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Cationic cobaltammines as anion receptors: Synthesis and characterization of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$, $[Co(NH_3)_6](2,4\text{-dnp})_3$ and $[Co(NH_3)_6](2,4,6\text{-tnp})_3$ (where np = nitrophenolate, dnp = dinitrophenolate, tnp, trinitrophenolate), single crystal X-ray structure and packing of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$

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Abstract

In an effort to utilize $[Co(NH_3)_6]^{3+}$ cation as a new host for mono-, di- and tri-substituted nitrophenolate anions, yellow solids of composition $[Co(NH_3)_6](4\text{-np})_3.4H_2O$, $[Co(NH_3)_6](2,4\text{-dnp})_3$, and $[Co(NH_3)_6](2,4,6\text{-tnp})_3$ were obtained in high yields by reacting sodium salts of 4-np, 2,4-dnp and 2,4,6-tnp (where np = nitrophenolate, dnp = dinitrophenolate and tnp = trinitrophenolate,) with $[Co(NH_3)_6]Cl_3$ respectively in 3:1 molar ratio in hot aqueous medium. These cobalt(III) complex salts have been characterized by elemental analyses and spectroscopic techniques (UV/Visible, IR and NMR). Single crystal X-ray structure determination of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$ revealed the presence of discrete ions, $[Co(NH_3)_6]^{3+}$ and $C_6H_4NO_3^-$ in addition to four lattice water molecules in the solid state. A strong network of hydrogen bond interactions (N–H···O (phenolate), N–H···O (nitro), O–H···O (water) stabilize the crystal lattice. The formation of these salts and measurement of solubility products suggests that $[Co(NH_3)_6]^{3+}$ present in $[Co(NH_3)_6]Cl_3$ may be used as anion receptor for the nitrophenolate ions.

Keywords: Anion receptor; Cobalt(III); Coordination chemistry; Inorganic synthesis; Nitrophenolates; X-ray crystallography

1. Introduction

The current interest [1–2] in developing new anion receptors is due to the role played by anions in many chemical, biological and environmental processes [3–7]. Several reasons why reliable sensing of anions is a particularly challenging area of research are: (a) anions are larger than isoelectronic cations and therefore have lower charge-to-radius (surface) ratio, a feature that makes the electrostatic binding of anions to the receptors less effective [8–9]. (b) Anions have a wide range of geometries and are often present in delocalized forms, which results in higher complexity in design and synthesis of receptors and (c) pH sensitivity. Anion receptors could be valuable if they are capable of anion binding in wastes or recognizing their presence. During last thirty years, many organic based anion receptors have been reported e.g. cationic cyclic polyamines[10–12], tripodal amines [13], calixarenes [14], sapphyrins [15], azacryptands [16] and azacages or open chain counterparts [17] but sporadic reports are available with cationic transition metal complexes based anion receptors i.e. alkoxide-bridged dinuclear Zn(II) complex [18], urea based Pt(II) receptor [19] and bipyridine Ru(II) complexes [20]. Therefore, the development of selective anion binding agents, which may find potential applications [21] and especially in polar solvents such as water is of particular interest [22–23].

Hexaamminecobalt(III) cation possesses all the characteristic features to act as a potential anion receptor (binding agent): (i) hydrogen bond donor groups, (ii) a positively

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charged component for effective electrostatic interactions and (iii) a suitable framework onto which these structural components can be assembled. This cationic cobaltammine is tri-positively charged, contains eighteen hydrogen bond donor. N–H groups which can interact with properly oriented atoms of the hydrogen bond accepters (oxygens of phenolate and nitro groups as well as water molecule) involving second sphere coordination and stable structural framework. We have undertaken an extensive research program to explore hexaamminecobalt(III) cation as anion receptor because it is relatively easy to synthesize from readily available materials and could be stored for months without any noticeable decomposition.

Mono-, di- and tri-substituted nitro-phenol and its salts are biologically and commercially important class of compounds. Nitrophenols are used to manufacture drugs (e.g. acetaminophen), fungicides, insecticides, and dyes and to darken leather [24]. Acute (short-term) inhalation or ingestion of nitrophenols in humans causes headaches, drowsiness, nausea, and cyanosis (blue color in lips, ears, and fingernails) [25]. Contact with eyes causes irritation in humans. Besides, picric acid (2,4,6-trinitrophenol) has been used in ammunitions and explosives during World War I as Lyddite or Melinite. Therefore, we report here the binding of biologically and commercially important mono-, di- and tri- substituted nitro-phenolate ions with the help of hexaamminecobalt(III) cation i.e. synthesis and characterization of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$, $[Co(NH_3)_6](2,4\text{-dnp})_3$, and $[Co(NH_3)_6](2,4,6\text{-tnp})_3$, (where np is nitrophenolate, dnp is dinitrophenolate and tnp is trinitrophenolate). And single crystal X-ray structure determination of one of the newly synthesized salt, $[Co(NH_3)_6](4\text{-np})_3.4H_2O$. We have already reported the use of hexaamminecobalt(III) as anion receptor for teraoxo-metallates [26–28], methanesulphatnate [29], carboxylates [30], fluoroanion [31] and halates [32].

2. Experimental

2.1. General remarks

Analytical grade reagents were used without any further purification. $[Co(NH_3)_6]Cl_3$ has been prepared by air oxidation of Co(II) salt in ammonical solution in the presence of activated charcoal as a catalyst according to method described by Bjerrum and McReynold [33]. Cobalt was determined by standard gravimetric method of estimation [34] and C, H, N were estimated micro analytically by automatic PERKIN ELMER 2400CHN elemental analyzer. The non-crystalline samples were dried in the desiccator before elemental analyses. UV/Visible spectra were recorded using HITACHI 330 spectrometer in water as solvent. Infrared spectra of the title complex salts were recorded using PERKIN ELMER spectrum RX FT-IR system using Nujol mull in KBr plates. ^{1}H-NMR and ^{13}C-NMR spectra of title complex salts were run in the solvent D_2O at 25 °C by using JEOL AL 300 MHz FT NMR spectrometer. The chemical shift values are expressed as δ value (ppm) down field from tetramethylsilane as an internal standard.

2.2. Synthesis of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$

Hexaamminecobalt(III) chloride (0.50 g., 0.0018 mol) was dissolved in 10 ml hot water taken in a beaker by mechanical stirring. In another beaker 0.907 g (0.0056 mol) of sodium 4-nitrophenolate was dissolved in 20 ml hot water. Both the solutions were mixed and allowed to cool slowly, yellow solid precipitated immediately, which was washed with ice-cold water and air dried. Orangish-yellow coloured shining crystals were obtained from hot aqueous medium, which were filtered and dried in air. The overall yield is nearly quantitative and salt decomposes at 398 K. Solubility (25 °C) in water: 0.876 g/100 ml. Elemental Anal. Calc. for $C_{18}H_{38}CoN_9O_{13}$, (F.W. = 647.50): C, 33.35; H, 6.86; N, 19.45; Co, 9.05. Found: C, 33.32; H, 5.84; N, 19.42, Co, 8.25%. IR. $\nu = 3410$ (b), 3232(b), 1618 (m), 1573 (m), 1521 (m), 1347(s), 1322(s), 803 (m) cm^{-1}. UV/Vis (solution): $\lambda_{max} = 346$, 399. NMR (solution): ^{1}HNMR (DMSO), $\delta = 7.6$–7.7 (d,6H), 6.0–6.1(d,6H), 3.7 (s,18H), ^{13}CNMR, $\delta = 179$, 129, 127,119 ppm.

2.3. Synthesis of $[Co(NH_3)_6](2,4\text{-dnp})_3$

Hexaamminecobalt(III) chloride (1 g, 0.003 mol) was dissolved in 20 ml of hot water taken in a beaker by mechanical stirring. In another beaker 2.33 g (0.011 mol) of sodium 2,4-dinitrophenolate was dissolved in minimum amount of hot water (20 ml). Both the solutions were mixed with stirring and yellow solid precipitated immediately, which was washed with ice-cold water and air-dried. The yield was 79% and salt decomposes at 474 K. Solubility (25 °C) in water: 0.056 g/100 ml. Elemental Anal. Calc. for $C_{18}H_{27}CoN_{12}O_{15}$, (F.W. = 781.9): C, 30.42; H, 3.80; N, 23.66; Co, 8.29 Found: C, 30.39; H, 3.75; N, 23.64, Co, 8.05%. IR. $\nu = 3232$(b), 1602 (m), 1554 (m), 1515 (m), 1331(s), 1324(s), 781 (m) cm^{-1}. UV/Vis (solution): $\lambda_{max} = 356$, 395. NMR (D_2O): ^{1}HNMR, $\delta = 8.69$ (s,3H,), 7.8–7.9 (d,6H), 6.4–6.5 (d, 6H), 3.45(18H), ^{13}CNMR, $\delta = 170$, 135, 128, 127, 126, 124 ppm.

2.4. Synthesis of $[Co(NH_3)_6](2,4,6\text{-tnp})_3$

Hexaamminecobalt(III) chloride (1 g, 0.003 mol) was dissolved in 20 ml of hot water taken in a beaker by mechanical stirring for 10–15 min. In another beaker 2.83 g (0.011 mol) of sodium 2,4,5-trinitrophenolate was dissolved in minimum amount of hot water (20 ml). Both the solutions were mixed with stirring and yellow solid precipitated immediately, which was washed with ice-cold water and air-dried. The yield was 80% and the salt decomposes at 483 K. Solubility (25 °C) in water: 0.039 g/100 ml. Elemental Anal. Calc. for C_{18} H_{24} Co N_{15} O_{21}, (F.W. = 844.9): C, 25.56; H, 2.84; N, 24.85, Co, 6.97) Found: C, 25.52; H, 2.84; N, 24.81; Co, 6.43%. IR. $\nu = 3232$(b), 1602 (m), 1554 (m), 1515 (m), 1331(s), 1324(s), 781 (m) cm^{-1}. UV/Vis (solution): $\lambda_{max} = 355, 395$. NMR (D_2O): ^{1}HNMR, $\delta = 8.69$ (s,3H), 7.8–7.9 (d,6H), 6.4–6.5 (d, 6H), 3.45(18H), ^{13}CNMR, 170, 135, 128,127, 126, 124 ppm.

2.5. Crystal structure determination

Good single crystal of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$ suitable for X-ray diffraction studies were grown from aqueous solution by slow evaporation method. A single crystal with dimension 0.28×0.19×0.17 mm was mounted along the largest dimension and used for data collection. The intensity data were collected on Siemens P4 single crystal diffractometer equipped with molybdenum sealed tube ($\lambda = 0.71073$ Å) and highly oriented graphite monochromator. Three reflections were used to monitor the stability and orientation of the crystal and were re-measured after every 97 reflections. The data were corrected for Lorentz and polarization factors and an empirical absorption correction based on psi scan method has also applied. All other relevant information about the data collection is presented in Table 1. The structure was solved by Direct Methods using SHELX-97 [35] package and also refined using the same one. All other information regarding the refinement is also recorded in Table 1.

3. Results and discussion

3.1. Synthesis

Three new hexaamminecobalt(III) complex salts i.e. $[Co(NH_3)_6](4\text{-np})_3.4H_2O$, $[Co(NH_3)_6]$ (2,4-dnp)$_3$ and $[Co(NH_3)_6]$(2,4,6-tnp)$_3$ have been synthesized by reacting appropriate metal salt- Na(4-np), Na(2,4-dnp), Na(2,4, 6-tnp), with $[Co(NH_3)_6]Cl_3$ respectively in 3:1 molar ratio in hot aqueous medium. Single crystals of $[Co(NH_3)_6]$-(4-dnp)$_3$.4H_2O were obtained from hot aqueous medium by allowing it to evaporate at room temperature. However, all efforts to obtain single crystals of $[Co(NH_3)_6]$(2,4-dnp)$_3$ and $[Co(NH_3)_6]$(2,4,6-tnp)$_3$ suitable for X-ray structure determination were unsuccessful. The chemical compositions of newly synthesized complex salts were initially indicated by elemental analyses. All the title complex salts are highly soluble in DMSO but insoluble in other organic solvents (e.g. chloroform, ethanol, acetone) except $[Co(NH_3)_6]$(2,4,6-tnp)$_3$ which is partially soluble in ethanol and acetone. These hexaamminecobalt(III) salts are slightly soluble in water but more soluble in hot water.

Table 1
Crystal data and structure refinement parameters of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$

Empirical formula	C_{18} H_{38} Co N_9 O_{13}
Formula weight	647.50
Temperature (K)	293(2)
Radiation used, wavelength (Å)	Mo Kα 0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 16.250(1)$ Å $b = 23.932(2)$ Å, $\beta = 95.35(1)°$ $c = 7.248(1)$ Å
Volume	2806.4(5) $Å^3$
Z, Calculated density (Mg/m^3)	4, 1.532
Absorption coefficient (mm^{-1})	0.690
F(000)	1360
Crystal size (mm)	0.28×0.19×0.17
Max. and min. transmission	0.880, 0.868
Theta range for data collection (°)	2.12–24.00
Scan type	$2\theta - \theta$
Scan speed	Variable, 2.0–60.0°/min. in ω
Scan range (ω)	0.90° plus Kα separation
Background measurement	Stationary crystal and stationary counter at the beginning and end of scan, each for 25.0% of total scan time
Index ranges	$-18 \leq h \leq 18$, $-27 \leq k \leq 0$, $0 \leq l \leq 8$
Reflections collected	4802
Independent reflections	4410 [R(int) = 0.0190]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4410/0/371
Goodness-of-fit on F^2	1.013
Weighting scheme	$1/[\sigma^2 (Fo^2) + (0.0408P)^2 + 1.00P]$, $P = (max(F_o^2, 0) + 2 * F_c^2)/3$
Data to parameter ratio	11.89:1
Final R indices, 3319 reflections [$I > 2s(I)$]	$R1 = 0.0345$, $wR2 = 0.0806$
R indices (all data)	$R1 = 0.0529$, $wR2 = 0.0895$
Extinction coefficient	0.0025(3)
Largest diff. peak and hole	0.198 and −0.256 e $Å^{-3}$

3.2. Measurement of solubility products

Solubility of ionic salts in water differs to a great extent and on the basis of solubility criterion, the salts are classified into three categories (a) solubility >0.1 M (soluble), (b) solubility between 0.01 and 0.1 M (slightly soluble) and (c) solubility <0.01 M (springly soluble). The solubility measurements at room temperature (Table 2) show that $[Co(NH_3)_6](4\text{-np})_3 \cdot 4H_2O$ is slightly soluble in water whereas $[Co(NH_3)_6]$(2,4-dnp)$_3$ and $[Co(NH_3)_6]$(2,4,6-tnp)$_3$ are springly soluble. It is

Table 2
Solubility products (K_{sp}) of hexaamminecobalt(III) salts

Complex salts	Solubility (M)	K_{sp}
$[Co(NH_3)_6]Cl_3$	0.26052	0.123
$[Co(NH_3)_6](4\text{-np})_3 \cdot 4H_2O$	0.01352	9.0×10^{-7}
$[Co(NH_3)_6]$(2,4-dnp)$_3$	0.00079	1.0×10^{-11}
$[Co(NH_3)_6]$(2,4,6-tnp)$_3$	0.00046	1.2×10^{-12}

observed that the binding (association) of 2,4,6-trinitrophenolate and 2,4-dinitrophenolate ions with $[Co(NH_3)_6]^{3+}$ is much more as compared to 4-nitrophenolate ion i.e. the binding affinities are in the order $[Co(NH_3)_6](2,4,6\text{-tnp})_3 > [Co(NH_3)_6](2,4\text{-dnp})_3 \gg [Co(NH_3)_6](4\text{-np})_3 \cdot 4H_2O$. This may be ascribed to increase in number of nitro groups on phenolate ion. As reported in the experimental section, when the appropriate amounts of the reactants were mixed in minimum amount of water the precipitation occurred immediately resulting in the formation of title complex salts. This is because ionic products are greater than solubility products, K_{sp} (Table 2).

3.3. Spectroscopy

The vibrational spectra of newly synthesized hexaamminecobalt(III) complex salts shows that the stretching vibration of the coordinated NH_3 molecule are lower than those of the free NH_3 molecules for two reasons, one is the effect of coordination and the other is the effect of the counter ions i.e. 4-np, 2,4-dnp and 2,4,6-tnp. This is attributed to the weakening of the N–H bond due to the formation of N–H···O type of hydrogen bond. It is seen that the antisymmetric stretch and symmetric NH_3 stretch, NH_3 degenerate deformation, NH_3 symmetric deformation and NH_3 vibrations appear in the regions of 3400–3000, 1650–1550, 1370–1200 and 800–900 cm^{-1} respectively for $[Co(NH_3)_6]Cl_3$ [36] which are comparable with newly synthesized hexaamminecobalt(III) complex salts. For the anionic groups, i.e. for mono, di and tri substituted nitrophenolates, the hydrogen bonding weaken the N=O bond resulting in absorption of lower frequency and the sharp peaks are observed in the range 1521–1515 and 1331–1347 cm^{-1} for NO_2 (ν_s) and NO_2 (ν_{as}) respectively. The peak assignments have been made in consultation with literature [37] values.

As reported in the literature [38] the two transitions $^1A_{1g} \rightarrow T_{1\,g}$ and $^1A_{1g} \rightarrow {}^1T_{2\,g}$ for hexaamminecobalt(III) complexes are observed around 470 and 340 nm respectively producing the familiar orange yellow colour for number of classical coordination compounds containing cobalt(III). For these entire complex salts the λ_{max} were not observed at 470 and 340 nm (showing d–d transitions typical for low spin Co(III) d^6 octahedral complex) but shifted to left i.e. 355 and 395 this is due to outer-sphere charge transfer from nitro substituted phenolate ion to central metal ion. These values of λ_{max} in the newly synthesized complex salts are also in agreement with those of the earlier reported complex salts [39] but quite different from our earlier reported hexaamminecobalt(III) salts [26–32].

In the title complex salts, ^1H and ^{13}C NMR chemical shift values are in good agreement with the literature values reported for mono-, di- and tri- substituted nitrophenols [40]. The ^1H NMR spectrum of all complex salts shows a broad peak at 3.45 ppm, which is a characteristic of coordinated NH_3 group [41]. In ^{13}C NMR, chemical shift values for carbon atom ($C–O^-$) in 4-np, 2,4-dnp and 2,4,6-tnp salts are 179, 170 and 160 ppm respectively. The lowering trend is due to presence of number of electron withdrawing groups on phenolate rings.

3.4. X-ray crystallography

The X-ray crystal structure of the $[Co(NH_3)_6](4\text{-np})_3.4H_2O$ has been unambiguously determined by single crystal X-ray crystallography. The salt crystallizes in Monoclinic, space group $P2_1/c$, having cell dimensions, $a = 16.250(1)$ Å, $b = 23.932(2)$ Å, $c = 7.248(1)$ Å $\beta = 95.35(1)°$, $V = 2806.4(5)$ Å^3, $Z = 4$ and $R = 0.0345$. The crystal structure not only conclusively establishes the existence of single salt of $[Co(NH_3)_6](C_6H_4NO_3)_3.4H_2O$ but also rules out the possibility of a mixture of salts or double salt. Furthermore, this revealed for the first time that it is a first ionic salt which contains discrete ions $[Co(NH_3)_6]^{3+}$ and $C_6H_4NO_3^-$ in addition to four lattice

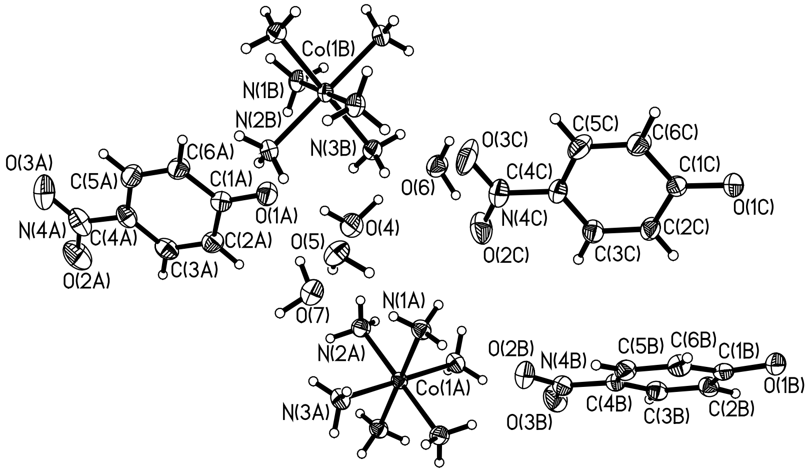

Fig. 1. ORTEP Diagram of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$.

water molecules in the solid state. The ORTEP diagram of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$ complex salts is shown in Fig. 1.

In $[Co(NH_3)_6]^{3+}$, the cobalt(III) metal ion is surrounded by six nitrogen atoms originating from six coordinating ammonia molecules resulting in a nearly octahedral geometry. The Co–N bond distances are in the range 1.958(2)–1.970(19) Å, while *cis* N–Co–N bond angles are in the range 88.02(8)–92.33(8)° and trans N–Co–N bond angles are in the range 180.00(9)–180.00(12)°. This study showed that octahedron is

Table 3
Selected bond lengths [Å] and angles [°] of $[Co(NH_3)_6](4\text{-np})_{3.}4H_2O$

Co(1A)–N(2A)	1.958(2)	Co(1B)–N(2B)#2	1.9645(19)
Co(1A)–N(2A)#1	1.958(2)	Co(1B)–N(2B)	1.9645(19)
Co(1A)–N(3A)	1.961(2)	Co(1B)–N(1B)	1.9665(19)
Co(1A)–N(3A)#1	1.961(2)	Co(1B)–N(1B)#2	1.9665(19)
Co(1A)–N(1A)	1.9690(19)	Co(1B)–N(3B)	1.9708(19)
Co(1A)–N(1A)#1	1.9690(19)	Co(1B)–N(3B)#2	1.9708(19)
O(1A)–C(1A)	1.311(3)	O(1B)–C(1B)	1.302(3)
O(2A)–N(4A)	1.237(4)	O(2B)–N(4B)	1.240(3)
O(3A)–N(4A)	1.235(4)	O(3B)–N(4B)	1.242(3)
N(4A)–C(4A)	1.434(4)	N(4B)–C(4B)	1.422(3)
C(1A)–C(6A)	1.402(4)	C(1B)–C(6B)	1.414(4)
C(1A)–C(2A)	1.409(4)	C(1B)–C(2B)	1.418(4)
C(2A)–C(3A)	1.371(4)	C(2B)–C(3B)	1.366(4)
C(3A)–C(4A)	1.383(4)	C(3B)–C(4B)	1.390(4)
C(4A)–C(5A)	1.382(4)	C(4B)–C(5B)	1.382(4)
C(5A)–C(6A)	1.371(4)	C(5B)–C(6B)	1.365(4)
O(1C)–C(1C)	1.302(3)	C(1C)–C(2C)	1.409(4)
O(2C)–N(4C)	1.226(3)	C(2C)–C(3C)	1.369(4)
O(3C)–N(4C)	1.242(3)	C(3C)–C(4C)	1.380(4)
N(4C)–C(4C)	1.427(3)	C(4C)–C(5C)	1.383(4)
C(1C)–C(6C)	1.408(4)	C(6C)–C(5C)	1.368(4)
N(2A)–Co(1A)–N(2A)#1	180.00(9)	N(2B)#2–Co(1B)–N(2B)	180.00(11)
N(2A)–Co(1A)–N(3A)	90.74(9)	N(2B)#2–Co(1B)–N(1B)	89.42(8)
N(2A)#1–Co(1A)–N(3A)	89.26(9)	N(2B)–Co(1B)–N(1B)	90.58(8)
N(2A)–Co(1A)–N(3A)#1	89.26(9)	N(2B)#2–Co(1B)–N(1B)#2	90.58(8)
N(2A)#1–Co(1A)–N(3A)#1	90.74(9)	N(2B)–Co(1B)–N(1B)#2	89.42(8)
N(3A)–Co(1A)–N(3A)#1	180.00(10)	N(1B)–Co(1B)–N(1B)#2	180.0
N(2A)–Co(1A)–N(1A)	88.55(9)	N(2B)#2–Co(1B)–N(3B)	91.98(8)
N(2A)#1–Co(1A)–N(1A)	91.45(8)	N(2B)–Co(1B)–N(3B)	88.02(8)
N(3A)–Co(1A)–N(1A)	89.24(9)	N(1B)–Co(1B)–N(3B)	87.67(8)
N(3A)#1–Co(1A)–N(1A)	90.76(9)	N(1B)#2–Co(1B)–N(3B)	92.33(8)
N(2A)–Co(1A)–N(1A)#1	91.45(8)	N(2B)#2–Co(1B)–N(3B)#2	88.02(8)
N(2A)#1–Co(1A)–N(1A)#1	88.55(9)	N(2B)–Co(1B)–N(3B)#2	91.98(8)
N(3A)–Co(1A)–N(1A)#1	90.76(9)	N(1B)–Co(1B)–N(3B)#2	92.33(8)
N(3A)#1–Co(1A)–N(1A)#1	89.24(9)	N(1B)#2–Co(1B)–N(3B)#2	87.67(8)
N(1A)–Co(1A)–N(1A)#1	180.0	N(3B)–Co(1B)–N(3B)#2	180.00(12)
O(3A)–N(4A)–O(2A)	121.8(3)	O(2C)–N(4C)–O(3C)	121.2(2)
O(3A)–N(4A)–C(4A)	119.4(3)	O(2C)–N(4C)–C(4C)	120.5(2)
O(2A)–N(4A)–C(4A)	118.8(3)	O(3C)–N(4C)–C(4C)	118.3(3)
O(1A)–C(1A)–C(6A)	121.2(2)	O(1C)–C(1C)–C(6C)	122.0(2)
O(1A)–C(1A)–C(2A)	121.9(2)	O(1C)–C(1C)–C(2C)	121.9(2)
C(6A)–C(1A)–C(2A)	116.9(2)	C(6C)–C(1C)–C(2C)	116.1(2)
C(3A)–C(2A)–C(1A)	121.4(3)	C(3C)–C(2C)–C(1C)	122.4(2)
C(2A)–C(3A)–C(4A)	119.9(3)	C(2C)–C(3C)–C(4C)	119.5(2)
C(5A)–C(4A)–C(3A)	120.3(3)	C(3C)–C(4C)–C(5C)	120.3(2)
C(5A)–C(4A)–N(4A)	119.2(3)	C(3C)–C(4C)–N(4C)	120.0(2)
C(3A)–C(4A)–N(4A)	120.6(3)	C(5C)–C(4C)–N(4C)	119.7(2)
C(6A)–C(5A)–C(4A)	119.8(3)	C(5C)–C(6C)–C(1C)	121.8(3)
C(5A)–C(6A)–C(1A)	121.8(3)	C(3B)–C(2B)–C(1B)	121.6(3)
O(2B)–N(4B)–O(3B)	121.4(2)	C(2B)–C(3B)–C(4B)	119.3(2)
O(2B)–N(4B)–C(4B)	119.2(3)	C(5B)–C(4B)–C(3B)	120.9(2)
O(3B)–N(4B)–C(4B)	119.4(3)	C(5B)–C(4B)–N(4B)	119.2(3)
O(1B)–C(1B)–C(6B)	121.4(2)	C(3B)–C(4B)–N(4B)	119.9(3)
O(1B)–C(1B)–C(2B)	121.8(2)	C(6B)–C(5B)–C(4B)	119.8(3)
C(6B)–C(1B)–C(2B)	116.8(2)	C(5B)–C(6B)–C(1B)	121.4(2)
C(6C)–C(5C)–C(4C)	120.0(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1,-y+1,-z+2$ #2 $-x,-y+1,-z+1$.

slightly distorted. In the hexaamminecobalt(III) chloride [42], the average Co–N distance is 1.963 Å and the maximum deviation of cis N–Co–N bond angles from their ideal values is 2.1° with a standard deviation of 0.7°. These values of the $[Co(NH_3)_6](4\text{-np})_3.4H_2O$ salt are also in the agreement with the earlier reported hexaamminecobalt(III) complex salts [26–32]. The selected bond angles and bond lengths are listed in Table 3.

The conformation of the 4-np ion is similar to that found in other 4-np salts/complexes [43–48]. The comparison of the C–O bond length of the 4-np ion in the various 4-np containing compounds indicate that there is no dependence of the C–O bond length of the para-nitrophenolate ion on the metal ion present (ionic and coordinated). The average C–O bond length is 1.305(3) Å and 1.311(2) Å in $Na(C_6H_4NO_3)\cdot 2H_2O$ [45] and $Mg(C_6H_4NO_3)\cdot 8H_2O$ [46], respectively, whereas in the $[Co(NH_3)_6]$ $(C_6H_4NO_3)_3.4H_2O$ salt is 1.305(3) Å. This indicate that the complex under study in ionic.

In the crystal lattice, there are two independent $[Co(NH_3)_6]^{3+}$ cations and both are placed on center of inversion. As a result, they have near octahedral coordination geometry around the central metal ion (Table 3). The packing of title complex salt shows some interesting structural features. There are four molecules of water as solvent of crystallization in the lattice. They are all clustered together with $[Co(NH_3)_6]^{3+}$ cations forming linear columns perpendicular to the *bc* plane (Fig. 2). Out of these four water molecules, there are two hydrogen bonded water dimers formed between O4, O6 [O6···H4A = 1.828 Å, O4–H4A···O6 = 165.70°] and O5, O7 [O7···H5B = 1.955 Å, O5–H5B···O7 = 168.22°]. These water dimers form an intricate network of hydrogen bonds with $[Co(NH_3)_6]^{3+}$ cations and stabilize the linear columns (see a typical one in the middle of Fig. 3). Six of such columns present at the inversion center of the unit cell forms a tubular cavity in which the 4-nitrophenolate anions reside, forming hydrogen bonding linkages to adjacent columns from both ends (using both $-O^-$ and $-NO_2$ groups) i.e. head to tail bonding of 4-np ion which we have observed for the first time. It is interesting that all the four water molecules of the columns are involved in holding the anions at the middle of the tubular cavity through strong hydrogen bonds with the negatively charged phenolate oxygen atoms. Indeed these oxygen atoms are involved in multiple hydrogen bonds to impart maximum stability (see the last six entries in Table 4). The other side of the anion (nitro part) is also anchored to the linear columns by hydrogen bonds simulating a molecular ladder. It is noteworthy that

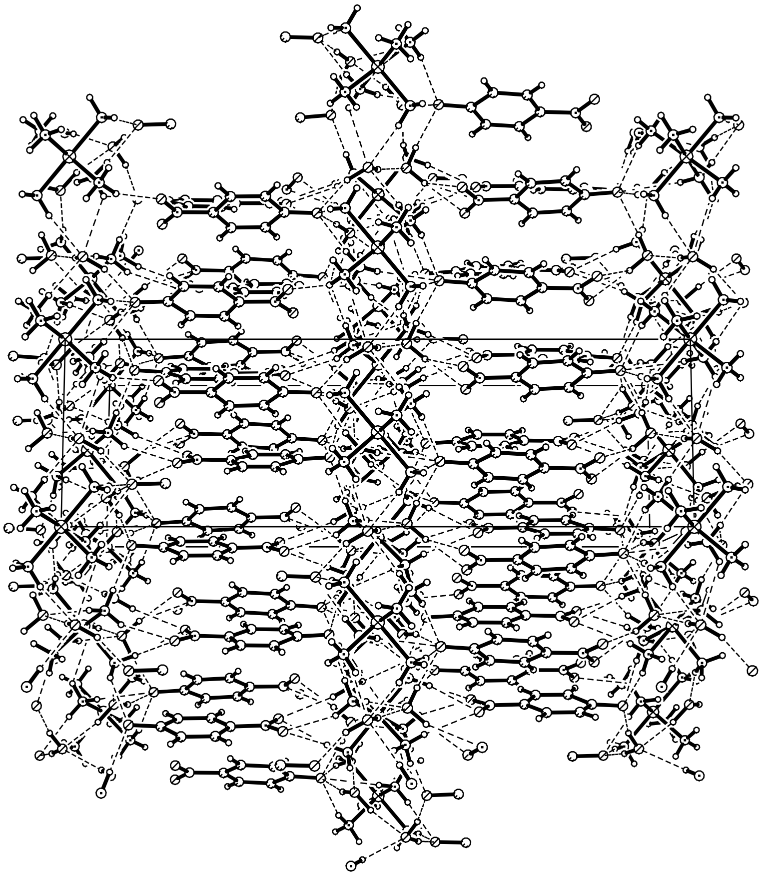

Fig. 2. Packing of $[Co(NH_3)_6](4\text{-np})_3\cdot 4H_2O$ viewed down *a*-axis. Note the formation of columns in which $[Co(NH_3)_6]^{3+}$ cation and water molecules participate through H-bonding. These columns are linked by 4-np ions on both sides. (hydrogen bonds are shown with dotted lines).

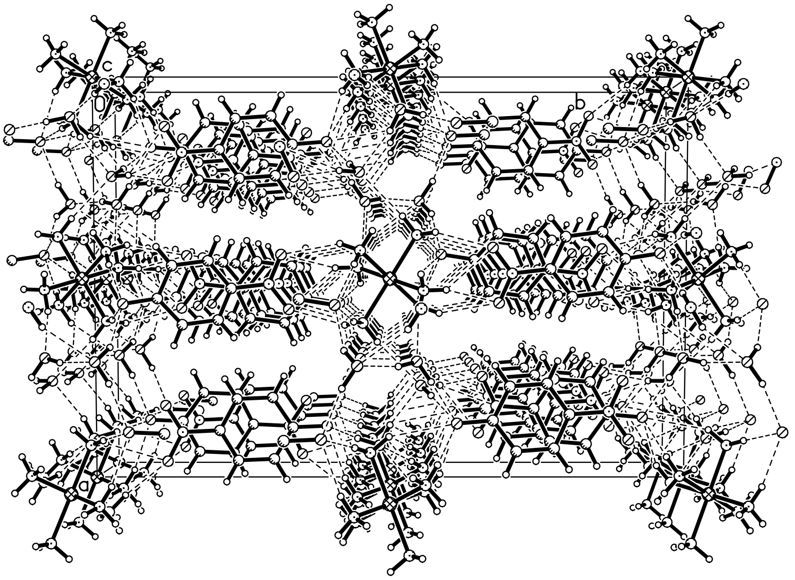

Fig. 3. Packing of $[Co(NH_3)_6](4\text{-np})_3\cdot 4H_2O$ viewed down 'ab' plane showing the π stacking of aromatic planes. See all the four water molecules bonded to a column of $[Co(NH_3)_6]^{3+}$ (hydrogen bonds are shown with dotted lines).

the hydrophilic parts of the structure are placed in the close proximity and are linked through hydrogen bonds imparting stability to the lattice. Due to such an arrangement, the hydrophobic aromatic part of the anions is stacked one over other generating additional stabilizing π···π stacking interactions (the interplanar distance between the benzene rings of the nearest neighbour is 3.54 Å). Thus a view from the one edge of a unit cell (Fig. 2) shows repeating array of *column*-π···π stack, column-π···π *stack*..., arrangement that are stabilized through hydrogen bonds and π···π interactions.

4. Conclusion

The selective complexation of hexaamminecobalt(III) cation with nitrophenolates results in the formation of yellow coloured complex salts which have been characterized on the basis of elemental analyses and spectroscopic studies. The measurements of solubility products show that relative affinities of nitrophenolate ions for hexaamminecobalt(III) is in the order $[Co(NH_3)_6](2,4,6\text{-tnp})_3 > [Co(NH_3)_6](2,4\text{-dnp})_3 \gg [Co(NH_3)_6](4\text{-np})_3\cdot 4H_2O$. In the case of $[Co(NH_3)_6](4\text{-np})_3\cdot 4H_2O$, the single crystal

Table 4
Hydrogen bonding parameters *(Å) and (°) of $[Co(NH_3)_6](4\text{-np})_3.4H_2O$

D-H···A	D-H	H···A	<DHA	D···A	Symmetry operations
N1A-H1AA···O2B	0.890	2.271	148.16	3.063	
N1A-H1AC···O1B	0.890	2.113	165.95	2.985	$[x, -y+3/2, z-1/2]$
N2A-H2AA···O4	0.890	2.095	163.45	2.959	
N2A-H2AC···O1B	0.890	2.272	145.33	3.047	$[-x+1, y-1/2, -z+3/2]$
N3A-H3AC···O1B	0.890	2.022	164.01	2.888	$[-x+1, y-1/2, -z+5/2]$
N1B-H1BA···O3C	0.890	2.104	157.63	2.946	$[-x, -y+1, -z+1]$
N1B-H1BB···O1A	0.890	2.169	161.74	3.027	
N2B-H2BA···O1C	0.890	2.183	166.71	3.056	$[-x, y-1/2, -z+3/2]$
N2B-H2BB···O5	0.890	2.205	156.24	3.041	
N2B-H2BC···O1A	0.890	2.077	158.43	2.923	
N3B-H3BB···O3C	0.890	2.460	125.88	3.068	
N3B-H3BC···O1C	0.890	2.082	174.82	2.969	$[x, -y+3/2, z-1/2]$
O4-H4A···O6	0.988	1.828	165.70	2.796	
O5-H5B···O7	0.872	1.955	168.22	2.814	
O4-H4B···O1A	0.891	1.916	164.01	2.783	
O5-H5A···O1C	0.970	1.767	162.58	2.709	$[x, -y+3/2, z+1/2]$
O6-H6A···O1B	0.932	1.918	153.92	2.786	$[x, -y+3/2, z-1/2]$
O6-H6B···O1C	0.961	1.931	165.04	2.870	$[x, -y+3/2, z-1/2]$
O7-H7A···O2A	0.958	2.027	169.63	2.975	$[x, -y+1/2, z+1/2]$
O7-H7B···O1A	0.904	1.996	172.17	2.894	

Relatively strong hydrogen bonds are only depicted in this Table (distance less than 2.28 Å between d(H···A)). There are short contacts in the range (2.28–2.6 Å d(H···A)) present in the hydrophilic region of the structure providing additional stability to the lattice.

X-ray structure determination revealed the presence of N–H···O, O–H···O and N–O···H charge assisted hydrogen bond interactions apart from coulombic attractions in the solid state which may be present in the other two title complex salts also. The present study shows that $[Co(NH_3)_6]^{3+}$ present in $[Co(NH_3)_6]Cl_3$ may find application as anion receptor for toxic and commercially important mono, di and tri-subsituted nitrophenolate ions in aqueous medium in contrast to other synthetic receptors which are effective in non aqueous medium.

5. Supplementary material

Crystallographic data for the structural analysis of $[Co(NH_3)_6](C_6H_4NO_3)_3.4H_2O$ compound has been deposited at the Cambridge Crystallographic Data Center,12 Union Road,Cambridge, CB2 1EZ, UK, and are available free of charge from the Director on request quoting the deposition number CCDC 250897 (Fax: 44 1223 336033, email: deposit@ccdc.cam.ac.uk)

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