Synthesis, spectroscopy, thermal studies and supramolecular structures of two new alkali-earth 4-nitrobenzoate complexes containing coordinated imidazole

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Abstract.   The reaction of hydrated magnesium or calcium 4-nitrobenzoate (4-nba) generated *in situ*, with imidazole (Im) results in the formation of the complexes $[Mg(H_2O)_2(Im)_2(4\text{-nba})_2]$ **1** and $[Ca(H_2O)_3(Im)(4\text{-nba})_2] \cdot Im$ **2**, which exhibit the same metal:4-nba:Im ratio but different degrees of hydration. Complex **1** crystallizes in the triclinic $P\bar{1}$ space group and the Mg atom is located on an inversion centre, while **2** crystallizes in the monoclinic $P2_1/c$ space group and all atoms are located in general positions. In **1** the Im ligands, which are *trans* to each other, are coordinated to Mg, while **2** contains coordinated as well as free Im. The monodentate 4-nba ligands are disposed *trans* to each other in **1**, while they adopt a *cis* orientation in **2** resulting in different supramolecular structures. Complex 1 exhibits two types of H-bonding interactions namely O–HΛO and N–HΛO, while in **2** three varieties of H-bond, viz. O-HΛO, N–HΛO and O–HΛN are observed. The Im ligand functions as a bifurcated H-bond donor in **1** while the O atom of the nitro group functions as a H-bond acceptor. In contrast, the nitro group in **2** is not involved in any H-bonding interactions. The free Im in **2** functions as a bifurcated acceptor and forms an extended chain linking adjacent complex molecules. The chains thus formed are further cross-linked with the aid of H-donor bonds from both the free as well as the coordinated Im. Both **1** and **2** exhibit π–π stacking interactions. Complex **1** is thermally more stable as compared to **2**, and both complexes can be dehydrated to the corresponding anhydrous complexes by heating at 140 and 100°C respectively. At elevated temperatures, both the complexes can be pyrolysed to the corresponding oxide. The anhydrous complexes can be rehydrated to obtain the starting hydrated materials.

Keywords.   4-Nitrobenzoate; imidazole; supramolecular; monodentate; H-bonding interactions; bifurcated donor; bifurcated acceptor; π–π interactions.

1.   Introduction

The designed construction of extended metal-organic network systems is an area of intense research investigations in recent years[1] and a variety of organic–inorganic compounds containing benzene substituted carboxylic acid and or N-donor ligands as the organic part have been structurally characterized. The structures of these compounds are held together by strong metal–ligand bonding and further stabilized by weaker bonding forces such as hydrogen bonding and π–π interactions. The importance of H-bonding interactions for the assembly of supramolecular structures is well documented in the literature.[2,3] A convenient way to build infinite polymeric structures

is by using a multi-functional ligand to link metal ions to form an infinite configuration. In this context, substituted benzene carboxylic acids have been shown to be very useful reagents by several research groups, as evidenced by the impressive array of interesting metal-organic molecular architectures synthesized from these types of ligands.[4-8] The advantage of using benzene-based ligand systems is due to the fact that donor groups like –COOH, –SH, –NH$_2$ etc. can be anchored onto the rigid six-membered benzene ring and the resulting supramolecular structures will largely depend on the positioning of the donor groups on the ring. The donor groups on the six-membered ring can also participate in weak H-bonding interactions in addition to the formation of a metal–ligand bond. Further, the positioning of the different donor moieties with respect to each other on the

benzene ring can be changed. In this context, a rich structural chemistry of the biologically relevant alkali and alkali-earth metals has been recently developed with amino as well as mercapto benzoic acids.[9–15] As part of an ongoing programme, we are investigating the chemistry of metal complexes of 4-nitrobenzoic acid (4-nbaH) to exploit the H-bonding capabilities of the nitro functionality.[16–18] The versatile ligational behaviour of the 4-nitrobenzoate (4-nba) ligand is well documented in the literature.[17–30] Although the nitro group lacks the donor characteristics of the amino functionality to exhibit strong metal-ligand interactions, it can participate in H-bonding interactions by forming H-acceptor bonds and these interactions not only affect the properties of the resulting compounds but also lead to interesting supramolecular architectures.[17,18] In continuation of this theme, we wish to present the synthesis, spectroscopic, thermal and structural characterization of two new alkali-earth 4-nitrobenzoates containing imidazole (Im) ligands.

2. Experimental

2.1 *Materials and methods*

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 routinely prepared under normal laboratory conditions. The complex $[Mg(H_2O)_6](4\text{-}nba)_2\cdot 2H_2O$ was prepared as described earlier.[16] Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FTIR spectrometer in the range 4000–400 cm^{-1}. The samples for the IR were prepared as KBr diluted pellets in the solid state and the signals referenced to polystyrene bands. Electronic spectra were recorded using matched quartz cells on a Shimadzu (UV-2450) spectrophotometer. The water content of the synthesised complexes were estimated by Karl-Fischer titration. NMR spectra were recorded on a Bruker WT 300 MHz FT-NMR spectrophotometer. Single crystal X-ray diffraction study was performed at the single crystal X-ray facility at IIT, Kanpur (**1**) and at University of Hyderabad (**2**). The insoluble 4-nbaH obtained on acid treatment of the complexes was weighed as described earlier[16] and metal analysis was performed titrimetrically following a standard procedure.[31] Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller.

2.1 *Preparation of $[Mg(H_2O)_2(Im)_2(4\text{-}nba)_2]$ 1 and $[Ca(H_2O)_3(Im)(4\text{-}nba)_2]\cdot Im$ 2*

Method 1 – A mixture of magnesium carbonate (0·84 g, 10 mmol) and 4-nbaH (3·34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO_2. At this stage the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered into a warm aqueous solution (5 ml) of Im (2·72 g, 40 mmol) and the entire reaction mixture was concentrated to half the volume and left undisturbed for 3–4 days. The crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuo. Yield: 77%. The use of $CaCO_3$ instead of $MgCO_3$ in the above reaction resulted in the formation of $[Ca(H_2O)_3(Im)(4\text{-}nba)_2]\cdot Im$ **2** in 78% yield. The crystals obtained in this method were suitable for X-ray structure investigations.

Analysis – Found (calc.) for $C_{20}H_{18}MgN_6O_{10}$, **1**: Mg 4·65 (4·62); 4-nbaH 62·08 (63·46); MgO 7·83 (7·66)%.

IR data in cm^{-1}: 3375(*s*), 3151(*s*), 3078(*m*), 3049(*m*), 1686(*w*), 1614(*m*), 1566(*s*), 1537(*s*), 1517(*s*), 1493(*m*), 1423(*m*), 1385(*s*), 1348(*s*), 1334(*s*), 1321(*s*), 1256(*m*), 1157(*w*), 1103(*m*), 1072(*s*), 1012(*w*), 975(*w*), 943(*m*), 891(*m*), 842(*m*), 804(*s*), 758(*s*), 727(*s*), 706(*s*), 662(*s*), 613(*s*), 521(*s*).

^{1}H NMR (DMSO-d_6): δ (in ppm); 8·19 (*d*, 2H, $J = 9$ Hz), 8·13 (*d*, 2H, $J = 9$ Hz), 7·69 (*s*, 1H), 7·04 (*s*, 2H).

^{13}C NMR (DMSO-d_6): δ (in ppm) 169·5 (C1), 148·9 (C5), 144·1 (C2), 135·8 (C10), 130·8 (C4, C6), 123·3 (C3, C7), 122·06 (C8, C9).

Analysis – Found (calc.) for $C_{20}H_{22}CaN_6O_{11}$ **2**: Ca 7·32 (7·13); 4-nbaH 59·55 (59·06); CaO 10·37 (9·97)%.

IR data in cm^{-1}: 3640–2560(*br*), 2440(*w*), 1952(*w*), 1813(*w*), 1626(*s*), 1591(*s*), 1514 (*s*), 1493(*m*), 1402(*s*), 1352(*s*), 1321(*s*), 1280(*w*), 1256(*s*), 1173(*m*), 1142(*w*), 1126(*w*), 1105(*m*), 1069(*s*), 1013(*m*), 980(*w*), 934(*m*), 912(*m*), 878 (*m*), 878(*m*), 864(*w*), 839(*s*), 799(*s*), 758(*s*), 725(*s*), 662(*s*), 613(*m*), 565 (*w*), 513 (*s*).

^{1}H NMR (D$_2$O): δ (in ppm); 8·05 (*d*, 2H, $J = 9$ Hz), 7·78 (*d*, 2H, $J = 9$ Hz), 7·57 (*s*, 1H), 6·93 (*s*, 2H).

^{13}C NMR (D$_2$O): δ (in ppm) 173·4 (C7, C8), 148·7 (C3, C12), 142·5 (C6, C9), 136 (C15), 129·5 (C4,

C2, C11, C13), 123·3 (C1, C5, C10, C14), 121·7 (C16, C17).

Method II – An aqueous solution of sodium 4-nba generated *in situ* from 4-nbaH (3·34 g, 20 mmol), NaHCO₃ (1·68 g 20 mmol) and water (20 ml) was added into [Mg(H₂O)₆]Cl₂ (2·03 g, 10 mmol) in water (5 ml). This resulted in the formation of a clear solution, which was filtered into an aqueous solution of Im (2·72 g, 40 mmol) in water (5 ml). The pale yellow solution was then concentrated to half its volume by heating on a water bath. The concentrated reaction mixture was kept aside for crystallization. Crystals that separated after 4–5 days were filtered, washed with little ice-cold water (≈ 2 ml), followed by ether and dried in air. The product obtained in this method (yield 63%) analysed satisfactorily and exhibited an identical IR spectrum to that of the product from method I. The use of anhydrous CaCl₂ (1·11 g, 10 mmol) instead of [Mg(H₂O)₆]Cl₂ afforded complex **2** in 62% yield, which analysed satisfactorily.

Method III – A powdered sample of [Mg(H₂O)₆](4-nba)₂·2H₂O (1 mmol, 0·500 g) was heated on a water bath for 15 min. The bright yellow-coloured partially dehydrated compound thus obtained was reacted with an aqueous solution (≈ 5 ml) of imidazole (4 mmol, 0·272 g). The clear solution thus obtained was left aside for crystallisation. The product was isolated as described above. **1** can also be prepared by mechanically grinding [Mg(H₂O)₆](4-nba)₂·2H₂O (0·500 g) and Im (0·136 g) for ≈ 20 min, in a mortar and pestle. The compound analysed satisfactorily and exhibited an identical IR spectrum as that of the product from method **1**.

2.2 *Preparation of anhydrous complexes*

A powdered sample of **1** (0·488 g) was heated in an oven at 140°C for ~ 20 min. This resulted in the formation of the anhydrous compound **3**. The observed mass loss of 7·65% is in very good agreement with the expected value (7·29%) for the loss of two moles of water. **2** can be similarly dehydrated, by heating at 100°C on a water bath to obtain **4**.

IR data for **3** in cm⁻¹: 3282(*m*), 3132(*s*), 2955(*m*), 2860(*m*), 1639(*s*), 1618(*s*), 1584(*s*), 1516(*s*), 1414(*s*), 1346(*s*), 1258(*w*), 1163(*w*), 1101(*m*), 1066(*s*), 1012(*m*), 977(*w*), 937(*m*), 875(*m*), 827(*s*), 800(*s*), 767(*s*), 727(*s*), 665(*s*), 617(*s*), 522(*s*).

IR data for **4** in cm⁻¹: 3222(*s*), 3161 (*sh*), 3143(*sh*) 3114(*sh*), 3063(*sh*), 2950(*m*), 2853(*m*), 2702(*w*), 1947(*w*), 1713(*w*), 1618(*sh*), 1607(*sh*), 1583(*s*), 1522(*s*), 1489(*w*), 1434(*w*), 1403(*s*), 1347(*s*), 1321(*s*), 1262(*m*), 1168(*w*), 1149(*w*), 1134(*w*), 1106(*w*), 1069(*s*), 1016(*m*), 973(*w*), 964(*w*), 936(*s*), 916(*m*), 880(*s*), 872(*s*), 826(*s*), 802(*s*), 767(*m*), 753(*s*), 741(*s*), 723(*s*), 706(*m*), 692(*m*), 660(*s*), 621(*s*), 556(*w*), 511(*s*), 498(*s*).

2.3 *Rehydration studies*

The anhydrous compounds were prepared as mentioned above. Equilibriation of a powdered sample of **3** or **4** over water vapour, resulted in the formation of the starting compounds **1** or **2** in near quantitative yield in about a day. However, the rehydration of **4** is a slow process and requires a longer duration of about 3 days. The IR spectra of the rehydrated products are identical to that of **1** or **2**.

2.4 *Single crystal X-ray diffractometry*

Intensity data for both the compounds were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71069$ Å). The data integration and reduction were processed with SAINT-PLUS software.[32] An empirical absorption correction was applied to the collected reflections with SADABS[33]. The structures were solved using the WINGX program package[34] with direct methods using SHELXS-97[35] and refinement was done against F^2 using SHELXL-97.[35] All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The H atoms on the N atoms of imidazole ring as well as those of all the coordinated water molecules were located in the difference Fourier maps and refined with fixed isotropic displacement parameters. The technical details of data acquisition and some selected refinement results for both the compounds are summarized in table 1.

3. Results and discussion

3.1 *Synthesis*

The aqueous reaction of Mg or Ca carbonate with 4-nbaH in a 1 : 2 mole ratio followed by addition of Im

Table 1. Technical details of data acquisition and selected refinement results for **1** and **2**.

Compound	$[Mg(H_2O)_2(Im)_2(4\text{-nba})_2]$	$[Ca(H_2O)_3(Im)(4\text{-nba})_2]\cdot Im$
Formula	$C_{20}H_{20}MgN_6O_{10}$	$C_{20}H_{22}CaN_6O_{11}$
Temperature [K]	100(2)	273(2)
Wavelength [pm]	71·073	71·073
Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_{1/C}$
a [Å]	5·533(5)	7·6011(5)
b [Å]	8·122(5)	9·9690(6)
c [Å]	12·775(5)	32·407(2)
α [°]	74·80(1)	90
β [°]	87·39(1)	95·42(1)
γ [°]	87·43(1)	90
Volume [Å³]	553·1(6)	2444·7(3)
Z	1	4
μ [mm⁻¹]	0·154	0·329
$F(000)$	274	1168
Molecular weight [g/mol]	528·73	562·52
Density (calc) [g cm⁻³]	1·587	1·528
hkl Range	−7/6, −10/10, −16/13	−9/9, −12/12, −39/39
2θ range	2·60–28·34	2·14–26·04
Reflections collected	3704	24780
Reflections unique	2636	4822
Data ($Fo > 4\sigma(Fo)$)	2636	4822
R_{int}·	0·0127	0·0304
Min/max transmission		0·9342/0·8743
$\Delta\rho$ [e/Å³]	0·318/−0·381	0·308/−0·187
Parameters	209	379
$R1$ [$Fo > 4\sigma(Fo)$]	0·0446	0·0414
$WR2$ for all unique data	0·1209	0·1042
Goodness of fit	1·010	1·048

results in the formation of the Im coordinated complexes **1** or **2** in good yields. Initially, the hydrated Mg or Ca nitrobenzoates are formed *in situ*,[16,17] which then react with Im to yield the Im containing products. The use of freshly precipitated metal carbonate in the reaction reduces the reaction times for the formation of the hydrated nitrobenzoate complexes as compared to the use of commercial carbonate samples. It is interesting to note that the Im coordinated *bis*(imidazole) complex **1** or the mono Im complex **2** can be obtained by maintaining the metal and Im in a 1 : 4 ratio. The use of reduced amounts of Im, i.e. metal : Im in a 1 : 2 mole ratio results in the formation of an initial product, which contains no Im and the Im ligated complexes are obtained in low yields in the second crop. The reason for this behaviour is not clear. It has also been observed that the use of an excess of Im (metal : Im ratio 1 : 6) leads to the formation of only the complexes **1** and **2**. In the case of complex **2** the use of excess Im does not lead to the coordination of a second Im to

Ca. Another interesting observation is with respect to the amount of water for the preparation of complex **1**. The product is formed in good yields if the reaction mixture is concentrated and the volume of water is reduced. In the presence of large amounts of water the previously reported complex $[Mg(H_2O)_6](4\text{-nba})_2\cdot 2H_2O$ is obtained[16]. **1** can also be prepared by partially dehydrating $[Mg(H_2O)_6](4\text{-nba})_2\cdot 2H_2O$ followed by reaction with Im or by mechanical grinding of $[Mg(H_2O)_6](4\text{-nba})_2\cdot 2H_2O$ with Im in a 1 : 2 ratio. The use of alternate starting materials like the alkali-earth metal chloride and sodium 4-nitrobenzoate result in the formation of the same product, indicating the high formation tendency of complexes **1** and **2**. The reaction of **1** or **2** with dilute HCl leads to the decomposition of the complexes and formation of 4-nbaH in quantitative yields, which was analysed gravimetrically. The water content of the complexes was estimated by Karl Fischer titrations. Pyrolysis of the complexes resulted in the formation of a white residue, which was identified as the oxide based on

the mass loss as well as metal analysis. Both the complexes could be characterized and formulated based on these experiments.

3.2 *Spectral and thermal studies*

The IR spectra of the complexes **1** and **2** are very similar below 2000 cm^{-1}. The similarity of the spectra in the region between 1750 and 1300 indicates that the ligational mode of the 4-nitrobenzoate can be same in both the compounds. A very important difference in the IR spectra is the observation of a very strong and broad signal for the Ca complex between 3650 to 2550 centred at 3242 cm^{-1} while the Mg complex exhibits a sharper band at 3375 cm^{-1}. In contrast, the anhydrous compound **3** is devoid of any signals in this region. The IR spectra of the rehydrated complexes are identical with those of **1** and **2** indicating that the signals in this region originate from the –OH functionality. The observation of several sharp signals in the mid IR in **1** and **2** indicates the presence of organic moieties in both the complexes and these signals are also observed in the dehydrated complexes **3** and **4**. The characteristic absorptions of the carboxylate and nitro functionalities are observed as expected. The complexes **1** and **2** absorb strongly at 274 nm in the UV region, which can be attributed to intramolecular charge transfer transition of 4-nbaH. The ^{1}H NMR spectra of both the complexes exhibit signals characteristic of 4-nba and Im protons and the chemical shifts of these protons are in the normal range, indicating the presence of both 4-nba and Im. The ^{13}C NMR spectra of **1** and **2** exhibit seven signals each, which can be assigned to the carbons of the 4-nitrobenzoate and imidazole. Complex **1** is thermally stable till about 100°C as no mass loss is observed when the complex is heated on a water bath. However, when **1** is heated at ∼ 140°C, a mass loss of 7·4% is observed, which corresponds to the loss of two moles of water. Further the dehydrated complex exhibits a rich IR spectrum and the band due to –OH vibration is not observed. By equilibriating the anhydrous complex **3** over water vapour, the original complex **1** was obtained in near quantitative yield as evidenced by its characteristic IR spectrum. It is to be noted that this phenomenon of de- and rehydration has been observed for hydrated 4-amino as well as 4-nitrobenzoate complexes in our earlier work.[15–18] In the case of **2**, a mass loss of 9·02% is observed at 100°C corresponding to the loss of three moles of water. Here again the dehydrated Ca complex **4**

could be rehydrated. Pyrolysis of **1** and **2** at elevated temperatures ∼ 800°C resulted in decomposition and the observed mass loss for this process is in good agreement for the formation of metal oxide. The complete loss of organic part could also be evidenced from the featureless IR spectra.

3.3 *Description of crystal structures*

The complex [Mg(H$_2$O)$_2$(Im)$_2$(4-nba)$_2$] **1** crystallizes in the centrosymmetric triclinic space group P$\bar{1}$ and the Mg(II) is located on a centre of inversion (figure 1). **1** is isostructural with the corresponding Ni(II),[28] Co(II)[29] and Mn(II)[30] analogues (table 2) and the cell volume of the Mg complex is very close to that of the corresponding Ni(II) complex. The central metal in **1** is hexacoordinated and is bonded to two *trans* water molecules and two *trans* monodentate 4-nba anions through O atoms, which lie on an approximate square plane. Two *trans* Im ligands complete the octahedral coordination around Mg. The *trans* O–Mg–O and N–Mg–N angles show the ideal value of 180°, while the *cis* O–Mg–O and N–Mg–O angles range from 87·01(5) to 92·99(5)° (table 3) indicating a slight distortion of the (MgO$_4$N$_2$) octahedron. The observed intra–ligand bond lengths of the Im and 4-nba ligands are in the normal range and are in agreement with those reported in related compounds.[28–30] The Mg–O(H$_2$O) and Mg–O(4-nba) distances of **1** (table 3) are in good agreement with those observed for the isostructural Co and Ni complexes and slightly shorter than those of the Mn(II) complex. The Mg–N distance of 2·1726(17) Å for **1** is relatively longer than the observed distances of
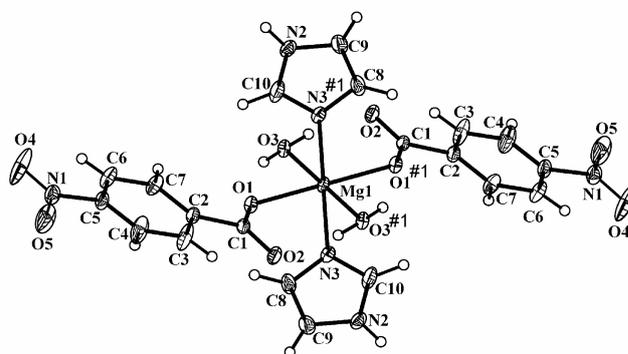
Figure 1. The asymmetric unit of [Mg(H$_2$O)$_2$(Im)$_2$ (4-nba)$_2$] **1** showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: #1 −x + 1, −y + 1, −z + 1.

Table 2. Comparative metric parameters of $[M(H_2O)_2(Im)_2(4\text{-nba})_2]$ complexes M = Mg, Mn, Co, Ni.

Metric parameters	$[Mg(H_2O)_2(Im)_2$ $(4\text{-nba})_2]^*$	$[Mn(H_2O)_2(Im)_2$ $(4\text{-nba})_2]^{30}$	$[Co(H_2O)_2(Im)_2$ $(4\text{-nba})_2]^{29}$	$[Ni(H_2O)_2(Im)_2$ $(4\text{-nba})_2]^{28}$
a (Å)	5·533(5)	5·6745(3)	5·6482(10)	5·644(2)
b (Å)	8·122(5)	8·1082(3)	8·0559(12)	8·0547(18)
c (Å)	12·775(5)	12·8399(6)	12·7628(11)	12·716(2)
α (°)	74·80(1)	76·73(2)	75·62(1)	75·03(1)
β (°)	87·39(1)	88·14(1)	87·92(1)	87·76(2)
γ (°)	87·43(1)	86·33 (2)	86·92(1)	87·08(2)
V (Å^3)	553·1(6)	573·71(5)	561·56(14)	557·5(3)
Interplanar distance (in Å)**	3·583	3·624(16)	3·555(14)	3·535(14)

All the complexes crystallise in the centrosymmetric triclinic space group $P\bar{1}$. *This work. **Perpendicular distance from the centre of gravity of one Im ring to another Im ring in a neighbouring complex

Table 3. Selected bond lengths and angles (Å, °) for $[Mg(H_2O)_2(Im)_2(4\text{-nba})_2]$ **1**.

Mg(1)–O(3)	2·0822(15)	Mg(1)–O(1)	2·1210(13)
Mg(1)–O(3)#1	2·0822(15)	Mg(1)–N(3)	2·1726(17)
Mg(1)–O(1)#1	2·1210(13)	Mg(1)-N(3)#1	2·1726(17)
O(3)–Mg(1)O(3)#1	180·00(1)	O(3)#1–Mg(1)–N(3)	89·63(5)
O(3)–Mg(1)O(1)#1	91·79(6)	O(1)#1–Mg(1)–N(3)	87·01(5)
O(3)#1Mg(1)O(1)#1	88·21(6)	O(1)–Mg(1)–N(3)	92·99(5)
O(3)–Mg(1)–O(1)	88·21(6)	O(3)–Mg(1)–N(3)#1	89·63(5)
O(3)#1–Mg(1)–O(1)	91·79(6)	O(3)#1–Mg(1)–N(3)#1	90·37(5)
O(1)#1–Mg(1)–O(1)	180·00(1)	O(1)#1–Mg(1)–N(3)#1	92·99(5)
O(3)–Mg(1)–N(3)	90·37(5)	O(1)–Mg(1)–N(3)#1	87·01(5)
N(3)–Mg(1)–N(3)#1	180·00(6)		

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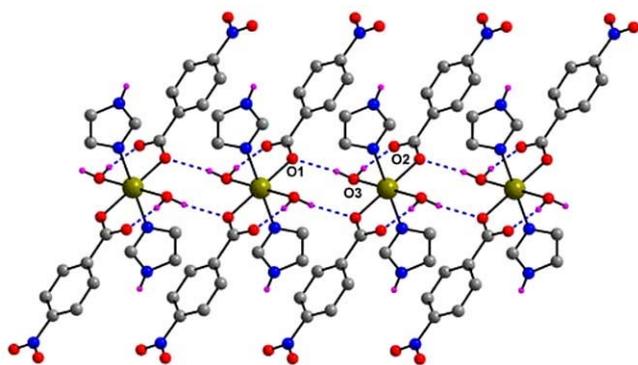

Figure 2. Formation of a H-bonded chain along *a* axis via O–H···O interaction showing the linking of coordinated water (O3) with a coordinated 4-nitrobenzoate of a neighbouring molecule (O1). H atoms attached to C are not shown for clarity.

2·0602(4) and 2·0944(14) Å for Ni and Co complexes but slightly shorter than the Mn–N distance of 2·2127(14) Å. The affinity of Ni and Co(II) for N donor ligands as well as the larger size of the Mn(II) ion can probably account for this observation.

A careful analysis of the structure reveals that the coordinated water, 4-nitrobenzoate as well as the imidazole in **1** are involved in two types of H-bonding interactions namely O–HΛO and N–HΛO. Each molecule of the Mg(II) complex is linked to six other molecules with the aid of O–HΛO and N–HΛO bonds (see web version). The coordinated water (O3) is linked intramolecularly to the free carboxylate oxygen atom (O2) at a very short distance of 1·823 Å and with a coordinated carboxylate (O1) of a neighboring molecule resulting in the formation of a H-bonded chain along *a* axis (figure 2). The amine nitrogen (N2) of the coordinated imidazole is H-bonded to the free carboxylate oxygen (O2) of a neighbouring molecule with O2 functioning as a bifurcated acceptor. In addition, the coordinated imidazole, which functions as a bifurcated hydrogen donor, is linked to the oxygen atom of the nitro group in a neighbouring complex thus extending the network. In all four OΛH contacts ranging from 1·823 to 2·518 Å (table 4) are observed and all these OΛH interactions are shorter than the sum of their van der Waals radii.[36] The short ring interactions

Table 4. Hydrogen-bonding geometry (Å, °) for [Mg(H$_2$O)$_2$(Im)$_2$(4-nba)$_2$] **1**.

D–HΛA	d(D–H)	d(HΛA)	d(DΛA)	<DHA	Symmetry code
O3–H2W2ΛO2	0·857	1·823	2·652	162·18	[−x + 1, −y + 1, −z + 1]
O3–H1W1ΛO1	0·826	2·002	2·807	164·52	[−x, −y + 1, −z + 1]
N2–H3N2ΛO2	0·871	2·260	3·011	144·28	[−x + 1, −y, −z + 1]
N2–H3N2ΛO5	0·871	2·518	3·132	128·14	[x + 1, y − 1, z + 1]
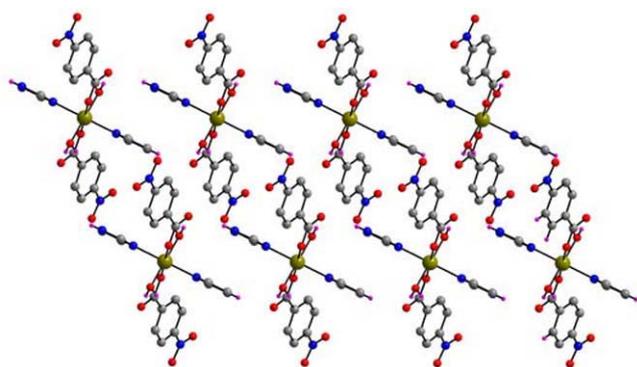
Figure 3. Diagram showing the nearly overlapped arrangement of imidazole rings in adjacent molecules of **1**. H-bonds as well as H atoms attached to C are not shown for clarity.
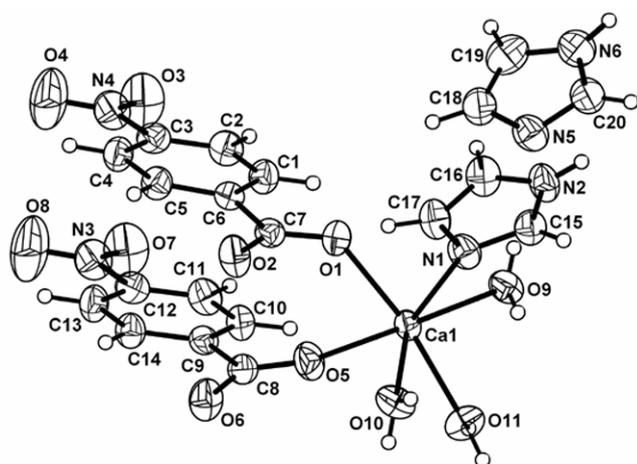
Figure 4. The asymmetric unit of [Ca(H$_2$O)$_3$(Im) (4-nba)$_2$]·Im **2** showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50 % probability level except for the H atoms, which are shown as circles of arbitrary radius.

and distances between the ring centroids (Cg–Cg) were analysed by using the program Platon.[37] A nearly overlapped arrangement of parallel imidazole ligands in neighbouring complex molecules is observed in the crystal structure of **1** (figure 3) and the

perpendicular distance of 3·583 Å accompanied by Cg–Cg distance of 3·6382 Å between the imidazole rings indicates π–π stacking interactions. A similar feature has been reported in the related isostructural Mn, Co and Ni complexes.[28–30] The observed interplanar distance between two imidazole rings of the neighbouring molecules in **1** is found to be slightly less than the value reported for the Mn(II) complex (3·624 Å) but longer than that reported for Ni(II) (3·535 Å) and Co(II) (3·555 Å) analogues. For the 6-membered 4-nba rings, the observed Cg–Cg distance of 4·3576 Å and the perpendicular distance from the centre of one ring to the next ring at 3·345 Å indicate π-π interactions but the rings do not overlap.

[Ca(H$_2$O)$_3$(Im)(4-nba)$_2$]·Im **2** crystallises in the monoclinic space group P2$_1$/c and all atoms are located in general positions (figure 4). The observed bond distances and bond angles of the 4-nba ligand are in good agreement with those observed for **1**. The observed values of the *trans* O–Ca–O and O–Ca–N bond angles between 160·19(6) to 177·33(6)° and the *cis* O–Ca–O angles ranging from 80·78(6) to 98·73(5)° (table 5) indicate that the {CaO$_5$N} octahedron is severely distorted. The coordination sphere of **2** consists of five oxygen atoms, with two from *cis* monodentate nitrobenzoate ligands and the remaining three oxygens from aquo ligands. The sixth position is occupied by an Im nitrogen and is coordinated to Ca at a longer distance of 2·4652(16) Å unlike in **1** where the imidazoles are bonded to Mg at 2·1726(17) Å. The second imidazole is free and linked to the metal complex with the aid of O–HΛN and N–HΛO bonds. In addition, the coordinated water molecules, imidazole, as well as the carboxylate oxygens of the 4-nitrobenzoate, are involved in H-bonding. Unlike in **1**, the oxygen atom of the nitro group is not involved in any intermolecular interactions in **2**.

A careful analysis of the structure reveals that **2** is involved in three varieties of intermolecular interactions namely O–HΛO, N–HΛO and O–HΛN bonds ranging from 1·789 to 2·535 Å (table 6). Each hexacoordinated Ca(II) complex is H-bonded to four

Table 5. Selected bond lengths and angles (Å, °) for [Ca(H₂O)₃(Im)(4-nba)₂]· Im **2**.

Ca(1)–O(5)	2·2952(13)	Ca(1)–O(11)	2·3413(15)
Ca(1)–O(10)	2·3373(16)	Ca(1)–O(9)	2·3621(14)
Ca(1)–O(1)	2·3380(14)	Ca(1)–N(1)	2·4652(16)
O(5)–Ca(1)–O(10)	97·84(6)	O(1)–Ca(1)–O(9)	89·90(5)
O(5)–Ca(1)–O(1)	87·89(5)	O(11)–Ca(1)–O(9)	96·49(6)
O(10)–Ca(1)–O(1)	92·75(5)	O(5)–Ca(1)–N(1)	98·73(5)
O(5)–Ca(1)–O(11)	85·59(6)	O(10)–Ca(1)–N(1)	160·19(6)
O(10)–Ca(1)–O(11)	83·19(6)	O(1)–Ca(1)–N(1)	98·63(5)
O(1)–Ca(1)–O(11)	171·77(5)	O(11)–Ca(1)–N(1)	87·34(6)
O(5)–Ca(1)–O(9)	177·33(6)	O(9)–Ca(1)–N(1)	83·07(6)
O(10)–Ca(1)–O(9)	80·78(6)		

Table 6. Hydrogen-bonding geometry (Å, °) for [Ca(H₂O)₃(Im)(4-nba)₂]·Im **2**.

| D–H∧A	D(D–H)	D(H∧A)	d(D∧A)	<DHA	Symmetry code
O11–H11B∧N5	0.791	2.092	2.875	170.03	[x − 1, y, z]
O9–H9B∧O2	0.871	1.885	2.748	171.10	[−x + 1, −y, −z]
O11–H11A∧O6	0.903	1.789	2.681	168.94	[−x, −y, −z]
O9–H9A∧N5	0.754	2.196	2.939	168.65	
N2–H2X∧O2	0.808	2.084	2.883	169.52	[x, y + 1, z]
O10–H10A∧O1	0.831	1.975	2.805	175.86	[−x + 1, −y, −z]
O10–H10B∧O5	0.773	2.326	3.033	152.53	[−x, −y, −z]
O10–H10B∧O11	0.773	2.535	3.034	123.82	[−x, −y, −z]
N6–H6X∧O6	0.850	2.155	2.948	154.98	[x + 1, y + 1, z]
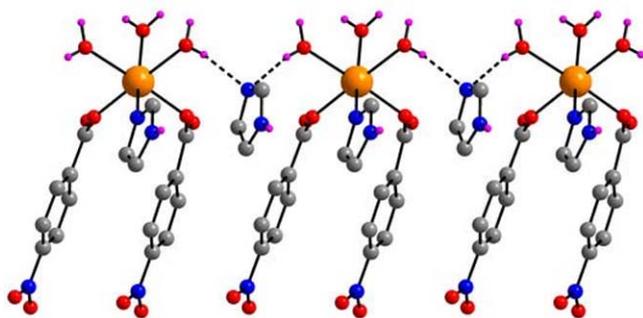
Figure 5. Linking of hexacoordinated Ca(II) complexes by the free Im with the aid of O–H···N interactions leading to the formation of a H-bonded chain along the *b* axis. H atoms attached to C are not shown for clarity.

other complexes resulting in the formation of a three-dimensional H-bonded network (see web version). The free imidazole is involved in three short H-bonding contacts and links three different complex molecules. The imine N atom (N5) of the free imidazole functions as a bifurcated H-bond acceptor linking adjacent complex molecules of **2** along *b* with the aid of O–H∧N interactions leading to the formation of an extended H-bond chain of hexaco-
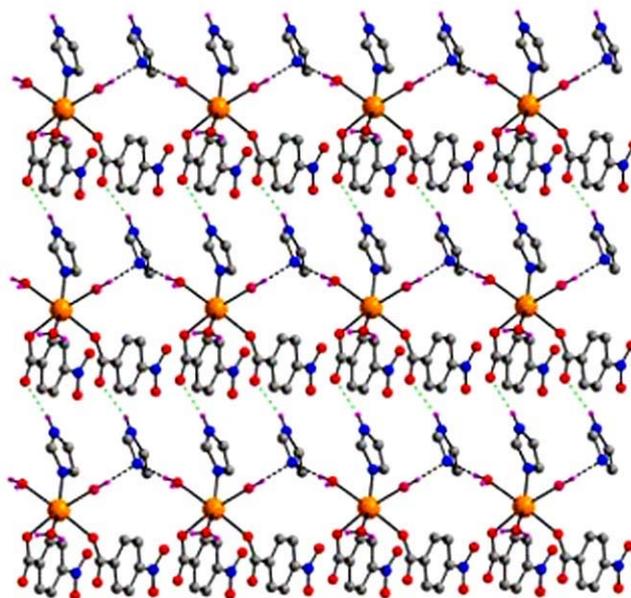
Figure 6. Cross-linking of H-bonded chains of hexacoordinated Ca(II) complexes by free as well as coordinated imidazole through N–H···O interactions. H atoms attached to C are not shown for clarity.

ordinated Ca(II) complexes linked by the free imidazole (figure 5) The chains of complex molecules
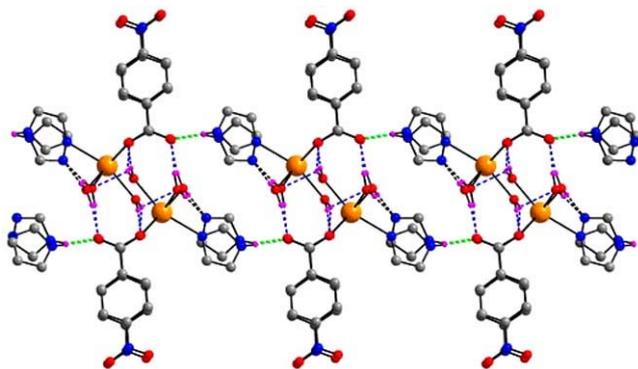
Figure 7. Formation of an intricate H-bonded network in **2**, showing three varieties of H-bonding interactions namely O–H⋯O, N–H⋯O and O–H⋯N. H atoms attached to C are not shown for clarity.

thus formed are further cross-linked by a H-donor bond formed by the amine N atom (N6) of the free imidazole with the free O6 atom of a coordinated carboxylate. In addition, the amine nitrogen (N2) of the coordinated imidazole forms a H-donor bond with the free oxygen (O2) of a coordinated carboxylate and this N–H⋀O interaction serves to cross-link the H-bonded complex chains (figure 6) In addition to the earlier mentioned O–H⋀N interactions which link adjacent Ca complexes, the coordinated water ligands (O9), (O10) and (O11) participate in several H-bonding interactions and are linked with the carboxyl oxygens O2, O1, O5 and O6 as well as a co-ordinated water. In all five short O–H⋀O interactions ranging from 1·789 to 2·535 Å are observed. One water ligand (O10) functions as a bifurcated donor and is linked with the coordinated carboxyl oxygen (O5) at 2·326 Å and with O11 at a longer distance of 2·535 Å. In addition, O9, O10 and O11 are also H-bonded to the carboxyl oxygens O2, O1, O6 respectively. These interactions further link the already formed chains, forming an intricate H-bonded network (figure 7) An analysis of the ring interactions[37] reveals that the Cg–Cg distances for the five-membered and the six-membered rings are 3·8269 and 3·7543 Å respectively. The corresponding perpendicular distances from the centre of the first ring to the second ring are 3·551 and 3·494 Å respectively. These values are indicative of π–π interactions.

4. Conclusions

The aqueous reactions of Mg/Ca carbonate with 4-nbaH or the corresponding alkali metal dichloride with sodium 4-nba in a 1 : 2 mole ratio followed by

the addition of excess Im results in the formation of the Im coordinated complexes **1** or **2** in good yields. Complex **1** can also be synthesized from the hydrated magnesium complex and imidazole by mechanical grinding. Both **1** and **2** can be dehydrated and the anhydrous complexes **3** and **4** thus formed can be rehydrated. At elevated temperatures, the complexes **1** and **2** decompose to the corresponding metal oxides. It is interesting to note that **1** and **2**, which are prepared under similar experimental conditions, have the same metal : nitrobenzoate : imidazole ratio but exhibit different degrees of hydration and different structures. **1** crystallizes in the triclinic $P\bar{1}$ space group and is isostructural with the corresponding Mn, Co, and Ni complexes, while complex **2** crystallizes in the monoclinic $P2_1/c$ space group. In complex **1**, both the Im ligands are coordinated to the central Mg metal, while in **2** both coordinated as well as free imidazole are found. The monodentate 4-nba ligands are disposed *trans* to each other in **1**, while they adopt a *cis* orientation in **2**, leading to different supramolecular structures. The complexes differ in terms of the intermolecular interactions. Complex **1** exhibits two types of H-bonding interactions namely O–H⋀O and N–H⋀O, while in **2** three types of intermolecular interactions, viz. O–H⋀O, N–H⋀O and O–H⋀N are observed. The imidazole ligand functions as a bifurcated H-bond donor in **1** and the O atom of the nitro group functions as a H-bond acceptor. In contrast the nitro group in **2** is not involved in any H-bonding interactions. Further the imine nitrogen of the free imidazole functions as a bifurcated acceptor and forms an extended chain linking adjacent complex molecules. The analysis of ring interactions in both complexes indicates π–π interactions. The isostructural nature of the diamagnetic complex **1** with the corresponding paramagnetic transition metal complexes indicates the possibilities for the preparation of novel doped magnetic materials. Efforts are underway in our laboratory for the synthesis of mixed metal 4-nitrobenzoates containing imidazole coligands.

Supplementary material

Illustrations describing the H-bonding situation around each complex of **1** and **2**, are available on the web version of this paper. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 605292 (**1**) CCDC 605291 (**2**). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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