## Notes

# Reversible hydration of tetraaquabis(4-aminobenzoato)cobalt(II)

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The octahedral red complex tetraaquabis(4-amino-benzoato)cobalt(II) (**1**) exhibits a water induced crystalline-amorphous-crystalline transformation accompanied by chromotropism. The loss of coordinated water from $[Co(4\text{-}aba)_2(H_2O)_4]$ (**1**) (4-aba=4-aminobenzoate) on heating, leads to the formation of tetrahedral anhydrous $[Co(4\text{-}aba)_2]$ (**2**). The amorphous blue compound (**2**) can be rehydrated to original composition by equilibrating (**2**) over water vapour. The rehydrated crystalline compound exhibits properties identical with (**1**). The variation in the structure and properties of (**1**) due to the coordination and decoordination of water are studied by spectral, thermal, magnetic and conductivity measurements.

Progress and development of science and technology relies mostly on the possibility of obtaining various materials with properties designed to meet practical purposes. This possibility is mainly based on the correlation between structure and properties of materials. Thus careful studies of material properties and correlating the corresponding structural changes can serve as a lead in exploring and devising synthetic methodologies that can help to design materials of potential applications. Several publications have appeared in recent literature, showing the growing research interest in metal-organic materials with flexible and dynamic frameworks especially in those that reversibly change their structures and properties in response to external stimuli as they have many applications[1-5]. These types of changes especially the ones accompanied by loss of coordinated or lattice water have also been reported for zero-dimensional systems for example hydrated organic ammonium salts[6,7] or tetra(aqua)Co(II) complexes[8]. Cobalt is a typical metal ion that shows chromism upon ligand exchange in the solid state. In an earlier work we have shown that tetraaquabis(paranitrobenzoato)cobalt(II) dihydrate can be reversibly hydrated[8]. In this work we have chosen the known zero dimensional cobalt complex, namely tetraaquabis(4-aminobenzoato)cobalt(II) (**1**), which contains only coordinated but no lattice water molecules[9] for investigating changes in the property on the dehydration and rehydration. The results are described herein.
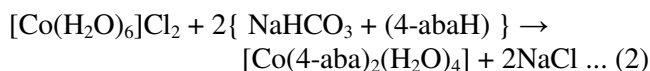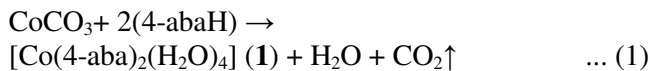
## Experimental

All the chemicals used in this study were of reagent grade and all the syntheses were carried out using doubly distilled water. Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000–400 cm$^{-1}$. UV-vis diffuse-reflectance spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer. BaSO$_4$ powder was used as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka-Munk function ($a/S=(1\text{-}R^2/2R$ where $a$ is the absorption coefficient, $R$ the reflectance and $S$ the scattering coefficient). TG-DTA studies were carried out on Netzsch, STA 409 PC (Luxx) analyzer, from RT to 1000 °C in dry air, with a heating rate of 10 K min$^{-1}$. Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller and on a steam bath. The X-ray powder pattern were recorded using Cu-Kα radiations of λ= 1.5418 Å (filtered through Ni) in steps of 0.02 degrees on a RIGAKU Ultima IV diffractometer. The variation of electrical resistivity, as a function of temperature was measured using two probe electrical conductivity setup. The temperature variation of resistance was measured from room temperature to 350 °C using a Keithley electrometer. The magnetic susceptibility in air was determined by Guoy method at room temperature in a field of 9600 gauss using sensitive analytical balance. A Quantum Design PPMS-VSM magnetometer was used for magnetic characterization of the pelletized compounds. The variation of the dc-susceptibility of each sample with temperature was measured from 2 K to 300 K in the ZFC (zero field cooling) and FC (field cooling) modes using a magnetic field of 500 Oe. The magnetization with varying magnetic field of up to 140 kOe was also measured at 2 K and 100 K.

For the synthesis of tetraaquabis(4-aminobenzoato) cobalt (II) (**1**), cobaltous carbonate was freshly prepared by mixing a solution of $Na_2CO_3$ (1.06 g, 10 mmol) in water (10 mL) with $[Co(H_2O)_6]Cl_2$ (2.37 g, 10 mmol) in water (10 mL). To this, 4-aminobenzoic acid (2.74 g, 20 mmol) in water (50 mL) was added and the reaction mixture was heated on a water bath.. The reaction was complete within 30 min as compared to commercial $CoCO_3$, which requires a prolonged reaction time. The reaction mixture containing a very small amount of insoluble material was filtered and the filtrate was left undisturbed for crystallization. After 4-5 days, red coloured crystals (**1**) were obtained (yield: 78%). Alternatively, these crystals can also be isolated in 85% yield from a solution containing the sodium salt of 4-aminobenzoic acid and cobalt chloride in 1:2 mole ratio.

To study the formation and rehydration of $[Co(4-aba)_2]$ (**2**), a powdered sample of (**1**) (500 mg) was taken in a silica crucible and heated in an oven for ~ 15 min at 140 °C. This resulted in the formation of dark blue coloured complex (**2**) (408 mg). The crucible with complex (**2**) was equilibrated over water in a dessicator. After a day, the colour of the complex changed from dark blue to the original red, resulting in isolation of the rehydrated compound.

## Results and discussion

Aqueous reaction of $CoCO_3$ (Eq. 1) with 4-aminobenzoic acid (4-abaH) in a 1:2 mole ratio results in the formation of a hexacoordinate red compound $[Co(4-aba)_2(H_2O)_4]$ (**1**). Freshly precipitated $CoCO_3$ is solubilised by hot aqueous 4-abaH in ~30 min while commercial $CoCO_3$ requires a longer reaction time. The reaction of $[Co(H_2O)_6]Cl_2$ with *in situ* generated sodium salt of 4-aminobenzoic acid can also be used as an alternate method (Eq. 2) for compound synthesis.

$CoCO_3 + 2(4\text{-abaH}) \rightarrow$
$[Co(4-aba)_2(H_2O)_4]$ (**1**) $+ H_2O + CO_2\uparrow$          ... (1)

$[Co(H_2O)_6]Cl_2 + 2\{ NaHCO_3 + (4\text{-abaH}) \} \rightarrow$
$[Co(4-aba)_2(H_2O)_4] + 2NaCl$ ... (2)

The product was unambiguously characterized with the aid of single crystal X-ray crystallography and confirmed to be the known tetraaquabis (4-aminobenzoato)cobalt(II); the compound was formulated as $[Co(4-aba)_2(H_2O)_4]$ (**1**) based on the unit cell data (Supplementary data, Tables S1-S3),

which is in agreement with literature[9]. The single crystal work reveals that in (**1**), the central metal is six coordinated and 4-aba anion functions as a monodentate carboxylate ligand. The central metal ion, i. e., Co(II) is surrounded by six oxygen atoms, four of which are from aqua ligands forming a square plane and the two monodentate carboxylate ligands disposed *trans* to each other complete the octahedral coordination around cobalt (Supplementary data, Fig. S1).

During the dehydration and rehydration studies, on heating at 140 °C the red coloured (**1**) changes to the anhydrous blue compound (**2**), which regains its original colour on equilibrating over water. The colour changes can be explained as dehydration of (**1**) resulting in the formation of blue anhydrous compound (**2**) as evidenced by the loss in mass accompanied by a characteristic IR spectrum. It is interesting to note that dehydration results in loss of crystallinity of (**1**) as evidenced by the X-ray powder pattern (Fig. 1). Although the anhydrous compound (**2**) is amorphous, both (**1**) and the rehydrated compound (**3**) are crystalline, showing that rehydration results in the transformation of the amorphous material to a crystalline solid. In the rehydration process, on exposure to moisture the dehydrated form of (**1**) attains its original colour. The rehydrated compound labeled as (**3**) is actually compound (**1**) which can be inferred by comparison of its spectral, thermal and conductivity characteristics with that of (**1**). In view of the quantitative formation of the rehydrated compound, the entire process of dehydration and rehydration can be schematized as shown below.
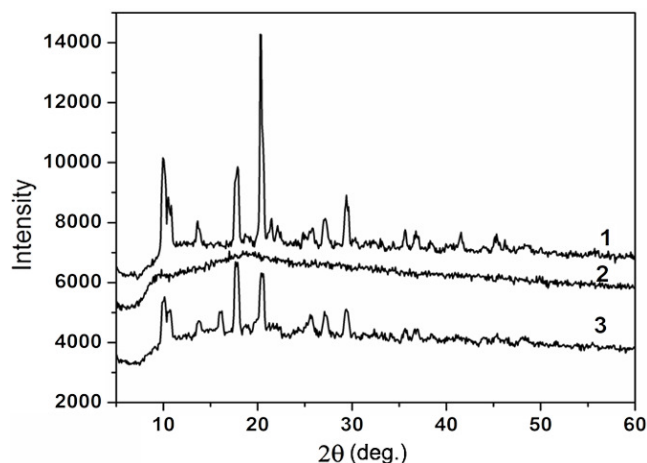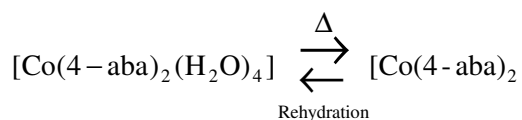


Fig. 1 – X-ray powder patterns of the red $[Co(H_2O)_4(4-aba)_2]$ (**1**), anhydrous blue $[Co(4-aba)_2]$ (**2**) and the rehydrated compound (**3**).

$$[Co(4-aba)_2(H_2O)_4] \underset{Rehydration}{\overset{\Delta}{\rightleftarrows}} [Co(4-aba)_2]$$

The coinciding of the IR spectra of (**1**) and the rehydrated compound (**3**) serve to demonstrate that they are one and the same (Fig. 2). The free acid 4-abaH does not show broad band above 3100 cm$^{-1}$ unlike the hydrated compound $[Co(4-aba)_2(H_2O)_4]$, indicating the presence of water in (**1**). The hydrated and rehydrated complexes exhibit very strong and broad absorption bands in the region 3500–3000 cm$^{-1}$, corresponding to the asymmetric and symmetric stretching vibrations of coordinated water which appears broad due to extensive intermolecular hydrogen bonding[10,11]. Further the $\nu(M-O)$ at 472 cm$^{-1}$ and 555 cm$^{-1}$ are indicative of coordinated aqua complex and the band at 640 cm$^{-1}$ may be due to wagging mode of coordinated water[11]. The IR spectrum of (**1**) heated at 140 °C shows several IR bands while the broad signal due to water disappears. The absence of the broad O-H band in the heat-treated sample can be attributed to the formation of the corresponding anhydrous complex. The two signals at 3354 and 3221 cm$^{-1}$ of medium intensity (Supplementary data, Fig. S2) clearly visible in anhydrous complex (**2**) and are masked by the broad O-H absorption signal in (**1**) and rehydrated complex can be assigned to the N-H asymmetric and symmetric stretching vibrations as seen for a primary amine[10]. The absence of bands $\nu(M-O)$ at 472 cm$^{-1}$, 555 cm$^{-1}$ and $\rho_w(H_2O)$ at 640 cm$^{-1}$ bands (Supplementary data, Fig. S3) further supports the anhydrous nature. In view of this, the band at 502 cm$^{-1}$ can be assigned to $\nu(Co-O)$ where oxygen is from
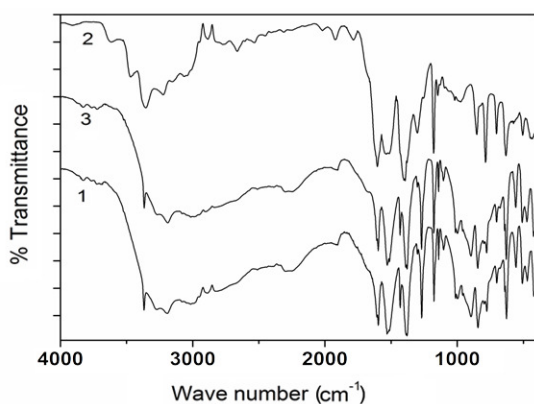


Fig. 2 – Infrared spectra of the red $[Co(H_2O)_4(4-aba)_2]$ (**1**), anhydrous blue $[Co(4-aba)_2]$ (**2**) and the rehydrated compound (**3**).

carboxylate. The bands (Supplementary data, Fig. S4) at 1528 cm$^{-1}$ and 1379 cm$^{-1}$ are assigned as asymmetric and symmetric stretch of carboxylate in (**1**) and rehydrated compound. The binding modes of metal ions to the carboxylate ligands has been a subject of interest and structural diagnosis using carboxylate stretching frequencies have been investigated in several studies[12-17]. In this study we report the vibrational spectra and correlate the binding modes of carboxylate ligand for both the crystalline (**1**) and the amorphous (**2**). The vibrations of the carboxylate group are closer in (**2**) (1539 cm$^{-1}$ and 1393 cm$^{-1}$) with a slightly smaller difference in asymmetric and symmetric stretch than in (**1**). The bands are split indicating that the carboxylate is bidentate in the dehydrated compound[11-17]. The blue colour of (**2**) which is characteristic of the tetrahedral Co (II) also supports this assignment. It is observed that the intensity of the asymmetric stretch of carboxylate is slightly less than that of the symmetric stretch in (**1**) and this intensity difference increases in (**2**) (Fig. S4). Bidentate chelation makes both C-O bonds symmetrical and hence the C-O stretch initially seen in hydrated complex and free acid disappears in the dehydrated complex and the spectrum exhibits symmetric and asymmetric vibrations of carboxylate shifted to higher frequency region. The band at 1177 cm$^{-1}$ can be assigned to C-N stretch. The rehydration of (**2**) resulted in the isolation of the rehydrated compound (**3**).

Removal of coordinated water from Co(II) leads to energy changes of the *d* orbitals of the central metal, as evidenced by the characteristic blue colour of tetrahedral Co(II).The forbidden *d-d* transitions in octahedral complexes with a center of symmetry are observed as weak bands due to vibrational motions which break this symmetry. In tetrahedral complexes with no center of symmetry the transitions are relatively intense (Fig. 3). The data show very weak *d-d* transition for (**1**) and (**3**) as expected (Supplementary data, Fig. S5). Secondly since $\Delta_t$ is much lower than $\Delta_o$ complexes of the same ion with ligands occupying nearby positions in spectrochemical series have their absorption maxima for *d-d* spectra at longer wavelengths for tetrahedral complexes. UV-DRS data show the absorption maxima for complex (**1**) and (**3**) at 479 nm, 502 nm and for complex (**2**) at 577 nm. Charge transfer bands are seen for both complexes (**1**) and (**2**).

The isothermal mass loss studies reveal a mass loss of 12.35% on heating the tetraaqua compound (**1**) at 100 $^o$C, which corresponds to a loss of three moles of water. This value is in agreement with the theoretical mass loss of 13.39%. A second mass loss (5.04%) occurs between 110–150 °C, corresponding to the loss of one water molecule. The total mass loss (17.39%) at this temperature is in very good agreement with the calculated mass loss of 17.85%, which corresponds to the total loss of 4 moles of water resulting in the formation of blue colored complex. The DTA curve of (**1**) exhibits an endothermic peak at 118 $^o$C which can be assigned for the loss of coordinated water from the central metal. The endothermic peak at 330 $^o$C and corresponding weight loss of 21.83% indicates the loss of two moles of $CO_2$. The decaboxylation of
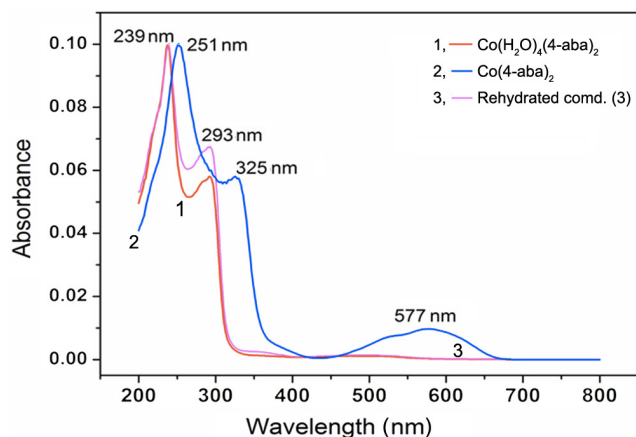


Fig. 3 – UV-vis spectra of (**1**), (**2**) and rehydrated compound (**3**).

organic ligand is followed by an exothermic event at 421 °C which can be attributed to the decomposition of the remaining organic moiety. The assignment of the first thermal event for the dehydration process can be confirmed by the absence of this signal in (**2**), and the absence of the O-H vibration in the IR spectrum of (**2**). No mass loss is observed for (**2**) in this temperature range while the rehydrated complex exhibits an identical weight loss profile as that of (**1**). The identical nature of (**1**) and (**3**) can also be evidenced from the TG-DTA graphs (Fig. 4a). It is interesting to note that the thermal profiles of (**1**) and (**2**) are identical after the first event clearly indicating that the first step in the decomposition of (**1**) is removal of coordinated water.

The different nature of (**1**) and (**2**) can be further evidenced by a sudden decrease in DC resistivity of the hydrated and rehydrated compounds (Fig. 5), however no such change is observed for the anhydrous blue compound which exhibits a straight line parallel to the X-axis. This change is observed between 110–130 $^o$C for complex (**1**) and (**3**). This is the same temperature range when the loss of last coordinated water molecule causes change in the coordination sphere of cobalt and hence resulting in the structural rearrangement from octahedral to tetrahedral with loss of crystalline nature.

A magnetic moment of 5.11 µB consistent with an octahedral arrangement of the metal centre indicates a high spin cobalt complex[18], was measured for (**1**). The magnetic moment of the anhydrous compound (**2**) decreased to 4.01 µB. The M-T plots (Fig. 6 &
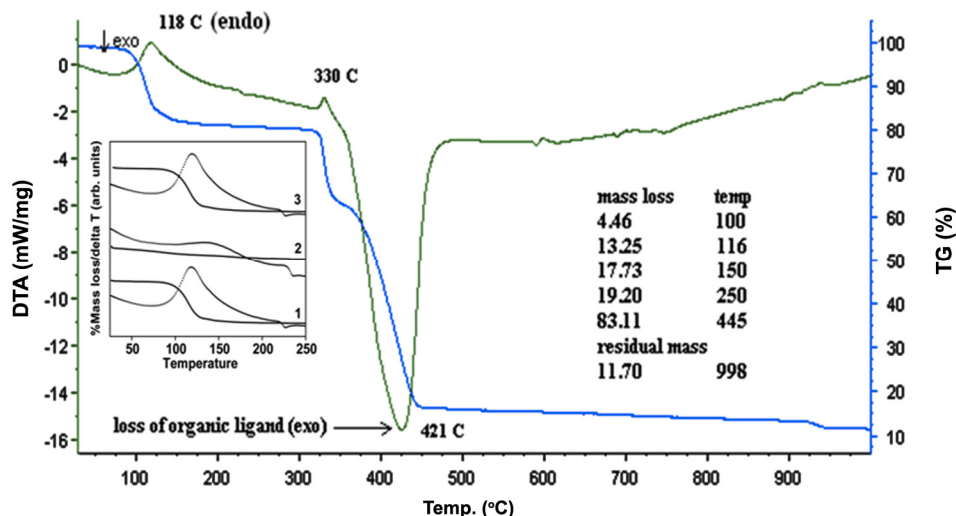


Fig. 4 – TG-DTA curves of tetraaquabis(4-aminobenzoato)cobalt(II). [Inset: TG-DTA profiles of $[Co(H_2O)_4(4\text{-aba})_2]$ (**1**) $[Co(4\text{-aba})_2]$ (**2**) and the rehydrated compound (**3**)].
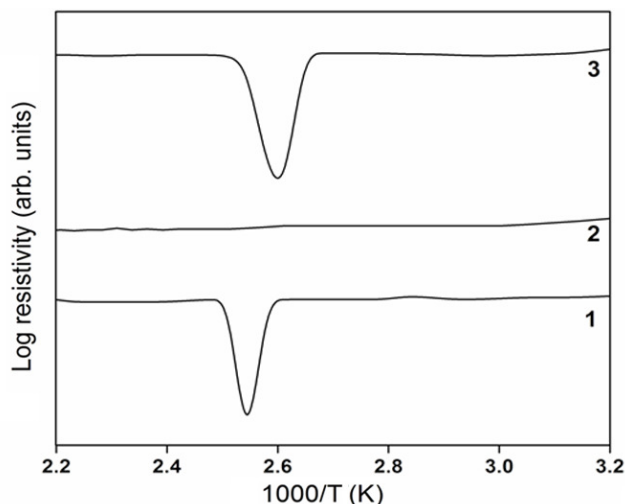
Fig. 5 – DC resistivity plot of [Co(H$_2$O)$_4$(4-aba)$_2$] (**1**), [Co(4-aba)$_2$] (**2**) and the rehydrated compound (**3**).
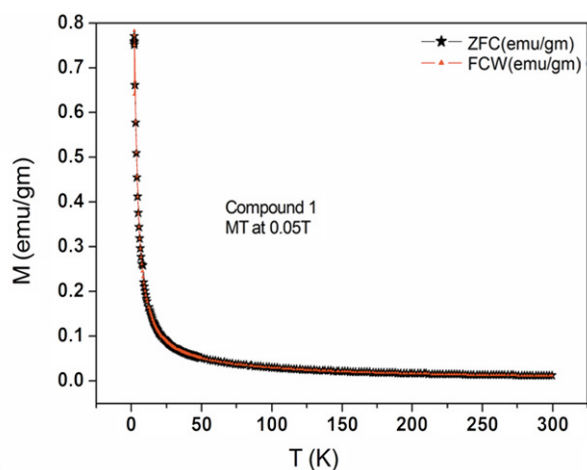


Fig. 6 – *M* versus *T* plot of [Co(H$_2$O)$_4$(4-aba)$_2$] (**1**). [For the *M* versus *T* plot of [Co(4-aba)$_2$] (**2**) see Supplementary data, Fig. S6].

Supplementary data, Fig. S6) shows the same trend in magnetization behavior for both the samples with variation in temperature and not much difference is seen in their magnetization values. The M-H plot (Supplementary data, Figs S7 & S8) shows that both compounds are paramagnetic even below 100 K. However below 8 K some changes are shown in the M-T plots leading to increase in the magnetization values. The magnetism of the material is entirely due to the high spin cobalt (II) ions which are far apart to interact with one another and hence even at temperature as low as 50 K, there is no effective magnetization observed for complex. Both complexes are paramagnetic at room temperature. The magnetic moments start aligning themselves with the applied magnetic field at very low temperature and the magnetization increases with increase in field. However both the complexes produce

hysteresis curves with zero remanance and coercivity at 2 K which is typical of a superparamagnetic material.

In this work it is shown that compound (**1**) undergoes crystalline–amorphous-crystalline transformation. The six cordinated octahedral tetraaquabis(4-amino-benzoato)cobalt(II) (**1**) can be fully dehydrated to four coordinated tetrahedral amorphous bis(4-amino-benzoato)cobalt(II) (**2**). Compound (**2**) can be rehydrated to the starting material thereby regaining its original properties.

## Supplementary data

Supplementary data associated with this article, i.e., Figs S1-S8, and, Tables S1–S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(07)867-871_SupplData.pdf.

## Acknowledgement

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