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Synthesis, crystal structures and properties of six new mixed ligand cobalt(II) 4-nitrobenzoates

Dedicated to Prof. Sabyasachi Sarkar on the occasion of his 75th birthday

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Abstract

The synthesis, spectral characteristics, thermal properties and single crystal structures of $[Co(N\text{-}meim)_2(4\text{-}nba)_2]$ (N-meim = N-methylimidazole; 4-nba = 4-nitrobenzoate) (**1**), $[Co(2\text{-}meim)_2(4\text{-}nba)_2]$ (2-meim = 2-methylimidazole) (**2**), $[Co(pyr)_3(4\text{-}nba)_2]$ (pyr = pyrazole) (**3**) $[Co(H_2O)_2(form)_2(4\text{-}nba)_2]\cdot form$ (form = formamide) (**4**), $[Co(H_2O)(aceta)_2(4\text{-}nba)_2]$ (aceta = acetamide) (**5**) and $[Co(H_2O)_3(N\text{-}mepyr)(4\text{-}nba)](4\text{-}nba)$ (N-mepyr = N-methylpyrazole) (**6**) are reported. The central Co(II) exhibits tetrahedral geometry in **1** and **2**, and trigonal bipyramidal geometry in **3** and octahedral geometry in **4-6**. In the anhydrous compounds **1-3** as well as the diaqua compound **4**, the monoaqua compound **5** and the triaqua compound **6**, the neutral N-donor coligands or the O-donor amides function as terminal ligands. The aromatic 4-nba ligand exhibits monodentate binding mode in **1-4** and monodentate and bidentate binding in **5**, while **6** contains a free uncoordinated 4-nba in addition to a bidentate 4-nba ligand. A single C-H···O interaction links molecules of **1** into an infinite chain while the N-H···O bonds in **2** result in a two-dimensional network. Compounds **4** and **5** exhibit three varieties of H-bonding. Thermal decomposition of **1-6** results in the formation of spinel oxide. A comparative study of thirty-one structurally characterized cobalt-4-nitrobenzoates is described.

Keywords: Cobalt(II); 4-nitrobenzoate; crystal structure; N-donor ligand; amide; H-bonding

Introduction

As part of our long-standing research interest, we are investigating the chemistry of 4-nitrobenzoic acid (4-nbaH) with both *d*-block [1-3] and *s*-block metals [4, 5]. Our studies using 4-nitrobenzoate (4-nba) as an organic linker have resulted in the structural characterization of molecular solids of Co(II) [1], Ni(II) [2, 3], Mg(II) [4, 6, 7] and Ca(II) [8] as well as several coordination polymers of Ca(II) [9-13], Sr(II) [4] and Ba(II) [5, 14]. The isomeric nitrobenzoic acids (Scheme S1) and their corresponding phthalic acid counterparts obtained by replacement of a $–NO_2$ group by the –COOH group are isoelectronic. However, in terms of their reactivity characteristics towards metal ions nitrobenzoic and phthalic acid 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 report on $[Zn_4O(1,4\text{-BDC})_3(DMF)_8(C_6H_5Cl)]$ (DMF=dimethylformamide) referred to as MOF-5 [15]. 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 [16]. 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. Although nitro oxygen binding has been reported for some *s*-block metals [17-19], the oxygen of the nitro group is generally not involved in metal binding in the case of transition metals. One example of a Cu(II) compound showing nitro oxygen coordination has been reported [20]. In 4-nbaH, the oxygen atoms of the nitro group disposed *trans* to the –COOH moiety function as H-acceptors resulting in interesting supramolecular network structure as reported by us in a very early study on $[Co(H_2O)_4(4\text{-nba})_2]\cdot 2H_2O$ **1a** [1].

In a recent paper, we reported that an attempted synthesis of anhydrous Co(II)-bis(4-nitrobenzoate) via a mechanochemical route starting from the tetraaquadihydrate compound **1a** resulted in the formation of a diaqua compound viz. $[Co(H_2O)_2(DMSO)_2(4\text{-nba})](4\text{-nba})$ containing coordinated as well as free 4-nba [21]. A later synthesis aimed at the substitution of the cis(diaqua) ligands by a bidentate N-donor ligand viz 2,2-bipyridine (bpy) afforded a mixed ligand binuclear Co(II) compound containing monodentate and free 4-nba in addition to bridging and terminal aqua ligands as well as bidentate bpy ligand [22]. In continuation of this theme, we have undertaken the present study to investigate the reactivity characteristics of *in situ* generated **1a** towards a few N-donor and O-donor ligands (Fig. 1) viz. N-methylimidazole (N-meim), 2-methylimidazole (2-meim), pyrazole (pyr), N-methylpyrazole (N-mepyr), formamide (form) and acetamide (aceta), which resulted in the synthesis and characterization of six new mixed ligand Co(II) compounds viz. $[Co(N\text{-meim})_2(4\text{-nba})_2]$ **1**, $[Co(2\text{-meim})_2(4\text{-nba})_2]$ **2**, $[Co(pyr)_3(4\text{-nba})_2]$ **3** $[Co(H_2O)_2(form)_2(4\text{-nba})_2]form$ **4**, $[Co(H_2O)(aceta)_2(4\text{-nba})_2]$ **5** and $[Co(H_2O)_3(N\text{-mepyr})(4\text{-nba})](4\text{-nba})$ **6**. The details of these investigations are described in this paper.

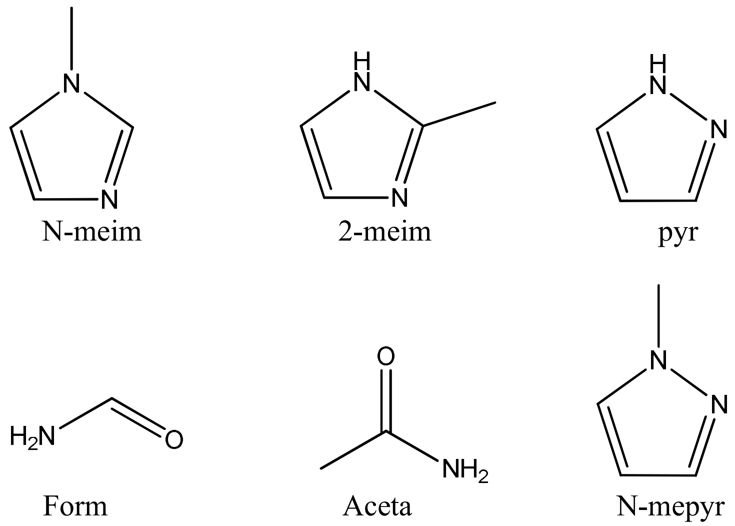


Fig. 1 – Neutral N / O donor ligands used in this study

Experimental Section

All the chemicals were used as received from commercial sources (Table S1) without any further purification. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions in air. The tetraaqua dihydrate compound $[Co(H_2O)_4(4\text{-}nba)_2]\cdot 2H_2O$ **1a** was prepared by a reported procedure [1]. Elemental analyses (C, H and N) were performed on a Variomicro cube CHNS analyser. 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}. Diffuse-reflectance spectra were recorded using a Shimadzu UV-2450 double beam spectrophotometer using $BaSO_4$ as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka-Munk function ($a/S = (1-R)2/2R$, where a is the absorption coefficient, R the reflectance, and S the Scattering coefficient. TG-DTA study was performed in flowing air in Al_2O_3 crucibles at heating rate of 10 min^{-1} using a STA-409 PC simultaneous thermal analyzer from Netzsch. A temperature-controlled furnace was used for pyrolysis. X-ray powder patterns were recorded on a Rigaku SmartLab powder diffractometer using Cu-Kα radiation with Ni filter. The morphology of the cobalt oxides was investigated by scanning electron microscope (FEI-Quanta FEG 200F). The crystal structures of compounds **1 - 6** were determined using a Bruker D8 Quest Eco X-ray diffractometer. Intensity data were collected using monochromated Mo (Kα) ($\lambda = 0.7107$ 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 [23]. The structures were solved with SHELXT [24] and subsequent refinements were performed with SHELXL [25]. In compound **3**, one unique pyrazole ligand exhibits substitutional disorder. The N22 and C21 atoms attached to N21 as well as C22 and C23 are disordered over two positions in the ratio of 50:50 due to the two-fold axis along the Co1-N21 bond. In compound **6**, the unique N-methylpyrazole ligand is disordered over two positions (0.7:0.3) and was refined using a split model. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the aromatic ring were introduced in calculated positions and refined by riding on their respective parent C atoms. The crystallographic details of data acquisition and selected crystal refinement results are given in Table 1.

((Table 1 (in landscape setting is given at the end of the manuscript.))

Synthesis of di(N-methylimidazole)bis(4-nitrobenzoato)cobalt(II) ***1****, bis(2-methylimidazole)-bis(4-nitrobenzoato)cobalt(II)* ***2****, tris(pyrazole)bis(4-nitrobenzoato)cobalt(II) (****3****), trans-di(aqua)di(formamide)bis(4-nitrobenzoato)cobalt(II) formamide solvate* ***4****, mono(aqua)-di(acetamide)bis(4-nitrobenzoato)cobalt(II)* ***5****, tri(aqua)(N-methylpyrazole)4-nitrobenzoato)-cobalt(II) 4-nitrobenzoate (****6****)*

A mixture of commercial cobaltous carbonate (0.250 g, 2.10 mmol) and 4-nitrobenzoic acid (0.668 g, 4.00 mmol) were taken in water (40 mL) and heated on a water bath. On heating, both the insoluble reactants slowly dissolved with the evolution of carbon dioxide resulting in the formation of a red-colored solution. After ~1 h, the above solution containing little undissolved carbonate was filtered and concentrated to 20 mL by heating it over a steam bath followed by the addition of neutral ligands. N-methylimidaole (2.00 mL) for **1** or 2-methylimidazole (0.328 g, 4.00 mmol) for **2** dissolved in ~5 mL water was added to the filtrate. The beaker was left undisturbed at room temperature for crystallization. Within a day, purple-colored crystals were observed. The crystals were washed with diethyl ether and dried to obtain [Co(N-meim)$_2$(4-nba)$_2$] **1** or [Co(2-meim)$_2$(4-nba)$_2$] **2** in 68.1 (0.756 g) or 64.5 % (0.716 g) yield. The use of pyrazole (0.544 g, 8.00 mmol) for **3**, 5 mL of formamide for **4**, acetamide (0.236 g, 4.00 mmol) or 2.00 mL of N-methylpyrazole for **6** afforded crystals of **3** to **6** in 71.3 % (0.849 g), 78.4 % (0.881 g), 76.5 % (0.807 g) and 67.5 % (0.712 g) yield respectively isolated as above. Alternatively, addition of N-methylimidaole (1.00 mL) or formamide (2.50 mL) or N-methylpyrazole (1.00 mL) to a finely powdered sample of tetraaquadihydrate compound **1a**

(0.500 g, 1.00 mmol) resulted in the formation of a clear solution on addition of water (~8 mL). From this, compounds **2** or **4** or **6** could be isolated as above in high yield. Mechanical grinding of **1a** (0.500 g, 1.00 mmol) with 2-methylimidazole (0.164 g, 2.00 mmol) or pyrazole (0.340 g, 5.00 mmol) or acetamide (0.118 g, 2 mmol) for ~20 minutes followed by addition of water (~8 mL) afforded compounds **1** or **3** or **5** which were isolated as above in ~80% yield.

Anal. Calc. for $C_{22}H_{20}CoN_6O_8$ (555.37 g/mol) **1**: C, 47.57; H, 3.64; N, 15.13; Found: C, 47.24; H, 3.52; N, 15.07; IR (KBr, cm^{-1}): 3136, 1959, 1625, 1587, 1514, 1342, 1290, 1238, 1161, 1107, 1010, 952, 877, 831, 796, 742, 723, 673, 655, 631, 567, 526; DTA (^oC): 258(endo), 409(exo).

Anal. Calc. for $C_{22}H_{20}CoN_6O_8$ (555.37 g/mol) **2**: C, 47.57; H, 3.64; N, 15.13; Found: C, 47.16; H, 3.44; N, 14.92; IR (KBr, cm^{-1}): 3275, 1944, 1625, 1587, 1568, 1523, 1344, 1274, 1153, 1130, 1105, 1089, 1012, 933, 879, 833, 798, 758, 725, 673, 582, 528; DTA (^oC): 258(endo), 317(endo), 393(exo)

Anal. Calc. for $C_{23}H_{20}CoN_8O_8$ (595.40 g/mol) **3**: C, 46.39; H, 3.39; N, 18.82; Found: C, 46.02; H, 3.16; N, 18.33; IR (KBr, cm^{-1}): 3317, 1936, 1579, 1523, 1475, 1344, 1273, 1240, 1149, 1107, 1066, 1012, 939, 908, 875, 827, 781, 725, 653, 601, 522; DTA (^oC): 203(endo), 408(exo)

Anal. Calc. for $C_{17}H_{21}CoN_5O_{13}$ (562.32 g/mol) **4**: C, 36.30; H, 3.77; N, 12.46; Found: C, 35.89; H, 3.70; N, 12.25; IR (KBr, cm^{-1}): 3600-2500(br), 1961, 1681, 1568, 1519, 1392, 1346, 1168, 1138, 1105, 1083, 1043, 1012, 887, 819, 800, 773, 729, 640, 526; DTA (^oC): 106(endo), 207(endo), 400(exo)

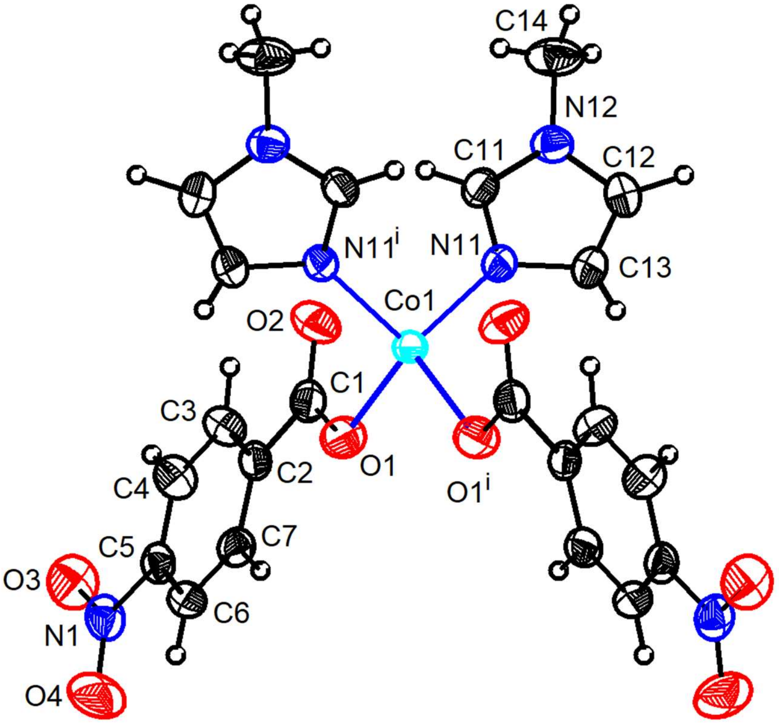
Anal. Calc. for $C_{18}H_{20}CoN_4O_{11}$ (527.31 g/mol) **5**: C, 40.99; H, 3.83; N, 10.62; Found: C, 40.71; H, 3.52; N, 10.27; IR (KBr, cm^{-1}): 3600-2500(br), 1955, 1664, 1579, 1512, 1409, 1346, 1105, 1047, 1010, 875, 798, 723, 580, 514; DTA (^oC): 114(endo), 418(exo)

Anal. Calc. for $C_{18}H_{20}CoN_4O_{11}$ (527.31 g/mol) **6**: C, 40.99; H, 3.83; N, 10.62; Found: C, 40.65; H, 3.57; N, 10.40; IR (KBr, cm^{-1}): 3600-2500(br), 1957, 1587, 1523, 1409, 1346, 1276, 1213, 1170, 1103, 1080, 1049, 1010, 989, 873, 790, 771, 721, 607, 540, 514; DTA (^oC): 112(endo), 222(endo), 395(exo)

Results and Discussion

Description of crystal structures of 1 - 6

In all the six Co(II) compounds described in this section, the geometric parameters (Table S2) of the organic ligands *viz*. 4-nitrobenzoate (4-nba) in **1**-**6**, N-methylimidazole (N-meim) in **1**, 2-methylimidazole (2-meim) in **2**, pyrazole (pyr) in **3**, formamide (form) in **4**, acetamide (aceta) in **5** and N-methylpyrazole (N-mepyr) in **6** are in normal range and are in agreement with reported data [26]. Compounds **1**-**3** crystallize in the centrosymmetric monoclinic space group *C*2/*c* with the central Co(II) situated on a two-fold axis in **1** and **3**. The crystal structure of [Co(N-meim)$_2$(4-nba)$_2$] **1** consists of a central Co(II) situated in a special position, a crystallographically unique monodentate 4-nba ligand and a crystallographically independent N-meim ligand (Fig 2). The coordination environment around the central metal in **1** and **2** is very similar, with the ligands bonded tetrahedrally to the central metal atom resulting in a {CoN$_2$O$_2$} tetrahedron.



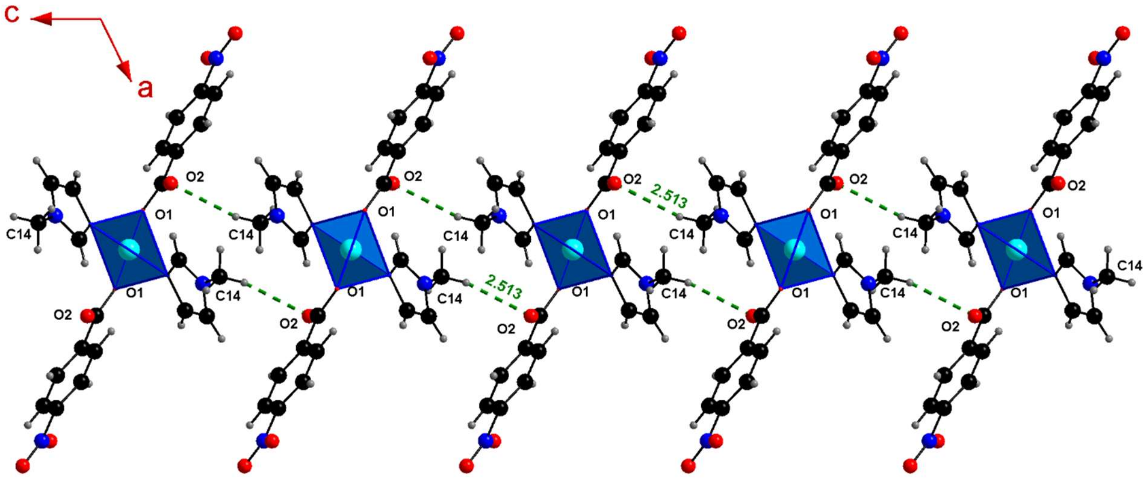


Fig. 2- The crystal structure of **1** showing the atom labelling scheme and the coordination sphere of Co(II). Displacement ellipsoids are drawn at the 30% probability for all the non-hydrogen atoms. Symmetry code: (i) -x+1, y, -z+3/2 (**Top**). Intermolecular C-H···O H-bonding results in the formation of an infinite chain extending along *c*-axis (**Bottom**).

The Co-N bond lengths at 2.026(2) Å are slightly longer than the Co-O bond distances at 1.991(2) Å in **1** (Table 2). The O-Co-O, N-Co-N and O-Co-N bond angle bond angles scatter in a wide range between 92.57(14) 124.55(11)^{o} indicating that the $\{CoN_2O_2\}$ tetrahedron is highly distorted (Table 2). The hydrogen atom (H14B) bonded to C14 is linked via H-bonding (C14-H14B···O2) with the carboxylate oxygen atom of an adjacent molecule (Table 3). This single C-H···O interaction accompanied by a large DHA angle results in the formation of a hydrogen bonded chain of **1** extending along *c*-axis (Fig 2).

((Table 2 (in landscape setting) is given at the end of the manuscript))

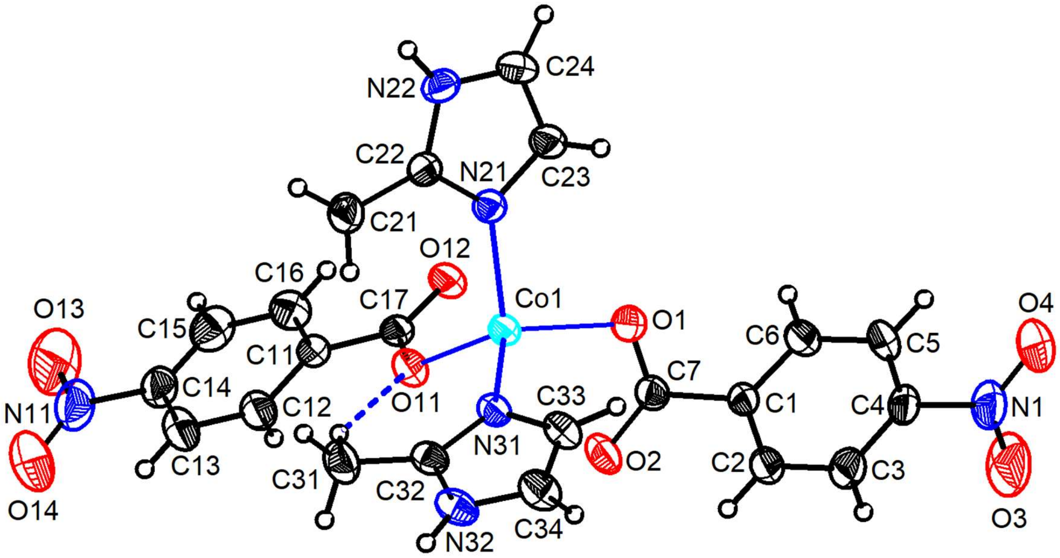
Table 3. Hydrogen bonding geometry [Å and °] for compounds **1 – 6**

D-H···A	*d*(DH)	*d*(H···A)	<(DHA)	*d*(D···A)	Symmetry code
[Co(N-meim)$_2$(4-nba)$_2$] **1**					
C14-H14B···O2	0.87(5)	2.51(6)	3.369(5)	166(5)	-x+1,-y+2,-z+1
[Co(2-meim)$_2$(4-nba)$_2$] **2**					
C21-H21B···O2	0.96	2.55	3.317(4)	136.1	x,y+1,z
N22-H22···O12	0.85(3)	2.31(3)	3.084(3)	152(3)	x,y+1,z
N22-H22···O12	0.85(3)	2.40(3)	3.007(3)	129(3)	-x+3/2,-y+5/2,-z+1
C31-H31C···O11	0.96	2.32	3.188(4)	149.5	x,y,z
N32-H32···O2	0.86	1.92	2.755(3)	163.0	-x+3/2,y+1/2,-z+3/2
C34-H34···O4	0.93	2.65	3.176(4)	116.7	-x+2,y+1,-z+3/2

$[Co(pyr)_3(4\text{-}nba)_2]$ **3**					
N12-H12···O2	0.86	1.83	2.657	161.3	-x+1,y,-z+3/2
$[Co(H_2O)_2(form)_2(4nba)_2]form$ **4**					
O1W-H1W···O41	0.83(3)	1.91(3)	2.734(2)	170(3)	x+1,y,z
O1W-H2W···O22	0.83(3)	1.94(3)	2.724(2)	157(3)	x,y,z
O2W-H3W···O41	0.79(2)	1.93(3)	2.712(2)	173(3)	x,y,z
O2W-H4W···O32	1.01(4)	1.63(4)	2.618(2)	165(3)	x,y,z
C1-H1···O41	0.93	2.64	3.283(2)	126.6	x+1,y-1,z
N1-H1A···O21	0.81(3)	2.23(3)	2.929(3)	145(3)	x,y,z
N1-H1B···O22	0.84(3)	2.34(3)	3.124(3)	157(2)	x,y-1,z
N11-H11A···O1W	0.78(3)	2.49(3)	3.174(2)	147(2)	x-1,y+1,z
N11-H11A···O1	0.78(3)	2.49(3)	3.141(2)	142(2)	x-1,y+1,z
N11-H11B···O2W	0.90(3)	2.32(3)	3.167(3)	158(2)	x,y+1,z
C25-H25···O22	0.93	2.61	3.445(3)	150.4	x-1,y,z
C35-H35···O32	0.93	2.55	3.369(2)	147.5	x+1,y,z
N41-H41A···O11	0.86	2.12	2.936(2)	159.4	x-1,y,z
N41-H41B···O32	0.86	2.20	2.954(2)	145.7	x-1,y+1,z
$[Co(H_2O)(aceta)_2(4nba)_2]$ **5**					
O1W-H1W···O32	0.83(3)	1.95(3)	2.7335(19)	157(3)	-x+1,-y+1,-z+1
O1W-H2W···O22	0.86(3)	1.81(3)	2.667(2)	177(2)	-x+1,-y+1,-z+1
N1-H1B···O31	0.82(3)	2.22(3)	3.040(3)	176(2)	x+1,y,z
N1-H1A···O22	0.85(3)	2.62(3)	3.410(3)	155(2)	x,y,z
C12-H12A···O21	0.96	2.59	3.259(3)	127	x,y,z
N11-H11A···O1	0.91(3)	2.47(3)	3.039(2)	121(3)	-x+1,-y,-z+1
N11-H11A···O11	0.91(3)	2.25(4)	3.122(3)	160(3)	-x+1,-y,-z+1
N11-H11B···O34	0.92(3)	2.48(3)	3.383(3)	168(3)	x,y-1,z+1
$[Co(H_2O)_3(N\text{-}mepyr)(4\text{-}nba)](4\text{-}nba)$ **6**					
O1W-H1WA···O11	0.83(5)	1.89(5)	2.711(4)	172(4)	-x,-y+1,-z+1
O1W-H1WB···O22	0.84(5)	1.89(5)	2.701(4)	163(5)	x,y,z
O2W-H2WA···O21	0.86(5)	1.85(5)	2.705(4)	178(5)	x,y,z
O2W-H2WB···O22	0.84(5)	1.90(5)	2.727(4)	167(5)	-x+1,-y+1,-z+1
O3W-H3WA···O21	0.76(5)	1.93(5)	2.684(4)	170(5)	x-1,y,z
O3W-H3WB···O12	0.81(6)	1.97(6)	2.769(4)	169(6)	-x,-y,-z+1
C23-H23···O24	0.93	2.53	3.395(6)	155	-x+1,y+1/2,-z+1/2

In $[Co(2\text{-}meim)_2(4\text{-}nba)_2]$ **2** all atoms are located in general positions and the structure consists of a unique Co(II) ion, two crystallographically independent monodentate 2-meim ligands and two unique 4-nba ligands (Fig. 3). As in **1**, the Co-O bond lengths 1.9550(19) and 1.9883(19) Å) are shorter than the Co-N bond distances 2.012(2) to 2.032(2) Å). The unique Co-O/N bond distances and the O-Co-N, O-Co-O and N-Co-N bond angles covering a wide range between 96.62(8) to 130.40(9)° indicate a severely distorted $\{CoN_2O_2\}$ tetrahedron in **2** (Table 2).

Unlike a single C-H···O interaction in **1**, a total of three N-H···O interactions involving the H22 and H32 atoms attached to N22 and N32 respectively of the unique imidazole ligands. The H22 atom is involved in a bifurcated hydrogen bond and is bonded to the uncoordinated carboxylate oxygen O12 of two symmetry-related molecules of **2** (Table 3), while the H32 atom is hydrogen-bonded with the free carboxylate oxygen O2 of a neighbouring molecule. The result of H-bonding is the formation of a two-dimensional hydrogen-bonded network in the crystallographic *bc*-plane (Fig. 3, Fig S1).



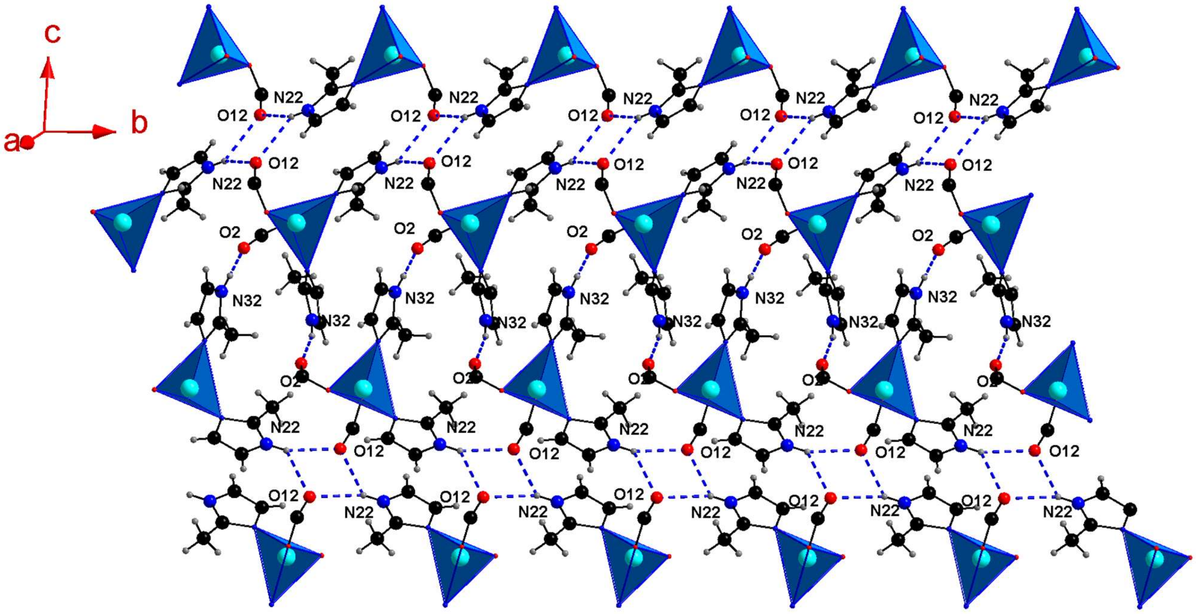


Fig. 3 - The crystal structure of **2** showing the atom labelling scheme and the coordination sphere of Co(II) (**Top**). Displacement ellipsoids are drawn at the 30% probability for all non-hydrogen atoms. Three different intermolecular N-H···O bonding results in the formation of 2D network in *bc*-plane (**Bottom**).

In addition to the central metal Co1 and N21 of a pyrazole (pyr) ligand located on a two-fold axis, the structure of [Co(pyr)$_3$(4-nba)$_2$] **3** consists of each of a crystallographically unique 4-nba and pyr ligands. The N22 and C21 atoms attached to N21 as well as C22 and C23 are disordered over two positions. Unlike **1** (or **2**) the central metal exhibits five coordination in **3** and is bonded to three pyrazole ligands via the imine N atoms (N11, N11$^{\mathrm{i}}$ and N21) and two oxygen atoms of 4-nba ligands resulting in a trigonal bipyramidal {CoN$_3$O$_2$} polyhedron (Fig. 4, Fig. S2).

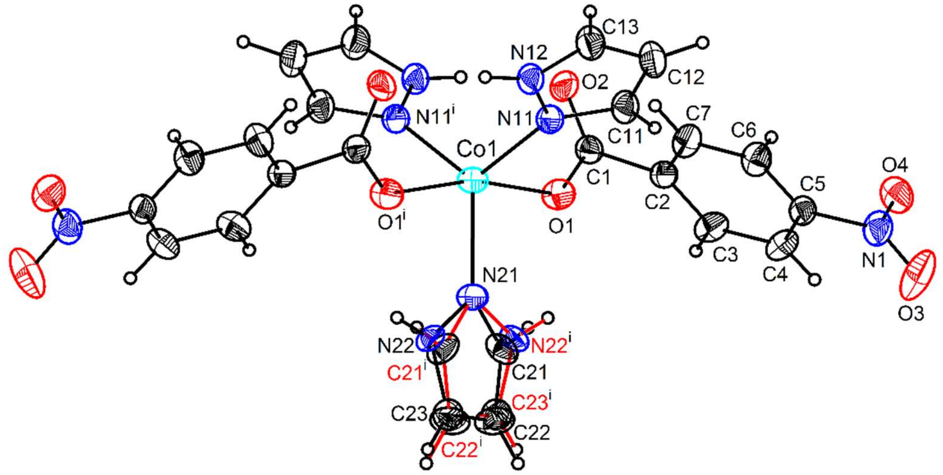


Fig. 4 - The crystal structure of **3** showing the atom labelling scheme and the coordination sphere of Co(II). Displacement ellipsoids are drawn at the 30% probability for all non-hydrogen atoms. Symmetry code: i) 1-x, y, 1.5-z. For a figure showing no disorder see Fig S2.

The pyrazole N atoms occupy the equatorial sites while the symmetry related 4-nba ligands occupy the axial sites. The Co-O bond distance at 2.145(13) Å is slightly longer compared with the Co-N bond lengths (Table 2) of 2.038(15) and 2.046(2) Å. The equatorial N-Co-N angles vary between 116.60(8) and 121.70 (4) °, while the axial O-Co-O angle at 166.84(7)° deviates considerably from the ideal value indicating a distortion of the $\{CoN_3O_2\}$ trigonal bipyramid. Although the H12 atom attached to N12 functions as a hydrogen donor and is hydrogen bonded to the uncoordinated oxygen O2, the disorder of one of the unique pyrazoles, precludes a detailed description of hydrogen bonding in this compound.

In compounds **4** – **6** the central metal exhibits octahedral geometry. The diaqua compound **4** and the monoaqua compound **5** crystallize in the centrosymmetric triclinic space group $P\bar{1}$ with all atoms situated in general positions. The crystal structures of **4** and **5** are nearly similar and consist of a unique Co(II), two crystallographically independent terminal formamide (or acetamide in **5**) ligands, two unique 4-nitrobenzoate ligands. In addition to two terminal aqua ligands (O1W, O2W) disposed trans to each other instead of a single aqua ligand in **5**, compound **4** additionally has a lattice formamide molecule (Fig. 5). Both the unique 4-nba ligands (O21, O31) in **4** are bonded to Co(II) in a monodentate fashion, while the unique 4-nba ligands in **5** exhibit both monodentate and bidentate coordination. The pair of unique formamide ligands in **4** are disposed *trans* to each other while in **5** the amide ligands adopt a cis geometry. It is interesting to note that the pair of aqua ligands as well as the unique 4-nba ligands in **4** are also *trans* to each other resulting in an all-*trans* orientation (Fig. 5). The Co-O bond distances scatter in a narrow range between 2.0598(13) and 2.1499(13) Å in **4** (2.0318(14) to 2.2974(15) Å in **5**). The Co-O(amide) bond distances in **4** at 2.1283(13) and 2.1499(13) Å are longer than the Co-O(aqua) bond lengths while the monodentate 4-nba exhibits the shortest bond distances of 2.0598(13) and 2.0624(13) Å respectively. In contrast, acetamide makes shorter Co-O bonds in **5** than the aqua as well the bidentate 4-nba ligand. The *cis* O-Co-O angles range from 85.35(6) to 96.48(6)°, while the *trans* bond angles vary from 174.80(5) to 177.79(5)° indicating a slight distortion of the $\{CoO_6\}$ octahedron in **4**. In contrast the $\{CoO_6\}$ octahedron in **5** exhibits a severe distortion with *cis* O-Co-O bond angles ranging from 59.19(5) to 115.59(6) and the *trans* O-Co-O bond angles between 147.37(5) and 179.04(6) °.

Compounds **4** and **5** exhibit three varieties of hydrogen bonding interactions viz. O-H···O, N-H···O and C-H···O. All the hydrogen atoms attached to the oxygens of the aqua ligands, and the H atoms attached to the amide N and a few of the H atoms attached to the carbon of the amide ligand or the aromatic C of 4-nba (H1, H25 and H35 in **4**; H12A in **5**) function as H-donors resulting in a total of fourteen hydrogen bonds in **4** (eight H-bonds in **5**) of which three (two in **5**) are intramolecular. The two weak C-H···O interactions in **4** organize the hexacoordinate Co(II) species into an infinite chain (Fig. 6).

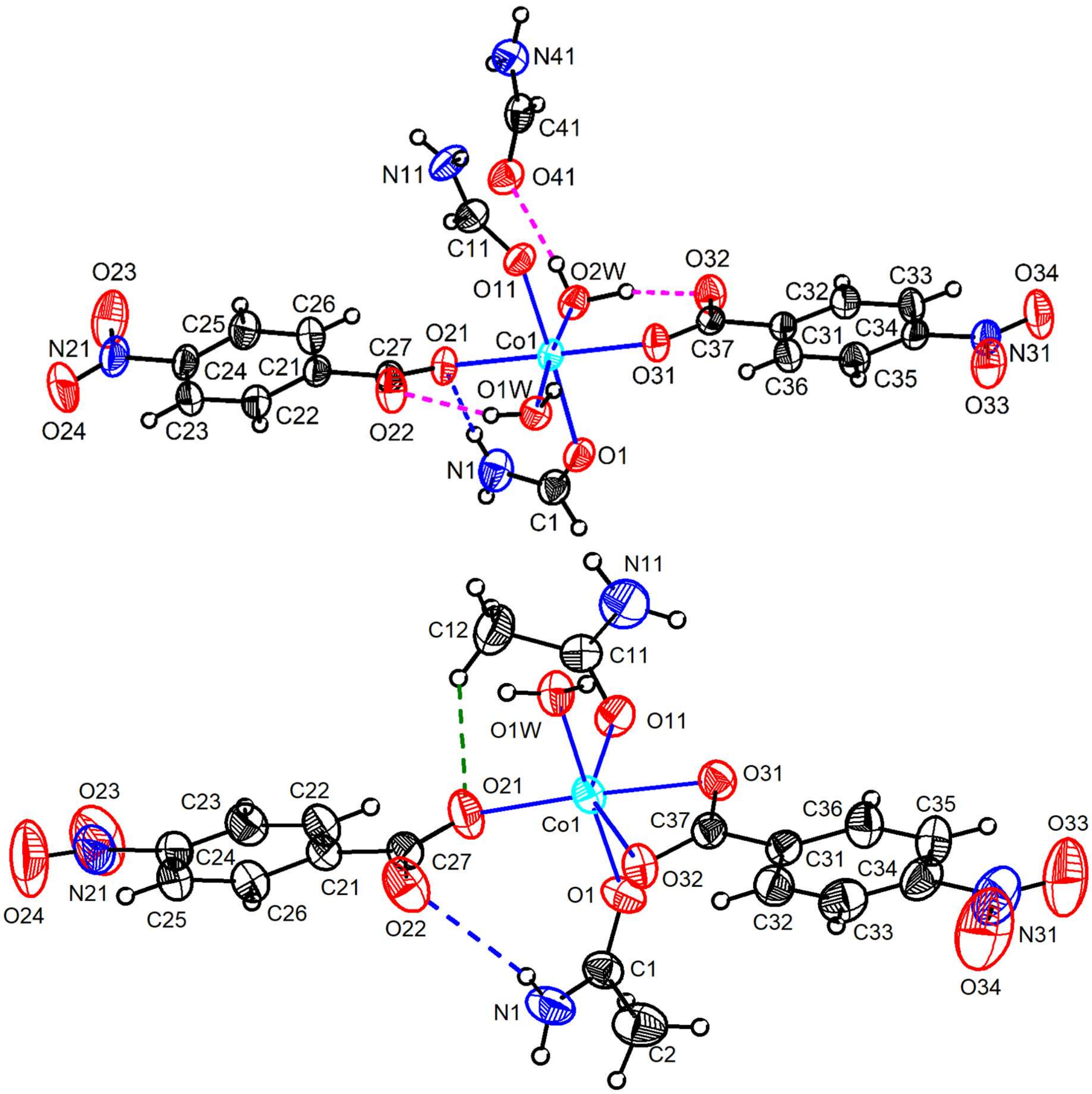


Fig. 5 - The crystal structure of **4** (**Top**) and **5** (**Bottom**) showing the atom labelling scheme and the coordination sphere of Co(II). Displacement ellipsoids are drawn at the 50% probability for all non-hydrogen atoms. Intramolecular H-bonds are shown as broken lines.

The lattice formamide is surrounded by three symmetry related $[Co(H_2O)_2(form)_2(4nba)_2]$ units with the aid of two O-H···O, two N-H···O and one C-H···O interaction (Fig. S3). Each $[Co(H_2O)_2(form)_2(4nba)_2]$ unit is linked via H-bonding with five symmetry related $[Co(H_2O)_2(form)_2(4nba)_2]$ species and two different lattice formamide molecules (Fig. S3). The net result is the formation of a two-dimensional network. As a result of H-bonding, each neutral molecule of **5** is linked with four symmetry related molecules resulting in a two-dimensional network (Fig. S4).

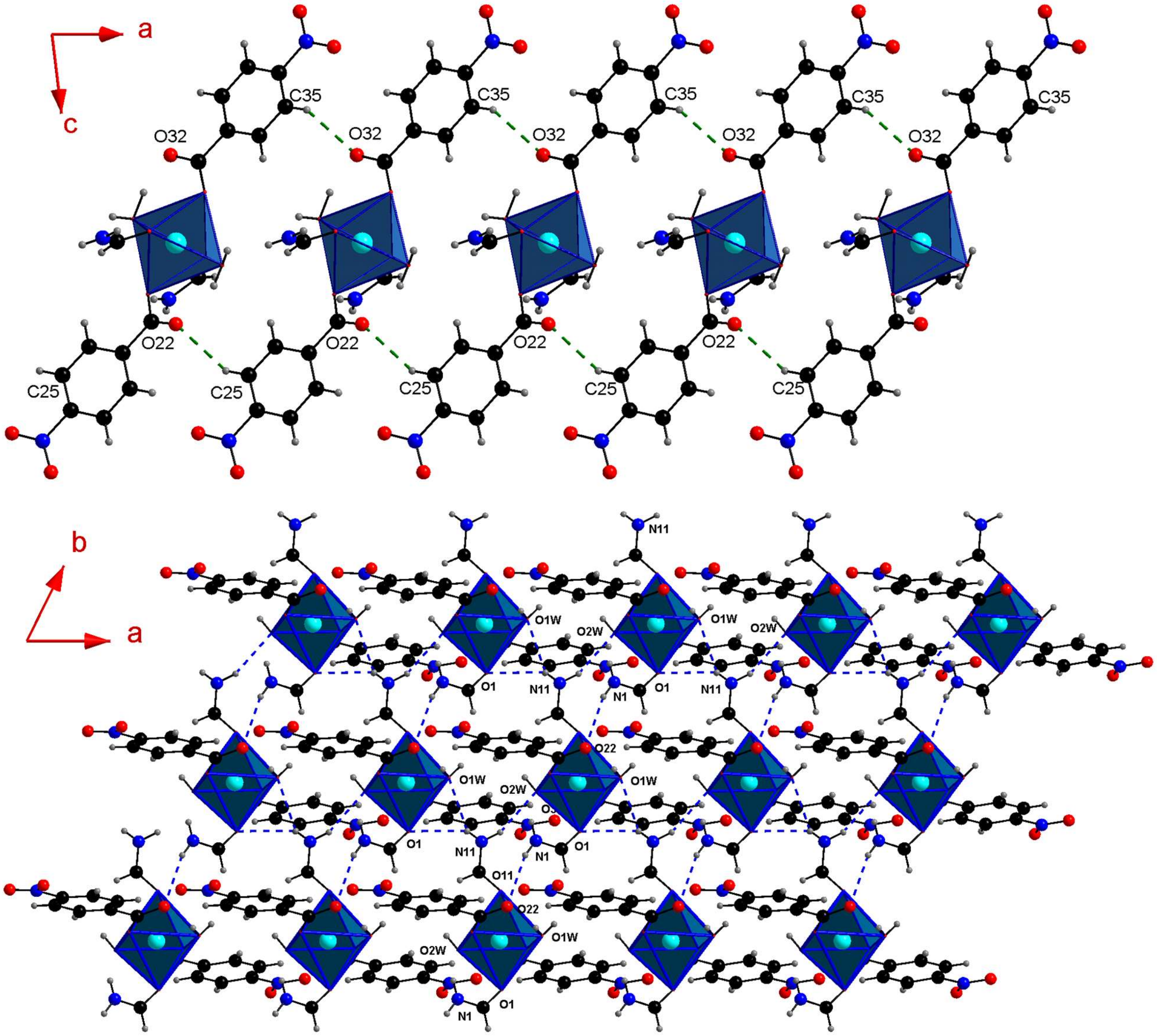


Fig. 6 - The C25-H25···O22 and C35-H35···O32 interactions link the $[Co(H_2O)_2(form)_2(4nba)_2]$ units into an infinite chain extending along *a*-axis (**Top**). The N1-H1B···O22, N11-H11A···O1W, N11-H11A···O1 and N11-H11B···O2W (x, y-1, z; x-1, y+1, z; x-1, y+1, z and x, y+1, z) interactions in **4** result in a 2D network (**Bottom**).

The crystal structure of $[Co(H_2O)_3(N\text{-}mepyr)(4\text{-}nba)](4\text{-}nba)$ **6** consists of a central Co(II), three crystallographically independent terminal aqua ligands (O1W, O2W and O3W), a terminal N-methylpyrazole ligand (N1) which is disordered over two positions (Fig. S5) in 0.7:0.3 ratio and two unique 4-nba one of which is outside the metal coordination sphere (Fig. 7). One unique 4-nba (O11, O12) functions as a bidentate ligand. As in **4** (or **5**), the central metal exhibits hexacoordination forming a $\{CoNO_5\}$ octahedron. The Co-O bond lengths vary from 2.064(3) to 2.260(2) Å. The Co1-N1 bond (2.127(5) Å) (Table 2) is longer than the Co-O(aqua) bond lengths but shorter than the Co-O(carboxylate) bond distances of 2.130(2) and 2.260(2) Å. The distinct bond distances and the *cis* O-Co-O bond angles ranging from 59.65(9) to 104.61(17) accompanied by *trans* O-Co-O bond angles between 156.70(11) and 175.77(13)° indicate a highly distorted $\{CoNO_5\}$ octahedron. All the H-atoms attached to the O of aqua ligands and the H23 attached to C of the free 4-nba function as H-donors. The disordered nature of the N-methylpyrazole ligand precludes a detailed description of the H-bonding.

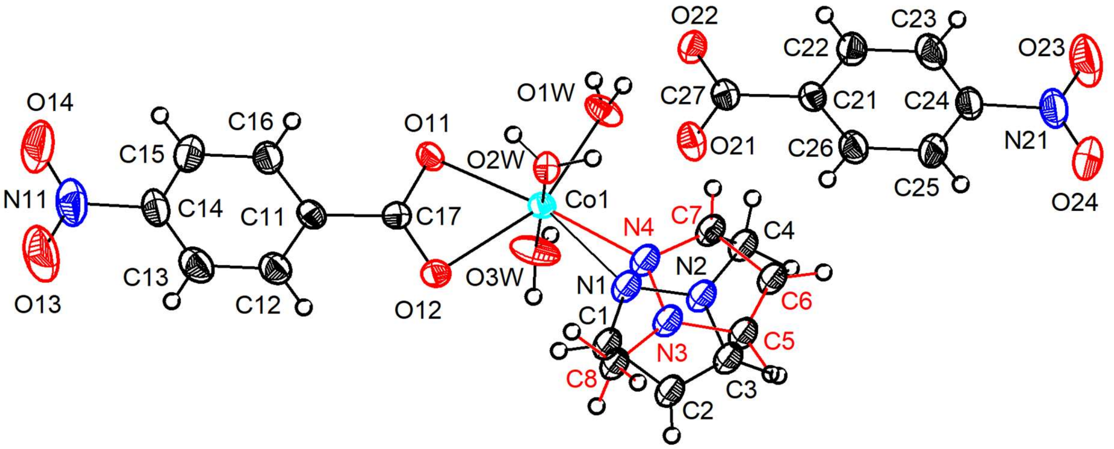


Fig. 7 - The crystal structure of **6** showing the atom labelling scheme and the coordination sphere of Co(II). Displacement ellipsoids are drawn at the 30% probability level for all non-hydrogen atoms. For the disordered N-methylpyrazole ligands see Fig S4.

In order to determine the ring centroid to ring centroid distances (Cg···Cg) between adjacent aromatic rings in **1**, **2**, **4** and **5**, Platon software [27, 28] was used. The values of these are found to be in the range 3.8259(2)–5.5132(2) Å in **1**, (3.5443(15)–5.766(2) Å in **2**, 3.7258(2)–5.1001(3) Å in **4** and 3.8177(15)–5.934(2) Å in **5**) (Table S3). As it has been documented that stacking interactions between aromatic rings can exist at a very long Cg···Cg distances [29], the observed data reveal π···π stacking in **1-2** and **4-5**.

Structural chemistry of cobalt 4-nitrobenzoates

In addition to the compounds described in this work, the structures of many cobalt compounds containing 4-nitrobenzoate are reported in the literature [1, 22, 30-51] and archived in the Cambridge Structural Database (Table 4). The compounds in Table 4 are organized based on the increasing coordination number of cobalt. For the sake of completeness, all known examples (seven entries) containing Co(III) are included. It is interesting to note that all the known compounds crystallize in the centrosymmetric triclinic (space group no. 2) or monoclinic (space group no. 14 and 15) space groups with the central cobalt exhibiting tetra, penta or hexacoordination. The octahedral geometry is the most common (twenty entries), followed by tetrahedral (nine examples) and trigonal bipyramidal geometry. Compound **3** described in this study is a new example of a pentacoordinate Co(II)-4-nitrobenzoate in this series. In all the compounds, excepting entry no. 30 which is organometallic, the central Co is bonded to O and or N donor ligands. Five examples which include compounds **4** and **5** containing exclusively $\{CoO_6\}$ coordination sphere (entry nos. 13, 14, 17, 18 and 21) and four compounds (entry no. 12, 25-27) contain exclusively $\{CoN_6\}$ coordination sphere. In all these compounds 4-nitrobenzoate functions not only as a charge balancing anion but also is coordinated to Co in many cases. In all the Co(III) compounds (entry nos 25-31) 4-nba functions as a charge balancing anion and one example of a Co(III) compound containing both coordinated and free 4-nba is known. Two examples of Co(II) compounds (entry nos 12, 13) containing only free uncoordinated 4-nba anions are known.

Table 4. Structural features of cobalt 4-nitrobenzoates

No	Compound	Space group	C.N (*)	C.S	Binding mode of 4-nba	H-bonding	D	Refcode
1	$[Co_2(datrz)_2(4\text{-nba})_2]_n$	$P\bar{1}$	4 (1)	$\{CoN_3O\}$	monodentate (η^1)	N-H···O	2	OVURUT
2	$[Co_2(atz)_2(4\text{-nba})_2]$	$P\bar{1}$	4 (2)	$\{CoN_2O_2\}$	monodentate (η^1)	N-H···O	2	GIWSEM
3	$[Co(4\text{-nba})_2(DMP)_2]\cdot 0.5H_2O$	$P\bar{1}$	4 (2)	$\{CoN_2O_2\}$	monodentate (η^1)	O-H···O N-H···O C-H···O C-H···C		ICOTIF
4	$[Co_2(4\text{-nba})_4(bix)_2]$	$P\bar{1}$	4(2)	$\{CoN_2O_2\}$	monodentate (η^1)		0	UGILON

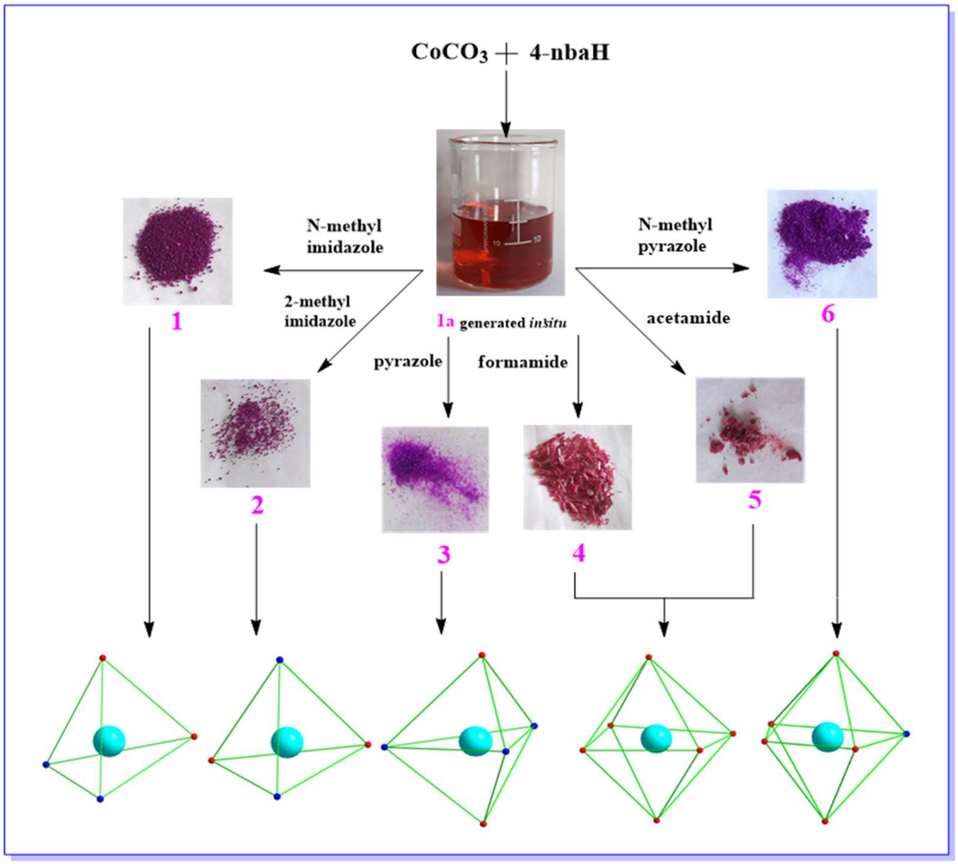
5	[(3,5-Pr$^{i}_{2}$pzH)$_2$Co$_2$(3,5-Pr$^{i}_{2}$pz)$_2$(4-nba)$_2$]	$P\bar{1}$	4(1)	{CoN$_3$O}	monodentate (η^1)	N–H···O	0	KIGHAK
6	[Co(4-nba)$_2$(py)$_2$]	*C2/c*	4 (2)	{CoN$_2$O$_2$}	monodentate (η^1)	C-H···O	0	TURKAT
7	[Co(NIT4-py)$_2$(4-nba)$_2$]	*C2/c*	4 (2)	{CoN$_2$O$_2$}	monodentate (η^1)	C-H···O	0	GUHGEX
8	[Co(N-meim)$_2$(4-nba)$_2$]	*C2/c*	4 (2)	{CoN$_2$O$_2$}	monodentate (η^1)	C-H···O	0	This work
9	[Co(2-meim)$_2$(4-nba)$_2$]	*C2/c*	4 (2)	{CoN$_2$O$_2$}	monodentate (η^1)	N-H···O C-H···O	0	This work
10	[Co(pyr)$_3$(4-nba)$_2$]	$P\bar{1}$	5(2)	{CoN$_2$O$_2$}	monodentate (η^1)	N-H···O C-H···O	0	This work
11	[Co$_2$(L$^{n\mathrm{Pr}}$)(4-nba)](PF$_6$)$_2$	$P\bar{1}$	5(1)	{CoN$_3$O$_2$}	bridging bidentate (μ_2- η^1: η^1)		0	QOZCEO
12	[Co(Im)$_6$](4-nba)$_2$ ·2H$_2$O	$P\bar{1}$	6 (0)	{CoN$_6$}	Uncoordinated	O-H···O N-H···O	0	KICDEG01
13	[Co(H$_2$O)$_6$](qno)(4-nba)$_2$(H$_2$O)$_3$	$P\bar{1}$	6 (0)	{CoO$_6$}	Uncoordinated		0	AYOFAX
14	[Co(H$_2$O)$_4$(4-nba)$_2$]·2H$_2$O	$P\bar{1}$	6 (2)	{CoO$_6$}	monodentate (η^1)	O-H···O	0	BELLEJ
15	[Co(H$_2$O)$_2$(Im)$_2$(4-nba)$_2$]	$P\bar{1}$	6 (2)	{CoN$_2$O$_4$}	monodentate (η^1)	O-H···O N-H···O C-H···O	0	IZAFEU
16	[Co$_2$(4-nba)$_2$(byp)$_2$(H$_2$O)$_4$](4-nba)$_2$	$P\bar{1}$	6(1)	{CoN$_2$O$_4$}	monodentate (η^1); uncoordinated	O-H···O C-H···O	0	PABMOY
17	[Co(H$_2$O)(form)$_2$(4nba)$_2$]·form	$P\bar{1}$	6(2)	{CoO$_6$}	monodentate (η^1)	O-H···O N-H···O C-H···O	0	This work
18	[Co(H$_2$O)$_2$(pmp)$_2$(4-nba)$_2$]·2H$_2$O	$P\bar{1}$	6(2)	{CoO$_6$}	monodentate (η^1)		1	BUXKIQ
19	[Co(4-nba)$_2$(py)$_2$(H$_2$O)$_2$]	*P2$_1$/c*	6 (2)	{CoN$_2$O$_4$}	monodentate (η^1)	O-H···O C-H···O	0	TURKEX
20	[Co(H$_2$O)$_2$(nic)$_2$(4-nba)$_2$]	*P2$_1$/n*	6 (2)	{CoN$_2$O$_4$}	monodentate (η^1)		0	PELLEX
21	[Co(H$_2$O)$_2$(DMSO)$_2$(4-nba)](4-nba)	*P2$_1$/c*	6 (1)	{CoO$_6$}	bidentate (η^2); uncoordinated	O-H···O C-H···O	0	SUKFEM
22	[Co(H$_2$O)$_3$(N-Mepyr)(4-nba)](4-nba)	*P2$_1$/c*	6(1)	{CoNO$_5$}	bidentate (η^2); uncoordinated	O-H···O C-H···O	0	This work
23	[Co(H$_2$O)(aceta)$_2$(4nba)$_2$]	$P\bar{1}$	6(2)	{CoO$_6$}	bidentate (η^2); monodentate (η^1)	O-H···O N-H···O C-H···O	0	This work
24	[Co$_4$O$_4$(4-nba)$_2$(bpy)$_4$](ClO$_4$)$_3$ CH$_3$CN·3H$_2$O	$P\bar{1}$	6(1)	{CoN$_2$O$_4$}	bridging bidentate (μ_2- η^1: η^1)		0	UBOSIN
25	[Co(NH$_3$)$_5$N$_3$](4-nba)$_2$·2H$_2$O$^{\#}$	*P2$_1$/c*	6 (0)	{CoN$_6$}	Uncoordinated	O-H···O N-H···O	0	CACPED
26	[Co(NH$_3$)$_6$]Cl(4-nba)$_2$$^{\#}$	$P\bar{1}$	6 (0)	{CoN$_6$}	Uncoordinated	N-H···O N-H···Cl	0	RENVIQ
27	[Co(dien)$_2$](4-nba)$_3$)·3H$_2$O$^{\#}$	$P\bar{1}$	6 (0)	{CoN$_6$}	Uncoordinated	O-H···O N-H···O	0	QIYGAI
28	[Co(phen)$_2$(CO$_3$)](4-nba)·5H$_2$O$^{\#}$	$P\bar{1}$	6 (0)	{CoN$_2$O$_4$}	Uncoordinated	O-H···O C-H···O	0	LIGSAX
29	[Co(bpy)$_2$(CO$_3$)](4-nba)·5H$_2$O	*P2$_1$/c*	6(0)	{CoN$_4$O$_2$}	Uncoordinated	O-H···O C-H···O	0	HARQEA
30	[Co(X)]4-nba·4-nbaH$^{\#}$	$P\bar{1}$	6(1)	{CoC$_2$N$_3$O}	Uncoordinated		0	VIDMUT
31	[Co(en)$_2$(NO$_2$)(4-nba)]4nba·4nbaH$^{\#}$	$P\bar{1}$	6 (1)	{CoN$_5$O}	monodentate (η^1); uncoordinated	O-H···O N-H···O	0	JEMCEK

Abbreviations: C.N (*) = Coordination No. The number in parentheses is the number of 4-nba ligands linked to each unique cobalt; CS = coordination sphere D = Dimensionality; $^{\#}$Co(III) compound; 4-nba=4-nitrobenzoate; Hdatrz = 3,5-diamino-1,2,4-triazole; atz = 3-amino-1,2,4-triazole; DMP = 3,5-dimethylpyrazole; bix = 1, 4-bis(imidazol-1-yl-methylene)-benzene); 3, 5-Pr$^{i}_{2}$pzH = 3,5-diisopropylpyrazole; py = pyridine; NIT4-py = 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide; py = pyridine; 1-meim = 1-mthylimidazole; 2-meim = 2-mthylimidazole; pyr = pyrazole; L$^{n\mathrm{Pr}}$ = *N*,*N*,*N*',*N*'-tetrakis(2-benzimidazolylalkyl)-2-hydroxy-1,3-diaminopropane; Im = imidazole; qno = quinolone N-oxide; byp = 2,2'-bipyridine; form = formamide; pmp = pyridin-3-yl)methylene)carbonohydrazonoyl)pyridine; nic = nicotinamide; DMSO = dimethylsulfoxide; 1-mepyr = 1-methylpyrazzole; aceta = acetamide; dien = diethylenetriamine; phen = 1,10-phenanthroline; en = ethylenediamine, X = 2-ethoxy-1-[4-nitrobenzene-1-(oxo)methoxy]-2-oxoethyl)-(3,11,17-triazatricyclo[11.3.1.15,9]octadeca-1(17),5(18),6,8,13,15-hexaen-18-yl).

Compound **6** is an example that contains both coordinated and free 4-nba. A survey of the binding modes of 4-nba reveals that the ligand exhibits monodentate (η^1) or bidentate (η^2) or bridging bidentate (μ_2-η^1:η^1) binding modes. The bridging mode results in the formation of a dinuclear compound (entry no 11). All the compounds excepting entry nos 1, 2 and 18 exhibit discrete structures and are zero-dimensional molecular solids. In entry nos 1 and 2, which are two-dimensional coordination polymers as well as entry no. 18 which is a 1D polymer, 4-nba exhibits monodentate binding. It is interesting to note that none of the tetracoordinate Co(II) compounds (entry nos. 1-9) contain coordinated aqua ligand. However, entry no. 3 is a hemihydrate. A study of the secondary interactions (H-bonding) reveals that these compounds can exhibit a maximum of four varieties of H-bonding interactions. Compounds **4** and **5** described in this study exhibit three varieties of hydrogen bonding.

Synthetic aspects, spectral and thermal studies

The tetaaquadihydrate compound $[Co(H_2O)_4)(4\text{-nba})_2]\cdot 2H_2O$ **1a** was first generated *in situ* by reaction of a 1:2 mixture of cobaltous carbonate with 4-nitobenzoic acid in boiling water. Without isolating **1a**, the respective neutral ligand viz. N-meim, 2-meim, pyr, form, aceta and N-mepyr was added to the reaction mixture resulting in the formation of **1** - **6** (Scheme 1). Although the reactions are performed in aqueous medium, only anhydrous compounds **1-3** are obtained in the case of N-meim, 2-meim and pyr. Compounds **1** - **6** can also be synthesized in very high yields by reaction of a finely powdered sample of **1a** with N-meim or form or N-mepyr or a grinding of **1a** with 2-meim or pyr or aceta followed by dissolution in water to isolate the product. A comparison of the X-ray powder pattern of the bulk samples (Fig. S6) with the calculated pattern from the single crystal data reveals that **1-6** are monophasic.



Scheme 1 - Synthetic methodology employed for the synthesis of compounds **1-6**

The infrared (IR) spectra of all the compounds described in this study exhibit several bands in the midIR region indicating the presence of organic moieties (Fig. S7). The anhydrous nature of compounds **1**-3 can be evidenced by the absence of a band in the –OH region (3500 cm^{-1}) The bands at at 3275 and 3317 cm^{-1} respectively in **2** and **3** can be assigned for –NH stretching vibration, which is absent in **1** due to the methylation of the imidazole N. The hydrated compounds (**4** - **6**) exhibit a strong and broad absorption band in the region 2500-3600 cm^{-1} which can be assigned to the –OH stretching vibrations. The symmetric stretching vibrations of -NO_2 group are observed at ~1340 cm-1 in all compounds. The diffused reflectance spectra of **1-6** exhibit two sets of bands in the 200-400 nm region and the 450-650 nm region (Fig. S8). The broad band in the longer wavelength region can be attributed to a *d*-*d* transition of Co(II) while the absorption around 280 nm can be assigned for the absorption of 4-nba.

In addition to TG-DTA experiments, a bulk sample (0.250 g) was pyrolysed in a furnace at 800°C to obtain the residue (Table S4). The IR spectrum (Fig. S9) of the residue is devoid of signals due to the organic moieties revealing formation of an oxidic phase. The powder pattern of the residue obtained upon pyrolysis at 800 °C reveals that Co_3O_4 is formed (matched with JCPDS card no. 00-042-1467) (Fig. S10), which exhibits a spherical morphology of homogeneously distributed particles as evidenced from its SEM image (Fig. S10). Thermal studies reveal that all compounds exhibit a very strong exothermic event at around 400 °C which can be assigned for the decomposition of 4-nba [13-15]. The anhydrous compounds **1** - **3** do not exhibit any significant mass loss till 200 °C. Between 200-320 °C the first endothermic event is observed accompanied by a mass loss which may be due to the loss of the neutral N-meim in **1** (Fig. S11) and 2-meim in **2** (Fig. S11). The absence of mass spectral analysis of the emitted fragments precludes a detailed discussion of the exact nature of the decomposition processes. The strong exothermic peak at ~ 400 °C in **1** and **2** can be attributed to the decomposition of 4-nitrobenzoate giving cobalt oxide, (Co_3O_4) as the final residue which is also confirmed by the pyrolysis study. Similarly, in compound **3**, loss of pyrazole is observed by an endothermic event followed by the exothermic decomposition at 400 °C to form residue (Fig. S11). Compounds **4** - **6** exhibit initial endothermic events that can be attributed to the loss of water followed by removal of neutral ligands. The exothermic signal centred around 400 °C can be assigned for the decomposition of 4-nba resulting in the formation of a spinel oxide.

Conclusions

The synthesis, spectra and structures of six new mixed ligand cobalt(II)-4-nitrobenzoate compounds are reported. The study demonstrates a series of Co(II) 4-nitrobenzoate compounds exhibiting variable coordination sphere and hydration depending on the type of the neutral ligands employed. H-bonding interactions in the compounds yield interesting supramolecular architectures. A comparative study of thirty-one cobalt compounds reveals a rich coordination chemistry of this group of compounds.

Acknowledgments

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Supporting information

CCDC No. 2152448 (**1**) 2152449 (**2**) 2152450 (**3**) 2152451 (**4**) 2152452 (**5**) and 2152453 (**6**) contain the supplementary crystallographic data in CIF format for this paper that have been deposited with the Cambridge Crystallographic Data Centre. 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). Additional figures related to the crystal structure and spectra, are available as 'Supplementary Data' for this article and can be found in the online version.

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Table 1. Crystal data and selected refinement results for compounds **1** - **6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	C_{22} H_{20} Co N_6 O_8	C_{22} H_{20} Co N_6 O_8	C_{23} H_{20} Co N_8 O_8	C_{17} H_{21} Co N_5 O_{13}	C_{18} H_{20} Co N_4 O_{11}	C_{18} H_{20} Co N_4 O_{11}
Formula weight (g mol^{-1})	555.37	555.37	595.40	562.32	527.31	527.31
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71076	0.71076
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions						
a (Å)	26.4960(11)	26.0215(19)	24.789(7)	7.3542(4)	7.469(3)	7.4606(7)
b (Å)	6.6107(3)	7.4081(5)	8.700(2)	7.5325(4)	11.643(4)	9.2330(10)
c (Å)	15.2447(6)	27.556(2)	14.490(4)	22.9600(14)	13.829(5)	32.119(3)
α (°)	90	90	90	85.101(2)	70.659(13)	90
β (°)	116.0900(10)	111.728(2)	125.436(7)	81.672(2)	87.520(14)	96.439(3)
γ (°)	90	90	90	63.349(2)	78.409(11)	90
Volume (Å^3)	2398.13(18)	4934.5(6)	2546.1(12)	1124.46(11)	1111.2(7)	2198.6(4)
Z	4	8	4	2	2	4
D_{calc} (mg/m^3)	1.538	1.495	1.553	1.661	1.576	1.593
Absorption coefficient (mm^{-1})	0.776	0.754	0.739	0.843	0.840	0.849
F(000)	1140	2280	1220	578	542	1084
Crystal size (mm^3)	0.24 x 0.20 x 0.05	0.25 x 0.14 x 0.05	0.26 x 0.22 x 0.13	0.15 x 0.13 x 0.07	0.21 x 0.17 x 0.06	0.19 x 0.14 x 0.04
θ range for data collection (°)	2.98 to 26.36	2.713 to 26.371	2.731 to 28.225	2.690 to 28.269	2.785 to 27.489	2.748 to 28.499
Index ranges	-32 ≤ h ≤ 32 -8 ≤ k ≤ 8 -19 ≤ l ≤ 19	-32 ≤ h ≤ 32 -9 ≤ k ≤ 9 -34 ≤ l ≤ 34	-32 ≤ h ≤ 32 -11 ≤ k ≤ 11 -19 ≤ l ≤ 19	-9 ≤ h ≤ 9 -10 ≤ k ≤ 10 -30 ≤ l ≤ 30	-9 ≤ h ≤ 9 -15 ≤ k ≤ 15 -17 ≤ l ≤ 17	-9 ≤ h ≤ 9 -11 ≤ k ≤ 11 -38 ≤ l ≤ 38
Reflections collected / unique	19223/ 2449 [R(int) = 0.0292]	40153 / 5047 [R(int) = 0.0479]	17177 / 3140 [R(int) = 0.0237]	16680/5551 [R(int) = 0.0327]	15021 / 5070 [R(int) = 0.0253]	24947 / 4084 [R(int) = 0.0395]
Completeness to θ	99.8 %	99.9 %	99.8 %	99.8 %	99.8 %	99.9 %
Absorption correction	MultiScan	Numerical	Numerical	MultiScan	MultiScan	MultiScan
Max. and min. Transmission	0.7454 and 0.6787	0.7247 and 0.6454	0.7114 and 0.6359	0.7457 and 0.6826	0.7458 and 0.6808	0.7448 and 0.6598
Refinement method	Full-matrix least-squares on F^2					
Data / restraints / parameters	2449 / 0 / 208	5047 / 0 / 343	3140 / 7 / 216	5551 / 0 / 357	5070 / 0 / 333	4084 / 3 / 322
Goodness-of-fit on F^2	1.053	1.092	1.058	1.051	1.026	1.219
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1146	R1 = 0.0369, wR2 = 0.0817	R1 = 0.0322, wR2 = 0.0758	R1 = 0.0356, wR2 = 0.0851	R1 = 0.0315, wR2 = 0.0731	R1 = 0.0562, wR2 = 0.1005
R indices (all data)	R1 = 0.0519, wR2 = 0.1230	R1 = 0.0690, wR2 = 0.1040	R1 = 0.0456, wR2 = 0.0873	R1 = 0.0482, wR2 = 0.0936	R1 = 0.0410, wR2 = 0.0797	R1 = 0.0692, wR2 = 0.1049
Largest diff. peak and hole (e Å^{-3})	1.010 and -0.383	0.355 and -0.333	0.248 and -0.305	0.295 and -0.435	0.268 and -0.249	0.383 and -0.405
CCDC No.	2152448	2152449	2152450	2152451	2152452	2152453

Table 2. Bond lengths [Å] and bond angles [°] for **1 - 6**.

1		**2**		**3**		**4**		**5**		**6**	
Co1-O1	1.991(2)	Co1-O11	1.955(19)	Co1-N11	2.038(15)	Co1-O31	2.059(13)	Co1-O21	2.031(14)	Co1-O1W	2.064(3)
Co1-O1^{i}	1.991(2)	Co1-O1	1.988(19)	Co1-N11^{i}	2.038(15)	Co1-O21	2.062(13)	Co1-O11	2.069(13)	Co1-O3W	2.067(3)
Co1-N11	2.026(2)	Co1-N21	2.012(2)	Co1-N21	2.046(2)	Co1-O1W	2.102(14)	Co1-O31	2.145(14)	Co1-O2W	2.070(3)
Co1-N11^{i}	2.026(2)	Co1-N31	2.032(2)	Co1-O1	2.145(13)	Co1-O2W	2.111(14)	Co1-O1	2.069(14)	Co1-N1	2.127(5)
				Co1-O1^{i}	2.145(13)	Co1-O1	2.128(13)	Co1-O1W	2.081(14)	Co1-O11	2.130(2)
						Co1-O11	2.149(13)	Co1-O32	2.297(15)	Co1-O12	2.260(2)
O1-Co1-O1^{i}	92.57(14)	O1-Co1-N21	96.62(8)	N11-Co1-N11^{i}	116.60(8)	O31-Co1-O1W	85.35(6)	O31-Co1-O32	59.19(5)	O1W-Co1-O3W	93.42(14)
N11-Co1-N11^{i}	102.64(13)	O11-Co1-N31	101.37(8)	N11-Co1-N21	121.70(4)	O1W-Co1-O1	87.15(6)	O11-Co1-O31	88.36(5)	O1W-Co1-O2W	90.62(12)
O1^{i}-Co1-N11	107.26(10)	O1-Co1-N31	104.83(9)	N11^{i}-Co1-N21	121.70(4)	O21-Co1-O11	87.78(5)	O1-Co1-O11	88.42(6)	O3W-Co1-O2W	175.77(13)
O1-Co1-N11^{i}	107.26(10)	O11-Co1-N21	110.63(9)	N11-Co1-O1	88.37(6)	O1W-Co1-O11	87.70(5)	O1-Co1-O32	88.22(6)	O1W-Co1-N1	104.61(17)
O1-Co1-N11	124.55(11)	N21-Co1-N31	113.12(9)	N11^{i}-Co1-O1	98.56(6)	O2W-Co1-O1	88.70(6)	O1W-Co1-O31	89.37(6)	O3W-Co1-N1	92.70(18)
O1^{i}-Co1-N11^{i}	124.55(11)	O11-Co1-O1	130.40(9)	N21-Co1-O1	83.42(4)	O31-Co1-O1	89.58(5)	O1-Co1-O31	89.81(6)	O2W-Co1-N1	85.07(16)
				N11-Co1-O1^{i}	98.56(6)	O21-Co1-O2W	90.14(6)	O21-Co1-O1W	90.16(7)	O1W-Co1-O11	97.10(11)
				N11^{i}-Co1-O1^{i}	88.38(6)	O31-Co1-O11	90.71(5)	O21-Co1-O1	90.62(6)	O3W-Co1-O11	90.11(14)
				N21-Co1-O1^{i}	83.42(4)	O31-Co1-O2W	91.65(6)	O1W-Co1-O32	90.93(6)	O2W-Co1-O11	90.63(11)
				O1-Co1-O1^{i}	166.84(7)	O21-Co1-O1W	92.96(6)	O11-Co1-O1W	92.05(6)	N1-Co1-O11	157.88(16)
						O21-Co1-O1	91.77(5)	O21-Co1-O11	96.90(6)	O1W-Co1-O12	156.70(11)
						O2W-Co1-O11	96.48(6)	O21-Co1-O32	115.59(6)	O3W-Co1-O12	88.53(12)
						O1-Co1-O11	174.80(5)	O11-Co1-O32	147.37(5)	O2W-Co1-O12	88.25(10)
						O1W-Co1-O2W	174.89(6)	O21-Co1-O31	174.74(5)	N1-Co1-O12	98.47(16)
						O31-Co1-O21	177.79(5)	O1-Co1-O1W	179.04(6)	O11-Co1-O12	59.65(9)

Symmetry transformations used to generate equivalent atoms: i) -x+1,y,-z+3/2