{l} N(1)-Co(1)-O(2) \\ O(1)-Co(1)-N(1) \\ O(2)-Co(1)-N(3) \\ O(1)-Co(1)-N(3) \\ N(1)-Co(1)-N(3) \\ O(2)-Co(1)-N(4) \\ O(1)-Co(1)-N(4) \\ O(1)-Co(1)-N(4) \\ \end{array}$	101.87(13) 88.75(12) 96.43(12) 93.18(13) 157.35(13) 115.12(12) 171.74(12)	96.32(11) 89.39(11) 94.89(12) 88.09(11) 168.71(11) 89.15(10) 174.39(10) 22.42(11)	95.45(11) 89.74(10) 94.24(11) 87.97(10) 170.22(11) 89.56(10) 174.18(10)
$ \begin{array}{l} N(1)-Co(1)-N(4) \\ N(3)-Co(1)-N(4) \\ O(2)-Co(1)-N(2) \\ O(1)-Co(1)-N(2) \\ N(1)-Co(1)-N(2) \\ N(3)-Co(1)-N(2) \\ N(4)-Co(1)-N(2) \end{array} $	85.13(12) 99.16(13) 162.36(12) 102.04(12) 80.41(13) 78.15(13) 82.43(12)	92.42(11) 89.11(11) 175.19(10) 88.84(10) 84.33(11) 84.62(11) 86.06(11)	90.98(11) 90.37(11) 175.98(10) 87.70(10) 85.78(11) 84.63(10) 86.59(10)



Fig. 3. Optical spectra of 1 and 1a (conc. = 0.1 mM) in acetonitrile.

low-spin cobalt(III)–salicylate complex, [(TPA)Co<sup>III</sup>(SA)](ClO<sub>4</sub>) (**1a**) was further confirmed from the diamagnetic <sup>1</sup>H NMR spectrum.

Two different crystalline forms of the cobalt(III)-salicylate complex, 1a and 1a 4H<sub>2</sub>O were isolated depending upon the condition of oxidation reaction and subsequent crystallization. Oxidation of 1 in dry acetonitrile or dry THF/MeOH leads to 1a. Single crystals of 1a were grown in dry THF/MeOH-diethyl ether mixture and crystallize in triclinic system with space group  $P\overline{1}$ . On the other hand, single crystals of 1a 4H<sub>2</sub>O, crystallized in a monoclinic unit cell with space group  $P2_1/c$ , were isolated from a moist acetonitrile solution of 1a. Crystalline 1a 4H<sub>2</sub>O could also be isolated from a reaction mixture containing equimolar amounts of TPA, cobalt(II) salt, salicylic acid and triethylamine, under air in moist acetonitrile. The solid state structures of 1a and its hydrated form (**1a**·**4H**<sub>2</sub>**O**) both reveal a similar complex cation with similar bond parameters within their estimated standard deviations (Fig. 4). The complex cation comprises a mononuclear distorted octahedral cobalt coordinated by four nitrogen donors of the N<sub>4</sub> ligand and two oxygen donors of dianionic salicylate. The salicylate group binds to the metal center in a bidentate fashion through one carboxylate oxygen atom (O1) and one phenolate oxygen atom (O2). The pyridine nitrogens (N1, N3 and N4) of the ligand and oxygen



Fig. 4. Structure of the cationic complex  $1a \cdot 4H_2O$ . The perchlorate anion and H atoms are omitted for clarity.

donor O1 form the equatorial plane with the average Co1-N<sub>py</sub> distances of 1.93 Å and Co1-O1 distance of 1.889(2) Å (Table 3). The amine nitrogen (N2) of the ligand and the phenolate oxygen (O2) of salicylate occupy the axial position with the Co1-N2 and Co1-O2 distances of 1.957(2) and 1.860(2) Å, respectively. The oxidation of cobalt(II) to cobalt(III) leads to a rearrangement in the binding of salicylate anion. In the cobalt(II)-salicylate complex (1), the carboxylate oxygen O1 binds to the metal center opposite to the amine nitrogen of the ligand. Upon oxidation, the carboxylate oxygen O2 binds to the metal center opposite to the amine nitrogen.

The carboxylate oxygen of monoanionic salicylate in **1** forms an intramolecular hydrogen bonding with the phenolic OH group. On the other hand, salicylate in **1a** (and in **1a**-4**H**<sub>2</sub>**O**) binds to the metal center in a bidentate fashion leaving one carboxylate oxygen atom for intermolecular hydrogen bonding interaction with guest solvent molecules. In the hydrated complex, **1a**-4**H**<sub>2</sub>**O**, one of the water molecules (O8) is in direct hydrogen bonding interaction with the cationic complex as well as with other three water molecules. The hydrogen boding motif associated with water molecules forms (H<sub>2</sub>O)<sub>6</sub> clusters in the crystal lattice (Fig. 5).



Fig. 5. Hexameric water cluster with 'pentamer planar+1' conformation.

2	2	0
,	-	h
~	-	v

Table 4				
Hydrogen	bonding	parameters	of	1a-4H <sub>2</sub> O.

$D\!\cdots\!H\!\cdots\!A$	Symmetry	D· · ·H (Å)	H···A (Å)	D···A (Å)	$D \cdots H \cdots A$ (°)
$O(8) \cdots H(8A) \cdots O(3)$	1 - x, $1 - y$ , $2 - z$	0.80	1.90	2.695(3)	170
$O(8) \cdots H(8B) \cdots O(10)$	x, y, z	0.98	1.75	2.733(4)	176
$O(9) \cdots H(9B) \cdots O(8)$	<i>x</i> , −1 + <i>y</i> , <i>z</i>	1.03	1.71	2.736(5)	173
$O(10) \cdots H(10A) \cdots O(8)$	1-x, $-1/2 + y$ , $3/2 - z$	1.00	1.81	2.801(4)	175
$O(10) \cdots H(10B) \cdots O(11)$	x, y, z	0.85	1.91	2.750(5)	167
$O(11) \cdots H(11B) \cdots O(9)$	x, y, z	1.14(11)	1.69(11)	2.766(5)	155(10)



Fig. 6. Propagation of hexameric water clusters in 1a·4H<sub>2</sub>O as one-dimensional tape along the crystallographic b axis.





Six water molecules in the cyclic repeating unit form strong hydrogen bonding with the  $0 \cdots 0$  distances in the range of 2.733–2.801 Å (Table 4). The average  $0 \cdots 0$  distance (2.76 Å) is very close to that found in the  $I_h$  structure of ice [1]. The average  $0 \cdots 0 \cdots 0$  angle of 116.8° deviates considerably from tetrahedral angle in ice  $I_h$  form. Among the six water molecules, oxygen atoms of five waters are in the same plane whether the rest one is out of the plane and makes an open envelop like 'pentamer planar+1' conformation with the dihedral angle of 36.8° (Fig. 5). Hexameric water clusters in complex lattice hosts with boat or chair like conformation have been reported in the literature. However, the water cluster in this case is one of the rare forms of 'pentamer planar+1' type conformation [86]. It is clear from the structural motif of **1a-4H<sub>2</sub>O** that the complex cation and perchlorate ions are involved in stabilizing the water cluster (Fig. 6). The salicylate oxygen (O3) strongly interacts with the water molecule (O8) of the cluster through H-bonding with a distance of 2.695 Å. On the other side, one oxygen atom of the perchlorate ion interacts with another water molecule (O11) of the cluster via a strong H-bonding interaction. Five water molecules, either act as two hydrogen bond acceptor or single hydrogen bond donor as well as acceptor, form a planar pentamer structure. The sixth water molecule interacting via two donors with two lone pairs of neighboring water molecules leads to tetrahedral angles and deviates from the pentameric plane [93]. This arrangement of water molecules gives rise to hexameric water clusters that



Fig. 8. XRPD patterns of 1, 1a·4H<sub>2</sub>O and 1a.

grow along the crystallographic *b* axis and form a one-dimensional tape (Fig. 6). In the tape each hexamer shares two water molecules (O8 and O10) and the overall cluster may be represented by T6(2) according to water cluster notation. T6(2) signifies a tape consisting of six-membered water rings involved in one-dimensional propagation along a particular direction where two water molecules are shared between the adjacent rings [94]. The edge-shared one-dimensional water tape observed in the small water clusters is considered to be a simplified model of ice [95,96].

Thermogravimetric analysis of  $1a \cdot 4H_2O$  in the temperature range 30–200 °C reveals a weight loss of 7.95%, close to a value for three water molecules (Fig. 7a). The difference between experimental and calculated values may be attributed to the release of some lattice water molecules below 30 °C. Thermogravimetric analysis of 1a also shows a step-wise weight loss of about 10% in the temperature range 30–200 °C that correspond to the loss of disordered solvent molecules (Fig. 7b).

The purity of bulk crystalline compounds was checked by comparing the experimental XRPD pattern with that of simulated pattern obtained from the single-crystal data (Fig. 8). The peaks for **1** and **1a**·**4H**<sub>2</sub>**O** do match well with the corresponding simulated patterns suggesting the purity of bulk crystalline compounds. It is important to mention here that the XRPD patterns of the sample after heating **1a**·**4H**<sub>2</sub>**O** up to 200 °C do not change much, suggesting that the lattice structure of the host remains same after removal of water molecules. On the other hand, the experimental XRPD data of **1a** do not match well with the simulated patterns. The experimental data for **1a**, however, match with the simulated pattern of **1a**-**4H**<sub>2</sub>**O**. This may be attributed to the fact that the crystal so **1a** lose the disordered solvent molecules present in the crystal lattice resulting in the formation of polycrystalline form with a very similar lattice structure as in **1a**-**4H**<sub>2</sub>**O**.

#### 4. Conclusion

We have synthesized and structurally characterized four mononuclear cobalt(II)-salicylate complexes of different tripodal N<sub>4</sub>-donor ligands. The cobalt(II)-salicylate complex of tris(2-pyridylmethyl)amine (TPA) ligand reacts with aerial oxygen to form the corresponding six-coordinate cobalt(III)-salicylate complex (**1a**) whereas other three complexes are unreactive towards dioxygen. Two different crystalline forms (hydrated and non-hydrated) of the cobalt(III)-salicylate complex were isolated depending upon the reaction/crystallization condition. In the lattice of hydrated crystalline form **1a**-**4H**<sub>2</sub>**0**, a hexameric water cluster is stabilized. The formation of the water cluster could be controlled during the crystallization process. The water hexamers in the crystal lattice adopt a rare 'pentamer planar+1' type conformation resulting in a one dimensional edge-shared water tape and represent a subunit of ice structure.

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#### Appendix A. Supplementary material

CCDC 818490, 818491, 818492, 818493, 818494, and 818495 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_re-quest/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.008.

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