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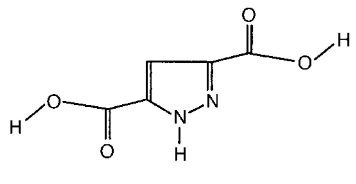
Novel Single- and Double-Layer and Three-Dimensional Structures of Rare-Earth Metal Coordination Polymers: The Effect of Lanthanide Contraction and Acidity Control in Crystal Structure Formation**

Long Pan, Xiaoying Huang, Jing Li,* Yonggang Wu, and Nengwu Zheng

The concept of rational design of micro- and mesoporous and other functional materials has attracted much attention because of the potential of these materials in various applications, such as molecular magnets, nonlinear optical devices, catalysts, molecular sieves, and sensors.[1] The construction of coordination networks possessing zeolite- or clay-like structures offers great challenges and opportunities in terms of controlling their shape and size for selective adsorption. Much of the work has so far been focused on coordination polymers containing transition metal (Groups 8 to 10) and post-transition metal (Groups 11 and 12) elements including Fe, Co, Ni, Cu, Ag, Zn, Cd, and Hg. Rare-earth metal compounds have seldom been investigated.[2] To date, no systematic investigation across the lanthanide series with a single ligand has been carried out. Due to their high coordination number and special magnetic and fluorescence properties, the lanthanide series is likely to provide new materials that possess specific properties and desired features. In this communication, we report the hydrothermal synthesis, structures, and properties of six novel lanthanide coordination polymers and the investigation of the effects of lanthanide contraction and solution pH on the crystal structures of these compounds.

Hydrothermal synthesis[3] is an effective and promising method for growing crystals of numerous inorganic compounds. Recently, we and others have successfully grown single crystals of a variety of transition metal coordination polymers using this approach.[4, 5] Our exploratory studies also show that the hydrothermal environment is suitable for preparation of lanthanide compounds.

In this work, we have chosen a single, multifunctional ligand, 3,5-pyrazoledicarboxylic acid (H_3pdc, **1**), based on the following considerations: a) it has multiple coordination sites that allow structures of higher dimensions; b) it has an asymmetric geometry that may lead to acentric crystal structures; and c) it has abstractable protons that allow various, acidity-dependant coordination modes. In general, the lanthanide series can be divided into three groups according to their masses: the lighter La–Pm (Group 1), the intermediate Sm–Dy (Group 2), and the heavier Ho–Lu (Group 3). Representative metals from each Group were selected and investigated.



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In a typical reaction 0.25 mmol of rare-earth metal(III) nitrate and 0.25 mmol of **1** in 10 mL H_2O was used. The mixture was placed into a 23 mL acid-digestion bomb lined with Teflon and heated at 150 °C for 3 days. Reactions with Group 1 lanthanide nitrates $Ln(NO_3)_3$ (Ln = La, Ce) generated $[Ln_2(Hpdc)_3(H_2O)_4]\cdot 2H_2O$, Ln = La (**2**), Ln = Ce (**3**). Group 2 nitrate $Eu(NO_3)_3$ produced $[Eu_2(Hpdc)_3(H_2O)_6]$ (**4**) and a minor product $[Eu_2(Hpdc)_3(H_2O)_4]\cdot 2H_2O$ that is isostructural to **2** and **3**, while Group 3 nitrates $Ln(NO_3)_3$ (Ln = Er, Lu) yielded $[Er_2(Hpdc)_3(H_2O)_6]$ (**5**), and $[Ln(Hpdc)(H_2pdc)(H_2O)_2]$, Ln = Er (**6**), Ln = Lu (**7**).

Single-phase polycrystalline samples of both **2** and **3** were obtained with 68 % and 71 % yields, respectively. Both compounds are stable in air and are not soluble in any common solvents. Single crystal X-ray diffraction analyses were performed on selected crystals of both compounds. Their crystal structures[6] are isotypic with a three-dimensional framework (see Figure 1 a) containing nine-coordinate lanthanide metal centers. There are two types of metal environments in this structure. As shown in Figure 1 b, three $Hpdc^{2-}$ ligands chelate to Ln1 through a carboxylate oxygen and adjacent nitrogen atoms (O3/N2, O5/N3, O9/N5), occupying six coordination sites of Ln1. The remaining three coordination sites of Ln1 are taken by another three $Hpdc^{2-}$ ligands, each through a single carboxylate oxygen atom (O2, O7, O12). The second metal environment has Ln2 bonding to a chelated carboxylate group of a $Hpdc^{2-}$ ligand (O1, O2) and to three carboxylate groups of three additional $Hpdc^{2-}$ ligands (O5, O9, O11). The remaining four coordination sites are occupied by the oxygen atoms of four water molecules (O13, O14, O15, O16). There are three crystallographically independent $Hpdc^{2-}$ molecules in the structure, each having a different coordination mode. The highly unsymmetric coordination pattern of the metal and the ligand led to a crystal structure

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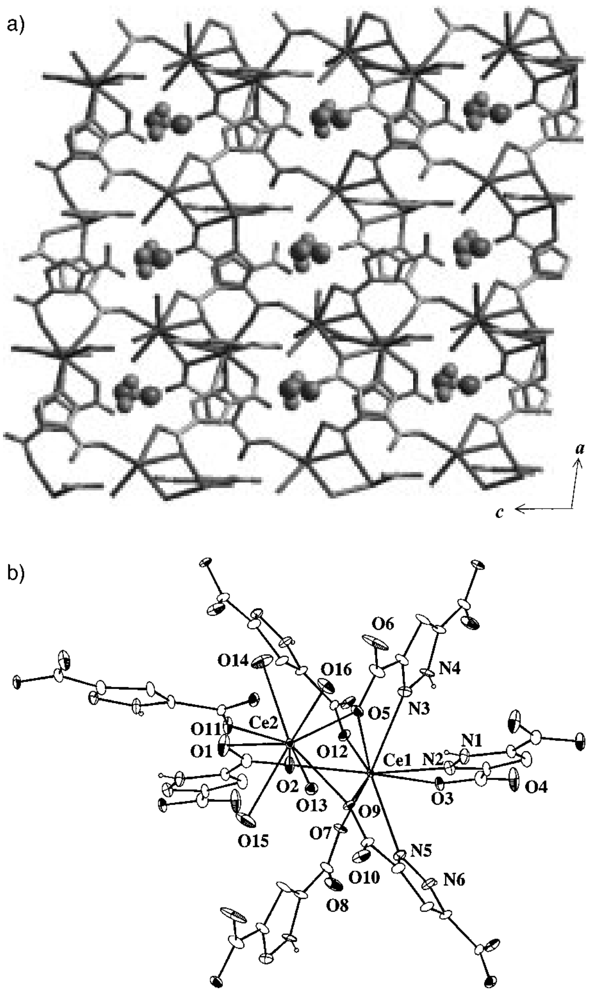

Figure 1. a) View of $[Ln_2(Hpdc)_3(H_2O)_4]\cdot 2H_2O$, Ln = La (**2**), Ln = Ce (**3**), along the *b* axis. Large and small solid spheres represent O and H atoms of the uncoordinated water molecules. b) ORTEP drawing of **3**. Both Ce1 and Ce2 atoms are nine coordinate. Selected distances [Å]: Ce1-Ce2 4.0381(12), Ce1-O7 2.427(5), Ce1-O3 2.456(5), Ce1-O12 2.458(5), Ce1-O2 2.469(5), Ce1-O5 2.610(5), Ce1-O9 2.616(4), Ce1-N5 2.628(6), Ce1-N3 2.632(7), Ce1-N2 2.654(6), Ce2-O16 2.413(5), Ce2-O11 2.427(5), Ce2-O13 2.530(5), Ce2-O15 2.541(6), Ce2-O5 2.547(5), Ce2-O1 2.589(5), Ce2-O9 2.595(4), Ce2-O14 2.596(6), Ce2-O2 2.668(5).

belonging to an acentric space group.[6] The resultant three-dimensional structure contains open channels along the *b* axis that are occupied by two noncoordinating water molecules. The approximate dimensions of these channels are 3.5 × 4.5 Å (Figure 1 a).

Europium was chosen as a representative metal from the Group 2 lanthanides, and compound **4** was synthesized under similar experimental conditions. A minor europium compound, isostructural with **2** and **3**, was also found in the reaction mixture. The crystal structure of **4** (Figure 2 a)[7] is a claylike double layer that is rare for coordination polymers.[8] As illustrated in Figure 2 b, the coordination polyhedron around each europium atom is a square antiprism with three sites occupied by oxygen atoms from three coordinated water molecules (O7, O8, O9) and the other three sites by carboxylate groups from three $Hpdc^{2-}$ ligands (O2, O3, O5). In the remaining two sites are a chelated carboxylate oxygen and adjacent nitrogen atom from the fourth $Hpdc^{2-}$ ligand (O1/N1). There are two types of $Hpdc^{2-}$ ligands in this structure: one type within the metal layer bonds to three Eu^{III} atoms through its O2′, O3′, and O1/N1; the other type lies between the two metal layers and connects them via two oxygen atoms from two different carboxylate groups (O5, O5″). This results in a unique double-layer structure with a distance of 6.3 Å between the two single layers (Figure 2 a). The double layers are connected through hydrogen bonding interactions. Worth mentioning here is that such a double-layer structure can be regarded as a unique molecular "floor" directly linked by pillars ($Hpdc^{2-}$) through covalent bonds.[9]

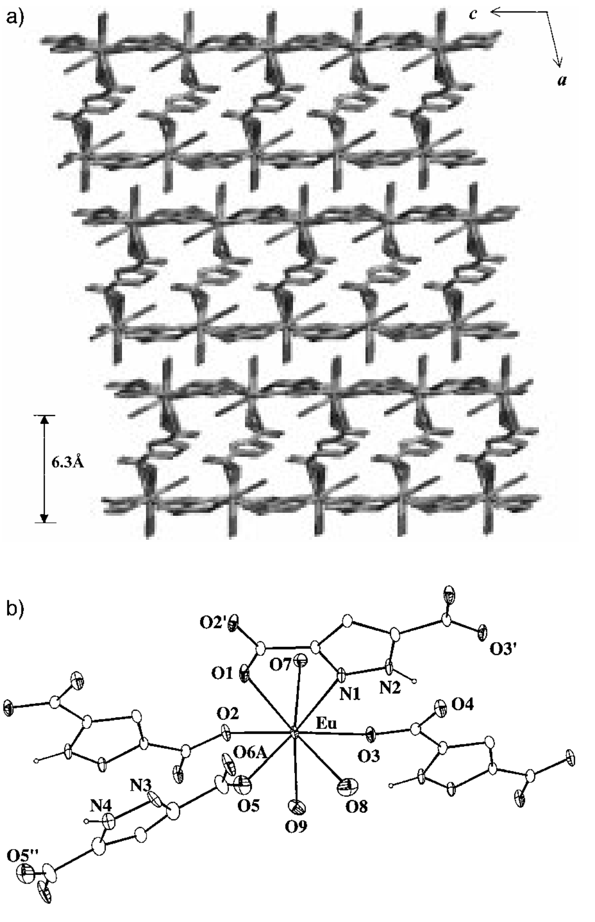

Figure 2. a) View of $[Eu_2(Hpdc)_3(H_2O)_6]$ (**4**) along the *b* axis. The interlayer interactions between the double layers are through hydrogen bonds (O4 ··· O7 = 2.767(4) Å, O2 ··· O7 = 2.785(4) Å, not shown). b) ORTEP drawing of **4**. Each Eu atom is eight coordinate. Selected bond lengths [Å]: Eu-O5 2.336(3), Eu-O7 2.375(3), Eu-O3 2.379(3), Eu-O2 2.416(3), Eu-O8 2.438(3), Eu-O9 2.441(3), Eu-O1 2.451(3), Eu-N1 2.523(3).

Two elements from Group 3, erbium and lutetium, were investigated. The double-layer structure was obtained for erbium (**5**)[7] and a new single-layered structure, $[Ln(Hpdc)(H_2pdc)(H_2O)_2]$, was obtained for both Er (**6**) and Lu (**7**).[10] Figure 3 a gives a view of this structure along the *a* axis. All metal atoms are eight coordinate. Each metal is coordinated by two $Hpdc^{2-}$ ligands (one through a chelating O1 and N1, and the other through a carboxylate oxygen O3), two H_2pdc^{-} ligands (one through a chelating O5 and N3, and the other through a carboxylate oxygen O6), and by two water molecules (O9, O10). This results in a single-layer structure

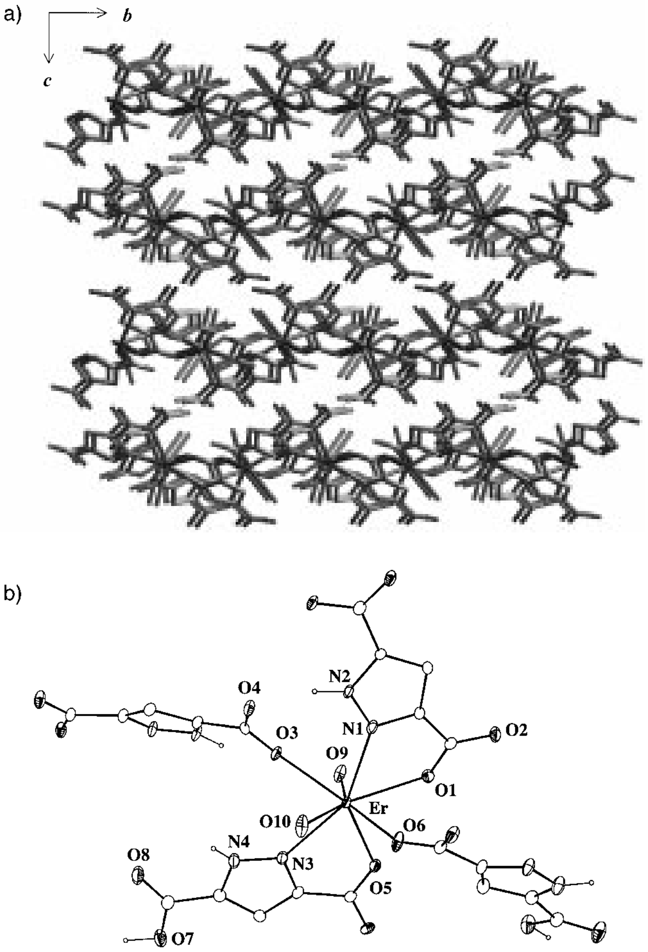

Figure 3. a) View of $[Ln(Hpdc)(H_2pdc)(H_2O)_2]$, Ln = Er (**6**), Ln = Lu (**7**), along the *a* axis. The interlayer interactions are through hydrogen bonds (not shown). b) ORTEP drawing of **6**. Er atoms are eight coordinate. Selected bond lengths [Å]: Er-O1 2.437(4), Er-O3 2.345(4), Er-O5 2.302(4), Er-O6 2.287(4), Er-O9 2.304(4), Er-O10 2.318(4), Er-N1 2.395(4), Er-N3 2.486(5).

$[Ln(Hpdc)(H_2pdc)(H_2O)_2]$. Both $Hpdc^{2-}$ and H_2pdc^- bond to two metal centers but with different coordination modes. The former uses two whereas the latter uses only one carboxylate group in bonding. The weak interactions between the layers are through hydrogen bonding.

It is interesting to observe the effect of lanthanide contraction through the structure formation of the title compounds. While Group 1 elements La and Ce form only the three-dimensional structures (**2**, **3**, nine-coordinate metal centers), the Group 2 element Eu gives rise to both double-layer (**4**, eight-coordinate metal centers) and three-dimensional structures. The analogous three-dimensional structures for Group 3 Er and Lu, however, have never been observed because of the considerably smaller atomic sizes of these elements. While the metal is eight-coordinate in both double- and single-layer structures, the size of the coordination sphere of the metal is larger in the former than in the latter due to the different number of coordinated water molecules. This is consistent with the observation that Er crystallizes in both structures (**5** and **6**) while smaller Lu only forms a single-layer structure (**7**).

The products of hydrothermal synthesis are often affected by the acidity of the reactions. In this study, it is clear that the pH of the reactions played a crucial role in the formation of the single- and double-layer structures. The coordination of ligand **1** can be controlled by the amount of H^+ in a reaction mixture: $H_3pdc \leftrightarrow H_2pdc^- + H^+ \leftrightarrow Hpdc^{2-} + 2H^+$. In $Hpdc^{2-}$ both carboxylate groups are available for coordination, while only one is in H_2pdc^-. In the single-layer structures (**6**, **7**), one half of the pyrazoledicarboxylate ligands participate in bonding as H_2pdc^- and the other half as $Hpdc^{2-}$, whereas in the double-layer structures (**4**, **5**) all ligands bond to metal centers as $Hpdc^{2-}$. By adjusting the pH value, we successfully isolated a single-phase, double-layer erbium structure (**5**) at pH 5, and its single-layer structure (**6**) at pH 1, respectively. That adjusting the pH value gives no effect in separating $[Eu_2(Hpdc)_3(H_2O)_6]$ (**4**, the double-layer structure) from $[Eu_2(Hpdc)_3(H_2O)_4] \cdot 2H_2O$ (the three-dimensional structure) is obvious, since both compounds contain the same number of $Hpdc^{2-}$ as the only ligand.

Thermogravimetric analysis (TGA) of the new compounds also revealed some interesting features. Compounds with both single- and double-layer structures cannot be recovered after loss of the water molecules through heating, whereas the crystal structure of the three-dimensional lanthanum and cerium compounds (**2**, **3**) are recoverable to a large degree during a heating–cooling and dehydration–hydration cycle. Figure 4 gives the PXRD patterns taken on lanthanum samples. The details of the characteristic peaks of the crystal structure began to disappear after the sample was heated to 125 °C, at which time two noncoordinated water molecules evolved from the sample (Figure 4b). The structure recovered almost completely when this sample was exposed to water for a short period of time, observed by comparing the PXRD pattern, taken after rehydrating the heated sample (Figure 4c), to the original powder pattern (Figure 4a). Figure 4d shows when the sample was heated to 220 °C, both noncoordinated as well as coordinated water molecules in **2** evolved from the sample. The crystal structure collapsed

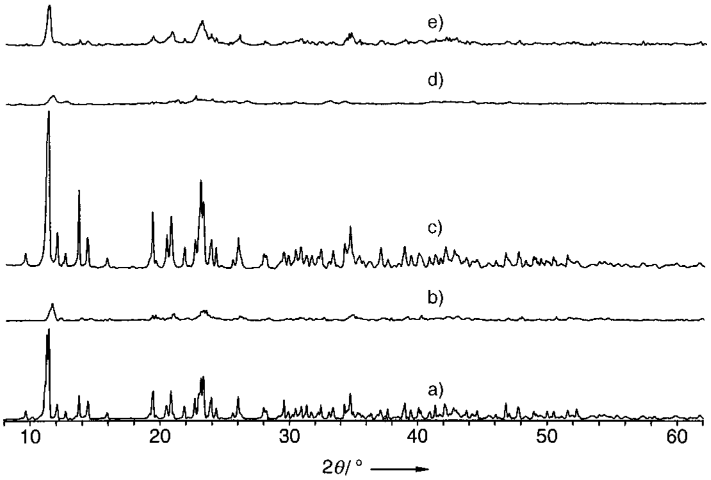

Figure 4. PXRD patterns for **2**, a) taken at room temperature, b) after heating to 125 °C, c) after rehydration for 30 min, d) after reheating to 220 °C, e) after rehydration for 36 h.

almost completely. After 36 hours in water, the structure began to recover and the major features reappeared in the powder pattern (Figure 4e). This remarkable phenomenon has also been observed, even more profoundly, in a number of transition metal 3,5-pyrazoledicarboxylate polymers.[11]

In summary, we have synthesized six novel lanthanide metal coordination polymers (**2**–**7**) via hydrothermal reactions. These compounds crystallize in three new structural types with the metal coordination number steadily decreasing from nine only (La, Ce) to nine and eight (Eu) to eight only (Er, Lu) as a result of lanthanide contraction. By controlling the reaction pH values, we have successfully and selectively isolated single-phase erbium compounds in different structures (**5**, **6**). The formation of a crystal structure in an acentric space group for compounds **2** and **3** shows it is possible to synthesize new materials for NLO devices using lanthanide metals in combination with asymmetric ligands. Furthermore, the structure recovery process that was observed in compounds **2** and **3** reveals an interesting phenomenon whose nature and possible applications deserve further investigation.

Experimental Section

Synthesis of **2, 3, 4, 7**: Reactions of $Ln(NO_3)_3 \cdot 6H_2O$ (La 0.105 g; Ce 0.108 g; Eu 0.112 g; Lu 0.118 g), **1** (0.043 g) and H_2O (10 mL) in the mole ratio of 1:1:2222 were conducted in a 23 mL acid digestion bomb at 150 °C for 3 days (pH 2–3). The products were collected after washing by H_2O (2 × 5 mL) and acetone (2 × 5 mL). La compound **2**: 0.048 g, 68 %; Ce compound **3**: 0.049 g, 71 %; Eu compound **4**: 0.038 g, which also contained $[Eu_2(Hpdc)_3(H_2O)_4] \cdot 2H_2O$ as a minor component; Lu compound **7**: 0.042g, 63 %.

Synthesis of **5**: Hydrated $Er(NO_3)_3$ (0.176 g), **1** (0.085 g), Et_3N (0.014 mL) and H_2O (10 mL) in the mole ratio of 1:1:2:1111 reacted in a 23 mL acid digestion bomb at 150 °C for 3 days (pH 5). The washing procedure described above was applied to the product. Compound **5** was collected in quantitative yield.

Synthesis of **6**: Hydrated $Er(NO_3)_3$ (0.176 g), **1** (0.085 g), HNO_3 (0.033 mL) and H_2O (10 mL) in the mole ratio of 1:1:1:1111 reacted in a 23 mL acid digestion bomb at 150 °C for 3 days (pH 1). The product was washed and collected as single-phase **6** in low yield.

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[6] a) Compound **2**: 0.22 × 0.10 × 0.02 mm, monoclinic, space group *Cc*, $a = 15.797(3)$, $b = 8.881(2)$, $c = 18.411(4)$ Å, $\beta = 98.37(3)°$, $V = 2555.4(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.205$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 3.395$ mm^{-1}, $F(000) = 1632$, ω-2θ scans, max./min. transmission 1.000/0.940, 6135 unique reflections ($\theta_{max} = 28°$), 4638 observed ($I > 2\sigma(I)$), 368 parameters, $R = 0.0573$, $R_w = 0.1183$, residual electron density max./min. 2.20/ – 2.24 e Å^{-3}. Compound **3**: 0.11 × 0.08 × 0.01 mm, monoclinic, space group *Cc*, $a = 15.724(3)$, $b = 8.849(2)$, $c = 18.354(4)$ Å, $\beta = 98.40(3)°$, $V = 2526.4(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.236$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 3.655$ mm^{-1}, $F(000) = 1640$, ω-2θ scans, max./min. transmission 1.000/0.766, 4919 unique reflections ($\theta_{max} = 26°$), 4802 observed ($I > 2\sigma(I)$), 371 parameters, $R = 0.0316$, $R_w = 0.0804$, residual electron density max./min. 1.61/ – 1.38 e Å^{-3}. b) X-ray diffraction studies were performed on single crystals using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) with an Enraf-Nonius CAD4 diffractometer at 293 K. Lorentz, polarization, and empirical absorption corrections were applied for all compounds. Direct phase determination yielded the position of the heavy atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. Most of the hydrogen atoms were located from difference Fourier maps while the rest were placed on calculated positions. Hydrogen atoms were not refined and their isotropic thermal parameters were set to $1.2 \times U_{eq}$ of the parent non-hydrogen atoms. A full-matrix least-squares refinement on F^2 reached final convergence. All computations were performed using the SHELX-97 program package (G. Sheldrick, University of Göttingen). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-129657–129661. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] Compound **4**: 0.15 × 0.06 × 0.06 mm, monoclinic, space group $P2_1/c$, $a = 10.985(2)$, $b = 10.187(2)$, $c = 10.462(2)$ Å, $\beta = 100.11(3)°$, $V = 1162.3(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.498$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 5.453$ mm^{-1}, $F(000) = 840$, ω-2θ scans, max./min. transmission 0.999/0.807, 2272 unique reflections ($\theta_{max} = 26°$), 2040 observed ($I > 2\sigma(I)$), 206 parameters, $R = 0.0239$, $R_w = 0.0646$, residual electron density max./min. 0.87/ – 0.80 e Å^{-3}.[6b] Compound **5**: 0.60 × 0.28 × 0.22 mm, monoclinic, space group $P2_1/c$, $a = 10.915(1)$, $b = 10.113(1)$, $c = 10.462(1)$ Å, $\beta = 100.475(9)°$, $V = 1135.58(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.646$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 7.447$ mm^{-1}, $F(000) = 860$, ω-2θ scans, max./min. transmission 1.000/0.637, 2220 unique reflections ($\theta_{max} = 26°$), 2091 observed ($I > 2\sigma(I)$), 206 parameters, $R = 0.0212$, $R_w = 0.0575$, residual electron density max./min. 1.10/ – 0.72 e Å^{-3}.[6b]

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[10] Compound **6**: 0.28 × 0.22 × 0.10 mm, monoclinic, space group $P2_1/n$, $a = 10.822(2)$, $b = 9.216(2)$, $c = 14.228(3)$ Å, $\beta = 104.79(3)°$, $V = 1372.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.481$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 6.188$ mm^{-1}, $F(000) = 980$, ω-2θ scans, max./min. transmission 0.999/0.527, 2691 unique reflections ($\theta_{max} = 26°$), 2326 observed ($I > 2\sigma(I)$), 227 parameters, $R = 0.0302$, $R_w = 0.0808$, residual electron density max./min. 1.74/ – 2.19 e Å^{-3}.[6b]

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