

## Three-dimensional hybrid networks based on aspartic acid

ANUPAMA GHOSH<sup>1,2,\*</sup> and R A SANGURAMATH<sup>2</sup>

<sup>1</sup>Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

<sup>2</sup>Chemistry and Physics of Materials Unit and CSIR Centre of Excellence in Chemistry,

Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064

e-mail: anupamag@jncasr.ac.in

**Abstract.** Three-dimensional achiral coordination polymers of the general formula  $M_2(D, L\text{-NHCH}(\text{COO})\text{CH}_2\text{COO})_2 \cdot \text{C}_4\text{H}_4\text{N}_2$  where  $M = \text{Ni}$  and  $\text{Co}$  and pyrazine acts as the linker molecule have been prepared under hydrothermal conditions starting with  $[\text{M}(\text{L-NHCH}(\text{COO})\text{CH}_2\text{COO}) \cdot 3\text{H}_2\text{O}]$  possessing a helical chain structure. A three-dimensional hybrid compound of the formula  $\text{Pb}_{2.5}[\text{N}\{\text{CH}(\text{COO})\text{CH}_2\text{COO}\}_2 \cdot 2\text{H}_2\text{O}]$  has also been prepared hydrothermally starting with aspartic acid and  $\text{Pb}(\text{NO}_3)_2$ . In this lead compound, where a secondary amine formed by the dimerisation of aspartic acid acts as the ligand, there is two-dimensional inorganic connectivity and one-dimensional organic connectivity.

**Keywords.** Aspartic acid; hybrid compounds; nickel aspartate; lead aspartate; achiral frameworks.

### 1. Introduction

Open-framework hybrid networks involving metal silicates, phosphates and sulphates have been areas of great interest in the past few decades.<sup>1–3</sup> Much attention is being paid in the last few years to organic–inorganic hybrid frameworks formed by metal carboxylates and phosphonates<sup>4–7</sup> because of their structural diversity and possible applications in catalysis<sup>8,9</sup>, separation<sup>10,11</sup> and hydrogen storage.<sup>12,13</sup> Natural amino acids have been used extensively to form coordination polymers with transition metals since both the carboxylate and the amino groups can coordinate to the metal depending upon the pH of the medium.<sup>14–16</sup>

Aspartic acid,  $\text{NH}_2\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ , is an acidic amino acid with one amino and two carboxylic acid groups. As these functional groups are capable of binding to the metal centres in different coordination modes it is exploited greatly to form hybrid metal-organic framework structures. Chiral and achiral metal aspartates with extended structures have been reported in the recent literature.<sup>17–19</sup> In the present work, we report two metal-organic framework structures derived from aspartic acid. We report a three-dimensional racemic structure of the formula  $\text{Ni}_2(\text{D, L-NHCH}(\text{COO})\text{CH}_2\text{COO})_2 \cdot \text{C}_4\text{H}_4\text{N}_2$ , **I**, by connecting helical nickel aspartate chains with

the bi-dentate aromatic linker pyrazine. We have obtained an analogous cobalt compound of the formula  $\text{Co}_2(\text{D, L-NHCH}(\text{COO})\text{CH}_2\text{COO})_2 \cdot \text{C}_4\text{H}_4\text{N}_2$ , **II**, starting with cobalt aspartate. We also report a three-dimensional hybrid lead compound of the formula  $\text{Pb}_{2.5}[\text{N}\{\text{CH}(\text{COO})\text{CH}_2\text{COO}\}_2 \cdot 2\text{H}_2\text{O}]$ , **III**, resulting from the hydrothermal reaction between  $\text{Pb}(\text{NO}_3)_2$  and aspartic acid, where the ligand is a secondary amine formed by the dimerisation of aspartic acid. In **III**, there is two-dimensional inorganic connectivity and one-dimensional organic connectivity.

### 2. Experimental

#### 2.1 Synthesis and initial characterization

In order to prepare  $\text{Ni}_2(\text{D, L-NHCH}(\text{COO})\text{CH}_2\text{COO})_2 \cdot \text{C}_4\text{H}_4\text{N}_2$ , **I**, 54.9 mg of Ni-asp [ $\text{Ni}(\text{L-NHCH}(\text{COO})\text{CH}_2\text{COO}) \cdot 3\text{H}_2\text{O}$ ] were dissolved in water (3 mL)–ethanol (2 mL) mixture to which pyrazine (16.90 mg) was added. The resultant solution with Ni-asp : pyrazine ratio of 1 : 1 was stirred for 1 h and transferred to a 23 mL PTFE-lined acid digestion bomb and heated at 150°C for 48 h. The pH of the solution was kept at around 5–6. Shiny bluish green coloured crystals so obtained were vacuum filtered and washed with water.

The cobalt analogue of **I**, was prepared as follows. 131.0 mg of Co-asp [ $\text{Co}(\text{L-NHCH}(\text{COO})\text{CH}_2\text{COO}) \cdot$

\*For correspondence

3H<sub>2</sub>O] were dissolved in water (5 mL)-ethanol (5 mL) mixture to which pyrazine (80.80 mg) was added. The resultant solution with Co-asp : pyrazine ratio of 1 : 2 was stirred for 1 h and transferred to a 23 mL PTFE-lined acid digestion bomb and heated at 150°C for 48 h. The pH of the solution was kept at around 5–6. Dark red coloured solid so obtained were vacuum filtered and washed with water.

Pb<sub>2.5</sub>[N{CH(COO)CH<sub>2</sub>COO}2H<sub>2</sub>O], **III**, was prepared as follows. 334.5 mg of Pb(NO<sub>3</sub>)<sub>2</sub> were dissolved in water (5 mL) to which L-aspartic acid (203.70 mg) was added. To the resultant mixture, with a Pb(NO<sub>3</sub>)<sub>2</sub>:aspartic acid ratio of 1 : 1.5, 1 molar NaOH solution was added drop-wise to make the pH of the solution equal to 5. The solution was stirred for an hour and transferred to a 23 mL PTFE-lined acid digestion bomb and heated at 150°C for 72 h. Beautiful colorless crystals so obtained were vacuum filtered and washed with water.

The precursor materials Ni-asp and Co-asp were prepared as follows. A 1 : 1 mixture of Ni(Co)Cl<sub>2</sub>·6H<sub>2</sub>O : aspartic acid was taken in a vial and dissolved in water. Triethylamine was added to maintain the pH at around 5. The resultant mixture was kept on a hot water bath for slow evaporation. After 3 days green crystals of the composition [Ni(L-NHCH(COO)CH<sub>2</sub>COO)·3H<sub>2</sub>O] and pink coloured crystals of [Co(L-NHCH(COO)CH<sub>2</sub>COO)·3H<sub>2</sub>O] were obtained. The crystals were vacuum filtered and washed with water. These precursors are similar in structure.<sup>14</sup>

Initial characterization of the compounds **I**, **II** and **III** were carried out by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and IR spectroscopy. PXRD patterns indicated the products to be new materials and monophasic, the patterns being consistent with those generated from single-crystal X-ray diffraction. Elemental analysis of **I**, **II** and **III** were satisfactory. Elemental analysis for **I**: C, 31.7%; H, 2.7% N, 12.3%. Observed: C, 31.8%; H, 3.7% N, 12.1%; for **II**: C, 31.7%; H, 2.7% N, 12.3%. Observed: C, 31.9%; H, 3.1% N, 12.0%; for **III**: Calculated: C, 12.5%; H, 1.3% N, 1.8%. Observed: C, 13.0%; H, 1.2% N, 1.9%; Infrared spectra of **I**, **II** and **III** show characteristic bands in the region 1400–1600 cm<sup>-1</sup> and 3300–3400 cm<sup>-1</sup> due to carboxylate and amine group stretching vibration of the aspartate moiety. Beside that, bands due to C–H and C–C stretching and bending vibrations have also been characterized.<sup>20</sup> A broad band in the 2800–3200 cm<sup>-1</sup> region in the spectra of those compounds

indicates the presence of extensive hydrogen bonding.

Thermogravimetric analysis of above compounds was carried out under constant flow of O<sub>2</sub> at a heating rate of 5°C min<sup>-1</sup> in the temperature range 30–900°C. Compound **I** showed a two-step weight loss corresponding to the loss of aspartic acid and pyrazine molecules in the range 350–450°C and 450–550°C (obs = 74.1%, calcd = 74.8%). Compound **II** showed the same type of TGA curve. Compound **III** showed a two-step weight loss corresponding to the loss of water molecules and aspartic acid dimer molecule in the range 200–450°C and 450–550°C (obs = 33.3%, calcd = 35.1%).

## 2.2 Single crystal structure determination

Suitable single crystals of **I** and **III** were carefully selected under a polarizing microscope and glued at the tip of a thin glass fibre with cyano-acrylate (super-glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-K<sub>α</sub> radiation, λ = 0.71073 Å) operating at 50 kV and 35 mA. A hemisphere of intensity data was collected at room temperature with ω space scans (width of 0.30° and exposure time of 10 or 20 s per frame). Pertinent experimental details of the structure determination for compounds **I** and **III** and are presented in table 1.

The structures were solved by direct methods using SHELXS-86,<sup>21</sup> which readily established the heavy atom position (Pb and Ni) and facilitated the identification of the light atoms (O, N, C, H) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS programme.<sup>22</sup> All the hydrogen positions were initially located in the difference Fourier maps and the hydrogen atoms were placed geometrically and held in the riding mode for the final refinement. With the single crystal X-ray data collected at room temperature, few of the hydrogen atoms of the water molecules of **III** could not be located from the difference Fourier maps. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against

**Table 1.** Crystal data and structure refinement parameters for compound **I** and **III**<sup>a</sup>.

Parameters	<b>I</b> <sup>b</sup>	<b>III</b>
Empirical formula	Ni <sub>2</sub> N <sub>4</sub> C <sub>12</sub> H <sub>12</sub> O <sub>8</sub>	Pb <sub>2.5</sub> NC <sub>8</sub> O <sub>10</sub> H <sub>10</sub>
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pmm2</i>	<i>P2(1)</i>
Crystal size (mm)	0.28 × 0.38 × 0.18	0.28 × 0.18 × 0.16
<i>a</i> (Å)	15.4137(6)	9.6521(6)
<i>b</i> (Å)	6.5818(2)	9.7770(6)
<i>c</i> (Å)	7.8808(3)	10.0407(6)
$\alpha$ (°)	90.0	89.9270(10)
$\beta$ (°)	90.0	70.0980(10)
$\gamma$ (°)	90.0	62.9510(10)
Volume (Å <sup>3</sup> )	799.51(5)	780.04(8)
<i>Z</i>	4	5
Formula mass	203.48	250.22
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.113	4.794
$\lambda$ (MoK $\alpha$ ) Å	0.71073	0.71073
<i>M</i> (mm <sup>-1</sup> )	5.796	48.418
$\theta$ range (°)	2.64 to 27.89	0.999 to 25.59
Total data collected	4266	10664
Limiting indices	-20 ≤ <i>h</i> ≤ 11, -5 ≤ <i>k</i> ≤ 8, -9 ≤ <i>l</i> ≤ 10	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -12 ≤ <i>l</i> ≤ 12
Unique data	1754	2926
Observed data ( <i>I</i> > 2σ( <i>I</i> ))	1266	2542
Refinement method	Full-matrix least squares on   <i>F</i> <sup>2</sup>	Full-matrix least squares on   <i>F</i> <sup>2</sup>
<i>R</i> <sub>int</sub>	0.0300	0.0382
<i>R</i> indexes [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0465, <i>wR</i> <sub>2</sub> = 0.1186	<i>R</i> <sub>1</sub> = 0.0521, <i>wR</i> <sub>2</sub> = 0.1391
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.0801, <i>wR</i> <sub>2</sub> = 0.1534	<i>R</i> <sub>1</sub> = 0.0629, <i>wR</i> <sub>2</sub> = 0.1575
Goodness of fit	1.082	1.186
No. of variables	118	197
Largest difference map peak and hole e.Å <sup>-3</sup>	0.712 and -0.749	5.817 and -1.998

<sup>a</sup>*R*<sub>1</sub> =  $\sum||F_o| - |F_c||/\sum|F_o|$ ; <sup>b</sup>*wR*<sub>2</sub> =  $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ ,  $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ , *a* = 0.0856 and *b* = 0.0000 for **I**

*a* = 0.0890 and *b* = 7.4879 for **III**

<sup>b</sup>Unit cell dimensions of **II**, the cobalt analogue of **I** are *a* (Å) = 16.01, *b* (Å) = 6.81, *c* (Å) = 8.34,  $\alpha$  (°) = 90.0,  $\beta$  (°) = 90.0,  $\gamma$  (°) = 90.0, volume (Å<sup>3</sup>) = 909.0

|*F*<sup>2</sup>| was carried out using the SHELXTL-PLUS package of programs.<sup>23</sup>

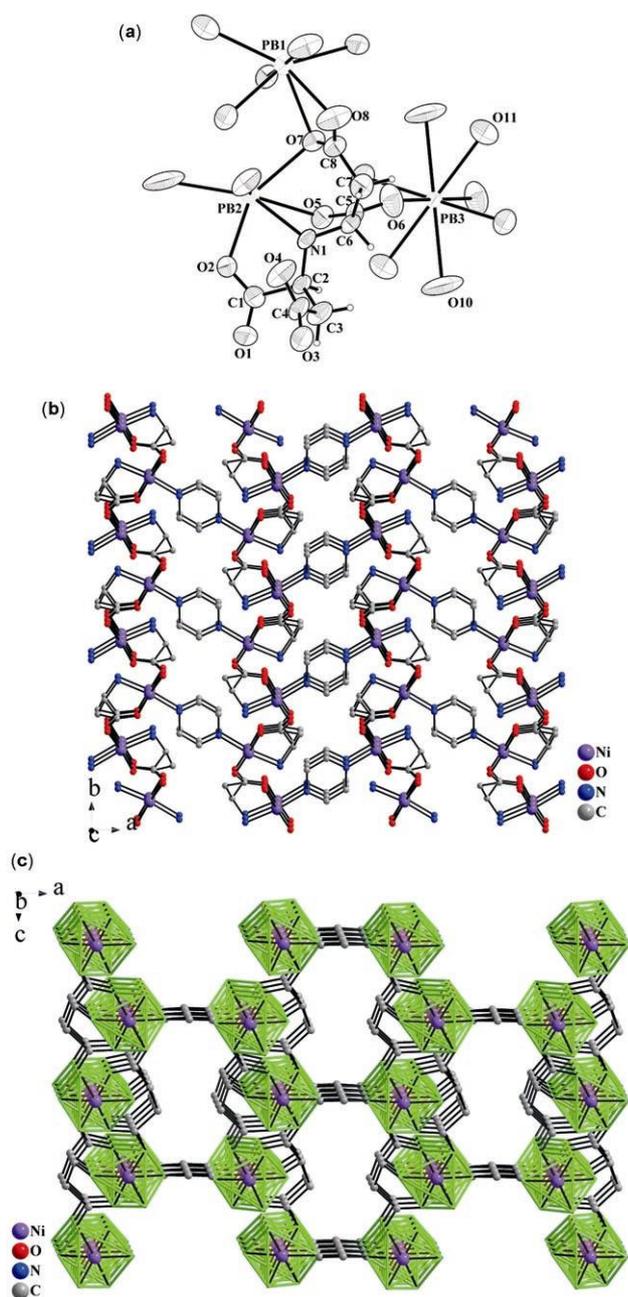
### 3. Results and discussion

We have prepared an achiral three-dimensional coordination polymer Ni<sub>2</sub>(D, L-NHCH(COO)CH<sub>2</sub>COO)<sub>2</sub>·C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>, **I**, by the hydrothermal reaction of nickel aspartate trihydrate salt Ni(L-NHCH(COO)CH<sub>2</sub>COO)·3H<sub>2</sub>O possessing a chiral one-dimensional helical extended chain structure with pyrazine. The asymmetric unit of **I** (figure 1a) contains 13 non-hydrogen atoms, with one Ni atom, one aspartate molecule and half of the pyrazine ligand. The coordination number Ni is six and coordinated to carboxylate oxygen and nitrogen atoms of the aspartic acid as well as nitrogen atom of pyrazine molecule. All the

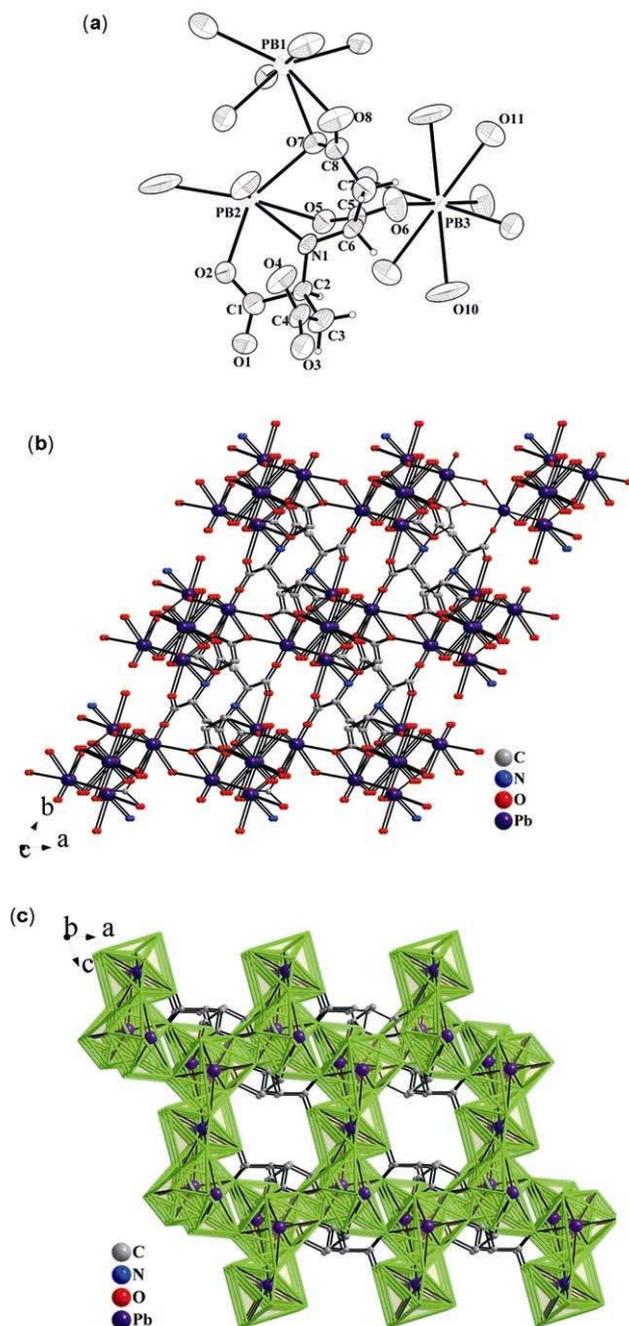
oxygen and nitrogens take part in coordination and aspartic acid act as quinque dentate ligand. At this high temperature L-acid undergoes racemisation and both the L- and D-acid exist in the structure which is reflected on the achiral space group of the crystal. Water molecules of the nickel aspartate trihydrate are replaced by aspartic acid oxygens and pyrazine nitrogens to give a three-dimensional structure. In **I**, L- and D-nickel aspartate helices are joined together by carboxylate bridges to form the *bc* plane of the crystals. These layers are joined together by pyrazine linkers in a zigzag fashion along the *a* direction of the unit cell to give a porous three-dimensional network (figure 1b). The polyhedral view of the structure down the *c* axis of the unit cell shows rectangular pores (figure 1c). The inorganic and organic connectivities in **I** are zero and three re-

spectively which can be specified as the  $\Gamma^0 O^3$  type. The Ni–O bond length in the nickel aspartate moiety of **I** is in the range of 2.038(0)–2.101(0) Å (average 2.068 Å) with Ni–N bond length being 2.079(0) Å. The average C–O, C–C and C–N distances of the

aspartic acid are 1.258, 1.577 and 1.552 Å respectively. The Ni–N (pyrazine) bond length is 2.098 Å while the average C–N distance in the pyrazine ring is 1.329 Å.



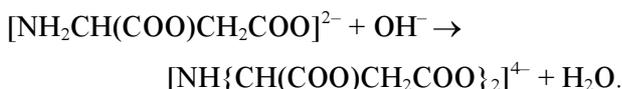
**Figure 1.** (a) ORTEP plot of Ni(D, L-NH-CH(COO)CH<sub>2</sub>COO).C<sub>2</sub>H<sub>2</sub>N, **I**. Thermal ellipsoids are shown at 50% probability. Only the asymmetric part is labelled. (b) Three-dimensional structure of **I** viewed along the *c* axis of the unit cell. Hydrogen atoms are not shown for clarity. (c) Polyhedral view of **I** viewed along the *b* axis of the unit cell.



**Figure 2.** (a) ORTEP plot of Pb<sub>2.5</sub>[N{CH(COO)CH<sub>2</sub>COO}2H<sub>2</sub>O], **III**. Thermal ellipsoids are shown at 50% probability. Only the asymmetric part is labelled. (b) Three-dimensional structure of **III** viewed along the *c* axis of the unit cell. Hydrogen atoms are not shown for clarity. (c) Polyhedral view of **III** viewed along the *b* axis of the unit cell.

The cobalt analogue  $\text{Co}_2(\text{D}, \text{L-NHCH}(\text{COO})\text{CH}_2\text{COO})_2 \cdot \text{C}_4\text{H}_4\text{N}_2$ , **II**, is isomorphous with **I** and gave an identical powdered X-ray diffraction pattern. The unit cell parameters of **II** are given in table 1.

We have obtained an achiral three-dimensional compound of the formula  $\text{Pb}_{2.5}[\text{N}\{\text{CH}(\text{COO})\text{CH}_2\text{COO}\}_2 \cdot 2\text{H}_2\text{O}]$ , **III**, from the high-temperature reaction of L-aspartic acid and  $\text{Pb}(\text{NO}_3)_2$ . This compound results from the dimerisation of aspartic acid to give a secondary amine as per the following reaction:



The asymmetric unit of **III** (figure 2a) contains 20 non-hydrogen atoms, with three crystallographically independent Pb atoms, two water molecules bridging the lead centers and one aspartic acid dimer molecule. The coordination number of Pb1 is seven and coordinated to water molecules as well as carboxylate oxygens of the ligand moiety while coordination number of Pb2 is six and is ligated through water molecules as well as the amine nitrogen and carboxylate oxygens of the ligand. Both of the lead atoms have somewhat distorted geometry and shows hemidirectionality. Pb3 is holodirectional with half occupancy in the asymmetric unit and has a regular eight coordinated geometry formed by both water and carboxylate oxygen atoms. Because of the high temperature and the basic condition of the reaction one of the amine hydrogens gets replaced by another aspartic acid moiety and forms the dimeric structure which is nothing but a secondary amine. Pb1 and Pb2 are joined together by carboxylate oxygens to form hybrid double chains along the *a* direction of the unit cell. These double chains are joined with one another through Pb–O–Pb linkage involving Pb3 and water oxygens to form hybrid layers parallel to the *ac* plane of the unit cell. These hybrid layers are joined together by ligand moiety through amine nitrogen and carboxylic oxygen atoms along the *b* direction of the unit cell to give the final three-dimensional  $\text{I}^2\text{O}^1$  hybrid structure (figure 2b). All the oxygen and the nitrogen atoms of the ligand are coordinated here. Polyhedral view of the structure shows rectangular pores formed by the three-dimensional network (figure 2c). The structure clearly reveals the inversion centre symmetry as reflected on the P-1 space group of the crystal. Two

types of Pb–O bonds are present in the structure, the Pb–O (water) bonds with a average bond length of 2.684 Å, the Pb–O (carboxylate) bonds with bond lengths in the ranges 2.408(1)–2.672(1) Å (average 2.592 Å) along with Pb–N bond length being 2.518 Å. The average C–O, C–N and C–C bond distances of the di-aspartate ligand are 1.263, 1.473 and 1.533 Å respectively.

#### 4. Conclusions

Reaction of  $\text{Ni}(\text{L-NHCH}(\text{COO})\text{CH}_2\text{COO}) \cdot 3\text{H}_2\text{O}$  with the pyrazine linker under hydrothermal conditions gives a new compound of the formula  $\text{Ni}_2(\text{D}, \text{L-NHCH}(\text{COO})\text{CH}_2\text{COO})_2 \cdot \text{C}_4\text{H}_4\text{N}_2$ , **I**, with extended three-dimensional connectivity. As the cobalt analogue of **I** has a similar structure, it may be surmised that similar compounds of other transition metals can also be prepared. The hydrothermal reaction of  $\text{Pb}(\text{NO}_3)_2$  and L-aspartic acid yields an achiral three-dimensional hybrid network with two-dimensional inorganic and one-dimensional organic connectivities. The compound has the composition  $\text{Pb}_{2.5}[\text{N}\{\text{CH}(\text{COO})\text{CH}_2\text{COO}\}_2 \cdot 2\text{H}_2\text{O}]$  wherein a secondary amine formed by the dimerisation of aspartic acid is the ligand.

CCDC-668748 and 668747 (**I** and **III**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))

#### Acknowledgement

The authors are grateful to Prof. C N R Rao for suggesting the problem and his constant support and guidance.

#### References

1. (a) Breck D W 1974 *Zeolite molecular sieves* (New York: Wiley); (b) Meier W M, Oslen D H and Baerlocher C 1996 *Atlas of zeolite structure types* (London: Elsevier)
2. (a) Cheetham A K, Férey G and Loiseau T 1999 *Angew. Chem. Int. Ed.* **38** 3268; (b) Rao C N R, Natarajan S, Choudhury A, Neeraj S. and Ayi A A 2001 *Acc. Chem. Res.* **34** 80
3. Rao C N R, Behera J N and Dan M 2006 *Chem. Soc. Rev.* **35** 375

4. (a) Rao C N R, Natarajan S, Vaidhyanathan R 2004 *Angew. Chem. Int. Ed.* **43** 1466; (b) Ocwig N C, D-Friedrichs O, O'Keefe M and Yaghi O M 2005 *Acc. Chem. Res.* **38** 176; (c) Forster, P M and Cheetham A K 2003 *Top Cat.* **24** 79
5. Cheetham A K, Rao C N R and Feller R K 2006 *Chem. Commun.* 4780
6. Kitagawa S, Kitaura R and Noro S 2004 *Angew. Chem. Int. Ed.* **43** 2334
7. Clearfield A 1998 *Prog. Inorg. Chem.* **47** 371
8. Clearfield A and Wang Z K 2002 *J. Chem. Soc., Dalton Trans.* 2937
9. Fujita M, Kwon Y J, Washizu S and Ogura K 1994 *J. Am. Chem. Soc.* **116** 1151
10. Kepert C J, Prior T J and Rosseinsky M J 2000 *J. Am. Chem. Soc.* **122** 5158
11. Chen B, Liang C, Yang J, Contreras D S, Clancy Y L, Lobkovsky E B, Yaghi O M and Dai S 2006 *Angew. Chem. Int. Ed.* **45** 1390
12. Zhao X B, Xiao B, Fletcher A J, Thomas K M, Bradshaw D and Rosseinsky M J 2004 *Science* **306** 1012
13. Wong-Foy A G, Matzger A J and Yaghi O M 2006 *J. Am. Chem. Soc.* **128** 3494
14. (a) Antolini L, Menabue L, Pellacani G C and Marco-trigiano G 1982 *Dalton Trans.* 2541; (b) Schmidbaur H, Bach I, RiedeMuller J, Helbig J and Hopf G 1988 *Chem. Ber.* **121** 795; (c) Doyne T H, Pepinsky R and Watanabe T 1957 *Acta Crystallogr.* **10** 438; (d) Kryger L and Rasmussen S E 1973 *Acta Chem. Scan.* **27** 2674
15. (a) Zhang Y, Saha M K and Bernal I 2003 *Cryst. Eng. Commun.* **5** 34; (b) Mizutani M, Maejima N, Jitsukawa K, Masuda H and Einaga H 1998 *Inorg. Chim. Acta* **283** 105; (c) Flook R J, Freeman H C and Scudder M L 1977 *Acta Crystallogr.* **B33** 801; (d) Gramaccioli C M 1966 *Acta Crystallogr.* **21** 600
16. (a) Dan M, Rao C N R 2005 *Chem. Eur. J.* **11** 7102; (b) Dan M 2004 *J. Mol. Struct.* **706** 127 (and references therein)
17. Anokhina E V and Jacobson A J 2006 *J. Am. Chem. Soc.* **128** 9957
18. Anokhina E V and Jacobson A J, Go Y B, Lee Y and Vogt T 2006 *J. Am. Chem. Soc.* **128** 9957
19. Vaidhyanathan R, Bradshaw D, Rebilly J N, Barrio J P, Gould J A, Berry N J and Rosseinsky M J 2006 *Angew. Chem. Int. Ed.* **45**
20. Nakamoto K 1978 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: Wiley Interscience)
21. (a) Sheldrick G M 1986 *SHELXS-86 program for crystal structure determination* (Gottingen, Germany: University of Gottingen); (b) Sheldrick G M 1990 *Acta Crystallogr.* **A46** 467
22. Sheldrick G M 1994 *SADABS: Siemens area detector absorption correction program* (Gottingen, Germany: University of Gottingen)
23. Sheldrick, G M 1993 *SHELXS-93 program for crystal structure solution and refinement* (Gottingen, Germany, University of Gottingen)