Synthesis, structure and characterization of tetraaquabis(4-nitrobenzoato)cobalt(II) dihydrate with O-donor Ligands

DISSERTATION

Submitted in partial fulfillment of

The Degree of M.Sc. (Inorganic chemistry)

By

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To

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April 2020

STATEMENT

I hereby declare that the matter presented in this dissertation entitled, '*Synthesis, structure and characterization of tetraaquabis(4-nitrobenzoato)cobalt(II) dihydrate with O-donor*' *Ligands* is based on the result of investigations carried out by me in the School of Chemical Sciences, Goa University under the supervision of Prof. B. R. Srinivasan and the same has not been submitted elsewhere for the award of a degree or diploma.

Ms. Froila Joyda Barbosa
CH-18-005

CERTIFICATE

This is to certify that the dissertation entitled, ‘*Synthesis, structure and characterization of tetraaquabis(4-nitrobenzoato)cobalt(II) dihydrate with O-donor*’ is a bonafide work carried out by Ms. Froila Joyda Barbosa under my supervision in partial fulfillment of the requirements for the award of the degree of Master in Science in Inorganic Chemistry at the School of Chemical Sciences, Goa University.

Prof. B. R. Srinivasan
Guiding Teacher

CERTIFICATE

This is to certify that the dissertation entitled, ‘*Synthesis, structure and characterization of tetraaquabis(4-nitrobenzoato)cobalt(II) dihydrate with O-donor*’ is a bonafide work carried out by Ms Froila Joyda Barbosa under the supervision of Prof. B.R. Srinivasan in partial fulfillment of the requirements for the award of the degree of Master in Science in Inorganic Chemistry at the School of Chemical Sciences, Goa University.

Prof. V. S. Nadkarni
Dean, School of Chemical Sciences

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INTRODUCTION

In recent years, coordination polymers or metal-organic framework(MOFs) have attracted much attention because of their topology and potential applications in catalysis, adsorption(gas storage), separation, luminescence, etc. Depending on the electronic and steric requirements of the central metal, the flexibility, binding modes and hydrogen bonding characteristics of the organic linker (ligand), coordination polymers of differing dimensionalities can be constructed [1]. The chemistry of metal-carboxylates continues to be 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, to their usefulness as novel materials in material science. An emerging area of interest is the construction of metal-carboxylate based supramolecular assemblies [2].

Transition metals have partially filled d-orbital, either in the atom or in the ion and can therefore hybridize differently depending on environment. The metals exhibit different oxidation states and can interact with a number of molecules called ligands which can be neutral or anionic [3]. The structural diversity encountered in metal-carboxylate complexes can be attributed to the versatile ligational behavior 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]. Benzene substituted carboxylate ligands are suitable reagents for the construction of metal-carboxylate supramolecular assemblies due to their ready availability in pure form. The advantage of using benzene based systems is that donor groups like –COOH, $-NH_2$, -OH, -SH, etc. can be anchored onto a rigid six-membered benzene ring and the resulting supramolecular structures will depend on the positioning of the donor groups on the ring [5]. This property, combined with the fact that many metal-carboxylates are hydrated and contain both coordinated as well as crystal water molecules that can participate in H-bonding interactions, are useful component for development of supramolecular assemblies based on carboxylate ligands.

Growing crystal is an important area of study in material science. A crystal is a solid material which can be regarded as constructed from regularly repeating structural elements, which may be atoms, molecules or ions extending in three dimensions. The pattern developed by the lattice points which is used to represent the position of repeating atoms, molecules or ions is called as "crystal lattice". There are seven different crystal systems. In three dimensional spaces, there are 14 Bravais lattices which are obtained by combining one of the seven systems with one of the centering types [6]. Single crystal XRD helps in understanding the structures of solids. A crystal structure can be either chiral or achiral. Achiral molecules usually crystallize in centrosymmetric space groups but examples of crystal having noncentrosymmetric space groups are known. In contrast, chiral molecules which do not possess any inversion center or mirror plane always crystallize in noncentrosymmetric space group [7,8].

The reported chemistry of 4-nitrobenzoic acid (4-nbaH) clearly demonstrates the versatile bonding nature of this ligand and that 4-nitrobenzoate (4-nba) can support different coordination geometries [9]. In this report, we have used reported compound "tetra-aquabis(para-nitrobenzoate)cobalt(ll) dihydrate [4] in order to synthesize two more compounds. The compounds were prepared by using the formamide (form) and acetamide (aceta) (see below). The synthesized compounds were characterized by spectral, thermal and single crystal X-ray diffraction method.

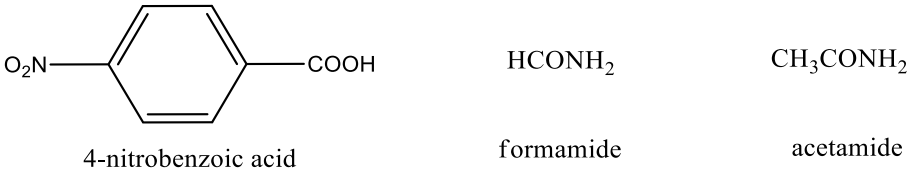

Fig 1: Structure of ligands used under study

EXPERIMENTAL DETAILS

Materials and Methods

All the chemicals used in the experimental work were of AR grade and used as received. Double distilled water was used as a solvent. The starting materials and reaction products are air stable and hence were routinely prepared under normal laboratory conditions. The products obtained were qualitatively analyzed following the standard procedures. The known compound $[Co(H_2O)_4(4\text{-}nba)_2]\cdot 2H_2O$ **1** was prepared by a reported procedure [4]. Infrared spectra of the solid samples were recorded in the region 4000 – 400 cm^{-1} using a Shimadzu (IR Prestige-21) FT-IR spectrometer, samples was diluted with KBr. TG-DTA study was performed in flowing air in Al_2O_3 crucibles at a heating rate of 10 min^{-1} using a STA-409 PC simultaneous thermal analyzer from Netzsch.

Single crystal X-ray structure determination

Single crystal X-ray diffraction study was performed. The structure was determined using a Bruker D8 Quest Eco X-ray Diffractometer. Intensity data were collected at room temperature using monochromated Mo (Kα) (λ = 0.7107 Å) radiation. The program suite APEX3 (Version 2019.1) was used i) to integrate the frames ii) to perform absorption correction and iii) to determine unit cell. The structures were solved with SHELXS and subsequent refinements were performed with SHELXL [10]. All non-hydrogen atoms were refined anisotropically. H atoms attached to the aromatic ring were introduced in calculated positions and included in the refinement by riding on their respective parent C atoms. The details of the refinement carried out are given in Appendix-I.

Synthesis of $[Co(4nba)_2(form)_2(H_2O)_2]$ **2** *(form = formamide)*

A mixture of 4-nitrobenzoic acid (4-nbaH) (1.6712 g, 10 mmol) and cobalt carbonate (0.547 g, 5 mmol) in water (50 mL) was taken in a 250 mL conical flask and placed over hot plate for heating for about 1 hour. The insoluble reactants started dissolving slowly with brisk effervescence. The heating of reaction mixture was stopped when there was no more evolution of CO_2. At this stage, the reaction mixture was almost clear, and pH was neutral. The solution turned red. On completion of the reaction, the reaction mixture was filtered in a beaker. Around 8 mL formamide was added to the clear filtrate and heated for some time (~10 mins). The beaker was left aside for crystallization at room temperature. After 2-3 day purple crystals obtained were collected by filtration, washed with diethyl ether and air dried.

IR data (cm^{-1}): 3418-3108, 2927, 2208, 1960, 1679, 1565, 1518, 1392, 1346, 1168, 1137, 1105, 1053, 1012, 887, 805, 769, 728, 638, 526

Calculations:

Theoretical Yield

$CoCO_3 \longrightarrow [Co(4nba)_2 (form)_2(H_2O)_2]form$

$118.94g \longrightarrow 562.32g$

$0.594g \longrightarrow x$

$x = 2.824g$

$$\text{Percentage Yield} = \frac{\text{Experimental Yield}}{\text{Theoretical Yield}} \times 100$$

$$= \frac{1.8012}{2.8243g} \times 100$$

$$= 63.77\%$$

Synthesis of $[Co(4nba)_2(aceta)_2(H_2O)]$ **3** *(aceta = acetamide)*

Cobalt carbonate (0.5947 g, 5mmol) and 4-nitrobenzoic acid (1.6712 g, 10mmol) were dissolved in around 50 mL double distilled water in a 250 mL conical flask and was heated on hot plate. Both the insoluble reactants slowly dissolved on heating the reaction mixture, with the evolution of carbon dioxide. The solution was heated for ~1h resulting in the formation of a red colored solution, was filtered. The pH of the solution was near to neutral. To the filtrate, acetamide (0.5907 g, 10 mmol) was added and heated for some more time. The beaker was left undisturbed at room temperature for crystallization. After 2 -3 days purple colored crystals were observed. The crystals were washed with diethyl ether and air dried.

IR data (cm^{-1}): 3441-2900, 2433, 1956, 1664, 1579, 1507, 1407, 1346, 1105, 1009, 873, 795, 722, 581, 514

Calculations:

Theoretical Yield:

$CoCO_3 \longrightarrow [Co(4nba)_2\,(aceta_2(H_2O)]$

$118.94g \longrightarrow 527.31g$

$0.5947g \longrightarrow x$

$x = 2.6365g$

$$\text{Percentage Yield} = \frac{\text{Experimental Yield}}{\text{Theoretical Yield}} \times 100$$

$$= \frac{1.7866g}{2.6365g} \times 100$$

$$= 67.76\%$$

RESULTS AND DISCUSSIONS

The reaction of $CoCO_3$ and 4-nbaH resulted in the formation of hydrated cobalt paranitrobenzoate compound **1** (parent compound). When metal carbonate is added to a hot aqueous solution of 4-nbaH, the insoluble MCO_3 goes into the solution with evolution of CO_2. The *in situ* reaction of parent compound **1** with stoichiometric amount of formamide and acetamide were studied in aqueous medium. This resulted in the formation of **2** and **3** wherein the aqua ligands in **1** were replaced by the neutral amide ligands. Purple colored crystals in both the cases were obtained from the reaction mixtures.

The compound formation can be represented as shown below in Eq. (1) and (2)

$$\begin{tikzcd}
CoCO_3 + 2\ 4\text{-nbaH} \arrow[r, "H_2O", "\text{heat}"'] & {[Co(4\text{-nba})_2 .\ x\ H_2O]} \arrow[d, "\text{formamide}"] \\
 & {[Co(4\text{-nba})_2(\text{form})_2(H2O)_2]\text{form}} \quad \mathbf{1}
\end{tikzcd}$$

$$\begin{tikzcd}
CoCO_3 + 2\ 4\text{-nbaH} \arrow[r, "H_2O", "\text{heat}"'] & {[Co(4\text{-nba})_2 .\ x\ H_2O]} \arrow[d, "\text{acetamide}"] \\
 & {[Co(4\text{-nba})_2(\text{aceta})_2H_2O]} \quad \mathbf{2}
\end{tikzcd}$$

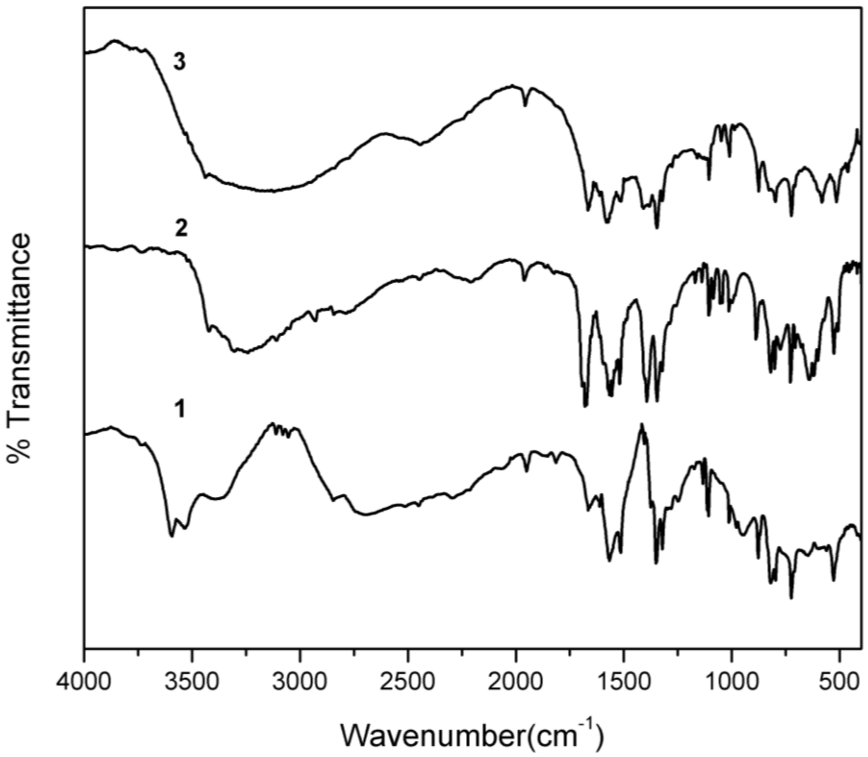

Fig 3.1 - Comparative infrared spectra of compound **1**, **2** and **3**

The synthesized complexes were studied by analytical techniques. Infrared spectroscopy has been extensively used in the present study in the mid-IR region ranging from 4000- 400 cm^{-1}. The IR spectra (Fig **3.1)** of the synthesized complexes exhibit several sharp bands, which confirm the presence of organic moiety. All the complexes exhibits very strong and broad absorption bands in the region 3500-3000 cm^{-1} corresponding to the -OH stretching vibrations. These signals clearly confirm the presence of water in all the synthesized complexes. The absorptions of the symmetric and asymmetric vibrations of the nitro group in the aromatic ring are observed at around 1550-1500 and 1360-1290 cm^{-1}as expected [11, 12]. The carbonyl absorption, which is observed at around 1700 cm^{-1} in the free acid, is shifted to lower energies in the Co (II) compounds and this is a typical feature observed in carboxylates.

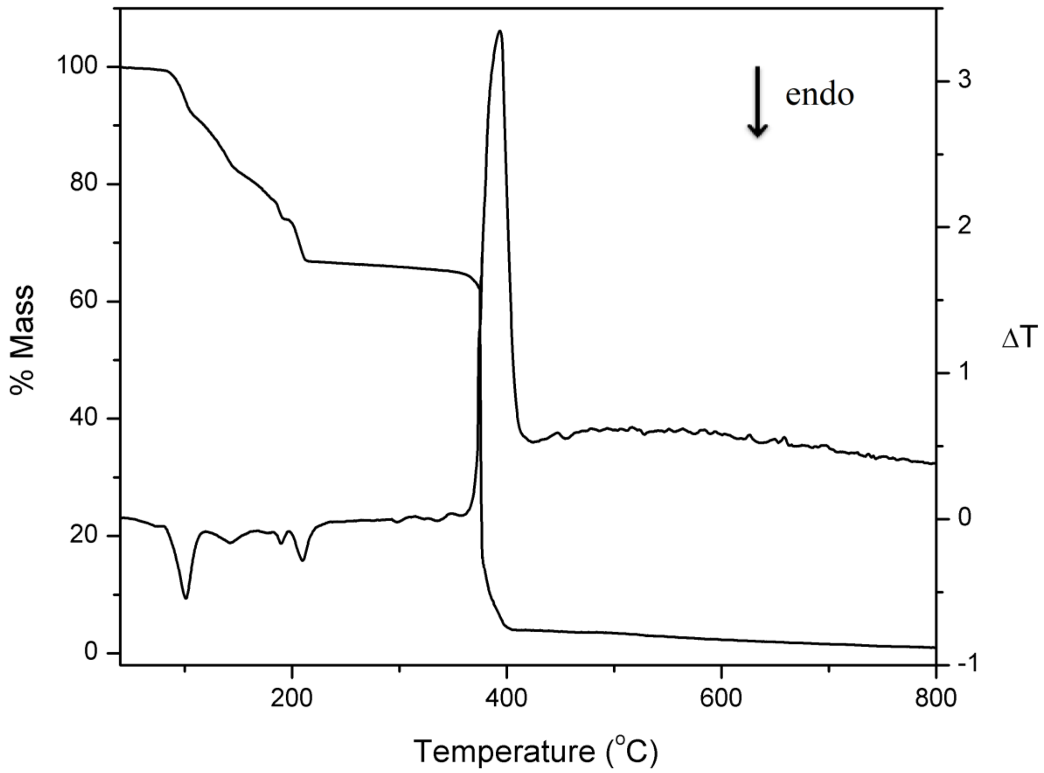

Fig 3.2 - TG and DTA curves of compound **2**

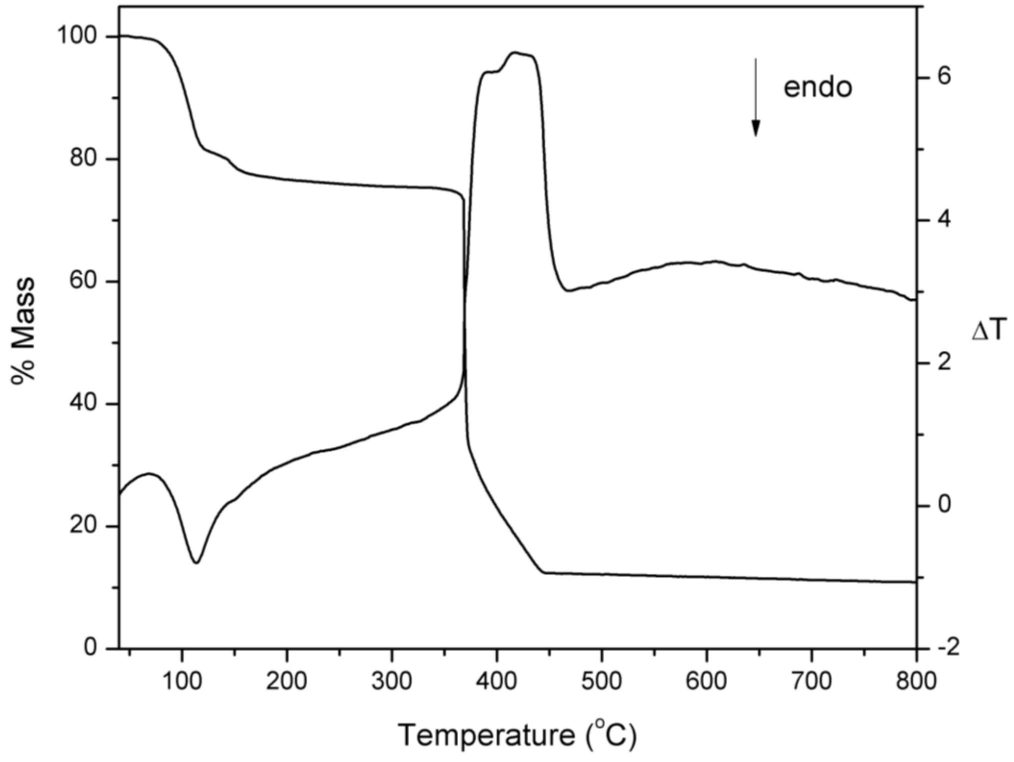

Fig 3.3 - TG and DTA curves of compound **3**

The TG-DTA curve for compounds **2** and **3** are shown in Fig: 3.2 and 3.3 respectively. In **2**, the TG curve shows a decrease in mass of approximately 6 % equivalent to loss of two water molecules around 100 °C. A mass loss of around 26 % and corresponding endothermic peak indicated the loss of three formamide ligands followed by the decomposition of the 4-nba. Similar trend is observed in compounds **3** wherein the anhydrous compound is obtained at 100 °C with the loss of one water molecule. Acetamide is lost between 150-300 °C followed by an exothermic event as shown in DTA corresponding to the decomposition of 4-nitrobenzoate (~65 %). Powder XRD was recorded for the residue obtained upon pyrolysis at 800 °C reveals that the final residue formed is Co_3O_4 (matched with JCPDS card no. 00-042-1467).

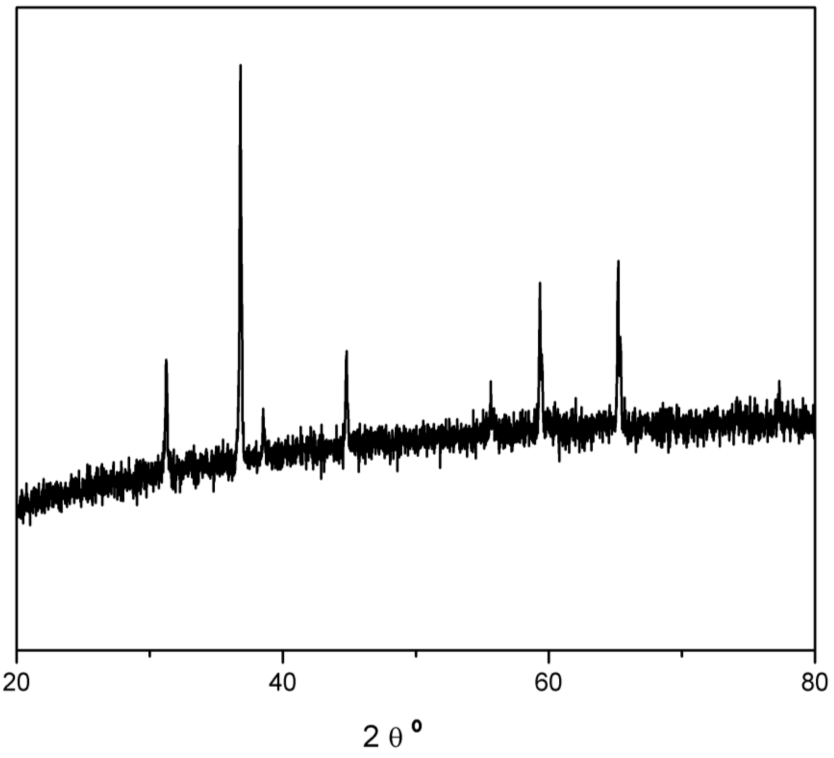

Fig 3.4 - Powder XRD of the residue obtained after pyrolysis at 800 °C.

The single crystal refinement results are given in Table 1.

Table 1. Crystal data and structure refinement for **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{17}H_{21}CoN_5O_{13}$	$C_{18}H_{20}CoN_4O_{11}$
Formula weight (g mol $^{-1}$)	562.32	527.31
Temperature(K)	293(2)	293(2)
Wavelength(A°)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a(Å)	7.3547(4)	7.4505(2)
b(Å)	7.5328(4)	11.6123(3)
c(Å)	22.9630(13)	13.8001(4)
α(°)	85.102(2)	70.7450(10)
β(°)	81.671(2)	87.4780(10)
γ(°)	63.350(2)	78.3320(10)
Volume (A ^{3})	1124.74(11)	1103.54(5)
Crystal size (mm $^{-1}$)	0.153×0.132×0.072	0.210 x 0.168 x 0.062
Z	2	2
D_{calc} (g/m ^{3})	1.660	1.587
Absorption coefficient (mm $^{-1}$)	0.843	0.846
F(000)	578	542
Theta range for data collection(°)	2.690to 28.266	2.792 to 28.296
Limiting indices	$-9 \leq h \leq 9$,	$-9 \leq h \leq 9$
	$-10 \leq k \leq 10$,	$-15 \leq k \leq 15$
	$-30 \leq l \leq 30$	$-18 \leq l \leq 18$
Reflections collected	16832	16460
Unique collected	5548 [R(int) = 0.0331]	5482[R(int) = 0.0265]
Completeness to theta = 25.242	99.8%	99.8 %
Absorption correction	Multiscan	
Refinement method	Full- matrix least-squares on F^2	
Data /restraints / parameters	5548 / 0 / 357	5482 / 0 / 333
Goodness –of-fit on F^2	1.053	1.031
Final R indices[I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0850	R1 = 0.0328, wR2 = 0.0762
R indices (all data)	R1 = 0.0483, wR2 = 0.0936	R1 = 0.0447, wR2 = 0.0844
Largest diff. peak and hole (e.Å $^{-3}$)	0.305 and -0.425	0.282 and -0.272

Single crystal data reveals that compound **2** crystallizes in the centrosymmetric triclinic P1̄ space group. The central metal atom is hexacoordinated and 4-nba anions function as monodentate carboxylate ligands. The central metal ion i.e. Co(II) is surrounded by 6 oxygen atoms, two of which are from aqua ligand, two monodentate carboxylate ligands disposed trans to each other and two monodentate formamide ligands complete the octahedral coordination around the cobalt. Additionally, this compound contains an uncoordinated formamide ligand which is not bonded to Co(II). The crystal structure of compound **2** is shown in Fig. 3.5. A view of the packing is given in Fig 3.6.

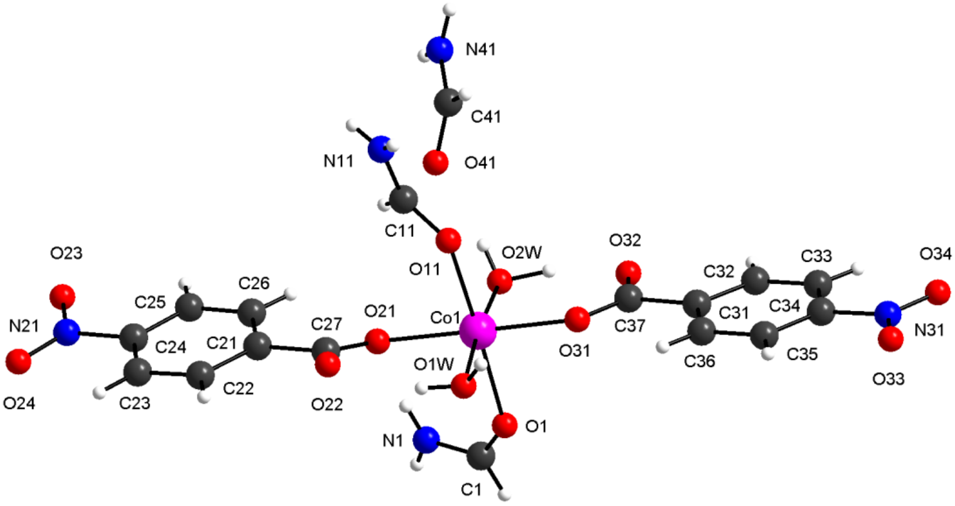

Fig 3.5 - The crystal structure of $[Co(4nba)_2(form)_2(H_2O)_2]$ **2** showing the atom labelling scheme and the coordination sphere of Co(II).

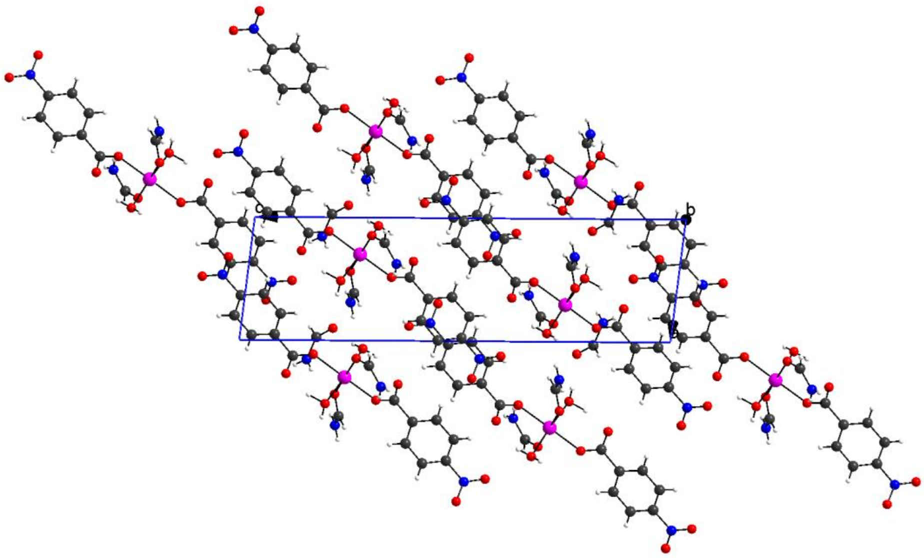

Fig 3.6 - A view along *b* axis showing the crystallographic packing of **2**.

Compound **3** crystallizes in the triclinic centrosymmetric space group P1̄. The structure of **3** consist Co(II) linked to the oxygen atoms of two acetamide ligands, one terminal water molecule and two 4-nba ligands one functioning as monodentate ligand and the other as bidentate ligand thereby completing the hexacoodination around Co(II). The crystal structure of compound **3** is shown in Fig. 3.6 showing the monodentate and bidentate bonding of 4-nba ligands. A view of the packing is given in Fig 3.8. For both the compounds the structure protocols contain the complete list of bond distances and bond angles.

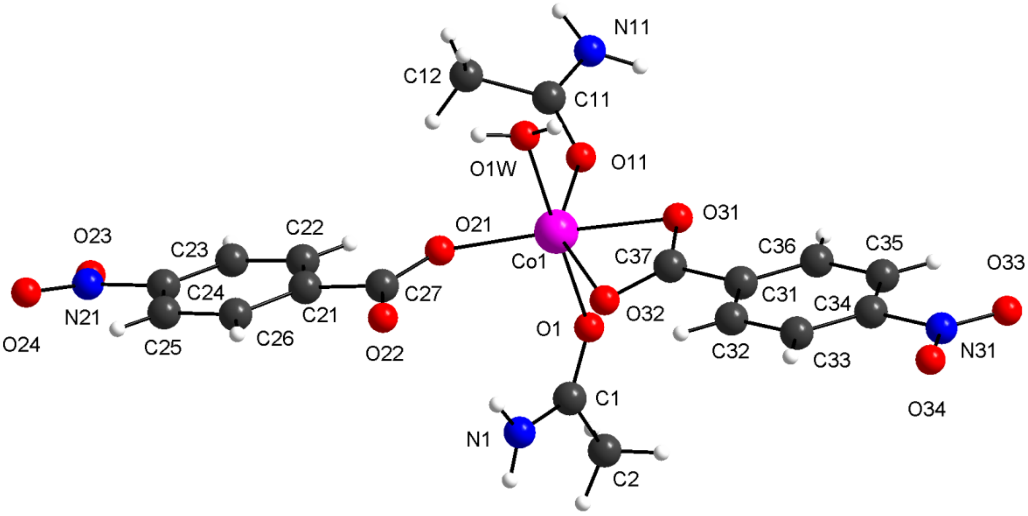

Fig 3.7 - The crystal structure of [Co(4nba)$_2$(aceta)$_2$(H$_2$O)] **3** showing the atom labelling scheme and the coordination sphere of Co(II).

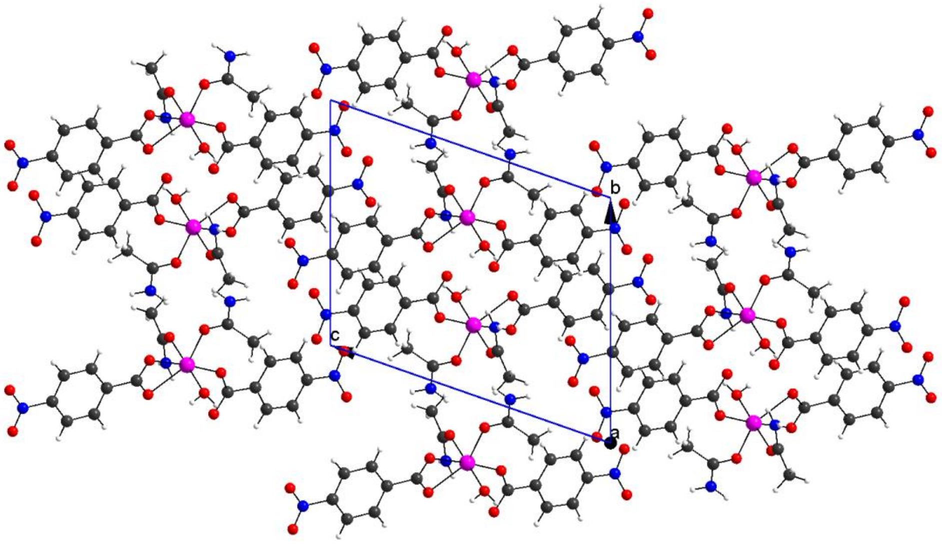

Fig 3.8 - A view along *a* axis showing the crystallographic packing of **3**.

CONCLUSIONS

All the products of reactions performed in this study were characterized exclusively using IR. The appearance of new bands or disappearance of existing bands in infrared, thermal studies and single crystal X-ray structure determination studies provides useful information for characterization.

The reaction of water rich compound **1** with formamide and acetamide resulted in the formation of amide containing compounds **2** and **3** in reasonably good yields. Compound **2** and **3** have been studied by thermal method (TG-DTA) and it is found that metal oxide is the preferred decomposition product at high temperature.

The structurally characterized compound **2** is hexacoordinated with both 4-nba ligands functioning as monodentate ligands whereas in **3**, one of the 4-nba anion functions as monodentate ligand whereas the other exhibits bidentate binding mode.

Compounds **2** and **3** described in this report are new additions to the growing list of structurally characterized cobalt compounds based on the 4-nitrobenzoic acid (4-nbaH).

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APPENDIX-I

Table 1. Crystal data and structure refinement for **2**.

Compound	**2**
Empirical formula	$C_{17}H_{21}CoN_5O_{13}$
Formula weight (g mol^{-1})	562.32
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P$\bar{1}$
Unit cell dimensions	
a (Å)	7.3547(4)
b (Å)	7.5328(4)
c (Å)	22.9630(13)
α (°)	85.102(2)
β (°)	81.671(2)
γ(°)	63.350(2)
Volume (A^3)	1124.74(11)
Crystal size(mm)	0.153×0.132×0.072
Z	2
D_{calc} (g/m^{-3})	1.660
Absorption coefficient (mm^{-1})	0.843
F(000)	578
Theta range for data collection (^{o})	2.690to 28.266
Limiting indices	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-30 \leq l \leq 30$
Reflections collected	16832
Unique collected	5548 [R(int) = 0.0331]
Completeness to theta = 25.242	99.8%
Absorption correction	Multiscan
Max. and min. transmission	0.746 – 0.679
Refinement method	Full- matrix least-squares on F^2
Data / restraints / parameters	5548 / 0 / 357
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0850
R indices (all data)	R1 = 0.0483, wR2 = 0.0936
Largest diff. peak and hole (e.$Å^{-3}$)	0.305 and -0.425

Table 2. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **2** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Co(1)	3002(1)	5183(1)	7452(1)	26(1)
O(1)	1138(2)	5672(2)	8242(1)	34(1)
N(1)	-5290(3)	7861(3)	10581(1)	39(1)
C(1)	-488(3)	6745(3)	6745(3)	27(1)
O(2)	2722(2)	6637(2)	8817(1)	40(1)
C(2)	-414(3)	7441(3)	9734(1)	34(1)
O(3)	-6746(3)	7580(3)	10498(1)	58(1)
C(3)	-1989(3)	7811(3)	10186(1)	36(1)
O(4)	-5145(3)	8439(3)	11046(1)	61(1)
C(4)	-3625(3)	7483(3)	10095(1)	31(1)

C(5)	-3756(3)	6807(3)	9570(1)	35(1)
C(6)	-2162(3)	6432(3)	9120(1)	34(1)
C(7)	1269(3)	6307(3)	8715(1)	28(1)
C(11)	6579(3)	3190(3)	5745(1)	30(1)
N(11)	11442(3)	2011(3)	4378(1)	50(1)
O(11)	4838(2)	4607(2)	6655(1)	34(1)
C(12)	6420(3)	2686(3)	5193(1)	35(1)
O(12)	3540(2)	3017(2)	6192(1)	45(1)
C(13)	7997(3)	2339(3)	4739(1)	40(1)
O(13)	13039(3)	1944(3)	4497(1)	74(1)
C(14)	9734(3)	2447(3)	4855(1)	37(1)
O(14)	11199(3)	1674(4)	3893(1)	83(1)
C(15)	9952(3)	2917(3)	5400(1)	40(1)
C(16)	8342(3)	3320(3)	5842(1)	36(1)
C(17)	4836(3)	3629(3)	6231(1)	30(1)
O(21)	1460(2)	8265(2)	7234(1)	36(1)
N(21)	3754(3)	8861(4)	6581(1)	45(1)
C(21)	2031(3)	9378(3)	6919(1)	37(1)
O(31)	4366(2)	2033(2)	7631(1)	35(1)
O(41)	5148(2)	5752(2)	7823(1)	34(1)
O(42)	664(2)	4863(2)	7111(1)	34(1)
C(51)	9739(3)	1428(3)	8223(1)	37(1)
O(51)	9005(2)	2820(2)	7865(1)	41(1)
N(51)	11558(3)	770(3)	8386(1)	41(1)
N(31)	6899(3)	-1081(3)	7532(1)	45(1)
C(31)	6162(3)	837(3)	7475(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **2**.

Bond lengths			
Co(1)-O(1)	2.0599(13	Co(1)-O(11)	2.0626(13)
Co(1)-O(42)	2.1029(14)	Co(1)-O(41)	2.1119(14)
Co(1)-O(21)	2.1289(13)	Co(1)-O(31)	2.1498(13)
O(1)-C(7)	1.257(2)	N(1)-O(3)	1.224(2)
N(1)-O(4)	1.224(2)	N(1)-C(4)	1.474(2)
C(1)-C(6)	1.391(3)	C(1)-C(2)	1.394(3)
C(1)-C(7)	1.510(2	O(2)-C(7)	1.257(2)
C(2)-C(3)	1.381(3)	C(2)-H(2)	0.9300
C(3)-C(4)	1.379(3)	C(3)-H(3)	0.9300
C(4)-C(5)	1.380(3)	C(5)-C(6)	1.386(3)
C(5)-H(5)	0.9300	C(6)-H(6)	0.9300
C(11)-C(12)	1.389(3)	C(11)-C(16)	1.393(3)
C(11)-C(17)	1.507(2)	N(11)-O(14)	1.219(3)
N(11)-O(13)	1.223(3)	N(11)-C(14)	1.475(3)
O(11)-C(17)	1.270(2)	C(12)-C(13)	1.388(3)
C(12)-H(12)	0.9300	O(12)-C(17)	1.247(2)
C(13)-C(14)	1.380(3)	C(13)-H(13)	0.9300
C(14)-C(15)	1.379(3)	C(15)-C(16)	1.381(3)
O(21)-C(21)	1.235(2)	N(21)-C(21)	1.298(3)
C(21)-H(21)	0.9300	O(31)-C(31)	1.239(2)
O(41)-H(41B)	0.80(3)	O(41)-H(41A)	1.01(4)
O(42)-H(42A)	0.83(3)	O(42)-H(42B)	0.85(3)
C(51)-O(51)	1.241(3)	C(51)-N(51)	1.302(3)
C(51)-H(51)	0.9300	N(51)-H(51A)	0.8600
N(51)-H(51B)	0.8600	N(31)-C(31)	1.298(3)

N(31)-H(31B)	0.77(3)	N(31)-H(31A)	0.89(3)

Bond angles

O(1)-Co(1)-O(11)	177.78(5)	O(1)-Co(1)-O(42)	85.34(6)
O(11)-Co(1)-O(42)	92.97(6)	O(1)-Co(1)-O(41)	91.65(6)
O(11)-Co(1)-O(41)	90.13(6)	O(42)-Co(1)-O(41)	174.90(6)
O(1)-Co(1)-O(21)	89.59(5)	O(11)-Co(1)-O(21)	91.77(5)
O(42)-Co(1)-O(21)	87.14(6)	O(41)-Co(1)-O(21)	88.72(6)
O(1)-Co(1)-O(31)	90.71(5)	O(11)-Co(1)-O(31)	87.78(5)
O(42)-Co(1)-O(31)	87.70(6)	O(41)-Co(1)-O(31)	96.47(6)
O(21)-Co(1)-O(31)	174.79(5)	C(7)-O(1)-Co(1)	129.70(12)
O(3)-N(1)-O(4)	123.37(18)	O(3)-N(1)-C(4)	118.28(18)
O(4)-N(1)-C(4)	118.35(18)	C(6)-C(1)-C(2)	119.69(17)
C(6)-C(1)-C(7)	120.82(16)	C(2)-C(1)-C(7)	119.47(16)
C(3)-C(2)-C(1)	120.30(18)	C(3)-C(2)-H(2)	119.9
C(1)-C(2)-H(2)	119.9	C(4)-C(3)-C(2)	118.60(18)
C(4)-C(3)-H(3)	120.7	C(2)-C(3)-H(3)	120.7
C(3)-C(4)-C(5)	122.68(17)	C(3)-C(4)-N(1)	118.34(17)
C(5)-C(4)-N(1)	118.97(17)	C(4)-C(5)-C(6)	118.19(18)
C(4)-C(5)-H(5)	120.9	C(6)-C(5)-H(5)	120.9
C(5)-C(6)-C(1)	120.53(18)	C(5)-C(6)-H(6)	119.7
C(1)-C(6)-H(6)	119.7	O(2)-C(7)-O(1)	125.71(17)
O(2)-C(7)-C(1)	117.15(16)	O(1)-C(7)-C(1)	117.13(16)
C(12)-C(11)-C(16)	119.67(17)	C(12)-C(11)-C(17)	120.01(17)
C(16)-C(11)-C(17)	120.30(17)	O(14)-N(11)-O(13)	123.8(2)
O(14)-N(11)-C(14)	118.0(2)	O(13)-N(11)-C(14)	118.2(2)
C(17)-O(11)-Co(1)	128.02(12)	C(13)-C(12)-C(11)	120.15(19)
C(13)-C(12)-H(12)	119.9	C(11)-C(12)-H(12)	119.9
C(14)-C(13)-C(12)	118.47(19)	C(14)-C(13)-H(13)	120.8
C(12)-C(13)-H(13)	120.8	C(15)-C(14)-C(13)	122.81(18)
C(15)-C(14)-N(11)	118.6(2)	C(13)-C(14)-N(11)	118.6(2)
C(14)-C(15)-C(16)	117.99(19)	C(14)-C(15)-H(15)	121.0
C(16)-C(15)-H(15)	121.0	C(15)-C(16)-C(11)	120.86(19)
C(15)-C(16)-H(16)	119.6	C(11)-C(16)-H(16)	119.6
O(12)-C(17)-O(11)	125.60(17)	O(12)-C(17)-C(11)	118.91(17)
O(11)-C(17)-C(11)	115.49(16)	C(21)-O(21)-Co(1)	131.80(13)
C(21)-N(21)-H(21A)	116.5(18)	C(21)-N(21)-H(21B)	117(2)
H(21A)-N(21)-H(21B)	126(3)	O(21)-C(21)-N(21)	126.7(2)
O(21)-C(21)-H(21)	116.6	N(21)-C(21)-H(21)	116.6
C(31)-O(31)-Co(1)	126.19(13)	Co(1)-O(41)-H(41B)	118.0(18)
Co(1)-O(41)-H(41A)	96.8(19)	H(41B)-O(41)-H(41A)	103(2)
Co(1)-O(42)-H(42A)	102(2)	Co(1)-O(42)-H(42B)	109.5(18)
H(42A)-O(42)-H(42B)	111(3)	O(51)-C(51)-N(51)	124.78(19)
O(51)-C(51)-H(51)	117.6	N(51)-C(51)-H(51)	117.6
C(51)-N(51)-H(51A)	120.0	C(51)-N(51)-H(51B)	120.0
H(51A)-N(51)-H(51B)	120.0	C(31)-N(31)-H(31B)	120(2)
C(31)-N(31)-H(31A)	121.1(18)	H(31B)-N(31)-H(31A)	118(3)
O(31)-C(31)-N(31)	125.22(19)	O(31)-C(31)-H(31)	117.4
N(31)-C(31)-H(31)	117.4		

Table 4. Anisotropic atomic displacement parameters (Å^2) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Co(1)	22(1)	28(1)	27(1)	- 5(1)	4(1)	-11(1)
O(1)	32(1)	45(1)	27(1)	-9(1)	6(1)	-21(1)
N(1)	37(1)	39(1)	32(1)	-2(1)	7(1)	-12(1)
C(1)	28(1)	27(1)	25(1)	-2(1)	0(1)	-10(1)
O(2)	31(1)	55(1)	36(1)	-9(1)	2(1)	-23(1)
C(2)	31(1)	39(1)	32(1)	-6(1)	-1(1)	-16(1)
O(3)	43(1)	78(1)	55(1)	-16(1)	16(1)	-34(1)
C(3)	39(1)	43(1)	24(1)	-10(1)	1(1)	-17(1)
O(4)	55(1)	90(1)	35(1)	-19(1)	13(1)	-33(1)
C(4)	29(1)	30(1)	28(1)	-1(1)	4(1)	-9(1)
C(5)	28(1)	42(1)	35(1)	-5(1)	1(1)	-17(1)
C(6)	33(1)	41(1)	28(1)	-7(1)	0(1)	-17(1)
C(7)	28(1)	26(1)	28(1)	-1(1)	0(1)	-9(1)
C(11)	31(1)	27(1)	28(1)	-2(1)	4(1)	-11(1)
N(11)	55(1)	41(1)	39(1)	-4(1)	18(1)	-13(1)
O(11)	35(1)	36(1)	31(1)	-10(1)	9(1)	-18(1)
C(12)	35(1)	37(1)	31(1)	-6(1)	-1(1)	-13(1)
O(12)	45(1)	59(1)	40(1)	-15(1)	10(1)	-32(1)
C(13)	47(1)	38(1)	25(1)	-5(1)	2(1)	-11(1)
O(13)	57(1)	93(2)	74(1)	-27(1)	32(1)	-42(1)
C(14)	39(1)	31(1)	31(1)	-4(1)	13(1)	-11(1)
O(14)	76(1)	114(2)	33(1)	-7(1)	17(1)	-23(1)
C(15)	37(1)	44(1)	41(1)	-6(1)	7(1)	-21(1)
C(16)	40(1)	40(1)	29(1)	-7(1)	4(1)	-19(1)
C(17)	31(1)	30(1)	27(1)	-2(1)	3(1)	-12(1)
O(21)	31(1)	30(1)	39(1)	-1(1)	6(1)	-11(1)
N(21)	47(1)	45(1)	47(1)	-4(1)	11(1)	-27(1)
C(21)	42(1)	30(1)	38(1)	-3(1)	2(1)	-16(1)
O(31)	27(1)	29(1)	41(1)	-1(1)	4(1)	-8(1)
O(41)	24(1)	37(1)	39(1)	-7(1)	1(1)	-13(1)
O(42)	31(1)	35(1)	36(1)	-1(1)	-1(1)	-16(1)
C(51)	35(1)	41(1)	36(1)	-8(1)	9(1)	-21(1)
O(51)	28(1)	42(1)	49(1)	0(1)	3(1)	-14(1)
N(51)	40(1)	44(1)	42(1)	1(1)	-3(1)	-22(1)
N(31)	27(1)	33(1)	63(1)	-2(1)	4(1)	-5(1)
C(31)	25(1)	35(1)	42(1)	-2(1)	-1(1)	-14(1)

Table 5. Hydrogen bonding geometry [Å and °] for **2**.

D-H···A	*d*(D-H)	*d*(H···A)	<(DHA)	*d*(D···A)	Symmetry code
C5-H5··· O2	0.930	2.546	147.55	3.368	x-1, y, z
C15-H15··· O12	0.930	2.606	150.38	3.445	x+1, y, z
N21-H21A··· O12	0.855	2.316	157.28	3.122	x, y+1, z
N21-H21B··· O11	0.794	2.249	144.24	2.930	x, y, z
C21-H21··· O51	0.930	2.641	126.66	3.283	x-1, y+1, z
O41-H41B··· O51	0.797	1.920	172.61	2.712	x, y, z
O41-H41A··· O2	1.007	1.635	164.15	2.618	x, y, z
O42-H42A··· O12	0.827	1.943	157.35	2.725	x, y, z
O42-H42B··· O51	0.853	1.892	169.15	2.734	x-1, y, z
N51-H51A··· O31	0.860	2.115	159.34	2.936	x+1, y, z
N51-H51B··· O2	0.860	2.205	145.66	2.956	x+1, y-1, z
N31-H31B··· O21	0.775	2.493	142.27	3.142	x+1, y-1, z
N31-H31B··· O42	0.775	2.501	146.20	3.174	x+1, y-1, z
N31-H31A··· O41	0.894	2.322	157.68	3.167	x, y-1, z

Table 1. Crystal data and structure refinement for **3**.

Compound	**3**
Empirical formula	C18 H20 Co N4 O11
Formula weight (g mol^{-1})	527.31
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	
a (Å)	7.4505(2)
b (Å)	11.6123(3)
c (Å)	13.8001(4)
α (°)	70.7450(10)
β (°)	87.4780(10)
γ (°)	78.3320(10)
Volume (A^3)	1103.54(5)
Z	2
D$_{calc}$ (g/m^{-3})	1.587
Absorption coefficient (mm^{-1})	0.846
F(000)	542
Crystal size (mm^3)	0.210 x 0.168 x 0.062
Theta range for data collection (^{o})	2.792 to 28.296
Limiting indices	$-9 \le h \le 9$
	$-15 \le k \le 15$
	$-18 \le l \le 18$
Reflections collected	16460
Unique collected	5482[R(int) = 0.0265]
Completeness to theta =25.242	99.8 %
Absorption correction	Multiscan
Max. and min. transmission	0.746 -0.662
Refinement method	Full- matrix least-squares on F^2
Data / restraints / parameters	5482 / 0 / 333
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0762
R indices (all data)	R1 = 0.0447, wR2 = 0.0844
Largest diff. peak and hole (e.Å^{-3})	0.282 and -0.272

Table 2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **3** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Co(1)	3962(1)	7149(1)	5111(1)	30(1)
N(1)	7991(3)	3047(2)	10976(2)	71(1)
C(1)	5860(2)	5064(2)	7981(1)	33(1)
O(1)	5601(2)	6805(1)	6451(1)	37(1)
C(2)	6714(3)	5633(2)	8523(2)	43(1)
O(2)	4008(2)	5391(1)	6507(1)	41(1)
C(4)	7255(3)	3745(2)	9923(2)	47(1)
O(4)	8663(4)	3595(2)	11437(2)	104(1)
O(3)	7858(4)	1957(2)	11338(2)	110(1)
C(3)	7411(3)	4966(2)	9507(2)	51(1)
C(6)	5738(3)	3825(2)	8426(2)	41(1)
C(5)	6449(3)	3147(2)	9405(2)	50(1)
C(7)	5113(2)	5793(2)	6915(1)	33(1)

N(11)	-2561(3)	8813(3)	-153(2)	69(1)
O(11)	2357(2)	7316(1)	3902(1)	50(1)
C(11)	366(2)	7212(2)	2673(1)	33(1)
O(12)	1450(2)	5528(1)	4160(1)	58(1)
C(12)	-439(3)	6480(2)	2275(2)	40(1)
O(13)	-3008(3)	9952(2)	-492(2)	101(1)
C(13)	-1374(3)	6992(2)	1346(2)	47(1)
O(14)	-2920(4)	8115(3)	-578(2)	112(1)
C(14)	-1546(3)	8251(2)	836(2)	46(1)
C(15)	-806(3)	9012(2)	1223(2)	47(1)
C(16)	166(3)	8475(2)	2147(2)	41(1)
C(17)	1478(2)	6622(2)	3666(1)	36(1)
O(21)	1770(2)	8026(1)	5743(1)	41(1)
C(22)	-1071(3)	8751(2)	6382(2)	58(1)
C(31)	5382(2)	9393(2)	3663(1)	35(1)
N(31)	6196(3)	10345(2)	3582(2)	60(1)
O(31)	4768(2)	8839(1)	4493(1)	38(1)
O(41)	6183(2)	6247(1)	4499(1)	38(1)
C(32)	5263(4)	9038(2)	2744(2)	56(1)
C(21)	195(2)	7861(2)	5969(1)	36(1)
N(21)	-449(3)	6925(2)	5876(2)	51(1)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Bond lengths			
Co(1)-O(11)	2.0286(13)	Co(1)-O(21)	2.0620(13)
Co(1)-O(31)	2.0656(12)	Co(1)-O(41)	2.0751(13)
Co(1)-O(1)	2.1420(12)	Co(1)-O(2)	2.2945(13)
N(1)-O(4)	1.218(3)	N(1)-O(3)	1.221(3)
N(1)-C(4)	1.478(3)	C(1)-C(6)	1.386(3)
C(1)-C(2)	1.392(3)	C(1)-C(7)	1.500(2)
O(1)-C(7)	1.257(2)	C(2)-C(3)	1.385(3)
C(2)-H(2)	0.9300	O(2)-C(7)	1.259(2)
C(4)-C(3)	1.370(3)	C(4)-C(5)	1.375(3)
C(3)-H(3)	0.9300	C(6)-C(5)	1.384(3)
C(6)-H(6)	0.9300	C(5)-H(5)	0.9300
N(11)-O(14)	1.220(3)	N(11)-O(13)	1.227(3)
N(11)-C(14)	1.471(3)	O(11)-C(17)	1.261(2)
C(11)-C(16)	1.386(3)	C(11)-C(12)	1.389(2)
C(11)-C(17)	1.512(2)	O(12)-C(17)	1.231(2)
C(12)-C(13)	1.375(3)	C(12)-H(12)	0.9300
C(13)-C(14)	1.380(3)	C(13)-H(13)	0.9300
C(14)-C(15)	1.379(3)	C(15)-C(16)	1.383(3)
C(15)-H(15)	0.9300	C(16)-H(16)	0.9300
O(21)-C(21)	1.237(2)	C(22)-C(21)	1.493(3)
C(22)-H(22A)	0.9600	C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600	C(31)-O(31)	1.235(2)
C(31)-N(31)	1.336(2)	C(31)-C(32)	1.468(3)
N(31)-H(31B)	0.90(4)	N(31)-H(31A)	0.91(3)
O(41)-H(41B)	0.83(3)	O(41)-H(41A)	0.84(3)
C(32)-H(32A)	0.9600	C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600	C(21)-N(21)	1.318(2)
N(21)-H(21A)	0.83(3)	N(21)-H(21B)	0.84(3)

Bond angles

O(11)-Co(1)-O(21)	90.61(6)	O(11)-Co(1)-O(31)	96.84(5)
O(21)-Co(1)-O(31)	88.47(5)	O(11)-Co(1)-O(41)	90.16(6)
O(21)-Co(1)-O(41)	179.05(6)	O(31)-Co(1)-O(41)	91.99(5)
O(11)-Co(1)-O(1)	174.74(5)	O(21)-Co(1)-O(1)	89.79(5)
O(31)-Co(1)-O(1)	88.41(5)	O(41)-Co(1)-O(1)	89.40(5)
O(11)-Co(1)-O(2)	115.63(5)	O(21)-Co(1)-O(2)	88.19(5)
O(31)-Co(1)-O(2)	147.38(5)	O(41)-Co(1)-O(2)	90.98(5)
O(1)-Co(1)-O(2)	59.14(4)	O(4)-N(1)-O(3)	124.0(2)
O(4)-N(1)-C(4)	118.3(2)	O(3)-N(1)-C(4)	117.7(2)
C(6)-C(1)-C(2)	119.63(17)	C(6)-C(1)-C(7)	120.78(16)
C(2)-C(1)-C(7)	119.59(16)	C(7)-O(1)-Co(1)	93.24(10)
C(3)-C(2)-C(1)	119.99(19)	C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0	C(7)-O(2)-Co(1)	86.27(10)
C(3)-C(4)-C(5)	122.95(18)	C(3)-C(4)-N(1)	118.2(2)
C(5)-C(4)-N(1)	118.9(2)	C(4)-C(3)-C(2)	118.67(19)
C(4)-C(3)-H(3)	120.7	C(2)-C(3)-H(3)	120.7
C(5)-C(6)-C(1)	120.82(18)	C(5)-C(6)-H(6)	119.6
C(1)-C(6)-H(6)	119.6	C(4)-C(5)-C(6)	117.92(19)
C(4)-C(5)-H(5)	121.0	C(6)-C(5)-H(5)	121.0
O(1)-C(7)-O(2)	121.35(16)	O(1)-C(7)-C(1)	118.78(15)
O(2)-C(7)-C(1)	119.87(16)	O(14)-N(11)-O(13)	124.2(2)
O(14)-N(11)-C(14)	117.8(2)	O(13)-N(11)-C(14)	118.0(2)
C(17)-O(11)-Co(1)	135.53(13)	C(16)-C(11)-C(12)	119.59(17)
C(16)-C(11)-C(17)	120.63(16)	C(12)-C(11)-C(17)	119.78(16)
C(13)-C(12)-C(11)	120.42(18)	C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8	C(12)-C(13)-C(14)	118.72(18)
C(12)-C(13)-H(13)	120.6	C(14)-C(13)-H(13)	120.6
C(15)-C(14)-C(13)	122.37(18)	C(15)-C(14)-N(11)	118.4(2)
C(13)-C(14)-N(11)	119.3(2)	C(14)-C(15)-C(16)	118.08(19)
C(14)-C(15)-H(15)	121.0	C(16)-C(15)-H(15)	121.0
C(15)-C(16)-C(11)	120.78(18)	C(15)-C(16)-H(16)	119.6
C(11)-C(16)-H(16)	119.6	O(12)-C(17)-O(11)	126.50(17)
O(12)-C(17)-C(11)	117.95(16)	O(11)-C(17)-C(11)	115.55(16)
C(21)-O(21)-Co(1)	134.82(12)	C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	O(31)-C(31)-N(31)	119.96(19)
O(31)-C(31)-C(32)	122.08(17)	N(31)-C(31)-C(32)	117.96(19)
C(31)-N(31)-H(31B)	118(2)	C(31)-N(31)-H(31A)	113.5(19)
H(31B)-N(31)-H(31A)	128(3)	C(31)-O(31)-Co(1)	135.07(12)
Co(1)-O(41)-H(41B)	117(2)	Co(1)-O(41)-H(41A)	116.7(17)
H(41B)-O(41)-H(41A)	105(2)	C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5	H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5	O(21)-C(21)-N(21)	123.65(18)
O(21)-C(21)-C(22)	119.44(17)	N(21)-C(21)-C(22)	116.91(18)
C(21)-N(21)-H(21A)	119.1(17)	C(21)-N(21)-H(21B)	119.7(18)
H(21A)-N(21)-H(21B)	121(2)		

Table 4. Anisotropic atomic displacement parameters (Å^2) for **3**.

	U11	U22	U33	U23	U13	U12
Co(1)	31(1)	28(1)	32(1)	-10(1)	-4(1)	-8(1)
N(1)	84(2)	72(2)	39(1)	-4(1)	-11(1)	2(1)
C(1)	32(1)	36(1)	31(1)	-12(1)	2(1)	-6(1)
O(1)	38(1)	37(1)	34(1)	-7(1)	-3(1)	-10(1)
C(2)	54(1)	39(1)	39(1)	-14(1)	-6(1)	-10(1)
O(2)	44(1)	42(1)	41(1)	-19(1)	-6(1)	-10(1)
C(4)	50(1)	52(1)	31(1)	-7(1)	0(1)	0(1)
O(4)	140(2)	109(2)	54(1)	-15(1)	-43(1)	-14(2)
O(3)	174(3)	72(1)	57(1)	10(1)	-31(1)	-12(2)
C(3)	60(1)	57(1)	39(1)	-20(1)	-9(1)	-8(1)
C(6)	46(1)	41(1)	40(1)	-13(1)	2(1)	-14(1)
C(5)	56(1)	41(1)	43(1)	-3(1)	4(1)	-10(1)
C(7)	32(1)	35(1)	33(1)	-15(1)	0(1)	-4(1)
N(11)	63(1)	101(2)	39(1)	-8(1)	-13(1)	-32(1)
O(11)	52(1)	55(1)	45(1)	-14(1)	-18(1)	-16(1)
C(11)	28(1)	40(1)	33(1)	-13(1)	-1(1)	-7(1)
O(12)	59(1)	42(1)	62(1)	-1(1)	-23(1)	-10(1)
C(12)	39(1)	42(1)	44(1)	-16(1)	-4(1)	-10(1)
O(13)	109(2)	98(2)	71(1)	16(1)	-46(1)	-31(1)
C(13)	45(1)	62(1)	45(1)	-28(1)	-1(1)	-19(1)
O(14)	149(2)	137(2)	60(1)	-27(1)	-43(1)	-50(2)
C(14)	38(1)	67(1)	32(1)	-11(1)	-4(1)	-15(1)
C(15)	47(1)	46(1)	41(1)	-3(1)	-7(1)	-14(1)
C(16)	40(1)	41(1)	44(1)	-13(1)	-8(1)	-13(1)
C(17)	29(1)	44(1)	35(1)	-14(1)	-3(1)	-4(1)
O(21)	30(1)	40(1)	56(1)	-20(1)	6(1)	-11(1)
C(22)	42(1)	53(1)	77(2)	-26(1)	10(1)	-1(1)
C(31)	34(1)	29(1)	40(1)	-9(1)	3(1)	-3(1)
N(31)	83(2)	49(1)	58(1)	-16(1)	12(1)	-37(1)
O(31)	51(1)	29(1)	35(1)	-11(1)	6(1)	-15(1)
O(41)	42(1)	33(1)	40(1)	-16(1)	-6(1)	1(1)
C(32)	77(2)	61(1)	35(1)	-17(1)	4(1)	-24(1)
C(21)	30(1)	36(1)	39(1)	-8(1)	-2(1)	-5(1)
N(21)	40(1)	51(1)	69(1)	-24(1)	11(1)	-21(1)

Table 5. Hydrogen bonding geometry [Å and °] for **3**.

D-H···A	*d*(D-H)	*d*(H···A)	<(DHA)	*d*(D···A)	Symmetry Code
N31-H31B···O21	0.895	2.465	121.62	3.032	-x+1, -y+2, -z+1
N31-H31B···O31	0.895	2.255	160.28	3.113	-x+1, -y+2, -z+1
N31-H31A···O3	0.913	2.480	167.75	3.377	x, y+1, z-1
O41-H41B···O2	0.828	1.942	157.50	2.726	-x+1, -y+1, -z+1
O41-H41A···O12	0.840	1.823	177.84	2.662	-x+1, -y+1, -z+1
C32-H32A···O11	0.960	2.588	126.55	3.253	x, y, z
N21-H21A···O1	0.826	2.207	176.18	3.032	x-1, y, z
N21-H21B···O12	0.840	2.620	155.03	3.399	x, y, z
D= Donor and A= Acceptor					