Solvothermal Syntheses and Structural Characterisation of Three Isostructural 3D Metal-Malate Coordination Polymers: $\{[M(C_4H_4O_5)(H_2O)]\cdot H_2O\}_n$ ($M = Co^{II}, Ni^{II}, Co^{II}/Ni^{II}$)

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Three isostructural coordination polymers with the general formula $\{[M(C_4H_4O_5)(H_2O)]\cdot H_2O\}_n$ [M = Co^{II} (**1**), Ni^{II} (**2**) and $1/3Co^{II} + 2/3Ni^{II}$ (**3**), $C_4H_4O_5$ = $Hmal^{2-}$, malate dianion] have been designed and synthesised via solvothermal routes. In these compounds, the malate acts as the unique quinque-dentate ligand with all five oxygen atoms participating in the coordination. The M^{II} ions are interconnected via α- and β-carboxyl groups from the malate ligands to generate zigzag chains and planes which are further linked together by the β-carboxyl groups leading to the 3D open frameworks. Variable temperature magnetic susceptibility measurements indicate the occurrence of antiferromagnetic (**1**), ferromagnetic (**2**) and ferrimagnetic (**3**) interactions between the M^{II} ions mediated by the *skew-skew* carboxylate bridges.

Introduction

Considerable effort has been made towards the construction of metal-organic frameworks by employing various organic linkers such as carboxylates, bipyridyl and other multifunctional ligands. The use of di- and polycarboxylates can generate a large number of coordination complexes composed of chains, sheets and 3D networks with an enormous variety of intriguing structural topologies. Such systems have received considerable attention due to their fascinating properties as well as their potential applications in many fields. A survey of the synthetic procedures attempted reveals that some of them deal with rigid bridging ligands such as benzenedi-,[1] benzenetri-,[2] benzenetetra-[3] and benzenehexacarboxylates[4] or nitrogen-containing heterocyclic dicarboxylates[5] while others employ flexible aliphatic dicarboxylates as bridging ligands such as malonate,[6] succinate,[7] maleate,[8] fumarate,[8,9] glutarate[10] and adipate.[11] However, the hydroxyl polycarboxylates (HPCs) such as malate, citrate and tartrate have been less studied as building blocks in the construction of metal-organic frameworks though they can display versatile coordination modes. In contrast to the aliphatic dicarboxylate compounds, the presence of the hydroxyl group in HPCs allows the formation of five- and six-membered rings which can stabilise the solid networks. In the metal-HPC systems, much attention has been focused on the compounds of V, Mo or W because malic or citric acid often act as a substitute for homocitric acid in synthetic model studies of nitrogenase and the extended networks of M-HPCs systems have not been further explored.

The malate ligand, besides two terminal carboxyl groups, contains a hydroxyl group in the α-position which can potentially provide an additional coordination site. In all known malate-bridged compounds, the oxygen atoms of the alkoxy or hydroxyl groups participate in coordination along with the α-carboxyl and/or β-carboxyl groups. As well as being an important biological ligand, malate has been found to be a versatile ligand in coordination chemistry. Structurally characterised metal-malate compounds include monomers,[12] dimers,[13] tetramers[14] and polymeric chain compounds[15] as well as a 3D coordination polymer based on copper ions and ternary mixed ligands.[16] To the best of our knowledge, no higher-dimensional network containing malate and water molecules as ligands has been constructed up to now. In addition, similar to the aliphatic dicarboxylates such as malonate or fumarate,[17] malate can also act as a suitable candidate for engineering the design of molecular magnets.

Our exploration of the solvothermal chemistry of the M-HPC systems has resulted in the discovery of some new

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compounds with unusual coordination modes. Herein we report the solvothermal syntheses, crystal structures and magnetic behaviour of three isostructural compounds $\{[M(C_4H_4O_5)(H_2O)]\cdot H_2O\}_n$ [$C_4H_4O_5$ = Hmal^{2-} (malate dianion), M = Co^{II} (**1**), Ni^{II} (**2**) and 1/3Co^{II} + 2/3Ni^{II} (**3**)] in which the coordination mode is unique and has not been previously reported.

Results and Discussion

Solvothermal reactions of the corresponding mixtures of cobalt(II) (or/and nickel) acetate (or chloride), malic acid, 4,4-bipyridine (4,4-bipy) and KOH in an alcohol-water medium yielded crystals of the title compounds. At first we try to synthesise the coordination polymers containing both malate and 4,4-bipy as bridging ligands. However, only the title compounds without 4,4-bipy were obtained under the selected reaction conditions. We also substituted the cobalt salts with iron dichloride to attempt to synthesise iron analogues of the title compounds under similar conditions but this was not successful.

Single-crystal X-ray structural analyses reveal that the metal centres M^{II} (Co^{II}, Ni^{II} and Co^{II}/Ni^{II}) in the title compounds are in distorted octahedral environments coordinated by three different malate ligands and one water molecule as shown in Figure 1. In each case three coordination positions are occupied by O(1), O(4) and O(3) coming from the α-carboxyl, β-carboxyl and hydroxyl groups of the same malate ligand, respectively. Two other coordination sites are occupied by O(2) and O(5) from the α-carboxyl and β-carboxyl groups from two different malato ligands and the sixth coordination site is occupied by OW(1) from a water molecule. The MO_6 polyhedra are severely distorted from idealised octahedral symmetry, the Co−O distances range from 2.0646(18) to 2.1126(19) Å with an average value of 2.0913(19) Å for compound **1**. The O−Co−O angles between neighbouring oxygen atoms range from 86.48(8) to 95.74(8)° except for two smaller angles [O(1)−Co−O(3), 79.04(7)°; O(3)−Co−O(4), 81.59(8)°] caused by the hydroxyl-oxygen atom. This is due to the formation of five- and six-membered chelate rings. For compound **2**, the Ni−O distances range from 2.035(2) to 2.088(2) Å with an average value of 2.056(2) Å. The O−Ni−O angles between neighbouring oxygen atoms range from 85.58(10) to 95.58(9)° except for the angles O(1)−Ni−O(3) [80.95(9)°] and O(3)−Ni−O(4) [82.38(9)°]. The corresponding bond lengths and angles of compound **3** are close to those in **1** and **2**.

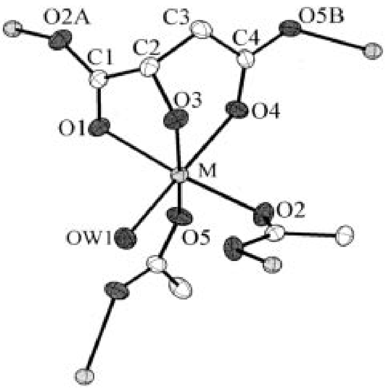

Figure 1. The coordination environment of M^{II} in **1**, **2** and **3**

The malate dianion coordinates to one M^{II} ion and acts as a tridentate ligand via its hydroxyl, α-carboxyl and β-carboxyl groups in a *face*-mode, while the α-carboxyl and β-carboxyl groups further coordinate in a monodentate fashion to the other M^{II} ions in the position trans to the hydroxyl group. The β-carboxyl groups bend back to chelate the M^{II} ions and the C(2)−C(3)−C(4) angles are reduced to 115.9(2)°, 115.7(3)° and 115.5(3)° for **1**, **2** and **3**, respectively. The angles of O(1)−C(1)−O(2A) are 125.1(2)°, 124.8(3)° and 125.3(3)°, and O(4)−C(4)−O(5B) are 123.4(2)°, 123.3(3)° and 124.1(3)° for compounds **1**, **2** and **3**, respectively. Both α-carboxyl and β-carboxyl groups adopt nonplanar *skew*-*skew* coordination modes and two bridged metal atoms on opposite sides of the carboxylate plane[18] and the corresponding torsion angles of compound **1** are as follow: Co−O(1)−C(1)−C(2) 8.12(29)°, Co−O(2A)−C(1)−C(2) 153.63(17)°; Co−O(4)−C(4)−C(3) 14.33(43)°, Co−O(5B)−C(4)−C(3) 164.53(20)°.

In the title compounds, each μ_3-malate dianion adopts a quinque-dentate coordination mode and all of the five oxygen atoms participate in the coordination towards three metal centres. It follows that each M atom in the crystal structure is attached to three different malate groups. As shown in Figure 2, the M^{II} ions are connected through α- and β-carboxyl groups to form zigzag chains in the [100] direction and the corresponding zigzag layers are further linked together by β-carboxyl groups of malate ligands roughly in the [010] direction leading to the formation of the 3D open frameworks (Figure 3). Figure 2 also shows the distribution of coordinated and lattice water molecules in the [001] direction. The OW(2) atoms of lattice water molecules form

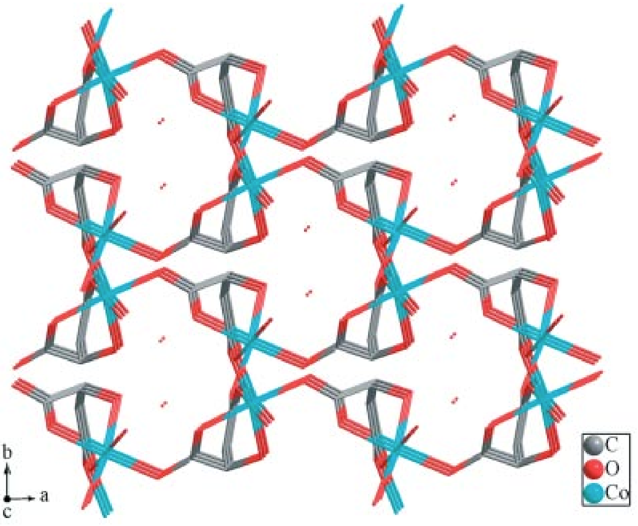

Figure 2. View of the network structure in the [001] direction, hydrogen atoms have been omitted for clarity

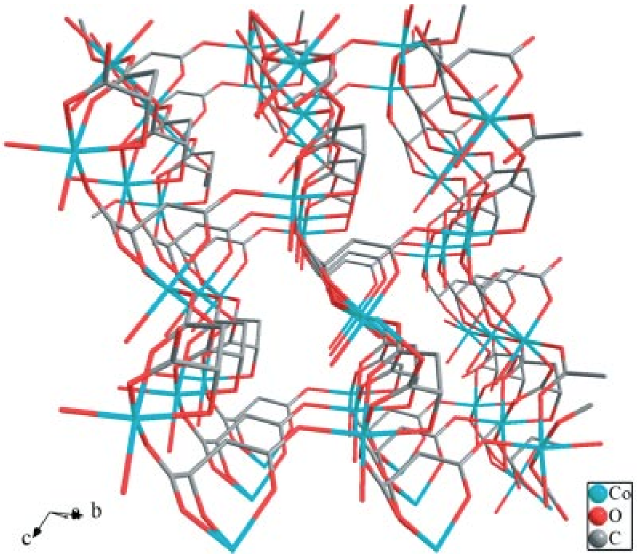

Figure 3. The packing diagram of compound **1** showing the 3D structure, hydrogen atoms and lattice water molecules have been omitted for clarity

hydrogen bonds with O(2) (symmetry mode: x, $-1 + y$, z) and the OW(2)···O(2) distance is 2.918(3) Å. The rhombic 16-membered channels consisting of M−O−C−O−M vectors along the [010] direction can be seen in Figure 4. The adjacent M···M distances are about 5.2 Å (through α-carboxyl groups) and 5.3 Å (through β-carboxyl groups).

The magnetic properties of compounds **1**, **2** and **3** were studied as a function of temperature (2−300 K) in a fixed magnetic field (5000 Oe). As the temperature is lowered, the χ_m values increase slowly until around 50 K in **1** and 20 K in **2** and **3**. They then dramatically increase at lower temperatures still. The data above 50 K can be fitted with Curie−Weiss functions with a Weiss constant $\theta = -20.21$ K and a Curie constant $c = 2.92$ cm^3·K·mol^{-1} for compound **1**, and $\theta = +2.38$ K and $c = 1.32$ cm^3·K·mol^{-1} for **2**. These are characteristic of overall antiferromagnetic (**1**) and ferromagnetic (**2**) interactions, respectively.

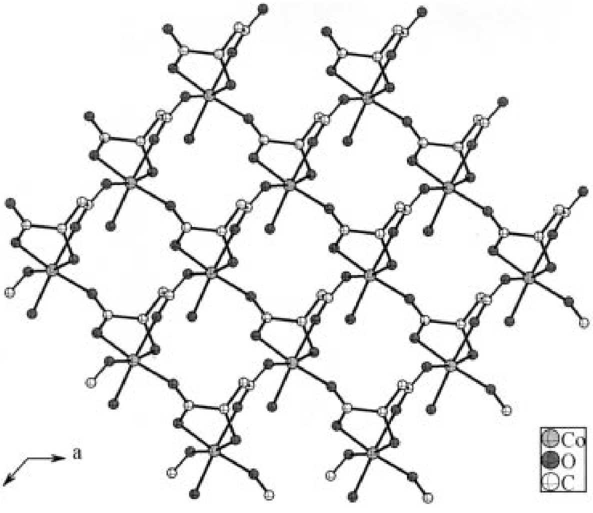

Figure 4. View of the network structure showing the channels in the [010] direction, hydrogen atoms and lattice water molecules have been omitted for clarity

Plots of μ_{eff} (the effective magnetic moment) versus T are shown in Figure 5 (compounds **1** and **2**). The μ_{eff} values of **1** decrease slowly from 4.65 μ_B at 300 K to 4.10 μ_B at 50 K and then decrease rapidly reaching 2.67 μ_B at 2 K. The μ_{eff} value of 4.65 μ_B at 300 K for compound **1** is larger than the spin-only value for high-spin cobalt(II) (3.87 μ_B per cobalt(II) ion with $g = 2.0$) and consistent with that expected for an octahedral cobalt(II) with an important orbital contribution.[19] For compound **2**, the μ_{eff} value of 3.18 μ_B at 300 K is close to the expected spin-only value (3.11 μ_B per nickel(II) with $g = 2.2$). Upon cooling, and in contrast to compound **1**, the μ_{eff} values of **2** increase slowly reaching 3.32 μ_B at 50 K and 3.42 μ_B at 30 K, then increase rapidly at low temperature. For compound **3**, as the temperature decreases, the μ_{eff} values (3.90 μ_B, 300 K) decrease slowly reaching steady values between 3.75 μ_B and 3.73 μ_B from 50 K to 24 K. This is then followed by a sharp increase below 24 K which is characteristic of ferrimagnetic behaviour.

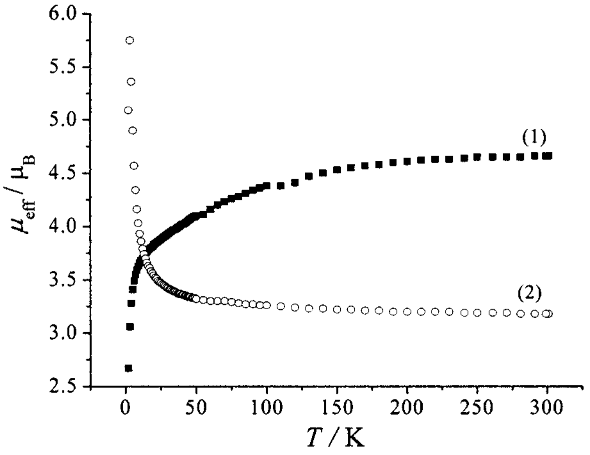

Figure 5. Thermal variations of μ_{eff} for compounds **1** and **2**

It should be noted that the magnetic coupling between the Co^{II} and/or Ni^{II} ions through the carboxylate-malate are antiferromagnetic, ferromagnetic and ferrimagnetic for compounds **1**, **2** and **3**, respectively. Different electronic configurations of the metal ions involving three (**1**) and two (**2**) unpaired electrons could account for this. The ferromagnetic couplings in **2** are very weak but the presence of one unpaired electron in a t_{2g} type orbital of Co^{II} in **1** would increase the possibility of net overlap between the magnetic orbitals,[19,20a] thus enhancing the antiferromagnetic contributions in **1** and the ferromagnetic terms would be overcome. Ferromagnetic interactions between the nickel(II) ions have been observed in some compounds involving *anti-syn* carboxylate bridged nickel(II).[20] The magnetic behaviour of the title compounds is related to their metal centres and the carboxylate-malate bridges. Detailed magnetic analyses are currently being carried out.

The assignment of oxidation states for the cobalt and nickel atoms in the three compounds is consistent with their coordination geometries and bond valence sum calculations[21] and is also confirmed by the results of XPS measurements. The electronic binding energies of $Co2p_{3/2}$ for **1** (Figure S1 in the Supporting Information) and $Ni2p_{3/2}$ for **2** (Figure S2) are 783.2 and 856.1 eV, respectively, indicating that the oxidation states of both Co and Ni are +2. For compound **3**, the peaks at 782.4 and 855.3 eV (Figure S3) are also in the range of the electronic binding energies for $Co2p_{3/2}$ in Co^{II} and $Ni2p_{3/2}$ in Ni^{II}, respectively, which confirms the coexisistence of Co^{II} and Ni^{II}.

The thermal behaviour of compounds **1**, **2** and **3** was studied from 30 to 800 °C in air. The TGA curves indicate that the three compounds have similar thermal properties (Figure S4, see Supporting Information). Taking compound **2** as an example, the sample slowly loses one lattice water molecule and one coordinated water from 120 to 330 °C with the weight-loss of 16.2% being consistent with the calculated value of 15.9%. Upon further heating, the sample decomposes rapidly and the occurrence of an exothermic process is very clear. The decomposition is complete by about 440 °C and the residue is most probably nickel(II) oxide.

Conclusion

In this work we have, for the first time, synthesised under solvothermal conditions three isostructural coordination polymers, $\{[M(C_4H_4O_5)(H_2O)]\cdot H_2O\}_n$, [M = Co^{II} (**1**), Ni^{II} (**2**) and $1/3Co^{II} + 2/3Ni^{II}$ (**3**)], based on bridging malate groups and water molecules. Compared with other metal-malate compounds, the most remarkable features of the title compounds are: (a) The malate acts as the unique quinquedentate ligand and all of the five oxygen atoms participate in the coordination. (b) Three isostructural compounds show antiferromagnetic, ferromagnetic and ferrimagnetic interactions in **1**, **2** and **3**, respectively, and this interesting magnetic behaviour is related to the nature of the metal centre and the carboxylate-malate bridges in each case. In the future, it would be worthwhile exploring the relationship between the structures and properties of extended networks based on transition metals and HPCs.

Experimental Section

Syntheses of 1, 2 and 3: The three compounds were prepared in an analogous manner and the detailed synthetic procedures are as follows. Compound **1** was prepared from a weakly acidic mixture of cobalt(II) acetate tetrahydrate (0.75 g, 3.0 mmol), malic acid (0.40 g, 3.0 mmol), 4,4-bipyridine dihydrate (0.20 g, 1.0 mmol), KOH (0.18 g, 3.2 mmol), distilled water (10 mL) and anhydrous alcohol (10 mL). The mixture was stirred for ca. 1 h. and was then heated under autogenous pressure at 160 °C for three days in a 30 mL Teflon-lined stainless steel vessel and finally cooled to room temperature. The purplish-red crystals were filtered, washed with distilled water and dried at ambient temperature. Yield: 0.46 g (67%, based on cobalt). X-ray quality crystals of **2** in the form of green blocks were prepared by the procedure detailed above for **1** but using nickel(II) acetate tetrahydrate instead of the cobalt(II) salt. Yield: 0.51 g (74%, based on nickel). Dark purple crystals of **3** were isolated by following the procedure detailed above for **1** but using cobalt(II) acetate tetrahydrate (0.30 g) and nickel(II) acetate tetrahydrate (0.50 g) instead of the cobalt(II) salt. Yield: 0.57 g (70%, based on cobalt). Analyses for **1, 2** and **3:**

1: $C_4H_8CoO_7$ (227.03): calcd. Co 25.96, C 21.16, H 3.55; found Co 25.47, C 21.45, H 3.38. Main IR features (KBr disk): $\tilde{\nu}$ = 3514.4 m, 3432.9 m, 2807.4 w, 1617.5 s, 1577.7 s, 1546.6 s, 1434.8 s, 1398.7 s, 1321.4 w, 1291.0 s, 1260.9 w, 1208.5 w, 1088.1 m, 1038.0 m, 806.2 m, 669.2 m, 609.5 m, 583.1 m, 545.8 m, 331.0 w cm^{-1}.

2: $C_4H_8NiO_7$ (226.81): calcd. Ni 25.88, C 21.18, H 3.56; found Ni 25.14, C 21.33, H 3.62. Main IR features (KBr disk): $\tilde{\nu}$ = 3511.1 m, 3426.4 m, 2806.9 w, 1609.2 s, 1579.8 s, 1541.4 s, 1435.0 s, 1400.0 s, 1321.8 w, 1292.1 s, 1261.6 w, 1207.1 w, 1087.7 m, 1039.1 m, 834.3 m, 680.9 m, 616.7 m, 588.9 m, 552.4 m, 355.7 w cm^{-1}.

3: $C_4H_8Co_{0.33}Ni_{0.67}O_7$ (226.89): calcd. Co 8.57, Ni 17.33, C 21.17, H 3.55; found Co 8.13, Ni 16.75, C 20.86, H 3.69. Main IR features (KBr disk): $\tilde{\nu}$ = 3509.0 m, 3428.4 m, 2807.1 w, 1609.2 s, 1573.4.8 s, 1541.9 s, 1434.5 s, 1399.5 s, 1321.6 w, 1291.7 s, 1261.3 w, 1207.3 w, 1087.8 m, 1038.7 m, 835.3 m, 678.3 m, 614.1 m, 586.6 m, 550.1 m, 349.4 w cm^{-1}.

X-ray Crystallographic Studies

Compound 1: $C_4H_8CoO_7$, M_r = 227.03, dimensions 0.299 × 0.229 × 0.100 mm, monoclinic, space group *Cc*, a = 13.211(3) Å, b = 7.564(2) Å, c = 9.758(2) Å, β = 130.83(3)°, V = 737.7(3) Å^3, Z = 4, D_c = 2.044 g/cm^3, $\mu(\text{Mo-}K_\alpha)$ = 2.325 mm^{-1}. X-ray data were collected on Rigaku RAXIS-RAPID diffractometer at 293 K in the range of $3.4 < \theta < 27.5°$. Unique reflections were used to solve the structure by direct methods using SHELXS-97 which was then refined on F^2 by full-matrix least-squares methods, converging at $R = 0.0237$ [$I > 2\sigma(I)$] with a goodness-of-fit on F^2 of 1.149 for 110 parameters and 1600 reflections, 1600 unique reflections.

Compound 2: $C_4H_8NiO_7$, M_r = 226.81, dimensions 0.594 × 0.393 × 0.353 mm, monoclinic, space group *Cc*, a = 13.103(3) Å, b = 7.526(2) Å, c = 9.629(2) Å, β = 130.88(3)°, V = 718.0(2) Å^3, Z = 4, D_c = 2.098 g/cm^3, $\mu(\text{Mo-}K_\alpha)$ = 2.701 mm^{-1}. X-ray data were collected on Rigaku RAXIS-RAPID diffractometer at 293 K in the range of $3.4 < \theta < 27.5°$. Unique reflections were used to solve the structure by direct methods using SHELXS-97 which was then refined on F^2 by full-matrix least-squares methods, converging at $R = 0.0269$ [$I > 2\sigma(I)$] with a goodness-of-fit on F^2 of 1.094 for 110 parameters and 1550 reflections, 1550 unique reflections.

Compound 3: $C_4H_8Co_{0.33}Ni_{0.67}O_7$, M_r = 226.89, dimensions 0.462 × 0.434 × 0.359 mm, monoclinic, space group *Cc*, a = 13.137(3) Å, b = 7.536(2) Å, c = 9.676(2) Å, β = 130.91(3)°, V = 724.0(2) Å^3, Z = 4, D_c = 2.082 g/cm^3, $\mu(\text{Mo-}K_\alpha)$ = 2.576 mm^{-1}. X-ray data were collected on Rigaku RAXIS-RAPID diffractometer at 293 K in the range of $3.4 < \theta < 27.3°$. Unique reflections were used to solve the structure by direct methods using SHELXS-97 which was then refined on F^2 by full-matrix least-squares methods, converging at $R = 0.0278$ [$I > 2\sigma(I)$] with a goodness-of-fit on F^2 of 1.064 for 119 parameters and 1528 reflections, 1528 unique reflections.

CCDC-241829 (for **1**), -241830 (for **2**) and -241831 (for **3**) 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 [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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