Supramolecular aggregation in alkaline earth metal 3- and 4-hydroxybenzoates using 1,10-phenanthroline auxiliary

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The interaction of group 2 metals with 3- and 4-hydroxybenzoic acids in presence of chelating N-donor ligand 1,10-phenanthroline (phen) has been investigated. The 3-hydroxybenzoate derivatives \([\text{Ca}(3\text{-hba})_2(\text{phen})_2(H_2O)_3]_n(1), [\text{Sr}(3\text{-hba})_2(\text{phen})_2(H_2O)_2]_n(2),\) and \([\text{Ba}(3\text{-hba})_2(\text{phen})_2(H_2O)_2]_n(3)\) have been obtained by treatment of the corresponding metal carbonates with 3-hydroxybenzoic acid and 1,10-phenanthroline, while the 4-hydroxybenzoate derivatives \([\text{Ca}(4\text{-hba})_2(\text{phen})_2(H_2O)](4), [\text{Sr}(4\text{-hba})_2(\text{phen})_2(H_2O)_4]_n(5), [\text{Ba}(4\text{-hba})_2(\text{phen})_2(H_2O)_2]_n(6)\) have been prepared by a similar method using 4-hydroxybenzoic acid. The compounds have been characterized by elemental analysis, thermal analysis, and infrared and \(^1\)H NMR spectroscopic studies. The solid-state structures of (2-4) and (6) have been established by single-crystal X-ray diffraction studies. The compounds are monomeric in the solid state although they exhibit considerable variations in their molecular structures in terms of binding mode of the hba ligands and the coordination geometry around the metal ions. All the compounds form polymeric networks in the solid state with the aid of O-H⋯O, C-H⋯O and N-H⋯O hydrogen bonding and π⋯π interactions.

Keywords: Coordination chemistry, Aggregation, Supramolecular aggregation, Benzoates, Auxiliary ligands, Crystal structures

The design and synthesis of new alkaline earth metal complexes has become an emerging area of research in inorganic chemistry during the past few decades owing to their potential applications in various fields such as catalysis\(^1\), material science\(^2\) and biochemistry\(^3,4\). Group 2 metal ions exhibit considerable versatility in coordination numbers and geometries, which give rise to the formation of a wide range of topologies and conformations with various ligands. Thus, calcium exhibits coordination numbers ranging from three to eleven, most common being six, seven and eight\(^5\)-\(^18\). Strontium and barium prefer coordination numbers\(^5\) of 6 to 12. The coordination chemistry of calcium has been a topic of current interest owing to the greater flexibility of the coordination number and geometry exhibited by the calcium ion (which results in variable metal ligand distances) compared to other alkaline earth metal ions.

Alkaline earth metal carboxylate complexes have been widely and well investigated due to the various coordination modes offered by the carboxylate ligand for metal binding\(^5\). We have reported the coordination behaviour of 2-aminobenzoic and related acids (3-aba-H, 4-aba-H, 2-mercapto benzoic acid, and 5-aminoisophthalic acid) towards alkaline earth metal ions\(^7\). Schmidbaur et. al\(^8\), Drake et. al\(^9\), and several others\(^10\) have unraveled the coordination chemistry of salicylic acid towards group 2 metal ions. While most of the work on hydroxybenzoic acids has been reported with salicylic acid, practically no studies are available in the literature for the corresponding 3- and 4-hydroxybenzoic acids. Significantly, incorporation of soft N-donor neutral ligands in the coordination sphere of hard group 2 metal ions is a difficult task.

In the present study a successful attempt has been made to incorporate chelating N-donor ligands such as 1,10-phenanthroline in one-half of the coordination sphere of these metal ions. The details of this study, including crystal structures of a number of derivatives, are described in this contribution.

Materials and Methods

Starting materials such as CaCO\(_3\), SrCO\(_3\), BaCO\(_3\), 3- or 4-hydroxy benzoic acid, and 1,10-phenanthroline were procured from commercial sources and used as received. All the starting materials and the products were found to be stable towards moisture and air, and no specific precaution was taken to rigorously exclude air. The melting
points were measured in glass capillaries and are reported uncorrected. Elemental analyses are performed on a Carlo Erba (Italy) (model 1106) Elemental Analyzer and Thermoquest Flash EA 1112 series CHNS analyzer. Infrared spectra were recorded on a Nicolet Impact 400 spectrometer as KBr diluted thin plates in the solid state. Thermogravimetric analysis and differential thermal analysis were carried out on a Perkin Elmer thermal analysis system under a stream of nitrogen gas. The $^1$H NMR spectra were recorded on a Varian 300 MHz instrument using Me$_2$Si as a reference. X-ray powder diffraction data were collected on a Philips X$^2$Pert PRO X-ray diffraction system using monochromated Cu-K$_{α1}$ radiation ($λ = 1.5406$ Å).

**Synthesis of complexes**

The compounds [Ca(3-hba)$_2$(phen)$_2$(H$_2$O)$_3$]$_n$ (1), [Sr(3-hba)$_2$(phen)$_2$(H$_2$O)$_3$]$_n$ (2), [Ba(3-hba)$_2$(phen)$_2$(H$_2$O)$_2$]$_n$ (3), [Ca(4-hba)$_2$(phen)$_2$(H$_2$O)] (4), [Sr(4-hba)$_2$(phen)$_2$(H$_2$O)$_2$] (5), and [Ba(4-hba)$_2$(phen)$_2$(H$_2$O)$_2$] (6) were prepared using a similar procedure. In a typical synthesis, the metal carbonate (2 mmol) suspended in H$_2$O (35-40 mL) was treated with 3- or 4-hydroxy benzoic acid (0.553 g, 4 mmol). The clear solution obtained was then treated with a methanol solution (40 mL) of 1,10-phenanthroline (0.721 g, 4 mmol). Crystals were obtained directly from the solution in all the cases except (1), where the product was instantly precipitated out.

**[Ca(3-hba)$_2$(phen)$_2$(H$_2$O)$_3$]$_n$ (1)**

M. pt.: 173-178 °C; Yield: 0.963 g (66 % based on CaCO$_3$). Anal. (%): Calcd for CaC$_{39}$H$_{52}$O$_{33}$N$_{7}$: C, 62.6; H, 4.4; N, 7.7; Found: C, 62.9; H, 4.1; N, 7.4. IR (KBr, cm$^{-1}$): 3388 (m), 1518 (s), 1424 (m), 1384 (s), 1281 (m), 1253 (m), 842 (m), 802 (m). $^1$H NMR (DMSO-$d_6$, 400 MHz): $δ$ 6.77 (dd, 2H, $H_d$), (J$_{HH}$ = 7.70, 4J$_{HH}$ = 1.47 Hz), 7.10 (t, 2H, $H_b$) (J$_{HH}$ = 7.70 Hz), 7.41 (d, 2H, $H_a$) (J$_{HH}$ = 7.33 Hz), 7.58 (s, 2H, $H_c$), 7.76-7.82 (dd, 4H, $H_e$), (J$_{HH}$ = 8.07, 4J$_{HH}$ = 4.40 Hz), 8.01 (s, 4H, $H_g$), 8.51 (dd, 4H, $H_f$), (J$_{HH}$ = 8.07, 4J$_{HH}$ = 2.20 Hz), 9.13 (dd, 4H, $H_i$) (J$_{HH}$ = 4.40, 4J$_{HH}$ = 1.47 Hz), 9.69 (s, 1H, OH) ppm. UV-vis (CH$_3$OH, $λ_{max}$ nm): 264; Fluorescence ($λ_{ex}$ = 264 nm, CH$_3$OH): 263 and 269 nm.

**[Sr(3-hba)$_2$(phen)$_2$(H$_2$O)$_3$]$_n$ (2)**

Colourless rod shaped crystals. M. pt.: 160-165 °C. Yield: 1.019 g (67 %). Anal. (%): Calcd for SrC$_{38}$H$_{52}$O$_{33}$N$_{7}$: C, 60.2; H, 4.0; N, 7.4; Found: C, 60.3; H, 3.3; N, 6.8. IR (KBr, cm$^{-1}$): 3460 (s), 3083 (w), 1555 (s), 1442 (s), 1423 (s), 1383 (s), 1349 (s), 1256 (s), 1228 (s), 1098 (s), 846 (m), 738 (w). $^1$H NMR (DMSO-$d_6$, 400 MHz): $δ$ 6.70 (m, 2H, $H_a$), (J$_{HH}$ = 8.07, 4J$_{HH}$ = 1.47 Hz), 7.06 (m, 2H, $H_b$) (J$_{HH}$ = 7.69 Hz), 7.29-7.38 (m, 4H, $H_c$, $H_f$) (J$_{HH}$ = 7.33 Hz), 7.76-7.81 (m, 4H, $H_e$) (J$_{HH}$ = 8.07, 4J$_{HH}$ = 4.40 Hz), 8.01 (s, 4H, $H_g$), 8.50 (m, 4H, $H_h$), (J$_{HH}$ = 8.07), (J$_{HH}$ = 2.20 Hz), 9.10 (m, 4H, $H_i$), (J$_{HH}$ = 4.03, 4J$_{HH}$ = 1.83 Hz), 9.56 (s, 2H, OH) ppm. UV-vis (CH$_3$OH, $λ_{max}$ nm, $ε$, cm$^{-1}$ M$^{-1}$): 264 (2.05 × 10$^5$). Fluorescence ($λ_{ex}$ = 264 nm, CH$_3$OH): 361 and 269 nm.

**[Ba(3-hba)$_2$(phen)$_2$(H$_2$O)$_3$]$_n$ (3)**

Colourless rod shaped crystals. M. pt.: 200-205 °C. Yield: 0.790 g (38 %). Anal. (%): Calcd for BaC$_{39}$H$_{52}$O$_{33}$N$_{7}$: C, 65.6; H, 4.1; N, 8.1. Found: C, 65.2; H, 4.1; N, 8.5. IR (KBr, cm$^{-1}$): 3325-2593 (m), 1602 (s), 1540 (s), 1508 (s), 1419 (s), 1385 (s), 1279 (m), 1245 (s), 845 (s). $^1$H NMR (DMSO-$d_6$, 400 MHz): $δ$ 6.68 (d, 2H, $H_a$), (J$_{HH}$ = 8.07 Hz) 7.76-7.86 (m, 4H, $H_e$, $H_f$), (J$_{HH}$ = 4.39 Hz), 8.0 (s, 2H, $H_d$), 8.51 (dd, 2H, $H_b$) (J$_{HH}$ = 1.467, 4J$_{HH}$ = 8.07 Hz), 9.1 (d, 2H, $H_i$) (J$_{HH}$ = 3.67 Hz), 9.96 (s, 2H, OH) ppm.; UV-vis (CH$_3$OH, $λ_{max}$ nm): 262; Fluorescence ($λ_{ex}$ = 262 nm, CH$_3$OH): 361 and 297 nm.

**[Sr(4-hba)$_2$(phen)$_2$(H$_2$O)$_3$]$_n$ (5)**

Colourless hexagonal plate-like crystals. M. pt.: >160-170 °C. Yield: 0.799 g (51 %). Anal. (%): Calcd for SrC$_{38}$H$_{52}$O$_{33}$N$_{7}$: C, 57.5; H, 4.3; N, 7.1. Found: C, 59.8; H, 4.1; N, 7.1. IR (KBr, cm$^{-1}$): 3445 (w), 1624 (s), 1574 (s), 1485 (s), 1457 (s), 1392 (s), 1342 (m), 1248 (m), 771 (s). $^1$H NMR (DMSO-$d_6$, 400 MHz):
δ 6.60-6.66 (m, 2H, \(H_e\)), \(\delta \) \(J_{HHr} = 7.332\), \(4J_{HH} = 1.47\) Hz, 6.64-6.68 (d, 2H, \(H_e\)), \(\delta \) \(J_{HHr} = 8.07\) Hz, 7.14-7.21 (m, 2H, \(H_e\)), \(\delta \) \(J_{HHr} = 7.70\), \(4J_{HH} = 1.83\) Hz, 7.70 (dd, 2H, \(H_e\)), \(\delta \) \(J_{HHr} = 1.83\), \(3J_{HH} = 7.70\) Hz, 7.80 (dd, 4H, \(H_e\)), \(\delta \) \(J_{HHr} = 8.07\), \(4J_{HH} = 4.40\) Hz, 8.01 (s, 4H, \(H_a\)), 8.52 (dd, 4H, \(H_a\)), \(\delta \) \(J_{HHr} = 8.43\), \(4J_{HH} = 1.83\) Hz, 9.13 (dd, 4H, \(H_a\)), \(\delta \) \(J_{HHr} = 4.40\), \(4J_{HH} = 1.47\) Hz, 9.93 (s, 2H, \(OH\)) ppm; UV-vis (CH\(_3\)OH, \(\lambda_{max}\), nm): 267.; Fluorescence (\(\lambda_{ex} = 267\) nm, CH\(_3\)OH): 304 and 243 nm.

**Table 1**—Crystalllographic cell parameters and experimental details of X-ray intensity data collection for metal complexes

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<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(6)</th>
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<td>(C_{3}H_{3}Ba_{2}N_{5}O_{5})</td>
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<td>692.72</td>
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<td>150(2)</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>P2(_1)/n</td>
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<td>(b) (Å)</td>
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<td>6593.7(1)</td>
<td>3284.8(9)</td>
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<td>(Z)</td>
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<td>1.628</td>
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<td>Abs. coeff. (mm(^{-1}))</td>
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<td>(F(000))</td>
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<td>1624</td>
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<tr>
<td>Crystal size (mm(^3))</td>
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<td>0.33 (\times) 0.28 (\times) 0.22</td>
<td>0.40 (\times) 0.21 (\times) 0.12</td>
<td>0.27 (\times) 0.21 (\times) 0.11</td>
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<td>3.10 to 25.00</td>
<td>3.04 to 25.00</td>
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<td>R1 = 0.0237</td>
<td>0.0445</td>
<td>0.0595</td>
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<td>wR2 [(I &gt; 2\sigma(I))]</td>
<td>0.1033</td>
<td>0.0523</td>
<td>0.0928</td>
<td>0.1613</td>
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**Crystal structure analysis**

The intensity data collection for all the new compounds (2-4 and 6) has been carried out on a Nonius MACH-3 diffractometer. The unit cell dimensions were determined using approximately 25 well-centered and well-separated high angle reflections. Intensity data collection and cell determination protocols were carried out using a graphite-monochromatized Mo-K\(_{\alpha}\) radiation (\(\lambda = 0.71073\) Å). The resultant intensity data have been corrected for Lorentz and polarization effect but not for absorption effects. Structure solution for each of the compound was obtained using direct methods (SHELXS-97)\(^{11}\) and refined using full-matrix least squares method on \(F^2\) using SHELXL-97\(^{12}\). The positions of hydrogen atoms were either located in the successive difference maps or were geometrically fixed and refined using a riding model. All non-hydrogen atoms were refined anisotropically. No disorder or symmetry related problems were encountered for the compound. The search for higher centrosymmetric space group for compound 3 using well known cell reduction programs such as Le Page did not yield any higher symmetry. The crystal data and details of refinement are listed in Table 1.
Results and Discussion

Synthesis and spectral studies

Synthesis of all the new compounds (1-6) has been achieved by a similar synthetic procedure. The hydroxyl benzoic acids 3-hba-H and 4-hba-H were treated with group 2 metal carbonates suspended in water, followed by the addition of 1,10-phenanthroline in MeOH/ H₂O mixture to yield compounds (1-6). All the new compounds are highly soluble in solvents like MeOH, EtOH and DMSO. All complexes have been obtained in good yield in an analytically pure form as crystalline products and characterized by both analytical (Table 2) and spectroscopic techniques. For compound (4), the isolated yield was comparatively less (38 %). Except (4) and (5), other complexes melt at around 160-170 °C. Complex (4) melts at around 200-205 °C, while (5) melts at 240 °C.

The empirical formula and composition of the products could easily be established from the analytical data listed in Table 1. In all the cases, the data obtained account for the presence of additional coordinated water molecules. The infrared spectra recorded in KBr diluted discs showed peaks corresponding to O–H and C=O stretching vibrations. The presence of water molecules in the complexes are indicated as broad absorptions in the region 3300-3400 cm⁻¹.

The 'H NMR spectra of the new complexes, the four protons of the hba ligands are manifested as four multiplets. The position as well as splitting pattern of these peaks depends upon the relative position of hydroxyl group. The labeling scheme of protons for the phen and hba ligands is shown in Scheme 1. The resonances due to phen protons are observed as additional four multiplets, and appear downfield compared to the carboxylate protons. The OH proton is observed as a singlet in the range 9.3 - 10.07 ppm. The aromatic region of the 'H NMR spectrum of (1) is given in Fig. 1 as a representative case.

Thermal analysis

Thermal analyses of complexes (1-6) have been carried out under a stream of nitrogen. The thermal decomposition studies show the loss of water molecules at around 100 °C. It was observed that the decomposition of 3-hba derivatives (1 – 3) was not complete even at 1200 °C. For compounds (4) and (5) the final decomposition product may be assumed to be the metal oxide product, based on the weight loss calculation. For (6), the final decomposition product is BaCO₃ (at 1013 °C). The thermogravimetric curve of the compound (6) is depicted in Fig. 2.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Yield (%)</th>
<th>M. pt. (°C)</th>
<th>Found (Calc.) %</th>
<th>pH</th>
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<td>4</td>
<td>38.1</td>
<td>200-205</td>
<td>65.2 (65.9)</td>
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<tr>
<td>5</td>
<td>50.6</td>
<td>&gt;240</td>
<td>59.8 (60.2)</td>
<td>4.1 (4.0)</td>
</tr>
<tr>
<td>6</td>
<td>56.5</td>
<td>170-175</td>
<td>57.5 (56.5)</td>
<td>3.6 (3.7)</td>
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</table>


![Scheme 1](image1)

Fig. 1—Aromatic region of the 'H NMR spectrum of (1) recorded in DMSO-δ₆.

![Table 2](image2)

In the 'H NMR spectra of the new complexes, the four protons of the hba ligands are manifested as four multiplets. The position as well as splitting pattern of these peaks depends upon the relative position of hydroxyl group. The labeling scheme of protons for the phen and hba ligands is shown in Scheme 1. The resonances due to phen protons are observed as additional four multiplets, and appear downfield compared to the carboxylate protons. The OH proton is observed as a singlet in the range 9.3 - 10.07 ppm. The aromatic region of the 'H NMR spectrum of (1) is given in Fig. 1 as a representative case.

Thermal analysis

Thermal analyses of complexes (1-6) have been carried out under a stream of nitrogen. The thermal decomposition studies show the loss of water molecules at around 100 °C. It was observed that the decomposition of 3-hba derivatives (1 – 3) was not complete even at 1200 °C. For compounds (4) and (5) the final decomposition product may be assumed to be the metal oxide product, based on the weight loss calculation. For (6), the final decomposition product is BaCO₃ (at 1013 °C). The thermogravimetric curve of the compound (6) is depicted in Fig. 2.

![Table 2](image2)
powder of these samples were identified by matching them with the powder diffractograms simulated from single crystal X-ray data, which agree well with the expected pattern. The experimental powder diffraction pattern and the simulated spectrum (from single crystal X-ray data, which agrees well with the bulk phase purity of the compounds reported herein. Powder X-ray diffraction and single crystal structures

The single crystal X-ray diffraction studies of the complexes [Sr(3-hba)$_2$(phen)$_2$(H$_2$O)$_2$]$_n$ (2), [Ba(3-hba)$_2$(phen)$_2$(H$_2$O)$_2$]$_n$ (3), [Ca(4-hba)$_2$(phen)$_2$(H$_2$O)] (4), and [Ba(4-hba)$_2$(phen)$_2$(H$_2$O)$_2$] (6) have been carried out. Repeated attempts to obtain suitable single crystals for [Ca(3-hba)$_2$(phen)$_2$(H$_2$O)$_2$] (1) and [Sr(4-hba)$_2$(phen)$_2$(H$_2$O)$_2$] (5) for X-ray investigations were unsuccessful. The hydrogen bond parameters responsible for supramolecular organization in compounds (2-4) and (6) are listed in Table 3, while selected bond lengths and angles are listed in Table 4. A comparison of selected structural parameters in these complexes is presented in Table 5.

Complexes (2-4) and 6 are all found to be monomeric in the solid state. The phenolic group is involved in the formation of hydrogen bonding and does not take part in metal coordination. It has been observed that the compounds (2) and (3) are isostructural with two phenanthroline ligands, with two carboxylate groups and two water molecules in the coordination sphere. However, the crystal structure of (3) consists of two crystallographically independent molecules [Ba(3-hba)$_2$(phen)$_2$(OH)$_2$] with the same coordination environment, but with slight structural difference in the periphery. Although compound (6) has a molecular formula similar to that of (2) and (3), the structural features are different. All the M–O$^{5c,13}$ and M–N$^{13d,14}$ bond lengths are in good agreement with the corresponding distances reported for alkaline earth metal complexes in the literature.

Molecular structure of (2) and (3)

The metal ions in 2 (Sr; Fig. 3) and 3 (Ba; Fig. 4) are eight coordinated with a donor set of four O atoms and four N atoms. The coordination geometry around the metal ions is distorted square antiprism. The phenanthroline ligands coordinate the metal from one side of the ion so that the nitrogen atoms occupy half of the coordination sphere and form one base of the antiprism. The other base is occupied by two water and two carboxylate oxygen atoms. The compound (2) crystallizes in centrosymmetric orthorhombic space group Pbnm, whereas (3) crystallizes in the non-centrosymmetric orthorhombic space group P2$_1$2$_1$2$_1$. It has not been possible to convert the unit cell of (3) to a centrosymmetric higher symmetry.

The phenanthroline units orient themselves in parallel planes with an eclipsed conformation with the interplanar distance between the two phen ligands only about ~3.5 Å, suggesting a strong π–π interaction within the complex (intramolecular π–π interaction). The phenolic –OH group is not involved in metal coordination.

While there are only two different Sr–N bond lengths in (2), eight different Ba–N bond lengths are present in 3. The Sr–N bond lengths in (2) are 2.705(2) and 2.869(2) Å, whereas the Ba–N bond lengths in (3) range from 2.841(4) to 3.145(4) Å for Ba(1) and 2.855(4) to 3.138(4) Å for Ba(2). Similar is the case with M–O bonds. The Sr–O bond lengths in (2) are 2.482(2) and 2.573(2) Å (Table 2), whereas the Ba–O bond lengths range from 2.649(3) to 2.875(3) around Ba(1) and 2.633(3) to 2.874(3) around Ba(2) in (3) respectively.

The presence of two water molecules and the phenolic group in the molecular structure results in the formation of extensive inter- and intramolecular hydrogen bonding in (2) and (3) (Figs 3 and 4) giving rise to a one-dimensional supramolecular architecture (Table 3). The meta-position of the phenolic hydroxyl group prevents it from forming intramolecular hydrogen bonding, but favours the formation of intermolecular hydrogen bonding with uncoordinated...
carboxylate oxygen of the neighbouring molecule. In compound (2), the 3-hba ligand coordinates to metal using oxygen atoms O(1) and O(1)’ from two different ligands, whereas the other carboxylate oxygens O(2) and O(2)’ remain uncoordinated. For compound (3), the carboxylate group binds to the metal in monodentate mode using the oxygen atoms O(1) and O(4) from two different ligands for Ba(1).
Table 4—Bond lengths (Å) and angles (°) in \([\text{Sr}(3\text{-hba})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (2), \([\text{Ba}(3\text{-hba})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (3), \([\text{Ca}(4\text{-hba})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (4) and \([\text{Ba}(4\text{-hba})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (6).

\[
\text{[Sr}(3\text{-hba})_2(\text{phen})_2(\text{OH}_2)_2]_n\) (2)
\]

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
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<tbody>
<tr>
<td>Sr(1)–O(1)</td>
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</tr>
<tr>
<td>Sr(1)–O(4)#</td>
<td>1.2573(2)</td>
</tr>
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<td>Sr(1)–N(2)</td>
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<tr>
<td>Sr(1)–N(1)#</td>
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<tr>
<td>O(1)–Sr(1)–O(1)#</td>
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</tr>
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</tr>
<tr>
<td>O(1)–Sr(1)–O(4)</td>
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</tr>
<tr>
<td>O(1)–Sr(1)–N(2)</td>
<td>82.74(6)</td>
</tr>
<tr>
<td>O(4)#–Sr(1)–N(2)</td>
<td>88.71(7)</td>
</tr>
<tr>
<td>O(1)–Sr(1)–N(2)#</td>
<td>140.46(7)</td>
</tr>
<tr>
<td>O(4)#–Sr(1)–N(2)#</td>
<td>113.58(7)</td>
</tr>
<tr>
<td>O(1)–Sr(1)–N(1)#</td>
<td>131.29(6)</td>
</tr>
<tr>
<td>O(4)–Sr(1)–N(1)#</td>
<td>69.10(7)</td>
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\[
\text{[Ba}(3\text{-hba})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (3)
\]

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
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<td>Ba(1)–O(1)</td>
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</tr>
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<td>Ba(1)–O(13)</td>
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<td>Ba(1)–O(14)</td>
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<td>90.41(12)</td>
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<td>126.94(12)</td>
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<td>O(13)–Ba(1)–O(4)</td>
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<td>O(13)–Ba(1)–N(1)</td>
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<td>132.87(10)</td>
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\[
\text{[Ca}(4\text{-hba})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (4)
\]

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<td>O(4)–Ca(1)–N(3)</td>
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<tr>
<td>O(1)–Ca(1)–N(3)</td>
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Contd.
Table 4—Bond lengths (Å) and angles (deg) in [Sr(3-hba)2(phen)2(H2O)2]n (2), [Ba(3-hba)2(phen)2(H2O)2]n (3), [Ca(4-hba)2(phen)2(H2O)] (4) and [Ba(4-hba)2(phen)2(H2O)2] (6)—Contd.

<table>
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<th>Contd.</th>
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<td>N(1)-Ca(1)-N(3)</td>
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<tr>
<td>Ba(1)–O(4)</td>
<td>2.586(5)</td>
<td>Ba(1)–O(2)</td>
<td>2.685(5)</td>
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<td>Ba(1)–O(8)</td>
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<td>Ba(1)–N(3)</td>
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<td>O(7)–Ba(1)–N(2)</td>
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<td>O(4)–Ba(1)–N(4)</td>
<td>75.6(2)</td>
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<td>O(2)–Ba(1)–N(4)</td>
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<td>O(7)–Ba(1)–N(4)</td>
<td>101.1(2)</td>
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<td>O(8)–Ba(1)–N(4)</td>
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<td>144.8(2)</td>
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<td>120.6(2)</td>
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<td>N(3)–Ba(1)–N(1)</td>
<td>154.3(2)</td>
<td>N(4)–Ba(1)–N(1)</td>
<td>135.0(2)</td>
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</table>

Symmetry: For (2) #1 -x+1, y+1/2, z.

Table 5—A comparison of structural features in compounds (2-4) and (6)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Nuclearity</th>
<th>M ion coord no.</th>
<th>Coord. geom. around M ion*</th>
<th>Carboxylate ion</th>
<th>Distinctive H-bonds</th>
<th>M-O bond lengths (Å)</th>
<th>M-N bond lengths (Å)</th>
</tr>
</thead>
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<td>(2)</td>
<td>Monomer</td>
<td>Eight</td>
<td>Square antiprism</td>
<td>Monodentate</td>
<td>O-H...O</td>
<td>2.482(2)-2.573(2)</td>
<td>2.705(2)-2.869(2)</td>
</tr>
<tr>
<td>(3)</td>
<td>Monomer</td>
<td>Eight</td>
<td>Square antiprism</td>
<td>Monodentate</td>
<td>O-H...O</td>
<td>2.649(3)-2.875(3)</td>
<td>2.841(4)-3.145(4)</td>
</tr>
<tr>
<td>(4)</td>
<td>Monomer</td>
<td>Seven</td>
<td>Pentagonal bipyramidal</td>
<td>Monodentate</td>
<td>O-H...O</td>
<td>2.633(3)-2.874(3)</td>
<td>2.855(4)-3.138(4)</td>
</tr>
<tr>
<td>(6)</td>
<td>Monomer</td>
<td>Eight</td>
<td>Square antiprism</td>
<td>Monodentate</td>
<td>O-H...O</td>
<td>2.586(5)-2.809(5)</td>
<td>2.955(6)-2.992(6)</td>
</tr>
</tbody>
</table>

*All the polyhedral arrangements around the metal are highly distorted from normal.

and O(10) and O(7) for Ba(2). The second O atom of the carboxylic group (O(2) and O(5) for Ba(1) and O(8) and O(11) for Ba(2)) are not involved in metal coordination. In both cases, the uncoordinated carboxylate oxygen atoms are involved in the formation of H-bonds with phenolic group of the neighbouring molecule as well as with coordinated water molecules. The coordinated water molecules further take part in intermolecular hydrogen bonding with water molecules of the neighbouring molecule. Apart from this, the molecule contains large amount of inter and intramolecular C–H…O hydrogen bonding, which further links different molecules together and imparts more stability to the compound. When viewed along the b axis, the three-dimensional structure of the molecule can be envisaged as layers of [M(3-hba)2(phen)2(OH2)2] units held to each other via intermolecular hydrogen bonding.

**Molecular structure of (4)**

Compound [Ca(4-hba)2(phen)2(H2O)] (4) is a monomer as in the case of (2) and (3) and crystallizes in the monoclinic space group P21/a. The calcium atom is hepta-coordinated displaying distorted pentagonal bipyramidal geometry (Fig. 5).
Fig. 3—(a) Molecular structure of \([\text{Sr(3-hba)}_2(\text{phen})_2(\text{OH}_2)_2]\) (2), (b) coordination polyhedron, (c) hydrogen bonding network.

Fig. 4—(a) Molecular structure of \([\text{Ba(3-hba)}_2(\text{phen})_2(\text{H}_2\text{O})_2]_n\) (3), (b) coordination polyhedron, (c) hydrogen bonding network.
The molecular structure of \([\text{Ca}(4\text{-hba})_2(\text{phen})_2(H_2O)]_n\) \((4)\) consists of a calcium atom, two \(p\)-hydroxybenzoate ligands, two phenanthroline ligands, and one water molecule. The two axial positions of the pentagonal bipyramid is occupied by the carboxylate oxygen atom (O(4)) from one of the \(p\)-hydroxy benzoate ligand and a coordinated water oxygen (O(1)). The four nitrogen atoms from the two phenanthroline ligands (N(1), N(2), N(3) and N(4)) and one oxygen from the second carboxylate ligand (O(2)) occupy the equatorial position, thus completing the coordination sphere. The carboxylate ligand coordinates in an anti-unidentate mode.

Quite contrary to the 3-hba analogues, the two phenanthroline ligands in \((4)\) coordinate to the metal from the opposite sides, forming a butterfly-like structure. However, the two phen ligands are not in the same plane; the molecular plane of one of the phenanthroline ligand is tilted from the plane, heavily distorting the pentagonal bipyramid. The phenolic groups are involved in hydrogen bonds with neighbouring water molecules and the uncoordinated carboxylate oxygen atom (Table 3). The presence of these weak bonds along with C–H⋯O hydrogen bonds results in the formation of a three-dimensional supramolecular network (Fig. 6). The Ca–O bond lengths are different, and range from 2.268(2) to 2.411(2) Å. Also, the four Ca–N distances are different in the molecule, the longest one being N(3)–Ca(1) (2.602(2)) and the shortest one N(2)–Ca(1) (2.519(2) Å).

Compound \([\text{Ba}(4\text{-hba})_2(\text{phen})_2(H_2O)]_2\) \((6)\) crystallizes in the monoclinic space group \(P2_1/n\). The barium atom is octacoordinated with a distorted square antiprismatic geometry (Fig. 7). The molecular structure of \((6)\) differs from that of \((4)\) in having one additional water molecule coordinated to the metal ion, thus taking the coordination number of the metal ion to eight. Thus the coordination environment of barium atom consists of two \(4\)-hydroxybenzoate ligands, two phenanthroline ligands, and two water molecules. Similar to its calcium analogue, the phen ligands in \((6)\) coordinates from the opposite directions. The two carboxylate oxygen atoms, O(2)
KORAH et al.: SUPRAMOLECULAR AGGREGATION IN ALKALINE EARTH METAL BENZOATES

and O(4), and the two phenanthroline nitrogen atoms, N(2) and N(3) occupy one base of the antiprism. The other base is occupied by the nitrogen atoms of N(1) and N(4) and the two water oxygen atoms, O(7) and O(8).

The molecule exhibits four different Ba–O bond lengths which range from 2.586(5) to 2.809(5) Å. The longer distances are associated with those arising from coordinated water molecule, while the shorter distances are due to the carboxylate oxygen atom in the axial position. Similarly, the four Ba–N distances are different in the molecule, the longest one being Ba(1)–N(1) (2.992(6)) and the shortest one Ba(1)–N(3) (2.975(6)).

The packing diagram of the compound exhibiting H-bonded network is shown in Fig. 8. The molecules are held together in the solid state via hydrogen bonding interactions. The presence of inter- and intramolecular hydrogen bonding results in the formation of a three-dimensional supramolecular architecture. One of the coordinated water molecule, O(8)W, forms intramolecular hydrogen bonding with the uncoordinated carboxylate oxygen, O(1). It also forms two other intermolecular hydrogen bonds: one with phenolic oxygen atom O(5) and the other a C–H⋯O bond with phenanthroline hydrogen atom H(6A) (Table 3).

Conclusions

It has been shown herein that it is possible to introduce N-donor ligands in the coordination sphere of group 2 metal cations. A comparison of the crystal structures of the complexes shows interesting structural variations. All the compounds form discrete monomeric which are units linked together by C–H⋯O, O–H⋯O and N–H⋯O hydrogen bonds. The formation of hydrogen bonds is evidenced by the hydrogen bond lengths and angles. The coordination sphere of the metal is occupied by one or more water molecules. Apart from the hydrogen bonding interactions, the molecules are assembled in solid state by π–π stacking interaction as well. The C–H⋯O interactions may afford additional stability and rigidity to the supramolecular framework and make the network more stable. It may be concluded from the studies that in the presence of a chelating amine such as phenanthroline, the carboxylate ligand

Fig. 7—(a) Molecular structure of [Ba(4-hba)₂(phen)₂(H₂O)₂] (6), (b) coordination polyhedron.

Fig. 8—Inter- and intramolecular hydrogen bonding in [Ba(4-hba)₂(phen)₂(H₂O)₂] (6).
may act as a monodentate ligand, thus inhibiting the expansion of polymeric framework. A comparison of key structural features of the compounds is given in Table 5.

Acknowledgement

The authors thank the DST and CSIR, New Delhi (RK was a recipient of CSIR JRF and SRF), for the financial support. SAIF, IIT-Bombay, Mumbai, is thanked for the spectral measurements.

Supplementary Data

CCDC numbers 822426–822429 contain the supplementary crystallographic data for (2)–(4) and (6). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References