More insight into the crystal structure of [Co(H$_2$O)$_4$(4-nba)$_2$]·2H$_2$O (4-nba=*para*-nitrobenzoate): An unprecedented hydrogen bonded supramolecular network[#]

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The title complex tetra-aquobis(*para*-nitrobenzoato)cobalt(II) dihydrate **1** crystallizes in the triclinic space group P$\overline{1}$ with the following unit cell dimensions for C$_{14}$H$_{20}$N$_2$CoO$_{14}$ (M=499.25) *a*=7.227(5) Å, *b*=7.341(5) Å, *c*=10.604(5) Å, α = 85.884(5)$^{\circ}$ β = 87.938(5)$^{\circ}$ γ = 60.178(5) $^{\circ}$ *V* = 486.8(5) Å^3, Z=1, D_c=1.703 g.cm^{-3}. In **1**, the *para*-nitrobenzoate anion functions as a monodentate ligand and the Co(II) metal is located on a centre of inversion. The central metal is bound by four oxygen atoms of four water ligands, which lie on a square plane and two monodentate nitrobenzoate ligands, which are *trans* to each other, complete a distorted octahedron around cobalt. The oxygen atom of the nitro group of the *para*-nitrobenzoate forms hydrogen bonds (H acceptor bonds) with a H atom of the coordinated water on an adjacent Co thus linking the complex in a chain. These chains are further linked by hydrogen bonding which use the crystal water. This gives rise to an unprecedented hydrogen bonded supramolecular network. The title complex can be fully dehydrated to the corresponding anhydrous complex, which in turn can be rehydrated to **1**. The synthesis, spectroscopic, thermal and X-ray structural characterization of the title complex **1** are described.
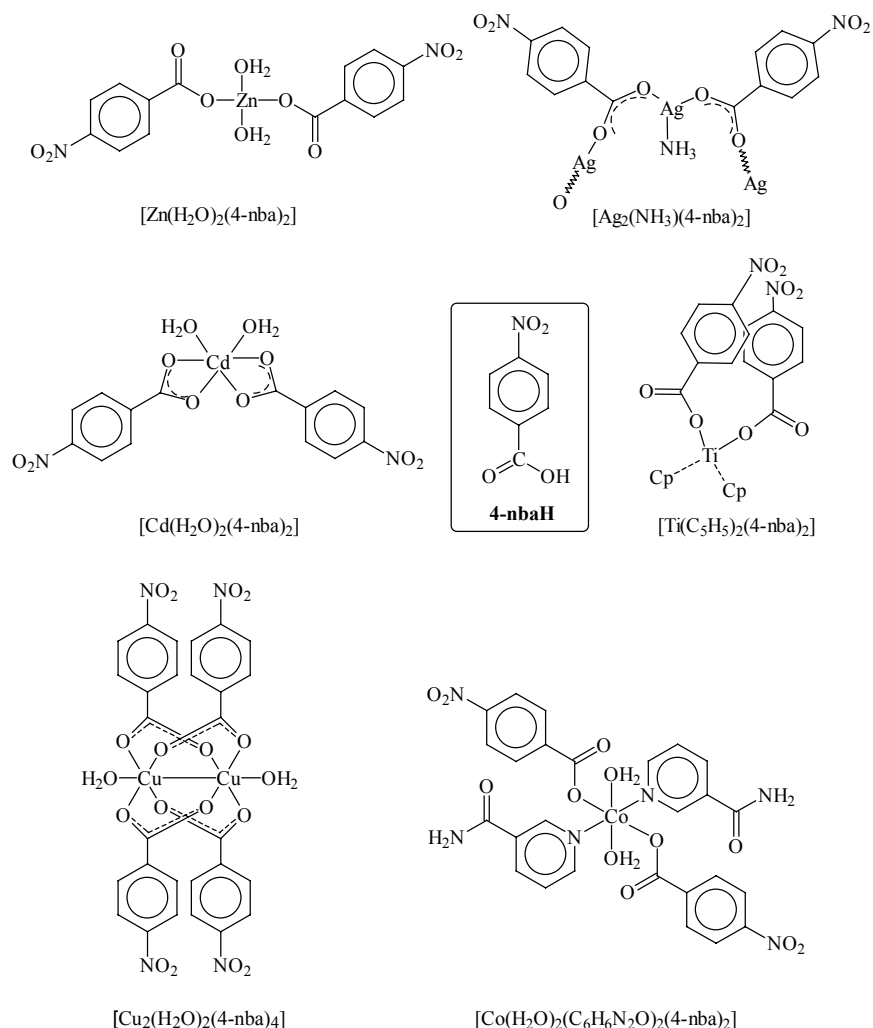
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The chemistry of metal-carboxylates is an area of intense research investigations in view of its diverse applications, ranging from the relevance of metal-carboxylate complexes as model systems for the metalloactive sites in bioinorganic chemistry[1,2] to their usefulness as novel materials in materials science. Metal oxides can be readily prepared from metal-carboxylate precursors by thermal decomposition methods[3]. The structural diversity encountered in metal-carboxylate complexes can be attributed to the versatile ligational behaviour of the carboxylate group which can function like a bidentate ligand binding to a single metal or alternatively as a bridging bidentate ligand coordinating to two metals or as a monodentate ligand[4,5].

An emerging area of interest is the construction of hybrid inorganic-organic polymer network systems in view of their applications as useful materials[6-10]. Carboxylate ligands that possess additional donor sites for example -NH$_2$, -SH etc. can be used as the organic component to synthesize metal complexes with novel extended network structural features. In this context, substituted aromatic carboxylic acids are expected to form rigid stable coordination polymers on account of their appropriately placed functional groups, which are attached to a rigid template such as a benzene ring. The formation of extended hydrogen bonded systems with interesting structural features has been well demonstrated in the case of metal complexes derived from amino and mercapto benzoic acids[11-13].

In our earlier work on the aminobenzoates of Mg(II) we have shown that the positioning of the amino group with respect to the carboxylate functionality in the six-membered ring is an important factor, which determines the stability characteristics of the complexes[14]. The investigations of the metal complexes of the corresponding nitrobenzoic acids can be useful to gain an insight into the substituent effect[15]. The nitro substituted carboxylates are expected to behave differently in view of the differing electronic nature of the –NH$_2$ (electron donating) and –NO$_2$ (electron withdrawing) substituents as evidenced in

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[#] Dedicated to Prof. S.K. Paknikar

[Zn(H$_2$O)$_2$(4-nba)$_2$]

[Ag$_2$(NH$_3$)(4-nba)$_2$]

[Cd(H$_2$O)$_2$(4-nba)$_2$]

4-nbaH

[Ti(C$_5$H$_5$)$_2$(4-nba)$_2$]

[Cu$_2$(H$_2$O)$_2$(4-nba)$_4$]

[Co(H$_2$O)$_2$(C$_6$H$_6$N$_2$O)$_2$(4-nba)$_2$]

Scheme 1

the thermal behaviour of Mg(II) complexes of substituted nitrobenzoic acids[16]. The reported chemistry of *para*-nitrobenzoic acid (4-nbaH) clearly demonstrates the versatile bonding nature of this ligand[17-33] and that *para*-nitrobenzoate (4-nba) can support different coordination geometries. Scheme 1 depicts a few structural types of metal complexes of the 4-nba ligand[17–22]. The differing nature of the amino and nitro carboxylates can be discussed in terms of the structural features of the complexes. An important structural feature of the reported aminobenzoate complexes is the identification of an extended hydrogen bonded network system[10-12]. Short H-bonding contacts of the type (N-H...O) are observed between a H atom of the amino group (H-donor bond) and the O atom of a coordinated water. In contrast, the nitro group is expected to hydrogen bond through its O atom rather
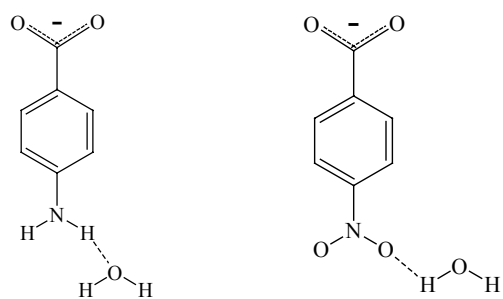
a) H –donor bonds between 4-aba and H$_2$O

b) H-acceptor bonds between 4-nba and H$_2$O

Scheme 2

than nitrogen. In this case, a H atom from a coordinated water can be hydrogen bond (H-acceptor bond) to the O atom of the nitro group to form hydrogen bonds of the type O...H-O. The present structural ex-

amination of the title complex nicely demonstrates this subtle difference in the H-bonding characteristics of the $-NO_2$ group as compared to the $-NH_2$ group (Scheme 2). A detailed investigation of the previously reported structure of the hydrated *para*-nitrobenzoate complex of Co(II)[23] indicates that the H-acceptor bonds between the O atom of the $-NO_2$ and the H atom of a coordinated water can give rise to an unprecedented hydrogen bonded supramolecular network. The synthesis, spectral, thermal and single crystal X-ray structural characterization of the hydrated cobalt *para*-nitrobenzoate complex are described in this paper.

Materials and Methods

Doubly distilled water was used as the solvent. All the chemicals used in this study were of reagent grade and used as received. The starting materials and reaction products are air stable and hence were routinely prepared under normal laboratory conditions. Infrared spectra were recorded on a Shimadzu (model 8101A) FTIR spectrometer in the range 4000-400 cm^{-1}. The samples for the infrared spectra were prepared as KBr diluted pellets in the solid state and the infrared signals referenced to polystyrene bands. Electronic spectra were recorded in DMSO using matched quartz cells on a Perkin-Elmer (Lambda 12) spectrophotometer. Single crystal X-ray diffraction study was performed at the National single crystal X-ray facility at IIT Kanpur. The insoluble *para*-nitrobenzoic acid obtained on acid treatment of the complexes was weighed and cobalt analysis was performed titrimetrically following a standard procedure[34]. Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller. TG-DSC analyses were performed in static air atmosphere in the temperature range 20°C to 800°C on a NETZSCH STA 409 PC/4/H (Luxx) instrument. A heating rate of 10°C/min was chosen for all the measurements.

Preparation of [Co(H₂O)₄(4-nba)₂].2H₂O 1
Method 1

A mixture of commercial cobaltous carbonate (1.20 g, ~10 mmol) and 4-nitrobenzoic acid (3.34 g, 20 mmol) was refluxed in 50 ml of water. Both the insoluble reactants slowly dissolved on heating the reaction mixture, with the evolution of carbon dioxide resulting in the formation of a coloured solution. After 4 h, the red coloured solution containing a small amount of insoluble material was filtered and the filtrate was left undisturbed for 3-4 days. The crystalline

blocks thus obtained were filtered, washed with cold water (5 ml), followed by ether and dried *in vacuo*. The crystals obtained in this method were suitable for X-ray studies. Yield (60%).

Anal. Found (Calcd.): Co 11.21 (11.80)%; 4-nbaH 65.21 (66.95)%; IR data: 3604, 3530, 3352, 3237, 1570, 1518, 1408, 1381, 1350, 1324, 1135, 1109, 1014, 952, 878, 821, 800, 726, 527 cm^{-1}.

Method 2

A solution of sodium bicarbonate (1.68 g, 20 mmol) in water (20 ml) was added into 4-nitrobenzoic acid (3.34 g, 20 mmol) to obtain the sodium salt of the carboxylic acid. $CoCl_2.6H_2O$ (2.37 g, 10 mmol) in water (10 ml) was slowly added into the carboxylate solution under stirring. This resulted in the instantaneous precipitation of copious amounts of the title complex. The fine pink coloured powder thus obtained was filtered off, washed thoroughly with cold water followed by ether and dried in vacuum. Yield (75%). The product analyzed satisfactorily. The product exhibited an identical IR spectrum to that of the product obtained from method 1.

Preparation of [Co(4-nba)₂] 2

The anhydrous blue complex **2** can be obtained in near quantitative yield by heating a powdered sample of **1** in an electric furnace for 30 min at 150°C. The complex thus obtained analyzed satisfactorily.

IR data: 1706, 1586, 1544, 1520, 1418, 1350, 1318, 1172, 1109, 1014, 878, 831, 799, 726, 548, 532 cm^{-1}.

**Reversible hydration of 1**

A powdered sample of **1** (500 mg) was taken in a silica crucible and heated in a furnace at 180°C for ~ 30 min. The crucible was cooled and the resultant anhydrous complex **2** was equilibrated over water in a dessicator for a day. This resulted in the isolation of the starting material **1** in quantitative yield. The infrared spectrum of the final product is identical to that of the starting material.

Results and Discussion

The reaction of $CoCO_3$ with 4-nitrobenzoic acid in a 1:2 mole ratio in water under reflux for 4 h results in the formation of the title complex **1** in good yields. Extended periods of refluxing does not increase the yield. However, the use of freshly prepared $CoCO_3$ reduces the reaction time as 4-nbaH can be solubilised in about 1 h. The insoluble reactants go into solution on refluxing in water and the product can be crystal-

lized from the nearly neutral reaction mixture. The complex formation can be represented as shown below in Eq. (1).

$$CoCO_3 + 2\ (4\text{-nbaH}) \xrightarrow[\text{H}_2\text{O}]{\text{Heat}} [Co(4\text{-nba})_2.\times H_2O]$$

… (1)
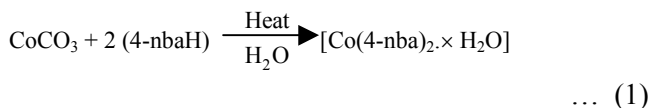
where 4-nbaH is *para*-nitrobenzoic acid.

Complex **1** can also be prepared as a fine powder by reacting aqueous cobaltous chloride with the sodium salt of the carboxylate in a 1:2 mole ratio. When the complexes **1** and **2** are acidified with HCl in slight excess, they react as shown in Eq. (2).

$$[Co(4\text{-nba})_2.\times H_2O] + H^+ \text{ (excess)} \rightarrow Co(II) + 2\ (4\text{-nbaH}) \downarrow$$

… (2)
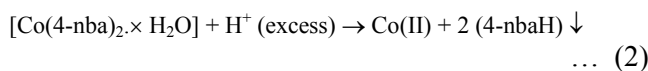
The Co(II) ions go into solution and the insoluble 4-nitrobenzoic acid is precipitated thus permitting the simultaneous analysis of both Co(II) content by EDTA titration as well as the organic acid gravimetrically. The complexes prepared in this work have been formulated based on metal analysis, and amount of 4-nbaH recovered on acidification. Further, heating the compounds to 800°C results in the formation of metal oxide. The formation of the oxide phase is evidenced by metal analysis of this product as well as featureless infrared spectra (*vide infra*).

The Co(II) complexes prepared in this work absorb strongly around 270 nm in the UV-region. The UV-absorption can be attributed to intramolecular charge transfer transition of the aromatic acid. In addition to this signal, **1** and **2** exhibit a very broad band around 567 nm. This weak signal can be attributed to a d-d transition. The ^{1}H NMR spectrum of **1** and **2** in DMSO-d_6 exhibit a single broad signal at δ 13.75 and 13.80 ppm respectively which can be assigned to the resonance of the aromatic protons. It may be noted that the diamagnetic complex [Mg(H$_2$O)$_6$](4-nba)$_2$.2H$_2$O exhibits a typical AB quartet for the two sets of aromatic protons in the 4-nitrobenzoate at δ 8.21 ppm and 8.10 ppm respectively[16]. Based on this, the down field shifting of the signal in **1** and **2** can be attributed to the paramagnetic nature of these complexes. The observed magnetic moments of **1** and **2** are 5.13 and 4.81 BM, respectively.

The Co(II) complexes prepared in this work, have been studied by infrared spectra. For the sake of comparison, the IR spectrum of the free 4-nitrobenzoic acid was also recorded[16]. Since IR has been used as a

fingerprint device to confirm the presence of water and the mode of binding of nitrobenzoate, the spectral assignments for only the water band, carboxylate group and the nitro group are discussed below. The IR spectra of the Co(II) complexes **1** and **2** exhibit several sharp bands in the mid infrared region, clearly indicating the presence of the organic moiety. The free acid does not exhibit any signals above 3100 cm^{-1} unlike the Co(II) complexes indicating that the –OH group of the caboxylic acid is strongly H-bonded to the nitro substituent in the solid state. The hydrated complex exhibits very strong and broad absorption bands in the region 3500-3000cm^{-1}. This band corresponds to the antisymmetric and symmetric stretching vibrations of water. In contrast, the anhydrous complex **2** does not show any signals in this region indicating the absence of water. The absorptions of the symmetric and antisymmetric vibrations of the nitro group in the aromatic ring are observed at around 1550-1500 cm^{-1} and 1360-1290 cm^{-1}, as expected[35]. The carbonyl absorption, which is observed at around 1700 cm^{-1} in the free acid, is shifted to lower energies in the Co(II) complexes and this is a typical feature observed in carboxylates[36]. Further, the difference between the symmetric and antisymmetric stretching vibrations of the carboxylate is of the order 200 cm^{-1} in **1** indicating that the carboxylate is monocoordinated. The IR spectrum of **1** heated at 150°C shows several IR bands while the broad signal due to water disappears. The absence of the broad –OH bands in the heat-treated sample can be attributed to the formation of the corresponding anhydrous complex. In addition, the IR vibrations of the carboxylate group are quite closer in the calcined complex and the bands are split indicating that the carboxylate is bidentate in this complex. The blue colour of the complex characteristic of tetrahedral Co(II) also supports this assignment. A similar behaviour has been reported[10] for the Co(II) complex [Co(BTEC)(H$_2$O)$_4$]$_n$. n(C$_4$H$_{12}$N$_2$). 4nH$_2$O (H$_4$BTEC is 1,2,4,5-benzenetetra-carboxylic acid). The IR spectra of the residues left after thermally decomposing the complexes **1** and **2** at 800°C are featureless and devoid of any absorption down to 600 cm^{-1} indicating oxide formation. The IR spectra of the residue formed in both the cases are identical indicating that the product formed is same.

The complexes prepared in this work have been investigated by isothermal weight loss studies and TG-DTA/DSC. The TG-DTA trace of complex **1** in flowing N$_2$ indicates that the complex is thermally

stable up to ~60°C, when its slow decomposition begins. The TG curve shows the first mass loss between 60 and 100°C, corresponding to the loss of five moles of water. In the DTA an endothermic event is observed for this process. The sixth water molecule is strongly bound and is lost around 150°C, resulting in the formation of the anhydrous complex. These assignments gain further credence, based on infrared spectral studies, isothermal weight loss and elemental analysis. When complex **1** is heated on a water bath the observed weight loss of 17.7% (expected loss is 18.04%) corresponds to the loss of five moles of H_2O. In contrast, the anhydrous complex **2** does not show any weight loss when heated on a water bath indicating its thermal stability compared to **1**. The IR spectrum of **1** heated on water bath shows a broad band at 3447 cm^{-1}. However, the IR spectrum of **1** recorded, after heating it to150°C is devoid of the broad water band. The observed mass loss of 20.83% can be attributed to the removal of six moles of H_2O. The IR spectrum of the calcined (at 150°C) sample after exposure to moisture is identical to that of the starting material. This feature indicates that the anhydrous complex **2** can be fully rehydrated. In other words, the original structure can be regenerated. This property is especially useful in the design of solid materials with selective inclusion behaviour[8]. We have observed a similar behaviour for the 4-nba complex of Mg(II)[16]. In addition, the IR spectrum of **1** recorded after heating it to 400°C is featureless, thus indicating the decomposition of the organic moiety. Heating the complexes **1** or **2** isothermally at 400°C results in the loss of the organic moiety and a voluminous product, which can be formulated as Co_2O_3 based on metal analysis. The DTA curve shows a strong exothermic signal at 385°C and a broad peak at 415°C. These signals can be attributed to the decomposition of carboxylate ligand. The TG residue (22%) corresponds to the formation of Co(II)-carbonate. Formation of metal-carbonates has been reported earlier for the thermal decomposition of alkali-earth metal aminobenzoates under inert atmosphere[12]. The TG-DSC data of complex **1** in static air can be similarly interpreted. The residue formed here corresponds to Co_2O_3 based on weight loss.

X-ray crystallographic study

A single crystal of **1** suitable for X-ray diffraction was mounted on an Enraf-Nonius CAD4 four-circle diffractometer for the cell determination and intensity data collection employing Mo-Kα radiation. The

measurements were performed at room temperature. Intensity data for the crystal were obtained with the use of a θ-2θ step scan technique. Lattice parameters were obtained by the least-squares analysis of 25 machine centered reflections. The intensities of three standard reflections were monitored periodically throughout the course of data collection and no significant decay was detected. The structure was solved (SHELXS-97)[37] and refined over F^2 by using the SHELXL-97[38] program. Anisotropic displacements were used for C, N, O and Co while the ring-H atoms were positioned in idealised geometry and refined using the riding model with fixed isotropic displacement parameters. The hydrogen atoms of cobalt-coordinated and crystal waters were located from difference Fourier maps, and their positions were refined isotropically. The technical details pertaining to data acquisition and some selected refinement results are summarised in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for **1** are tabulated in Table 2. Selected bond lengths and bond angles are collected in Table 3.

Table 1—Technical details of data collection and selected refinement results for [Co(H$_2$O)$_4$(4-nba)$_2$].2H$_2$O, **1**

Identification code	[Co-(4-nba)$_2$]
Empirical formula	C$_{14}$H$_{20}$CoN$_2$O$_{14}$
Formula weight	499.25
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	triclinic
space group	P$\bar{1}$
A	7.227 (5) Å
B	7.341 (5) Å
C	10.604 (5) Å
α	85.884 (5)°
β	87.938 (5)°
γ	60.178 (5)°
Volume	486.8 (5) Å^3
Z	1
Calculated density	1.703 mg/m^3
Absorption coefficient	0.961 mm^{-1}
F(000)	257
Crystal size	0.2 × 0.2 × 0.15 mm^3
Theta range for data collection	1.93 to 22.48 deg.
Limiting indices	0<=h<=7, -6<=k<=7, -11 <=l <=11
Reflections collected/unique	1391/1267 [R(int) = 0.0450]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1267 / 0 / 166
Goodness of fit on F^2	1.040
Final R indices [I>2σ (I)]	R1 = 0.0388, wR2 = 0.0993
R indices (all data)	R1 = 0.0515, wR2 = 0.1057
Largest diff. peak and hole	0.424 and – 0.437 e.Å^3

Table 2—Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters[a]   (Å^2 × 10^3)   for   [Co(H$_2$O)$_4$(4-nba)$_2$].2H$_2$O, **1**

Atom	X	Y	Z	U$_{eq}$
O (5)	2211 (6)	5661 (5)	-888(3)	55 (1)
Co (1)	5000	5000	0	36 (1)
O (4)	-1281 (5)	1866 (6)	6610 (3)	55 (1)
O (12)	968 (5)	1792 (7)	7880 (3)	76 (1)
N (8)	319 (6)	1937 (6)	6815 (3)	43 (1)
O (2)	4112 (4)	3670 (4)	1589 (2)	40 (1)
C (13)	1516 (6)	2238 (6)	5748 (4)	36 (1)
C (11)	3249 (6)	2430 (6)	5995 (4)	40 (1)
C (16)	799 (6)	2368 (6)	4544 (4)	38 (1)
C (14)	4910 (6)	3264 (6)	2697 (4)	37 (1)
C (15)	4337 (6)	2753 (6)	4996 (4)	38 (1)
C (9)	1909 (6)	2697 (6)	3551 (4)	38 (1)
C (10)	3675 (6)	2888 (6)	3755 (4)	35 (1)
O (6)	6610 (6)	3160 (6)	2960 (3)	60 (1)
O (3)	2214 (6)	1889 (6)	320 (4)	50 (1)
O (7)	6442 (7)	2222 (6)	-938 (4)	66 (1)

[a]The equivalent isotropic displacement parameter U$_{eq}$ is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

Crystal structure description of 1

The thermal ellipsoid plot of **1** showing the immediate coordination environment around the central metal is shown in Fig. 1. The compound crystallizes in the centrosymmetric triclinic space group P$\bar{1}$. The Co(II) ion is located on a centre of inversion and is hexacoordinated. The central metal is bound by four oxygen atoms of four water ligands, which lie on an approximate square plane and the monodentate nitrobenzoate ligands, which are *trans* to each other, complete the octahedral coordination. Such monodentate carboxylate coordination has been earlier reported for the Co(II) carboxylate complexes of acetic acid[39] and 1,2,4,5-benzenetetracarboxylic acid[10]. The observed cobalt-water (2.069 and 2.082 Å) and cobalt-oxygen (2.125 Å) distances of **1** are comparable with those of the Co-water (2.11 and 2.06 Å) and Co-oxygen (2.12 Å) reported for cobaltous acetate tetrahydrate. The lattice parameters and the geometric parameters of **1** are in very good agreement with the previously reported values[23]. In the earlier report, the H-bonding contacts, given below, were not described.

Table 3—Selected bond lengths [Å] and angles [^{0}] for [Co(H$_2$O)$_4$(4-nba)$_2$].2H$_2$O, **1**

Bond lengths

O(5)-Co(1)	2.069 (4)	O(2)-C(14)	1.279 (5)
Co(1)-O(5)#1	2.069 (4)	C(13)-C(11)	1.364 (6)
Co(1)-O(7)	2.082 (4)	C(13)-C(16)	1.375 (6)
Co(1)-O(7)#1	2.082 (4)	C(11)-C(15)	1.374 (6)
Co(1)-O(2)#1	2.125 (3)	C(16)-C(9)	1.380 (6)
Co(1)-O(2)	2.125 (3)	C(14)-O(6)	1.233 (5)
O(4)-N(8)	1.211 (5)	C(14)-C(10)	1.501 (6)
O(12)-N(8)	1.213 (5)	C(15)-C(10)	1.394 (6)
N(8)-C(13)	1.470 (5)	C(9)-C(10)	1.378 (6)

Bond angles

O(5)#1-Co(1)-O(5)	180.0	O(12)-N(8)-C(13)	119.4 (3)
O(5)#1-Co(1)-O(7)	86.27 (17)	O(4)-N(8)-C(13)	118.5 (4)
O(5)-Co(1)-O(7)	93.73 (17)	C(14)-O(2)-Co(1)	126.3 (3)
O(5)#1-Co(1)-O(7)#1	93.73 (17)	C(11)-C(13)-C(16)	123.0 (4)
O(5)-Co(1)-O(7)#1	86.27 (17)	C(11)-C(13)-N(8)	118.8 (4)
O(7)-Co(1)-O(7)#1	180.0	C(16)-C(13)-N(8)	118.2 (4)
O(5)#1-Co(1)-O(2)#1	91.11 (13)	C(15)-C(11)-C(13)	118.6 (4)
O(5)-Co(1)-O(2)#1	88.89 (13)	C(13)-C(16)-C(9)	117.6 (4)
O(7)-Co(1)-O(2)#1	86.11 (15)	O(6)-C(14)-O(2)	124.7 (4)
O(7)#1-Co(1)-O(2)#1	93.89 (15)	O(6)-C(14)-C(10)	118.1 (4)
O(5)#1-Co(1)-O(2)	88.89 (13)	O(2)-C(14)-C(10)	117.2 (3)
O(5)-Co(1)-O(2)	91.11 (13)	C(11)-C(15)-C(10)	120.6 (4)
O(7)-Co(1)-O(2)	93.89 (15)	C(16)-C(9)-C(10)	121.4 (4)
O(7)#1-Co(1)-O(2)	86.11 (15)	C(9)-C(10)-C(15)	118.8 (4)
O(2)#1-Co(1)-O(2)	180.0	C(9)-C(10)-C(14)	122.8 (4)
O(12)-N(8)-O(4)	122.1 (4)	C(15)-C(10)-C(14)	118.3 (4)

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

The complex $[Co(H_2O)_4(4\text{-}nba)_2].2H_2O$ is linked into a chain via O–H···O hydrogen bonds involving O7 water (coordinated water of Co) and O4 (of nitro) as shown in Fig. 2. It is to be noted that in the previously reported aminobenzoate complexes, the electron donating -NH₂ group forms H-donor bonds with the O atom of the coordinated water, whereas in **1** the electron withdrawing -NO₂ group makes H-acceptor bonds thus extending the network. These chains are then laterally linked through the crystal

This shows the linking region as O(7)–H(7B)···O(3)–H(3B)···O(2). This comprises two hydrogen bondings: O(7)–H(7B)···O(3) and O(3)–H(3B)···O(2). In the parallel chains, two complexes are linked laterally by two O(7)–H(7B)···O(3)–H(3B)···O(2) linkers in head to tail fashion. It is important to mention that, even though the coordination number of O(3) has been shown as 3 in Fig. 2, actually this is not the case (*vide infra*). The hydrogen bonding situation is much more complicated.

In the crystal structure, each cobalt complex is hydrogen bonded to its surrounding through all possible sites. Figure 3 outlines the hydrogen bonding situation around a complex, which also includes the intramolecular hydrogen bonding (between carboxylate oxygen O(6) and cobalt-coordinated water O(5)). The oxygen atoms, O(4) and O(12) of the nitro end of the complex are hydrogen bonded to cobalt-coordinated water (O(7)) of another complex unit and crystal water (O(3)) respectively. The coordinated water O(5), besides its intramolecular hydrogen bonding, is linked to a crystal water O(3). The water O(7), covalently linked to Co(II), is hydrogen bonded to oxygen (O(4)) of nitro group of a surrounding complex unit and a lattice water O(3) through its hydrogens H(7A) and H(7B) respectively.
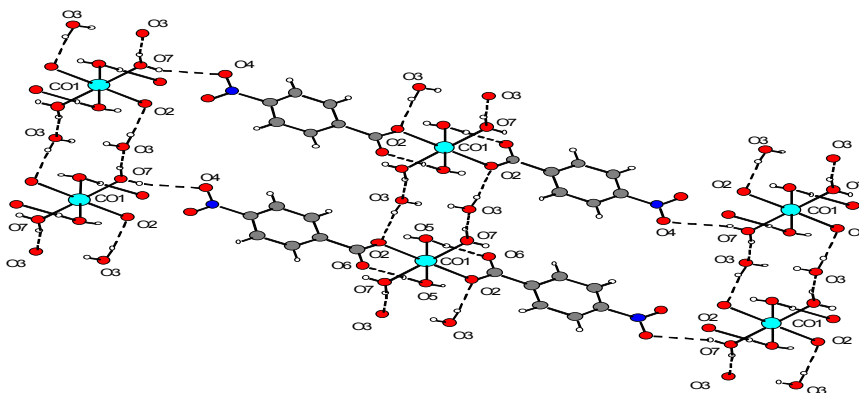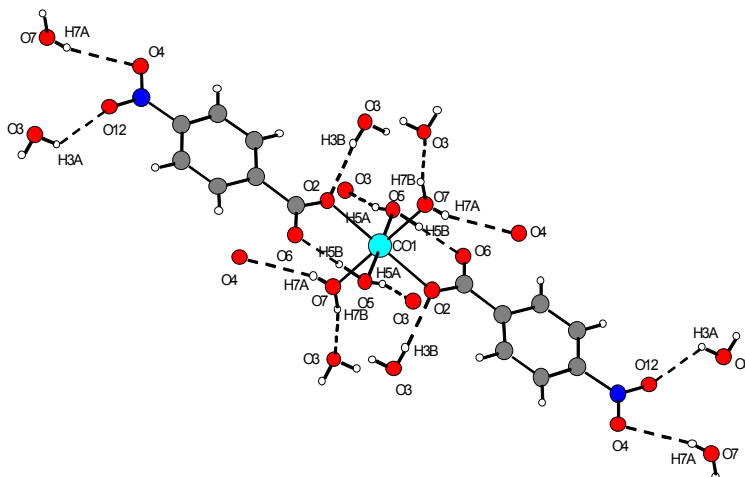

Fig 1—Crystal structure of **1** showing the atom–labelling scheme and displacement ellipsoids drawn at 50% probability level.

Fig. 2—The linking of the complex [Co(H₂O)₄(4-nba)₂].2H₂O **1** into a chain via intermolecular O–H···O hydrogen bonds (O(7)···O(4)) and water O(3) (Fig. 2).

Fig. 3—Hydrogen bonding situation around the complex **1** (for details, see text).

Table 4—Hydrogen-bonding geometry ($Å^0$) for [Co(H₂O)₂(4-nba)₂].2H₂O, **1**

D-H…A	d(D…H)	D(H…A)	d(D…A)	<DHA	Symmetry code
O(5)-H(5B)…O(6)	0.90 (6)	1.69 (6)	2.576 (5)	169 (5)	1-x, 1-y, -z
O(5)-H(5A)…O(3)	0.78 (5)	2.09 (5)	2.849 (5)	165 (5)	-x, 1-y, -z
O(7)-H(7A)…O(4)	0.68 (7)	2.36 (7)	2.983 (5)	153 (5)	1+ x, y, -1 + z
O(7)-H(7B)…O(3)	0.88 (9)	1.83 (9)	2.707 (6)	176 (7)	1-x, -y, -z
O(3)-H(3A)…O(12)	0.77 (5)	2.26 (5)	2.789 (5)	127 (4)	x, y, -1 + z
O(3)-H(3B)…O(2)	0.82 (6)	1.94 (6)	2.752 (5)	170 (5)	

D=Donor; A=Acceptor

The crystal water O(3) is additionally hydrogen bonded to carboxylate oxygen O(2). There are in all six types of O–H⋯O hydrogen bonds involving nitro groups, carboxylates, coordinated and crystal waters. The geometrical parameters of these six hydrogen bonds are presented in Table 4.

Interestingly, the crystal water O(3) is hydrogen bonded to four different complexes involving cobalt-coordinated waters (O(7) and O(5)), carboxylate group (O(2)) and nitro group (O(12)). The relevant hydrogen bonding interactions are shown in Fig. 4. The approximate geometry around O(3) is tetrahedral. It donates two protons to O(2) (carboxylate) and O(12) (nitro) respectively and accepts two protons from coordinated waters, O(5) and O(7) from two different complexes (Fig. 4). This tetrahedral arrangement of O(3) water is fundamentally important in the sense that, the crystal structures of most ice modifications consist of three-dimensional hydrogen
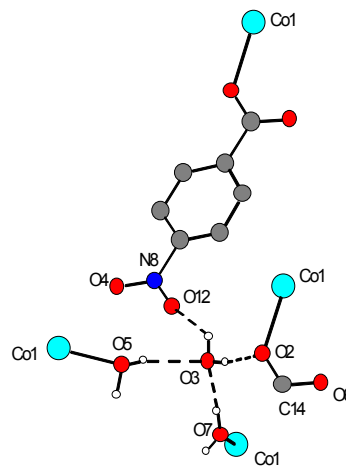

Fig 4—Hydrogen bonding environment around the solvent water O(3), which donates two protons as well as accepts two protons furnishing an approximate tetrahedral geometry around it.
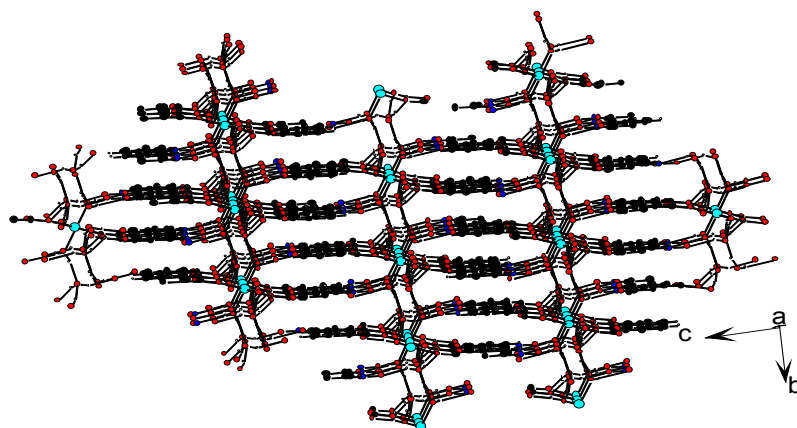
Fig. 5—The supramolecular hydrogen bonding network in **1**, when viewed down crystallographic *a* axis.

bonded networks of waters where each of oxygen atoms is tetrahedral (double donors and double acceptors)[40] — a similar situation, as observed around O(3) water in the present work. The resulting hydrogen bonding interactions from six types of O–H···O hydrogen bonds give rise to an unprecedented three dimensional supramolecular network as shown in Fig. 5. Well-defined channels are observed, when viewed along crystallographic *a* axis.

Conclusions

The reaction of 4-nbaH with $CoCO_3$ or with $CoCl_2.6H_2O$ in the presence of a weak base like bicarbonate leads to the formation of the hydrated para-nitrobenzoate complex **1** in good yields. Complex **1** can be fully dehydrated to get the anhydrous tetrahedral complex **2**, which in turn can be rehydrated. The hydrated Co(II) complex can be decomposed in air at $400^{o}C$ to yield oxide material. The formation of oxide at low temperatures promises scope for further investigations in this area to prepare newer materials.

The crystal structure of **1** is indeed interesting in terms of supramolecular hydrogen bonding interactions. Both functional groups of 4-nba ligand, the co-ordinated and crystal waters are exclusively involved in the formation of 3D-supramolecular network in the crystal structure of **1**. The tetrahedral arrangement of the crystal water O(3) mimics the basic unit of many ice modifications. The structural investigations of the title complex **1** also demonstrates the subtle difference in the hydrogen bonding characteristics of the nitro functionality as compared to that of the amino group.

Supporting information available

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 215133 for **1**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (Fax: +44-(0)1223-336033 or Email: deposit@ccdc.cam.ac.uk).

References

1   Wieghardt K, *Angew Chem Int Ed (Engl),* 28 (1989) 1153.
2   Pecoraro V L, Baldwin M J & Gelasco A, *Chem Rev,* 94 (1994) 807.
3   Rane K S & Verenkar V M S, *Bull Mater Sci,* 24 (2001) 39.

4   Mehrotra R C & Bohra R, *Metal carboxylates* (Academic Press, London) 1983.

5   Mehrotra R C & Singh A, *Prog Inorg Chem,* 46 (1997) 239.

6   Yaghi O M, Li H, Davis C, Richardson D & Groy T L, *Acc Chem Res,* 31 (1998) 474.

7   Yaghi O M, Li G & Li H, *Nature* 378 (1995) 703.

8   Yaghi O M, Davis C E, Li G & Li H, *J Am Chem Soc,* 119 (1997) 2861.

9   Yaghi O M, Li H & Groy T L, *J Am Chem Soc,* 118 (1996) 9096.

10   Murugavel R, Anantharaman G, Krishnamurthy D, Sathiyendiran M & Walawalkar M G, *Proc Indian Acad Sci (Chem Sci.),* 112 (2000) 273.

11   Wang R, Hong M, Luo J, Jiang F, Han L, Lin Z & Cao R, *Inorg Chim Acta* 357 (2004) 103.

12   Murugavel R, Karambelkar V V, Anantharaman G & Walawalkar M G, *Inorg Chem*, 39 (2000) 1381; Murugavel R, Karambelkar V V & Anantharaman G, *Indian J Chem*, 39A (2000) 843.

13   Murugavel R, Baheti K & Anantharaman G, *Inorg Chem,* 40 (2001) 6870.

14   Srinivasan B R, Sawant S C & Dhuri S N, *Indian J Chem*, 41A (2002) 290.

15   Srinivasan B R & Sawant S C, *Fourth National Symposium in Chemistry*, NCL Pune (2002) p.163.

16   Srinivasan B R & Sawant S C, *Thermochim Acta,* 402 (2003) 45.

17   Nacefoglu H, Clegg W & Scott A J, *Acta Cryst*, 57E (2001) m-472.

18   Jaber F, Charbonnier F & Faure R, *Eur J Solid State Inorg Chem,* 32 (1995) 25.

19   Rodesiler P F, Griffith E A H, Charles N G & Amma E L, *Acta Cryst,* 41C (1985) 673.

20   Kuntsevich T S, Gladkikh E A, Lebedev V A, Lineva A N & Belov N V, *Kristallografiya,* 21 (1976) 80.

21   Usubaliev B T, Movsumov E M, Amiraslanov I R & Mamedov Kh S, *Dokl Akad Nauk Az SSR,* 36 (1980) 40.

22   Hokelek T & Necefoglu H, *Acta Cryst,* 54C (1998) 1242.

23   Nadzhafov G N, Shnulin A N & Mamedov Kh S, *Zh Strukt Khim,* 22 (1981) 124.

24   Das B K & Chakravarty A R, *Inorg Chem,* 30 (1991) 4978.

25   Mandal S K & Chakravarty A R, *Indian J Chem,* 29A (1990) 1169.

26   Tahir M N, Ulku D, Movsumov E M & Hokelek T, *Acta Cryst,* 53C (1997) 176.

27   Jian-Fang M, Zhong-Sheng J & Jia-Zuan N, *Chinese J Struct Chem,* 15 (1996) 85.

28   Klinga M, *Cryst Struct Commun,* 10 (1981) 521.

29   Usubaliev B T, Amiraslanov I R, Nadzhafov G N, Movsumov E M, Musaev O N & Mamedov Kh S, *Koord Khim,* 7 (1981) 440.

30   Klinga M, *Finn Chem Lett,* (1976) 179.

31   Hokelek T, Budak K & Necefoglu H, *Acta Cryst,* 53C (1997) 1049.

32   Usubaliev B T, Shnulin A N, Musaev F N & Mamedov Kh S, *Zh Strukt Khim,* 23 (1982) 124.

33   Tahir M N, Ulku D & Muvsumov E M, *Acta Cryst,* 52C (1996) 593.

34   Bassett J, Denney R C, Jeffery G H & Mendham J, *Vogel's textbook of quantitative inorganic analysis*, 4th Edn (ELBS, London) 1978.

35   Silverstein R M, Bassler G C & Morril T C, *Spectrometric Identification of Organic Compounds,* Fifth Edn, (Wiley, New York), 1991, Chapt. 3.

36   Nakamoto K, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* Fourth Edn, (Wiley, New York), 1986.

37   Sheldrick G M, SHELXS-97: *Program for Crystal Structure Determination* (University of Göttingen, Germany) 1997.

38   Sheldrick G M, SHELXL-97 : *Program for the Refinement of Crystal Structures* (University of Göttingen, Germany) 1997.

39   Van Niekerk J N & Schoening F R L, *Acta Cryst*, 6 (1953) 609.

40   Ludwig R, *Angew Chem Int Ed Engl*, 40 (2001) 1808.