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Notes

Synthesis and structure characterization of $[Co(H_2O)_2(DMSO)_2(4\text{-nba})]4\text{-nba}$ (DMSO = dimethylsulfoxide; 4-nba = 4-nitrobenzoate)

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Dissolution of a fine powder obtained by mechanochemical grinding of cobaltous carbonate with 4-nitrobenzoic acid (4-nbaH) in hot dimethylsulfoxide (DMSO) followed by slow evaporation of the solvent resulted in the formation of *cis*-diaquabis(dimethylsulfoxide)4-nitrobenzoatocobalt(II) 4-nitrobenzoate **1** in good yield. The title compound $[Co(H_2O)_2(DMSO)_2(4\text{-nba})]4\text{-nba}$ **1** crystallizes in the centrosymmetric monoclinic $P2_1/c$ space group. The structure of **1** consists of two crystallographically independent Co(II) ions. Each unique cobalt exhibits octahedral geometry and is bonded to a pair of terminal aqua ligands situated *cis* to each other and a bidentate 4-nba ligand which form the square base of the octahedron. A pair of DMSO ligands disposed *trans* to each other complete the hexa coordination around the central metal. The $[Co(H_2O)_2(DMSO)_2(4\text{-nba})]^+$ cations and the 4-nba anions are interlinked with the aid of several weak H-bonding interactions. A comparative study of several 4-nitrobenzoate compounds of cobalt is described.

Keywords: Mechanochemical synthesis, 4-nitrobenzoate, Dimethylsulfoxide, Crystal structure, cis-diaquabis (dimethylsulfoxide)4-nitrobenzoatocobalt(II) 4-nitrobenzoate

The isomeric phthalic acids and their corresponding nitrobenzoic acid counterparts obtained by replacement of a –COOH group by a $–NO_2$ functionality are isoelectronic compounds. However, in terms of their reactivity characteristics towards metal ions they exhibit altogether different behavior. For example, terephthalic acid (also known as benzene 1,4-dicarboxylic acid and abbreviated as 1,4-BDC) has been extensively used as a linker to assemble metal-organic framework (MOF) materials since the first report[1] on $[Zn_4O(1,4\text{-BDC})_3(DMF)_8(C_6H_5Cl)]$ (DMF=dimethylformamide) referred to as MOF-5. The reaction of 1,4-BDC with Co(II) has been shown to result in the formation of [Co(1,4-BDC)DMF] designated as MOF-71 which is a framework constructed from rod-shaped secondary building units[2]. In contrast to 1,4-BDC which extends the structure due to metal binding by both the carboxylate moieties disposed *trans* to each other, only the –COOH group of 4-nitrobenzoic acid (4-nbaH) is involved in metal binding. Binding of nitro oxygen has been reported for a few alkali metals like Na, K, Rb and Cs[3,4]. In general, the oxygen of the nitro group is not involved in metal binding in the case of transition metals. The nitro functionality situated *trans* to –COOH moiety is not involved in metal binding but instead the oxygen atoms of the nitro group function as H-acceptors resulting in interesting supramolecular network structure as reported by us in a previous study on $[Co(H_2O)_4(4\text{-nba})_2]\cdot 2H_2O$ (4-nba=4-nitrobenzoate)[5].

We are investigating the chemistry of 4-nbaH with both *d*-block[6,7] and s-block[8] metals and our studies have revealed a rich structural chemistry of metal 4-nitrobenzoates. During the course of our studies, an attempt to synthesize an anhydrous Co(II)-bis (4-nitrobenzoate) via a mechanochemical route resulted in the formation of the title compound viz. *cis*-diaquabis(dimethylsulfoxide)4-nitrobenzoatocobalt(II) 4-nitrobenzoate **1**. The results of these investigations are described herein.

Experimental

All the chemicals used in this study were of reagent grade and were used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. The known compound $[Co(H_2O)_4(4\text{-nba})_2]\cdot 2H_2O$ **1a** was prepared by a reported procedure[5]. The infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000–400 cm^{-1}. Optical spectra were recorded using Agilent 8453 UV-Vis spectrophotometer. Raman spectra were recorded using 785 nm radiation for excitation on an Agiltron Peak Seeker Pro Raman instrument from 4000 to 200 cm^{-1}. Isothermal mass loss studies were performed in a temperature-controlled electric muffle furnace.

The crystal structure of compound **1** was determined using a Bruker D8 Quest Eco X-ray diffractometer. Intensity data were collected at room temperature (RT) using monochromated Mo (Kα) (λ = 0.7107 Å) radiation. The program suite APEX3 (Version 2018.1) was used (i) to integrate the frames, (ii) to perform absorption correction and (iii) to determine unit cell. The structure was solved with SHELXS and subsequent refinements were performed with SHELXL[9]. 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. Technical details of data acquisition and selected crystal refinement results are given in Table 1.

Synthesis of $[Co(H_2O)_2(DMSO)_2(4\text{-nba})]4\text{-nba}$ (1)

A mixture of cobaltous carbonate (0.297 g, 2.5 mmol) and 4-nitrobenzoic acid (0.835 g, 5 mmol) was ground well in a mortar and pestle for ~10 min. The fine powder obtained by grinding was taken in a beaker and to this DMSO (~3 mL) was added. The reaction mixture was heated on a water bath for some time (~10 min) in order to dissolve the mixture. On heating, the pale pink solution changed its colour to blue and after cooling regains its original colour. The reaction mixture was cooled and left undisturbed at room temperature for crystallisation. The pink crystals which were obtained after five days were filtered off and washed with dichloromethane and dried in air. Yield 1.02 g, IR data (KBr cm^{-1}): 3417, 3000–2500 (br), 1573, 1427, 1346, 1101, 1004, 950, 877, 840, 796, 723, 522, 439 cm^{-1}.

Table 1 — Selected refinement data for $[Co(H_2O)_2(DMSO)_2(4\text{-nba})]4\text{-nba}$ **1**

Empirical formula	$C_{18}H_{24}CoN_2O_{12}S_2$
Formula weight (g mol^{-1})	583.44
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	12.2689(3)
b(Å)	14.8553(4)
c (Å)	26.5011(8)
α(°)	90
β(°)	96.8470(10)
γ(°)	90
Volume (Å^3)	524.33(7)
Z	8
Density (calc.) (mg/m^3)	1.616
Absorption coefficient (mm^{-1})	0.955
F(000)	2408
Crystal size (mm^3)	0.27 × 0.18 × 0.09
Theta range for data collection (°)	2.54 to 28.29
Completeness to theta	99.9%
Index ranges	$-16 \leq h \leq 16, -19 \leq k \leq 19, -35 \leq l \leq 35$
Reflections collected	71117
Independent reflections	11890 [R(int) = 0.0510]
Refinement method	Full-matrix least-squares on F^2
Absorption correction	Multi Scan
Data / restraints / parameters	11890 / 0 / 671
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1086
R indices (all data)	R1 = 0.0865, wR2 = 0.1374
Largest diff. peak and hole (e.Å^{-3})	1.479 and –0.522

Raman Data (cm^{-1}): 3923, 3089, 3007, 2923, 1591, 1512, 1416, 1368, 1333, 1097, 988, 941, 866, 790, 714, 680, 624 cm^{-1}.

In another method compound **1a** (0.5 g) was crushed to a fine powder and then dissolved in ~5 mL DMSO and the clear solution thus obtained was left undisturbed for crystallization. After a few days pink crystals were obtained. These were filtered and washed with dichloromethane. Yield 90%. The IR spectrum of the product thus obtained was identical to the spectrum obtained earlier.

Results and Discussion

Synthesis, spectral and thermal studies

In an earlier study we demonstrated that an aqueous reaction of cobaltous carbonate with 4-nbaH followed by crystallization will result in the formation of the tetraaquadihydrate Co(II) compound $[Co(H_2O)_4(4\text{-nba})_2]\cdot 2H_2O$ **1a**, which on heating can be fully dehydrated to the blue anhydrous $[Co(4\text{-nba})_2]$ compound. With a view to prepare crystals of the anhydrous Co(II) compound for a structure study, a mixture of $CoCO_3$ and 4-nbaH were ground well and the finely powdered mixture was taken in hot DMSO for dissolution. While the hot DMSO solution appeared blue, crystallization of the reaction mixture afforded pink crystals of **1**. Our efforts to isolate a blue compound from this reaction mixture have not been fruitful. Analysis of the pink compound **1** revealed that it contains both water and DMSO in addition to Co and 4-nba with the composition being Co:water:DMSO: 4-nba being 1:2:2:2. In view of this, another experiment was performed by grinding compound **1a** and dissolving it in DMSO. This methodology also afforded pink crystals whose infrared spectrum is identical to that of compound **1**. A comparison of the IR spectra of compounds **1** and **1a** reveals noticeable similarities and differences (Supplementary data, Fig. S1). Both the spectra are nearly identical in the region 2000–1200 cm^{-1}. Although the profile of the spectra in the 3500–3000 cm^{-1} are quite different, the broad signal centred at ~3417cm^{-1} can be attributed for the –OH stretching vibration of the terminal water ligand. The band centred at 1573 cm^{-1} can be attributed to the carboxylate vibration and a band at 1346 cm^{-1} for the symmetric stretching vibration of the nitro group. The most intense signal that appears at around 1340 cm^{-1} in the Raman spectrum can be assigned for the symmetric stretching vibration of the nitro group (Supplementary data, Fig. S2). Uncoordinated (free) dimethylsulfoxide exhibits a strong signal at ~1050 cm^{-1} in its IR spectrum (Supplementary data, Fig. S3), which can be assigned for the S=O stretching vibration of DMSO[10]. A comparison of the IR spectra of **1** and DMSO (Fig. 1) reveals that the S=O vibration is shifted to lower energies (1004 cm^{-1}) in **1**, which can be explained due to the binding of the sulfoxide oxygen with Co(II) as observed in the single crystal structure (*vide infra*). Unlike the differing IR spectra, the UV-Vis spectra of both **1** and **1a** are nearly identical which can be attributed to the octahedral {CoO_6} chromophore in both compounds (Supplementary data, Fig. S4). The band around 273 nm can be assigned for the intra ligand charge transfer transition of 4-nitrobenzoate.

Unlike the nearly similar UV-Vis spectra, compounds **1** and **1a** exhibit different thermal properties as evidenced by a comparison of the mass loss determined at different temperatures (Supplementary data, Table S1). On heating at 100 °C a mass loss of 7.81% is observed for the water-deficient compound **1**, which is more than the value expected (6.18%) for the loss of two moles of water and can be assigned for a partial loss of DMSO in addition to water. In contrast, the water-rich compound **1a** exhibits a mass loss of 18.01%, accounting for the loss of five moles of water. On further heating, the mass loss increases progressively and at 250 °C a mass loss of 31.95% is observed for **1**, which is in reasonable agreement for the expected value (32.97%) for loss of two water and two DMSO molecules. The final mass loss of ~84.00% at 550 °C for **1** can account for the complete loss of organics and formation of oxide material as evidenced by a featureless IR spectrum of the residue.

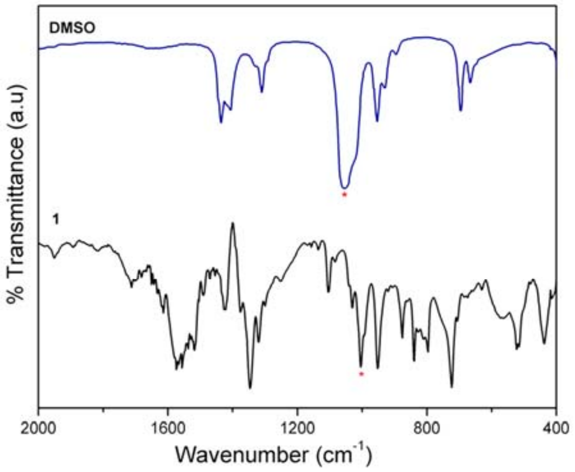

Fig. 1 — Infrared spectra of DMSO (top) and [$Co(H_2O)_2(DMSO)_2$(4-nba)]4-nba **1** (bottom). *is the S=O stretching vibration. For the spectra in the region (4000-2000 cm^{-1}) see Fig. S3. (*Note: The spectrum of DMSO is from https://webbook.nist.gov/cgi/cbook.cgi?ID=C67685&Type=IR-SPEC&Index=2#IR-SPEC*).

Description of crystal structure

The compound [$Co(H_2O)_2(DMSO)_2$(4-nba)](4-nba) **1** crystallizes in the centrosymmetric monoclinic $P2_1/c$ space group with all atoms located in general positions. Its crystal structure consists of two unique Co(II) ions (Co1 and Co2), four crystallographically independent 4-nba anions, four unique DMSO molecules and four crystallographically independent water molecules (Supplementary data, Fig S5). The bond angles and bond distances of the unique 4-nitrobenzoates and the DMSO molecules are in the normal range (Supplementary data, Table S2). Two of the four water molecules viz. O1W and O2W are bonded to Co1 while O11W and O12W are bonded to Co2. Of the four 4-nba anions in the crystal structure, two are uncoordinated while the other two function as bidentate ligands one each for the unique Co1 (O1, O2) and Co2 (O11, O12) respectively. Each unique cobalt in **1** exhibits octahedral geometry and is bonded to a pair of terminal aqua ligands situated *cis* to each other and a bidentate 4-nba ligand which form the square base of the octahedron (Fig. 2). A pair of

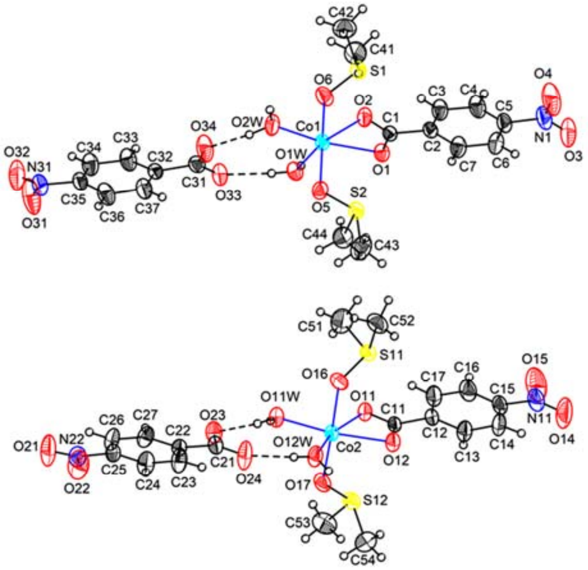

Fig. 2 — The hexa coordination around the unique cobalt (Co1 (top) and Co2 (bottom)) in the crystal structure of [$Co(H_2O)_2(DMSO)_2$(4-nba)](4-nba) **1**. Co-O bonds are shown in blue. Thermal ellipsoids are drawn at the 50% probability level excepting for the H atoms which are shown as spheres of arbitrary radii. Intramolecular H-bonds are shown as broken lines.

DMSO ligands disposed *trans* to each other complete the hexa coordination around the central metal by binding via the oxygen atom. Thus both the unique Co(II) are bonded only to O-donor sites of water (η^1 ligand), DMSO (η^1 ligand) and 4-nba (η^2 ligand).

The *trans* O-Co-O bond angles deviate from the ideal values of 180° and range from 163.64(9) to 176.57(9)° for Co1 (163.45(9) to 177.08(10)° for Co2) while the *cis* O-Co-O angles range from 60.16(7) to 104.24(8)° in Co1 (60.36(7) to 103.88(9)° for Co2) indicating a severe distortion of the $\{CoO_6\}$ octahedron (Table 2). The Co-O bond distances range from 2.046(2) to 2.193(2) Å for Co1 (Table 2) while the Co-O bond lengths vary from 2.049(2) to 2.1965(19) Å for Co2. The two longest Co-O distances of 2.1705(19) and 2.193(2) Å for Co1 (2.16693) and 2.1965(19) Å for Co2) are observed for the carboxylate binding with the unique central metal. The observed Co-O(DMSO) distances (2.073(2) & 2.087(2) for Co1 and 2.061(2) and 2.083(2) for Co2) are in agreement with data reported for Co(II) compounds containing DMSO ligands[11,12].

The H-atoms attached to the terminal water molecules function as H-donors and are involved in O-H···O interactions with the O atoms of the carboxylate of the 4-nba anions (Supplementary Data, Table S3). Each of the free uncoordinated 4-nba anions (O23,O24 and O33,O34) make two intramolecular H-bonds with the $[Co(H_2O)_2(DMSO)_2(4\text{-}nba)]^+$ cation. Out of a total of seven O-H···O bonds five are intramolecular. In addition to the O-H···O interactions, several H atoms attached to the carbon of the methyl group in DMSO and the one H each on the carbon atoms (C26 and C36) of the aromatic ring of the uncoordinated 4-nba anions are involved in several intermolecular C-H···O interactions with the O atoms of DMSO and 4-nba functioning as H-acceptors (Supplementary data, Table S3). The net result of H-bonding is the organisation of the $[Co(H_2O)_2(DMSO)_2(4\text{-}nba)]^+$ cations and the uncoordinated 4-nba anions into alternating layers as can be evidenced from a view of the crystallographic packing along *a* axis (Fig. 3). Based on an analysis of the short ring interactions in **1** using the program Platon[13], the ring centroid to ring centroid distances (Cg···Cg) between adjacent aromatic rings is found to be in the range 4.296 to 4.6032 Å (Supplementary data, Table S4). The shortest distance (Cg3-Cg4 = 4.296 Å) is observed between the free uncoordinated 4-nba anions. As it has been reported that stacking interactions between benzene rings can exist at a very long Cg···Cg distances[14], the observed data reveal the presence of π···π stacking in **1**. (Supplementary data, Fig. S6).

Table 2 — Selected geometric parameters [Å and °] for $[Co(H_2O)_2(DMSO)_2(4\text{-}nba)]4\text{-}nba$ **1**

Bond lengths

Co1-O2W	2.046(2)	Co2-O12W	2.049(2)
Co1-O6	2.073(2)	Co2-O17	2.061(2)
Co1-O5	2.087(2)	Co2-O11W	2.098(2)
Co1-O1W	2.098(2)	Co2-O16	2.083(2)
Co1-O1	2.1705(19)	Co2-O11	2.166(3)
Co1-O2	2.193(2)	Co2-O12	2.1965(19)

Bond angles

O6-Co1-O5	176.57(9)	O12W-Co2-O16	89.56(9)
O2W-Co1-O2	164.37(9)	O12W-Co2-O11W	92.56(10)
O2W-Co1-O1	163.64(9)	O16-Co2-O11W	89.64(9)
O2W-Co1-O6	92.53(10)	O17-Co2-O11	90.49(8)
O6-Co1-O1W	86.76(9)	O11W-Co2-O11	103.88(9)
O5-Co1-O1	89.31(8)	O17-Co2-O12	91.59(8)
O2W-Co1-O2	103.56(9)	O11W–Co2-O12	164.23(9)
O5-Co1-O2	90.57(8)	O12W-Co2-O17	92.06(10)
O1-Co1-O2	60.16	O17-Co2-O16	177.08(10)
O2W-Co1-O5	89.16(9)	O17-Co2-O11W	87.85(9)
O2W-Co1-O1W	92.06(10)	O12W-Co2-O11	163.45(9)
O5-Co1-O1W	90.19(9)	O16-Co2-O11	88.65(8)
O6-Co1-O1	89.91(8)	O12W-Co2-O12	103.22(9)
O1W-Co1-O1	104.24(8)	O16-Co2-O12	90.41(8)
O6-Co1-O2	91.94(8)	O11-Co2-O12	60.36(7)

Comparative study of cobalt 4-nitrobenzoates

In addition to the title compound described in this work, the structures of many cobalt compounds containing 4-nitrobenzoate are reported in the literature[5,15-25] (Table 3). All these compounds which crystallize in centrosymmetric space groups contain a central cobalt which is either tetra or hexa coordinated. Of the fourteen compounds listed in Table 3, the last

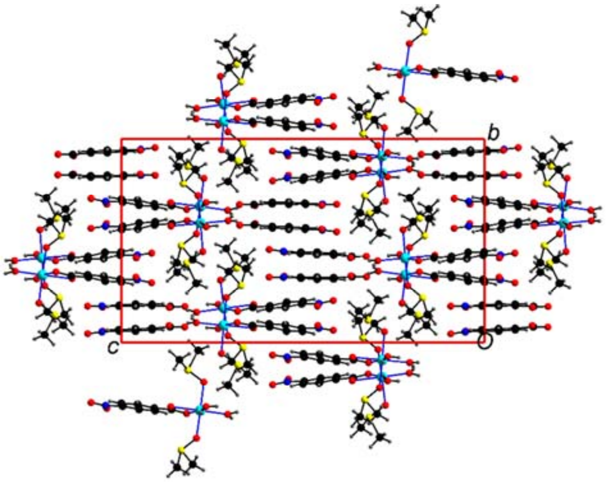

Fig. 3 — A view along *a* axis showing the crystallographic packing of **1**.

Table 3 — Structural features of cobalt 4-nitrobenzoates

No	Compound	Space group	C.N (*)	C.S	4-nba binding mode	Ref
1	[Co(H$_2$O)$_4$(4-nba)$_2$]·2H$_2$O	$P\bar{1}$	6 (2)	{CoO$_6$}	monodentate (η^1)	5
2	[Co(H$_2$O)$_2$(nic)$_2$(4-nba)$_2$]	$P2_1/n$	6 (2)	{CoN$_2$O$_4$}	monodentate (η^1)	15
3	[Co(H$_2$O)$_2$(Im)$_2$(4-nba)$_2$]	$P\bar{1}$	6 (2)	{CoN$_2$O$_4$}	monodentate (η^1)	16
4	[Co$_2$(datrz)$_2$(4-nba)$_2$]$_n$	$P\bar{1}$	4 (1)	{CoN$_3$O}	monodentate (η^1)	20
5	[Co(4-nba)$_2$(DMP)$_2$]	$P\bar{1}$	4 (2)	{CoN$_2$O$_2$}	monodentate (η^1)	21
6	[Co(4-nba)$_2$(py)$_2$]	$C2/c$	4 (2)	{CoN$_2$O$_2$}	monodentate (η^1)	22
7	[Co(4-nba)$_2$(py)$_2$(H$_2$O)$_2$]	$P2_1/c$	6 (2)	{CoN$_2$O$_4$}	monodentate (η^1)	22
8	[Co(Im)$_6$](4-nba)$_2$	$P\bar{1}$	6 (0)	{CoN$_6$}	uncoordinated	23
9	[Co(H$_2$O)$_2$(DMSO)$_2$(4-nba)](4-nba) **1**	$P2_1/c$	6 (1)	{CoO$_6$}	bidentate (η^2); uncoordinated	This work
10	[Co(NH$_3$)$_5$N$_3$](4-nba)$_2$·2H$_2$O$^{\#}$	$P2_1/c$	6 (0)	{CoN$_6$}	Uncoordinated	17
11	[Co(NH$_3$)$_6$]Cl(4-nba)$_2$$^{\#}$	$P\bar{1}$	6 (0)	{CoN$_6$}	Uncoordinated	18
12	[Co(dien)$_2$](4-nba)$_3$)·3H$_2$O$^{\#}$	$P\bar{1}$	6 (0)	{CoN$_6$}	Uncoordinated	25
13	[Co(phen)$_2$(CO$_3$)](4-nba)·5H$_2$O$^{\#}$	$P\bar{1}$	6 (0)	{CoN$_2$O$_4$}	Uncoordinated	24
14	[Co(en)$_2$(NO$_2$)(4-nba)]4nba·4nbaH$^{\#}$	$P\bar{1}$	6 (1)	{CoN$_5$O}	monodentatel(η^1); uncoordinated	19

Abbreviations: C.N (*) = Coordination No. The number in parentheses is the number of 4-nba ligands linked to each unique cobalt; C.S = coordination sphere; 4-nba = 4-nitrobenzoate; nic = nicotinamide; Im = imidazole; Hdatrz = 3,5-diamino-1,2,4-triazole; DMP = 3,5-dimethylpyrazole; py = pyridine; DMSO = dimethylsulfoxide; dien = diethylenetriamine; phen = 1,10-phenanthroline; ; en = ethylenediamine; $^{\#}$Co(III) compound.

five are octahedral Co(III) compounds. In four Co(III) compounds (entry nos 10–13) 4-nba functions as a charge balancing counter anion and is not bonded to Co and in three cases (entry nos 10-12) the central Co is bonded to only N-donor ligands. In the mixed ligand compound (entry no. 14) containing a {CoN$_5$O} octahedron, 4-nba is bonded to Co in a monodentate fashion (η^1). Additionally, this compound contains an uncoordinated 4-nba and a free acid namely 4-nbaH. In seven of the eight earlier reported Co(II) compounds (entry nos. 1–7), the charge balancing 4-nba anion is bonded to the central Co(II) via the carboxylate oxygen in a monodentate fashion (η^1). The title compound is an example containing both uncoordinated and a bidentate 4-nba (η^2) which binds to Co(II) via both the oxygen atoms of the carboxylate group.

Conclusions

The mixed ligand cobalt(II)-4-nitrobenzoate compound described in this report is a new addition to the growing list of structurally characterized cobalt compounds based on the 4-nitrobenzozate ligand.

Supplementary data

Crystallographic data in CIF format containing for the crystal structure of **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1915884. 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). Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(01)51-56_SupplData.pdf.

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References

1 Li H, Eddaoudi M, O'Keeffe M & Yaghi O M, *Nature* 402 (1999) 276.

2 Rosi N L, Kim J, Eddaoudi M, Chen B, O'Keeffe M & Yaghi O M, *J Am Chem Soc*, 127 (2005) 1504.

3 Srinivasan B R, Shetgaonkar S Y, Dhavskar K T, Sundar J K & Natarajan S, *Ind J Chem*, 51A (2012) 564.

4 Smith G, *Acta Crystall,* C71 (2015) 499.

5 Srinivasan B R, Sawant S C & Das S K, *Ind J Chem*, 43A (2004) 1066.

6 Srinivasan B R & G K Rane, *J Chem Sci,* 121 (2009) 145.

7 Srinivasan B R, Sawant J V & Raghavaiah P, *Ind J Chem*, 48A (2009) 181.

8 Srinivasan B R & Dhavskar K T, *Ind J Chem,* 56A (2017) 387 and references therein.

9 Sheldrick G M, *Acta Crystall,* C71 (2015) 3.

10 Silverstein R M, Bassler G C & Morrill T C, *Spectrometric identification of organic compounds*, Fifth Edition, John Wiley (1991) 129.

11 Chan E J, Cox B G, Harrowfield M, Ogden M I, Skelton B W & White A H, *Inorg Chim Acta*, 357 (2004) 2365.

12 Sudo R, Yoshioka D, Mikuriya M & Sakiyama H, *X-ray Structure Analysis Online* 28 (2012) 71.

13 Spek A L, *Acta Crystall,* D65 (2009) 148.

14 Ninković D B, Janjić G V, Veljković D Z, Sredojević D N & Zarić S D, *ChemPhysChem,* 12 (2011) 3511.

15 Hokelek T & Necefoglu H, *Acta Crystall,* 54C (1998) 1242.

16 Xu T G & Xu D J, *Acta Crystall,* E60 (2004) m1131.

17 Bala R, Kaur N & Kim J, *J Mol Struc,* 1003 (2011) 47.

18 Sharma R P, Bala R, Sharma R, Perez J & Miguel D, *J Mol Struc,* 797 (2006) 49.

19 Sharma R P, Sharma R, Bala R, Karaghiosoff K, Klapötke T M & Suter M, *J Coord Chem,* 59 (2006) 651.

20 Yang E C, Liu Z Y, Liu T Y, Li L L & Zhao X J, *Dalton Trans,* 40 (2011) 8132.

21 Chakravorty S, Platts J A & Das B K, *Dalton Trans,* 40 (2011) 11605.

22 Chakravorty S & Das B K, *Polyhedron,* 29 (2010) 2006.

23 Marsh R E, *Acta Crystall,* 65B (2009) 782.

24 Singh A, Sharma R P, Aree T & Venugopalan P, *Cryst Eng* Comm, 15 (2013) 1153.

25 Bala R, Kaur A, Kashyap M & Janzen D E, *J Mol Struct,* 1063 (2014) 203.