

Synthesis, crystal structure and properties of magnesium and calcium salts of *p*-anisic acid

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Abstract. The synthesis, crystal structure and properties of the magnesium and calcium salts of *p*-anisic acid *viz.* $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ ($\text{C}_8\text{H}_7\text{O}_3 = p$ -anisate or 4-methoxybenzoate) (**1**) and $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (**2**) are reported. The *p*-anisate ion is not coordinated to Mg(II) and functions as a charge balancing counter anion for the centrosymmetric octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ unit in **1**. The unique lattice water molecule links pairs of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations and *p*-anisate anions with the aid of O-H...O interactions. The μ_2 -bridging bidentate and the μ_3 -bridging tetradentate binding modes of the crystallographically unique *p*-anisate ligands in (**2**) result in a two-dimensional (2-D) coordination polymer.

Keywords. Magnesium; calcium; *p*-anisic acid; μ_2 -bridging bidentate; μ_3 -bridging tetradentate; coordination polymer.

1. Introduction

The study of coordination polymers is currently a topical area of research.¹ In its recent recommendations on the terminology of metal–organic frameworks (MOFs) and coordination polymers (CPs), the International Union of Pure and Applied Chemistry (IUPAC) defines a coordination polymer as one with repeating coordination entities extending in 1, 2, or 3 dimensions and the use of a prefix 1D-, 2D-, or 3D- to indicate the degree of extension of the coordination polymer.² The designed construction of such CPs began with the pioneering work of Robson^{3a} who employed a tetratopic tetranitrile ligand $[\text{C}(\text{C}_6\text{H}_4\text{CN})_4]$ ($\text{C}_6\text{H}_4\text{CN}=4$ -cyanophenyl) to link Cu(I) ions into a diamond-like network. Since then several other N and O donor ligands have been employed for the construction of CPs of varying dimensionality, a few notable ones being the ditopic benzene-1,4-dicarboxylic acid and the tritopic benzene-1,3,5-tricarboxylic acid introduced by the Yaghi group.^{3b} The structures of many compounds with repeating coordination entities extending in 1, 2, or 3 dimensions (for example the carboxylates of calcium)

are reported in older literature without referring to them as coordination polymers. Based on a study of several structurally characterized Ca(II) carboxylates, Einspahr and Bugg^{3c,3d} had reported that Ca(II) ions usually bind to several carboxylate groups. The past decade has witnessed several new additions to this list of Ca(II) compounds containing monocarboxylate linkers, for example, the aminobenzoates of Ca(II) reported by the Murugavel group⁴ and the nitrobenzoates of Ca(II) reported by the Srinivasan group.⁵ It is noted that the structure of the Ca(II) salt of *p*-anisic acid is not reported so far.

Anisic acid also known as methoxybenzoic acid exists in three forms depending on the disposition of the methoxy (-OCH₃) group with respect to the carboxylic acid functionality in the six membered phenyl ring. Although many examples of structurally characterized metal anisates are reported in the literature^{6–8} for the *para*-isomer (4-methoxybenzoic acid or *p*-anisic acid) in which the methoxy (-OCH₃) group is *trans* to -COOH moiety,^{9a} no structurally characterized *p*-anisate of Mg(II) or Ca(II) is known till date. However, the *p*-anisates of Sr(II) and Ba(II) are well documented in the literature.^{9b,9c} In view of our interest in the chemistry of alkaline-earth metal carboxylates, we have investigated the reactions of magnesium (or calcium) carbonate with *p*-anisic acid and have structurally characterized the products. The results of these studies are described in this paper.

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Dedicated to Prof. Subramanian Natarajan on the occasion of his 68th birth anniversary.

2. Experimental

2.1 Materials and Methods

All the chemicals used in this study were of reagent grade and were used as received without any further purification. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000-400 cm^{-1} at a resolution of 4 cm^{-1} . UV-Visible spectra were recorded in water using a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. Isothermal weight loss studies were performed in a temperature controlled furnace. TG-DTA study was performed in flowing oxygen in Al_2O_3 crucibles at a heating rate of 10 K min^{-1} using a STA-409 PC simultaneous thermal analyser from Netzsch. X-ray powder pattern were recorded on a Rigaku Miniflex II powder diffractometer using $\text{Cu-K}\alpha$ radiation with Ni filter.

2.2 Synthesis of $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ (1) and $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (2)

A mixture of *p*-anisic acid (1.217 g, 8 mmol) and basic magnesium carbonate (0.388 g, 0.8 mmol) was taken in water (~50 mL) and the reaction mixture was heated on a water bath. Brisk effervescence was observed and the heating was continued till all the insoluble carbonate dissolved to give a clear solution. The hot reaction mixture was filtered and left aside for crystallization. Colourless crystals which separated in a few days were collected by filtration in ~68% yield. The reaction of calcium carbonate (0.400 g, 4 mmol) with *p*-anisic acid (8 mmol) under the same conditions for MgCO_3 afforded crystals of **2** in ~80% yield.

2.3 X-ray crystal structure determination

Single crystal X-ray analysis of compounds **1** and **2** was done at the Sophisticated Analytical Instrument

Table 1. Crystal data and selected refinement results for (1) and (2).

| | | |
|---|---|---|
| Empirical formula | $\text{C}_{16}\text{H}_{30}\text{MgO}_{14}$ (1) | $\text{C}_{16}\text{H}_{16}\text{CaO}_7$ (2) |
| Formula weight (g mol^{-1}) | 470.71 | 360.37 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (\AA) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1$ |
| Unit cell dimensions | | |
| <i>a</i> (\AA) | 12.3938 (6) | 5.8212(2) |
| <i>b</i> (\AA) | 11.1553(4) | 6.9210(2) |
| <i>c</i> (\AA) | 8.2660(4) | 19.3962(6) |
| β ($^\circ$) | 103.549(2) | 94.369(5) |
| Volume (\AA^3) | 1111.02(9) | 779.17(4) |
| Z | 2 | 2 |
| D_{calc} (mg/m^3) | 1.407 | 1.536 |
| Absorption coefficient (mm^{-1}) | 0.148 | 0.439 |
| F(000) | 500 | 376 |
| Crystal size (mm^3) | $0.35 \times 0.30 \times 0.25$ | $0.35 \times 0.30 \times 0.30$ |
| θ range for data collection ($^\circ$) | 2.488 to 27.438 | 2.11 to 25.00 |
| Index ranges | $-16 \leq h \leq 15$; $-14 \leq k \leq 14$; $-10 \leq l \leq 10$ | $-6 \leq h \leq 6$; $-8 \leq k \leq 8$; $-23 \leq l \leq 22$ |
| Reflections collected / unique | 16213 / 2538 (R(int) = 0.0247) | 7394 / 2728 (R(int) = 0.0159) |
| Completeness to θ | 100% | 99.7 % |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. Transmission | 0.9699 and 0.9492 | 0.8815 and 0.8604 |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 2538 / 12 / 174 | 2728 / 4 / 229 |
| Goodness-of-fit on F^2 | 1.048 | 1.111 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0316, wR2 = 0.0796 | R1 = 0.0207, wR2 = 0.0539 |
| R indices (all data) | R1 = 0.0481, wR2 = 0.0898 | R1 = 0.0217, wR2 = 0.0547 |
| Absolute structure parameter | — | 0.38(3) |
| Extinction coefficient | — | 0.0055(10) |
| Largest diff. peak and hole (e \AA^{-3}) | 0.239 and -0.176 | 0.207 and -0.159 |

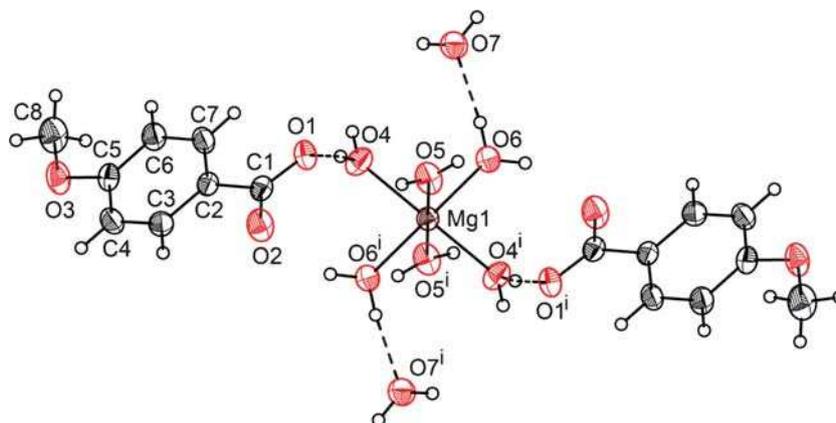


Figure 1. The crystal structure of $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ (**1**) showing the atom labeling scheme and the coordination sphere of Mg(II) in **1**. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown in broken lines. Symmetry code: i) $-x+2, -y, -z+1$.

Table 2. Selected bond lengths and bond angles [\AA , $^\circ$].

| | | | |
|---|------------|---|------------|
| $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ (1) ^a | | | |
| Mg1-O5 | 2.0306(10) | Mg1-O5 ⁱ | 2.0306(10) |
| Mg1-O6 | 2.0402(10) | Mg1-O6 ⁱ | 2.0402(10) |
| Mg1-O4 | 2.0677(10) | Mg1-O4 ⁱ | 2.0677(10) |
| O5 ⁱ -Mg1-O5 | 180.0 | O6-Mg1-O4 ⁱ | 89.72(5) |
| O5 ⁱ -Mg1-O6 | 88.71(5) | O6 ⁱ -Mg1-O4 ⁱ | 90.28(5) |
| O5 ⁱ -Mg1-O6 ⁱ | 91.29(5) | O5 ⁱ -Mg1-O4 | 93.54(5) |
| O5-Mg1-O6 ⁱ | 88.72(5) | O6-Mg1-O4 | 90.28(5) |
| O6-Mg1-O6 ⁱ | 180.0 | O6 ⁱ -Mg1-O4 | 89.72(5) |
| O5 ⁱ -Mg1-O4 ⁱ | 86.46(5) | O4 ⁱ -Mg1-O4 | 180.0 |
| O5-Mg1-O4 ⁱ | 93.54(5) | O5-Mg1-O6 | 91.28(5) |
| O5-Mg1-O4 | 86.46(5) | | |
| $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (2) ^b | | | |
| Ca1-O1 | 2.3984(13) | Ca1-O4 ⁱⁱ | 2.6013(13) |
| Ca1-O2 | 2.2755(11) | Ca1-O5 ⁱⁱⁱ | 2.3032(12) |
| Ca1-O3 | 2.3761(14) | Ca1...Ca1 ⁱ | 4.059(3) |
| Ca1-O4 | 2.4946(13) | Ca1...Ca1 ^{iv} | 5.821(0) |
| Ca1-O1 ⁱ | 2.4706(13) | Ca1...Ca1 ^v | 6.921(1) |
| O2-Ca1-O5 ⁱⁱⁱ | 109.83(5) | O5 ⁱⁱⁱ -Ca1-O4 | 83.77(5) |
| O2-Ca1-O3 | 81.57(5) | O3-Ca1-O4 | 106.58(5) |
| O5 ⁱⁱⁱ -Ca1-O3 | 165.63(5) | O1-Ca1-O4 | 170.30(4) |
| O2-Ca1-O1 | 90.74(6) | | |
| O5 ⁱⁱⁱ -Ca1-O1 | 89.90(5) | O1 ⁱ -Ca1-O4 | 69.02(4) |
| O3-Ca1-O1 | 81.00(6) | O2-Ca1-O4 ⁱⁱ | 150.73(5) |
| O2-Ca1-O1 ⁱ | 140.41(5) | O5 ⁱⁱⁱ -Ca1-O4 ⁱⁱ | 91.05(4) |
| O5 ⁱⁱⁱ -Ca1-O1 ⁱ | 96.42(5) | O3-Ca1-O4 ⁱⁱ | 75.29(5) |
| O3-Ca1-O1 ⁱ | 78.63(6) | O1-Ca1-O4 ⁱⁱ | 68.34(4) |
| O1-Ca1-O1 ⁱ | 119.18(4) | O1 ⁱ -Ca1-O4 ⁱⁱ | 51.18(4) |
| O2-Ca1-O4 | 84.54(6) | O4-Ca1-O4 ⁱⁱ | 118.96(4) |

^aSymmetry transformations used to generate equivalent atoms: i) $-x+2, -y, -z+1$.

^bSymmetry transformations used to generate equivalent atoms: i) $-x+3, y+1/2, -z+2$; ii) $-x+3, y-1/2, -z+2$; iii) $x+1, y, z$; iv) $x-1, y, z$; v) $x, 1+y, z$.

Facility (SAIF), Indian Institute of Technology (IIT) Madras. X-ray intensity data were collected using Bruker AXS Kappa Apex II CCD Diffractometer

equipped with graphite monochromated Mo ($K\alpha$) ($\lambda = 0.7107 \text{ \AA}$) radiation, through an optimized strategy which gave an average 4-fold redundancy. The

Table 3. Hydrogen bonding geometry [\AA , $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | \angle DHA | Symmetry code |
|--|-----------|-----------|------------|--------------|-----------------------|
| [Mg(H₂O)₆](C₈H₇O₃)₂·2H₂O (1) | | | | | |
| O7-H7A...O1 | 0.848(14) | 1.943(14) | 2.7773(15) | 167.4(19) | $x, -y+1/2, z-1/2$ |
| O7-H7B...O2 | 0.839(14) | 1.964(15) | 2.7908(17) | 168(2) | $-x+2, y+1/2, -z+3/2$ |
| O6-H6A...O3 | 0.839(15) | 2.002(17) | 2.7960(16) | 158(2) | $x+1, y, z$ |
| O6-H6B...O7 | 0.857(14) | 1.839(14) | 2.6920(16) | 173.3(19) | x, y, z |
| O5-H5A...O2 | 0.857(14) | 1.849(15) | 2.7021(15) | 173.5(19) | $x, y, z-1$ |
| O5-H5B...O7 | 0.841(15) | 1.990(17) | 2.7839(17) | 157.0(18) | $x, -y+1/2, z-1/2$ |
| O4-H4A...O1 | 0.862(14) | 1.918(15) | 2.7742(15) | 171.7(19) | x, y, z |
| O4-H4B...O1 | 0.827(14) | 2.046(15) | 2.8652(15) | 171(2) | $x, -y+1/2, z-1/2$ |
| [Ca(H₂O)(C₈H₇O₃)₂] (2) | | | | | |
| C16-H16B...O6 | 0.96 | 2.66 | 3.474(3) | 143.2 | $-x+2, y+1/2, -z+1$ |
| O3-H3A...O4 | 0.826(16) | 2.13(2) | 2.8940(19) | 154(2) | $-x+2, y-1/2, -z+2$ |
| O3-H3B...O5 | 0.864(17) | 1.948(17) | 2.807(2) | 173(3) | $-x+2, y-1/2, -z+2$ |

program APEX2-S SAINT (Bruker, 2004) was used for integrating the frames. Four-fold redundancy per reflection was utilized for achieving good multi-scan absorption correction using SADABS (Bruker, 2004). Besides absorption, Lorentz, polarization and decay corrections were applied to intensity during data reduction. The structures were solved by direct methods using SIR92^{10a} and refined by full-matrix least squares techniques using SHELXL-97.^{10b} The crystal used for the structure determination of **2** was twinned and hence a twin refinement with batch scale factor (BASF) of 0.38 was performed. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms attached to the aromatic ring were introduced in calculated positions and included in the refinement by riding on their respective parent C atoms. The technical details of data acquisition and selected crystal refinement results are summarised in table 1.

3. Results and Discussion

3.1 Synthetic aspects, spectral and thermal studies

In this work, we have employed acid-base chemistry for the synthesis of *p*-anisate salts of Mg and Ca. The insoluble carbonates of Mg (or Ca) were solubilised by reacting them with a hot aqueous solution of *p*-anisic acid in 1:2 mole ratio. The clear solution thus obtained afforded crystals of **1** (or **2**) in good yield on slow evaporation. The metal carbonates can be solubilised faster in aqueous *p*-anisic acid to obtain the same products, if the reaction is performed in a domestic microwave oven. The composition of **1** and **2** was arrived at based on elemental analytical data and analysis of the residue formed on pyrolysis. The optical spectra of **1** and **2** in water exhibit absorption maxima at 284 nm (figure S1 in Supplementary Information)

which is close to the λ_{max} of the free acid. This signal can thus be assigned for an intraligand charge transfer of the *p*-anisate. A comparison of the IR spectra of **1** and **2** with that of the free acid reveals that the band due to $-\text{COOH}$ group of the free acid occurring at 1686 cm^{-1} is shifted to lower energies in **1** and **2** due to the formation of anisate (figure S2). The presence of water in both **1** and **2** can be evidenced by the characteristic profile of the spectra in the $3500\text{--}3000 \text{ cm}^{-1}$ region. Compound **2** is thermally more stable as compared to **1** as evidenced by no change in mass on heating at 100°C . In the case of **1** a loss in mass of 17.56% corresponding to four water molecules is observed. On pyrolysis at 800°C both are converted to the corresponding binary oxide as evidenced by featureless IR

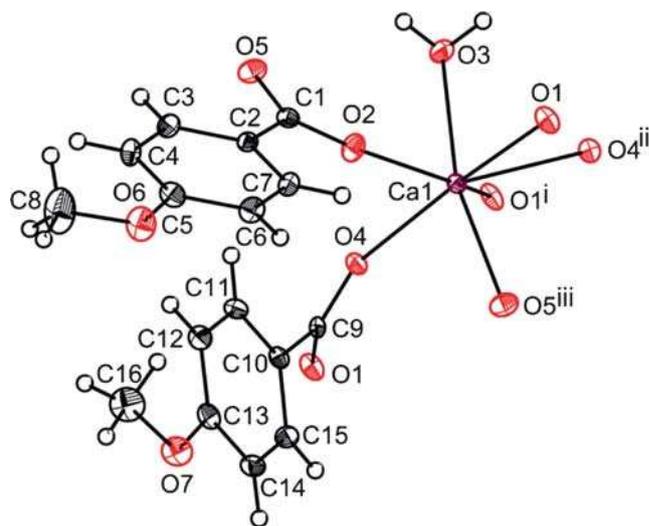


Figure 2. The crystal structure of $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (**2**) showing the atom labeling scheme and the coordination sphere of Ca(II) in **2**. Displacement ellipsoids are drawn at the 50% probability level excepting the H atoms, which are shown as circles of arbitrary radius. Symmetry code: i) $-x+3, y+1/2, -z+2$; ii) $-x+3, y-1/2, -z+2$; iii) $x+1, y, z$.

spectra for the loss of organics. In accordance with the observation of no mass loss on heating at 100°C, the TG-DTA curves of **2** exhibit the first weight loss corresponding to the loss of the coordinated water starting from 140°C (figure S3). The anhydrous compound thus formed can be rehydrated to the original composition as evidenced by IR spectra (figure S4). Exothermic events are observed at higher temperatures (382 and 489°C) which can be attributed to the decomposition of the ligand. Based on a combination of spectral data, weight loss study and elemental analytical data, both **1** and **2** are formulated as $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$, respectively.

3.2 Crystal structure of $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (**2**)

Compound **1** crystallises in the centrosymmetric monoclinic space group $P2_1/c$ with the Mg(II) located on an inversion centre. The crystal structure consists of

a central Mg(II) ion, three unique terminal water ligands, an independent *p*-anisate anion and a lattice water molecule (figure 1). In view of the special position of Mg(II), the asymmetric unit consists of a half of the formula unit. In **1** the *p*-anisate is not coordinated to Mg(II) but functions as a charge balancing counter anion. Its geometric parameters are in the normal range (table S1). The central metal is linked to six aqua ligands forming the well-known $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ unit^{4a,11} which has been observed in several Mg(II) carboxylates listed in the Cambridge Database^{11c} (table S2). The Mg-O bond distances range from 2.0306(10) to 2.0677(10) Å (table 2). The *trans* O-Mg-O angles exhibit ideal values of 180° while the *cis* O-Mg-O angles vary between 86.46(5) to 93.54(5)° indicating a slightly distorted $\{\text{MgO}_6\}$ octahedron.

An analysis of the crystal structure of **1** reveals that the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation, the *p*-anisate anion and the lattice water (O7) are interlinked with the aid of only O-H...O interactions (table 3). The O1, O2 and O3 atoms

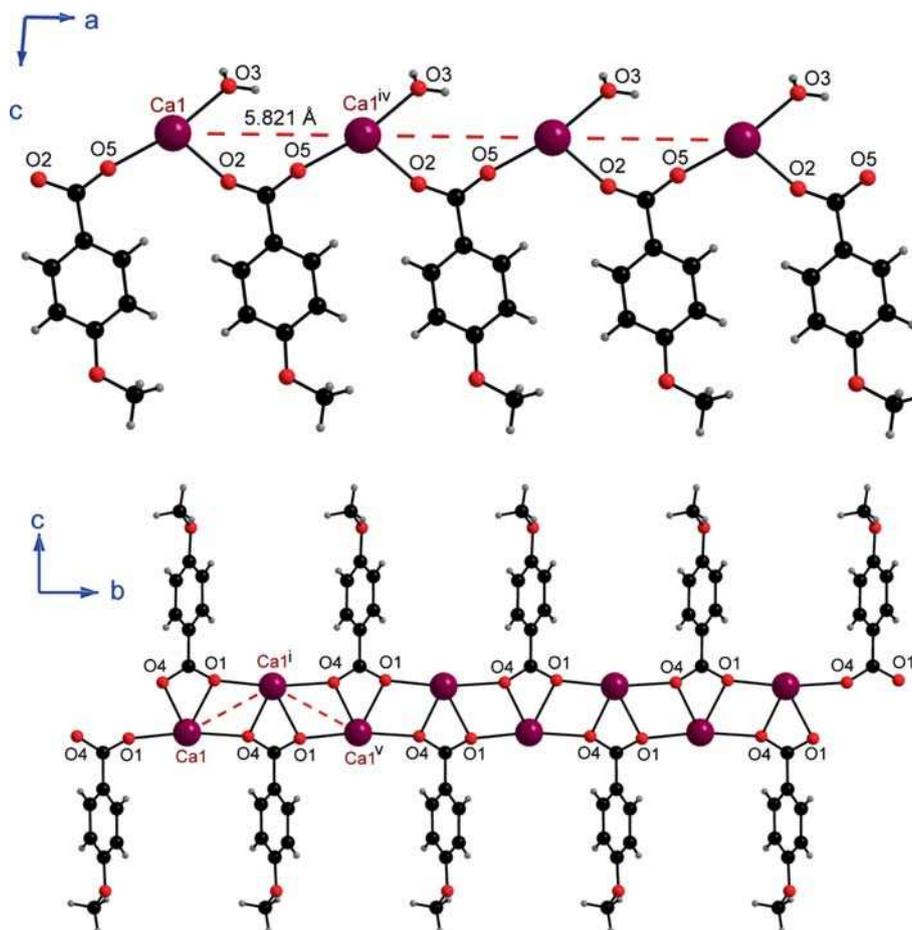


Figure 3. (Top) A portion of an infinite chain extending along *a*-axis due to the first unique *p*-anisate (O2, O5); For clarity the *p*-anisates (O1, O4) around each Ca(II) are not shown. (Bottom) A view of an infinite double chain along *b*-axis due to the second unique *p*-anisate (O1, O4). For clarity, the monodentate water ligand and the *p*-anisates (O2, O5) on each Ca(II) are not shown.

of the *p*-anisate and the O7 of lattice water function as H-acceptors while the H-atoms of the coordinated and lattice water molecules function as H-donors (figure S5). The oxygen atom (O7) of the lattice water forms H-acceptor bonds with two different $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations via O6-H6B \cdots O7 and O5-H5B \cdots O7 interactions (*x*, *y*, *z* and *x*, -*y*+1/2, *z*-1/2), while the H atoms of the lattice water further link it with two *p*-anisate anions via H-donor bonds in the form of O7-H7A \cdots O1 and O7-H7B \cdots O2 interactions. Thus, the lattice water (O7) serves as a link between the alternating layers of cations and anions.

Compound **2** crystallizes in the monoclinic Sohncke space group $P2_1$ with all atoms located in general positions. In view of the non-centrosymmetric nature of the space group, its choice for the structure model as well as the phase purity of **2** was confirmed by a comparison of its theoretical powder pattern with the experimental pattern (figure S6). The crystal structure of **2** consists of a unique Ca(II) ion, two crystallographically independent *p*-anisate ligands, and a monodentate water molecule (figure 2). The geometric parameters of the unique *p*-anisate ligands (table S1) are in the normal range. Each calcium is linked to

Table 4. List of structurally characterized calcium compounds with monocarboxylic acids.

| No. | Compound | C.N. | S. G. | Dimensionality | Ref |
|-----|--|-------|--------------|----------------|-----------|
| 1 | $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]$ | 8 | $P\bar{1}$ | 1-D | 5a |
| 2 | $[\text{Ca}(\text{H}_2\text{O})_2(\text{C}_8\text{H}_5\text{NO}_3)_2]$ | 7 | $P\bar{1}$ | 1-D | 5b |
| 3 | $[\text{Ca}(\text{H}_2\text{O})_3(2\text{-aba})_2]$ | 7 | <i>Pbcn</i> | 1-D | 4b |
| 4 | $[\text{Ca}(\text{H}_2\text{O})_2(3\text{-aba})_2]$ | 8 | <i>Pbcn</i> | 1-D | 4c |
| 5 | $[\text{Ca}_3(\text{H}_2\text{O})_4(\text{Sa})_6(4\text{-bpy})_2]$ | 7,6,7 | $P\bar{1}$ | 1-D | 4d |
| 6 | $[\text{Ca}(\text{Sa})_2(\text{Phen})]$ | 6 | <i>Pnab</i> | 1-D | 4d |
| 7 | $[\text{Ca}(\text{H}_2\text{O})_2(\text{C}_8\text{H}_5\text{O}_3)_2]$ | 8 | <i>C2/c</i> | 1-D | 12a |
| 8 | $[\text{Ca}(\text{H}_2\text{O})_2(\text{C}_7\text{H}_3\text{O}_2\text{F}_2)_2]$ | 8 | <i>C2/c</i> | 1-D | 12b |
| 9 | $[\text{Ca}(\text{H}_2\text{O})_3(4\text{-fba})](4\text{-fba})$ | 8 | $P2_1/c$ | 1-D | 12c |
| 10 | $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-CNbenz})_2]$ | 8 | $P2/n$ | 1-D | 12d |
| 11 | $[\text{Ca}(\text{H}_2\text{O})_3(\text{benz})](\text{benz})$ | 8 | $P2_1/c$ | 1-D | 12e |
| 12 | $[\text{Ca}(\text{H}_2\text{O})(\text{dnSa})]$ | 7 | $P2_1/c$ | 1-D | 12f |
| 13 | $[\text{Ca}(\text{H}_2\text{O})(\text{DMF})(\text{benz})_2]$ | 8 | $P2_1/n$ | 1-D | 12g |
| 14 | $[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]$ | 7 | $P2_1/n$ | 1-D | 5c |
| 15 | $[\text{Ca}(\text{H}_2\text{O})(\text{N-MeIm})(4\text{-nba})_2]$ | 6 | $P\bar{1}$ | 1-D | 5d |
| 16 | $[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]$ | 6 | $P\bar{1}$ | 1-D | 5f |
| 17 | $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}$ | 8 | $P\bar{1}$ | 1-D | 5g |
| 18 | $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-aba})_2]$ | 8 | $P2_12_12_1$ | 1-D | 4a |
| 19 | $[\text{Ca}(\text{H}_2\text{O})_2(\text{L}_1)_2]\cdot \text{H}_2\text{O}$ | 8 | $P2_1$ | 1-D | 5e |
| 20 | $[\text{Ca}(\text{H}_2\text{O})_2(\text{L}_2)_2]\cdot 2\text{H}_2\text{O}$ | 8 | $P2_1$ | 1-D | 5e |
| 21 | $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (2) | 7 | $P2_1$ | 2-D | This work |

C.N. = Coordination number; S.G. = Space group; 2-nba=2-nitrobenzoate; $(\text{C}_8\text{H}_6\text{NO}_3)$ = 2-carbamoyl-4-nitrobenzoate; 2-aba = 2-aminobenzoate; 3-aba = 3-aminobenzoate; Sa = salicylic acid; 4-bpy = 4,4'-bipyridine; phen = 1,10-phenanthroline; $(\text{C}_8\text{H}_5\text{O}_3)$ = 2-formylbenzoate; $(\text{C}_7\text{H}_3\text{O}_2\text{F}_2)$ = 2,6-difluorobenzoate; 4-fba = 4-fluorobenzoate; 4-CNbenz = 4-cyanobenzoate; benz = benzoate; dnSa = 3,5-dinitrosalicylate; 2-MeIm = 2-methylimidazole; 4-nba = 4-nitrobenzoate; N-MeIm = N-methylimidazole; pyr = pyrazole; dmp = 3,5-dimethylpyrazole; 4-aba = 4-aminobenzoate; L₁ = 4-methoxyphenylacetate; L₂ = 2-chlorophenylacetate.

Table 5. Structural details of alkaline-earth *p*-anisates.

| Compound | S.G. | C.N. | Binding mode | H-bonding | Ref |
|---|-------------|------|---|-------------------------------|-----------|
| $\text{C}_8\text{H}_8\text{O}_3$ (<i>p</i> -anisic acid) | $P2_1/a$ | — | — | O-H \cdots O | 9a |
| $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_7\text{O}_3)_2\cdot 2\text{H}_2\text{O}$ (1) | $P2_1/c$ | 6 | Counter ion | O-H \cdots O | This work |
| $[\text{Ca}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ (2) | $P2_1$ | 7 | μ_2 -bidentate; μ_3 -tetradentate | O-H \cdots O C-H \cdots O | This work |
| $[\text{Sr}(\text{H}_2\text{O})(\text{C}_8\text{H}_7\text{O}_3)_2]$ | <i>Pbca</i> | 8 | μ_2 -bidentate; μ_3 -tetradentate | — [#] | 9b |
| $[\text{Ba}(\text{C}_8\text{H}_7\text{O}_3)_2]$ | $P\bar{1}$ | 8 | μ_3 -tetradentate | — [#] | 9c |

S.G. = Space group; C.N. = Coordination number; [#]H-atom coordinates not reported.

a monodentate water and to six O atoms from five symmetry related *p*-anisate anions, resulting in a distorted monocapped trigonal prismatic {CaO₇} polyhedron (figure S7). The Ca-O bond distances vary between 2.2755(11) and 2.6013(13) Å (table 3), while the O-Ca-O angles scatter in a very broad range from 51.18(4) to 170.30(4)° indicating the distortion of the {CaO₇} polyhedron. The unique *p*-anisate ligands in the crystal structure exhibit different bridging binding modes (figure S8). The first unique ligand (O2, O5) functions as a μ_2 -bidentate bridge between two Ca(II) ions and links the metals into a chain extending along *a* axis (figure 3) with a Ca...Ca separation of 5.821 Å. The second unique ligand (O1, O4) functions as a μ_3 -tetradentate bridge for three Ca(II) ions and links them into an infinite double chain (ladder) extending along *b* axis with Ca...Ca separations of 4.059(3) and 6.921(1) Å respectively (figure 3). Each Ca(II) in this double chain is bonded to three symmetry related *p*-anisates (O1, O4).

The net effect of the metal binding of two unique *p*-anisate ligands is the organization of the Ca(II) ions into a two-dimensional (2D) layer in the *ab* crystallographic plane (figure S9) with each Ca(II) in the layer bonded to a monodentate water ligand and to six O atoms from five symmetry related *p*-anisate ligands two of which are (O2, O5) and the rest being (O1, O4). An analysis of the structure reveals that the H-atoms of the coordinated water and one H atom (H16B) of a methoxy group function as H-donors and the oxygen atoms O4, O5 and O6 function as H-acceptors (figure S10). It is interesting to note that the O6 oxygen of a methoxy group of the first unique anisate (O2, O5) is H-bonded to the H16B atom of the methoxy group in the second unique ligand thus serving as a link to two perpendicular chains (figure S10). We consider this as an important secondary interaction because i) no C-H...O interaction is observed for the Mg(II) anisate, ii) a 2D layer structure is observed for a Ca-carboxylate prepared using an aromatic monocarboxylic acid unlike the 1D chain structure for many Ca-carboxylates^{4,5,12} of aromatic monocarboxylic acids (table 4). Although the last four entries (Nos. 18-21) crystallize in non-centrosymmetric space groups, the preference for a centrosymmetric space group is shown by a majority of (80%) of the compounds in the list. It is interesting to note that **2** is the only example in the list of Ca(II) carboxylates in table 4 which exhibits a 2D connectivity for a monosubstituted benzoic acid.

A comparative study of the structural chemistry of four alkaline-earth *p*-anisates (table 5) is presented. It is interesting to note that the coordination number varies from 6 for Mg to 8 for Sr and Ba. The Mg(II)

compound is water rich and is a hexa aqua dihydrate while the Ca and Sr anisates contain a single coordinated water. Although the unique *p*-anisates in the Ca and Sr compounds exhibit same binding modes, the coordinated water functions as a μ_2 -bidentate bridging ligand in Sr thus accounting for its octa coordination. The Ba anisate is anhydrous. In the heavier congeners, Ca, Sr and Ba, the μ_3 -tetradentate bridge binding mode is observed for *p*-anisate and all three compounds are two-dimensional.

4. Conclusions

In summary, the synthesis, crystal structure and properties of the Mg and Ca salts of *p*-anisic acid are described. The Mg(II) salt is a hexa aqua dihydrate and exhibits a layer structure of alternating [Mg(H₂O)₆]²⁺ cations and *p*-anisate anions with the lattice water functioning as a link between the layers. The mono aqua Ca(II) salt is a two-dimensional coordination polymer and is a new example of a structurally characterized benzene carboxylate of calcium.

Supplementary Information (SI)

Crystallographic data (excluding structure factors) for the structures of [Mg(H₂O)₆](C₈H₇O₃)₂·2H₂O (**1**) and [Ca(H₂O)(C₈H₇O₃)₂] (**2**) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1431469 (**1**) and CCDC 1431470 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

Electronic supplementary information (for figures S1–S10 and tables S1–S3) is available at www.ias.ac.in/chemsci.

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References

- (a) Batten S R, Neville S M and Turner D R 2009 In *Coordination Polymers: Design, Analysis and Application* (RSC Publishing: Cambridge UK); (b) Robson R 2008 *Dalton Trans.* 5113; (c) Themed issue 'Coordination polymers: structure and function' 2010 Biradha K (Ed.) *New J. Chem.* **34** 2353–2681; (d) Biradha K, Ramanan A and Vittal J J 2009 *Cryst. Growth Des.* **9** 2969; (e) Natarajan S, Mahata P and Sarma D 2012 *J. Chem. Sci.* **124** 339; (f) Vishnoi P, Kalita A Ch and Murugavel R 2014 *J. Chem. Sci.* **126** 1385; (g) Suresh P and Prabusankar G 2014 *J. Chem. Sci.* **126** 1409; (h) Mudsainiyan R K, Jassal A K, Arora M and Chawla S K 2015 *J. Chem. Sci.* **127** 849
- (a) Coordination Polymers and metal Organic Frameworks: Terminology and Nomenclature guidelines, (<http://www.iupac.org/web/ins/2009-012-2-200>) Last update April 1, 2015; (b) Batten S R, Champness N R, Chen X M, Garcia M J, Kitagawa S, Öhrström L, O'Keeffe M, Suh M P and Reedijk J 2012 *Cryst. Eng. Comm.* **14** 3001
- (a) Hoskins B F and Robson R 1989 *J. Am. Chem. Soc.* **111** 5962; (b) Eddaoudi M, Moler D B, Li H, Chen B, Reineke T M, O'Keeffe M and Yaghi O M 2001 *Acc. Chem. Res.* **34** 319; (c) Einsphar H and Bugg C E 1980 *Acta Crystallogr.* **36B** 264; (d) Einsphar H and Bugg C E 1981 *Acta Crystallogr.* **37B** 1044
- (a) Murugavel R, Karambelkar V V and Anantharaman G 2000 *Indian J. Chem. A* **39** 843; (b) Murugavel R, Karambelkar V V, Anantharaman G and Walawalkar M G 2000 *Inorg. Chem.* **39** 1381; (c) Murugavel R and Banerjee S 2003 *Inorg. Chem. Commun.* **6** 810; (d) Murugavel R and Korah R 2007 *Inorg. Chem.* **46** 11048
- (a) Srinivasan B R, Shetgaonkar S Y and Raghavaiah P 2009 *Polyhedron* **28** 2879; (b) Srinivasan B R and Shetgaonkar S Y 2010 *J. Coord. Chem.* **63** 3403; (c) Srinivasan B R, Shetgaonkar S Y, Näther C and Bensch W 2009 *Polyhedron* **28** 534; (d) Srinivasan B R, Shetgaonkar S Y, Sawant J V and Raghavaiah P 2008 *Polyhedron* **27** 3299; (e) Srinivasan B R, Shetgaonkar S Y and Ghosh N N 2011 *J. Coord. Chem.* **64** 1113; (f) Srinivasan B R, Shetgaonkar S Y and Näther C 2011 *Z. Anorg. Allg. Chem.* **637** 130; (g) Srinivasan B R, Shetgaonkar S Y, Saxena M and Näther C 2012 *Indian J. Chem.* **51A** 435
- (a) McGregor D R and Speakman J C 1968 *J. Chem. Soc. A* 2106; (b) Lučanská B and Krätšmár-Šmogrovič J 1977 *Z. Chem.* **17** 113; (c) Ghyragov F M, Musaev F N, Gambarov D G, Abbasov R M and Mamedov K S 1987 *Koord. Khim.* **13** 1412; (d) Antsyshkina A S, Chyragov F M and Porai-Koshits M A 1989 *Koord. Khim.* **15** 1098; (e) Parulekar C S, Jain V K, Kesavadas T and Tiekink E R T 1990 *J. Organometallic Chem.* **387** 163
- (a) Eppley H J, deVries N, Wang S, Aubin S M, Tsai H L, Foltling K, Hendrickson D N and Christou G 1997 *Inorg. Chim. Acta* **263** 323; (b) Jin L, Wang R, Li L, Lu S and Huang S 1998 *Polyhedron* **18** 487; (c) Wang Z, Zhang Y, Razak I A, Shanmuga S R S, Fun H K, Li and Song H 2000 *Acta Crystallogr.* **C56** 161; (d) Wang J, Ping L, Chen Y and Liu Z 2004 *Acta Crystallogr.* **E60** m628
- (a) Hökelek T, Dal H, Tercan B, Tenlik E and Necefoglu H 2010 *Acta Crystallogr.* **E66** m910; (b) Hökelek T, Süzen Y, Tercan B, Tenlik E and Necefoglu H 2010 *Acta Crystallogr.* **E66** m784; (c) Hökelek T, Dal H, Tercan B, Tenlik E and Necefoglu H 2010 *Acta Crystallogr.* **E66** m891; (d) Hökelek T, Süzen Y, Tercan B, Tenlik E and Necefoglu H 2010 *Acta Crystallogr.* **E66** m807; (e) Hökelek T, Saka G, Tercan B, Tenlik E and Necefoglu H 2010 *Acta Crystallogr.* **E66** m1135; (f) Jin S W, Lin Z H, Zhou Y, Wang D Q, Chen G Q, Ji Z Y and Huang T S 2014 *Polyhedron* **74** 79; (g) Zhou X, Wong W T, Hau S C K and Tanner P A 2015 *Polyhedron* **88** 138
- (a) Colapietro M and Domenicano A 1978 *Acta Crystallogr.* **B34** 3277; (b) Cherkezova V R, Musaev F N, Karaev Z S, Surazhskaya M D, Larina T B and Koz'min P A 1988 *Koord. Khim.* **14** 1139; (c) Cherkezova V R, Musaev F N, Karaev Z S, Koz'min P A, Surazhskaya M D and Larina T B 1987 *Koord. Khim.* **13** 833
- (a) Altomare A, Cascarano G, Giacovazzo C, Guagliardi A, Burla M C, Polidori G and Camalli M 1994 *J. Appl. Cryst.* **27** 435; (b) Sheldrick G M 2008 *Acta Crystallogr.* **A64** 112
- (a) Wiesbrock F, Schier A and Schmidbaur H 2002 *Z. Naturforsch.* **B57** 251; (b) Srinivasan B R, Sawant J V, Näther C and Bensch W 2007 *J. Chem. Sci.* **119** 243; (c) Allen F H 2002 *Acta Crystallogr.* **B58** 380
- (a) Odabaşoğlu M and Büyükgüngör O 2007 *Acta Crystallogr.* **E63** m712; (b) Karipides A, White C and Peiffer K 1992 *Acta Crystallogr.* **C48** 1015; (c) Karipides A, McKinney C and Peiffer K 1988 *Acta Crystallogr.* **C44** 46; (d) Yuan R X, Xiong R G, Chen Z F, You X Z, Peng S M and Lee G H 2001 *Inorg. Chem. Commun.* **4** 430; (e) Senkovska I and Thewalt U 2005 *Acta Crystallogr.* **C61** m448; (f) Song W D, Guo X X and Zhang C H 2007 *Acta Crystallogr.* **E63** m399; (g) Yano S, Numata M, Kato M, Motoo S and Nishimura T 2001 *Acta Crystallogr.* **E57** m488