ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Solid State Chemistry 181 (2008) 373–381

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Hydrothermal chemistry of Th(IV) with aromatic dicarboxylates: New framework compounds and *in situ* ligand syntheses

Kate L. Ziegelgruber[a,b], Karah E. Knope[b], Mark Frisch[b], Christopher L. Cahill[b,c,*]

[a]*Department of Chemistry and Biochemistry, DePauw University, Greencastle, IN 46135, USA*
[b]*Department of Chemistry, The George Washington University, Washington, DC 20052, USA*
[c]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*

Received 26 September 2007; received in revised form 3 December 2007; accepted 9 December 2007
Available online 23 December 2007

Abstract

A novel thorium (IV) coordination polymer, $Th(C_5H_2N_2O_4)_2(H_2O)_2$ (**1**), has been prepared under the hydrothermal reaction of thorium nitrate tetrahydrate and 3,5-pyrazoledicarboxylic acid (H_3pdc). Compound **1** (orthorhombic, $P2_12_12_1$, $a = 6.9362(5)$ Å, $b = 10.7806(8)$ Å, $c = 17.9915(14)$ Å, $Z = 2$, $R_1 = 0.0210$, $wR_2 = 0.0470$) consists of thorium metal centers connected via H_3pdc linkages to form an overall three-dimensional structure containing π–π interactions between the pyrazole rings. 2,3-Pyrazinedicarboxylic acid (H_2pzdc) was explored as well to (1) study the effect of the location of the carboxylic groups around the aromatic ring and (2) produce heterometallic compounds. Thorium (IV) and copper (II) were combined with H_2pzdc, resulting in an interesting decomposition reaction characterized though the isolation of $Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$ (**2**) (monoclinic, $C2/c$, $a = 13.8507(12)$ Å, $b = 7.8719(7)$ Å, $c = 10.7961(16)$ Å, $\beta = 118.0310(10)^\circ$, $Z = 2$, $R_1 = 0.0160$, $wR_2 = 0.0349$), $Cu(C_6H_2N_2O_4)$ (**3**) (monoclinic, $C2/c$, $a = 11.499(3)$ Å, $b = 7.502(2)$ Å, $c = 7.402(2)$ Å, $\beta = 93.892(5)^\circ$, $Z = 4$, $R_1 = 0.0472$, $wR_2 = 0.0745$) and $Cu(C_5H_3N_2O_2)(NO_3)(H_2O)$ (**4**). The capture of these species provides mechanistic evidence for the formation of the oxalate anions observed in **2** via the decarboxylation of H_2pzdc to yield the linker in **4**: 2-pyrazinecarboxylate anions.

Keywords: Thorium (IV) coordination polymers; Decarboxylation; Oxalate formation; *In situ* ligand synthesis; Hydrothermal synthesis

---

1. Introduction

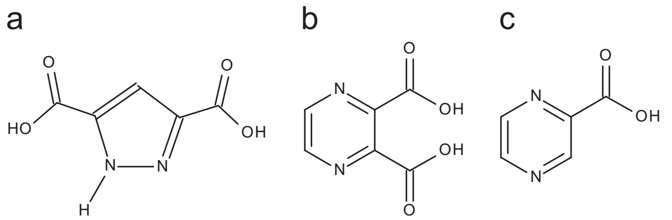
The synthesis of inorganic–organic hybrid materials containing either transition metals or lanthanides has been explored extensively partly due to their propensity to form extended framework structures with interesting structural topologies [1–12]. Moreover, these materials have shown potential in a vast range of applications including gas storage, magnetic materials, ion exchange, separations, optics and catalysis [13–21]. The most common approach for producing coordination polymers and metal organic framework materials is through the self-assembly of metal centers with appropriate organic linker species to promote extended topologies. This methodology (often applied under hydrothermal conditions) has resulted in extensive families of compounds based on transition metal compositions. Actinide containing coordination polymers (specifically U(VI) compositions) are somewhat less developed yet are increasing in number and application [22–44]. Materials containing Th(IV) have not been as widely explored and consequently the syntheses of these materials are considerably less developed [45–49]. Additionally, it is essential to investigate the hydrothermal synthesis of actinide compounds in a general sense as this relates to stewardship of spent nuclear fuel, reprocessing and other aspects of the nuclear fuel cycle [50–56].

As part of our efforts to synthesize thorium (IV) coordination polymers, we have chosen 3,5-pyrazoledicarboxylic acid, H_3pdc ($C_5H_4N_2O_4$), and 2,3-pyrazinedicarboxylic acid, H_2pzdc ($C_6H_4N_2O_4$), as our organic linker species (Scheme 1). The use of these molecules as linkers

---

[*] Corresponding author at: Department of Chemistry, The George Washington University, Washington, DC 20052, USA.
Fax: +1 202 994 5873.
E-mail address: cahill@gwu.edu (C.L. Cahill).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2007.12.008



Scheme 1. Organic linkers seen in this system: (a) 3,5-pyrazoledicarboxylic acid, H_3pdc ($C_5H_4N_2O_4$); (b) 2,3-pyrazinedicarboxylic acid, H_2pzdc, ($C_6H_4N_2O_4$) and (c) the decarboxylated species of H_2pzdc—2-pyrazinecarboxylic acid, Hpzca ($C_5H_4N_2O_2$).

was originally intended to allow study of the effect of functional group location on resulting topology. Each organic contains two distinct coordination sites involving both the carboxylic groups and the nitrogen atoms from either the pyrazole or pyrazine rings. These binding sites are highly accessible to metal ions and thus the promotion of higher dimensional structures is to be realized through the various binding modes. Further, carboxylate affinity for Th(IV) can be anticipated and incorporation of a second, softer metal may be explored at the N donor sites [23,26]. These linkers have recently been successful in producing coordination polymers involving transition metals [57–66], lanthanides [67–71] and U(VI) [26]; yet, to our knowledge, neither has been utilized with thorium as the metal center.

As hydrothermal methods have become an increasingly popular route for the synthesis of novel coordination polymers, so has the frequency with which *in situ* ligand synthesis has been observed. Briefly, *in situ* ligand synthesis results when an organic component, nominally the intended linker molecule, undergoes a re-arrangement, cleavage or redox and the resulting species are then observed in the crystalline reaction products as either a linker or a guest [72]. Researchers have described this synthetic pathway as a new approach to crystal engineering with benefits including a simplification of synthesis steps, the slow formation of ligands to promote single crystal growth, and environmental friendliness. Furthermore, it has been observed that materials produced through this synthetic route have been difficult or impossible to obtain otherwise [72]. As such, a number of examples of *in situ* ligand synthesis have been reported recently [24,29,72–81]. Oxalate anion formation under hydrothermal conditions is one such example and several pathways for its formation have been proposed, including the reductive coupling of carbon dioxide [82–86], the decomposition or oxidation of an organic compound [87–92], and the decarboxylation of an organic species [35,79,93–102] as viewed in this system.

Reported herein are the syntheses and crystal structures of two novel thorium (IV) coordination polymers, $Th(C_5H_2N_2O_4)_2(H_2O)_2$ (**1**) and $Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$ (**2**), produced under hydrothermal conditions. Interestingly, the oxalate anion ($C_2O_4^{2-}$) observed in compound **2** is believed to form via *in situ* ligand synthesis through decarboxylation of the organic precursor, H_2pzdc. We also report the first account (to our knowledge) of the isolation and subsequent characterization of all decomposition species within a single reaction product through a pair of secondary phases that co-crystallize with **2** (namely $Cu(C_6H_2N_2O_4)$, compound **3** and $Cu(C_5H_3N_2O_2)(NO_3)(H_2O)$ [103], compound **4**). Compound **4** contains the decarboxylated species, 2-pyrazinecarboxylic acid, bound to Cu(II) that was originally introduced to promote the synthesis of a bimetallic coordination polymer. The appearance of 2-pyrazinecarboxylic acid in the crystal structure of **4** provides additional evidence for the formation of the oxalate anions in **2** via decarboxylation of the H_2pzdc starting material.

2. Experimental

2.1. Synthesis

Caution: Standard precautions for handling radioactive substances should be followed when working with thorium (IV) nitrate tetrahydrate [$(Th(NO_3)_4 \cdot 4H_2O)$].

Copper (II) nitrate hemi(pentahydrate) [$Cu(NO_3)_2 \cdot 2.5H_2O$], H_2pzdc, and H_3pdc were purchased from Aldrich Chemicals, Inc. Thorium (IV) nitrate tetrahydrate [$Th(NO_3)_4 \cdot 4H_2O$] was obtained from Strem Chemicals. All reagents were used as received without further purification. Elemental analyses were conducted by Galbraith Laboratories, Inc., Knoxville, TN.

Compound **1**, $Th(C_5H_2N_2O_4)_2(H_2O)_2$, was synthesized when $Th(NO_3)_4 \cdot 4H_2O$ (0.552 g, 1 mmol) and H_2pzdc (0.347 g, 2 mmol) were dissolved in 3.19 g of distilled H_2O in the molar ratio of 1:2:177. The reactants were placed in a 23 mL Teflon-lined Parr bomb (starting pH = 0.86) and heated statically at 120 °C for 7 days. The reaction vessel was allowed to cool at room temperature for 1 h. A colorless solution was decanted (final pH = 0.41), and the remaining clear colorless block crystals were washed with distilled water and ethanol and allowed to air dry at room temperature (442 mg, yield: 76.2% based on thorium). Elemental analysis observed/found (%) for $Th(H_2O)_2(C_5H_2N_2O_4)_2$: C (20.83/20.85), H (1.45/1.40) and N (9.75/9.72).

Compound **2**, $Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$, was synthesized when $Th(NO_3)_4 \cdot 4H_2O$ (0.137 g, 0.25 mmol), copper (II) nitrate hemi(pentahydrate) (0.052 g, 0.25 mmol) and H_2pzdc (0.085 g, 0.50 mmol) were dissolved in 3.133 g of distilled H_2O in the molar ratio 1:1:2:695. The reaction solution was placed in a 23 mL Teflon-lined Parr bomb (starting pH = 0.92) and heated statically at 120 °C for 5 days, then cooled for 2 h at room temperature. A light blue solution (final pH = 1.73) was obtained and allowed to evaporate. Clear colorless crystals of compound **2** were produced along with both green crystals, $Cu(C_6H_2N_2O_4)$ (**3**), and dark blue crystals, [$Cu(C_5H_3N_2O_2)(NO_3)(H_2O)$] [103] **4**. Optical inspection suggests a ratio of 4:2:1 for the three phases (**2**:**3**:**4**). Compound **2** may also be obtained as a pure phase via reaction of H_2pzdc or Hpzca (in the

Table 1
Crystallographic data for $Th(C_5H_2N_2O_4)_2(H_2O)_2$, $Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$ and $Cu(C_6H_2N_2O_4)$

	$Th(C_5H_2N_2O_4)_2(H_2O)_2$ (**1**)	$Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$ (**2**)	$Cu(C_6H_2N_2O_4)$ (**3**)
Formula weight	1152.49	952.22	229.64
T (K)	298	298	298
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$	$C2/c$
a (Å)	6.9362(5)	13.8507(12)	11.499(3)
b (Å)	10.7806(8)	7.87196(7)	7.502(2)
c (Å)	17.9915(14)	10.7961(16)	7.402(2)
α (deg)	90	90	90
β (deg)	90	118.0310(10)	93.892(5)
γ (deg)	90	90	90
V (Å^3)	1345.34(17)	1039.0(2)	637.0(3)
Z	2	2	4
D_c (mg m^{-3})	2.845	3.044	2.394
μ(Mo$K\alpha$) (mm^{-1})	11.157	14.413	3.403
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
$F(000)$	1064	856	452
Crystal size (mm)	0.14 × 0.06 × 0.06	0.06 × 0.05 × 0.03	0.04 × 0.04 × 0.02
Theta range for data collection	2.20–30.33°	3.08–30.43°	3.24–24.70°
Index ranges	$-6 \leqslant h \leqslant 9$, $-14 \leqslant k \leqslant 15$, $-25 \leqslant l \leqslant 24$	$-19 \leqslant h \leqslant 19$, $-10 \leqslant k \leqslant 10$, $-14 \leqslant l \leqslant 14$	$-13 \leqslant h \leqslant 13$, $-8 \leqslant k \leqslant 8$, $-8 \leqslant l \leqslant 8$
Reflections collected	22125	9886	4259
R_{int} (independent reflections)	0.0602 (3821)	0.0308 (1477)	0.1414 (547)
Goodness-of-fit on F^2	1.051	1.079	1.041
R^a $[I > 2\sigma(I)]$	0.0210	0.0168	0.0472
wR_2^a	0.0470	0.0395	0.0745

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]^{1/2}$.

absence of Cu(II)) with $Th(NO_3)_4 \cdot 4H_2O$ at 120 °C for 1 day. This will be discussed further below.

2.2. Instrumentation

Representative single crystals of **1**–**4** were extracted and mounted on glass fibers with epoxy. The crystal structures were determined via single crystal X-ray diffraction. The crystallographic data are summarized in Table 1. Intensity data were collected on a Bruker SMART diffractometer equipped with an APEX II CCD detector. Data processing was performed using SAINT [104] and the structures were solved using direct methods. Refinements were carried out using SHELXL-97 [105] within the WINGX software suite [106]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located or calculated and refined isotropically, with the exception of hydrogen atoms on the unbound water molecules, which could not be located.

3. Results

3.1. Crystal structure of $Th(C_5H_2N_2O_4)_2(H_2O)_2$, compound 1

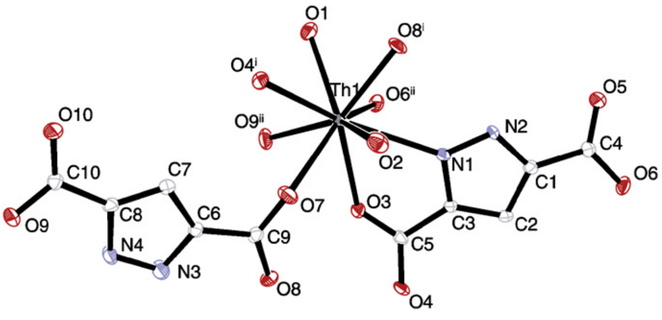


Fig. 1. The ORTEP of compound **1** [$Th(C_5H_2N_2O_4)_2(H_2O)_2$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

The crystal structure of compound **1** (Fig. 1) consists of a central thorium (IV) metal ion bound to six H_3pdc acid units. One H_3pdc is bound to the thorium center in a bidentate mode through a carboxylate oxygen atom, O3, at a distance of 2.436 Å and N1 from the pyrazole ring at a distance of 2.704 Å forming a N1–Th1–O3 angle of 60.327°. The remaining five H_3pdc acid units are bound through a single carboxylate oxygen atom at an average distance of 2.243 Å. Finally, two water molecules are bound to the thorium metal center at distances of 2.529 and 2.473 Å to complete the overall 9-coordination of thorium (IV). Coordination to the ligand is through deprotonated oxygen atoms at the carboxylate groups

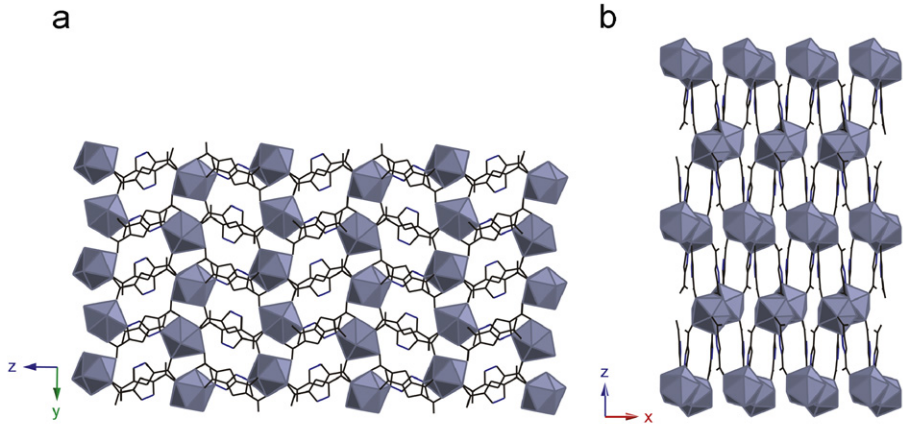


Fig. 2. View of compound **1**, $Th(C_5H_2N_2O_4)_2(H_2O)_2$, in the (a) [100] direction and (b) [010] direction.

exclusively. This is despite the presence of an acidic proton on the pyrazole ring; yet sterics and charge balance requirements likely leave this site uncoordinated.

The thorium metal centers are connected into chains by two separate bridging carboxylate groups, through O3 and O4 along with O7 and O8 as viewed down the [100] direction (Fig. 2a). These thorium chains are further linked by the H_3pdc linkers, resulting in the overall three-dimensional structure as seen in the y-direction (Fig. 2b).

The orientation of the pyrazole rings in $Th(C_5H_2N_2O_4)_2(H_2O)_2$ suggests π-stacking may be present. The closest center of gravity, $C(g)$, positions from the center of the pyrazole ring in H_3pdc as calculated using PLATON [107] is 3.726 Å, which is in the accepted range for π–π interactions [108].

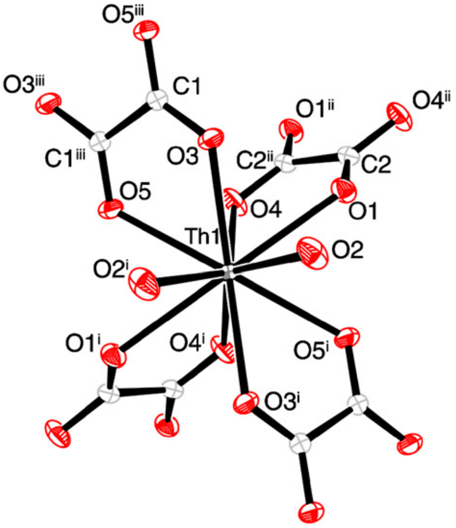


Fig. 3. The ORTEP of compound **2** [$Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x, y, -z+\frac{1}{2}$; (ii) $-x, -y, -z$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

3.2. *Crystal structure of $Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$, compound 2*

The crystal structure of compound **2** (Fig. 3) consists of a central thorium (IV) metal ion bound to four distinct oxalate anions. Each oxalate is coordinated to the metal center in a bidentate fashion. O3 and O5 (and their symmetry equivalents) are bound to thorium (IV) at a distance of 2.505 and 2.516 Å to form an O3–Th1–O5 angle of 63.989°, while O1 and O4 (and their symmetry equivalents) are bound at a distance of 2.568 and 2.503 Å, respectively, creating a similar O1–Th1–O4 angle of 62.727°. To complete the ten-member spherical coordination of the metal center, two symmetry equivalent water molecules are additionally coordinated at a distance of 2.462 Å.

The thorium metal centers are linked into one-dimensional chains through the bidentate coordination of O3 and O5 from the oxalate anion as demonstrated down the [001] direction (Fig. 4a). Viewing compound **2** in the [011] direction illustrates the additional dimensionality through the bonding of the oxalates in a bidentate fashion from O1 and O4 down the y-axis, resulting in the overall three-dimensional structure (Fig. 4b). Finally, there are two symmetry equivalent unbound water molecules (Ow1) located in the void space.

3.2.1. *Crystal structure of $Cu(C_6H_2N_2O_4)$, compound 3*

The crystal structure of compound **3** (Fig. 5) consists of a central copper (II) metal ion bound to two H_2pzdc units in a bidentate fashion. The Cu(II) is coordinated to a carboxylate oxygen atom, O1, at a distance of 1.935(5) Å along with N1 from the pyrazine ring at a distance of 1.980(5) Å to form the corresponding O1–Cu1–N1 angle of 82.9(2)°, respectively.

Through these linkages, one-dimensional chains are realized along [010] (Fig. 6a). Furthermore, two symmetry equivalent carboxylate oxygen atoms, O2, are bound at a distance of 2.454 Å, completing the overall distorted octahedral geometry of the copper metal center. These

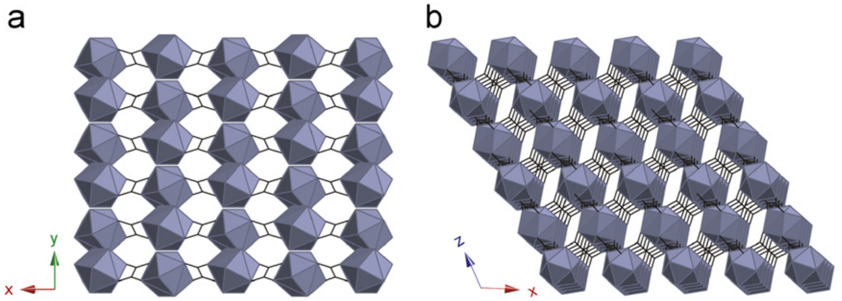


Fig. 4. View of compound **2**, $Th(C_2O_4)_2(H_2O)_2\cdot 2H_2O$, down the (a) [001] direction and (b) [010] direction. Unbound water molecules and hydrogen atoms are removed for clarity.

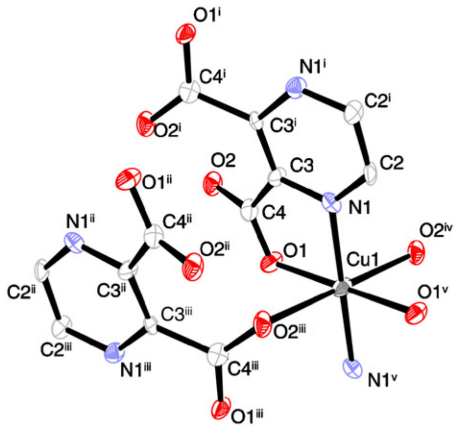


Fig. 5. The ORTEP of compound **3**, $Cu(C_6H_2N_2O_4)$. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x, y, -z+\frac{1}{2}$; (ii) $-x, -y, -z$; (iii) $x, -y, z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

Cu1–O2 bonds in the axial plane link the copper-2,3-pyrazinedicarboxylate chains into a three-dimensional structure (Fig. 6b).

3.3. *Crystal structure of $[Cu(C_5H_3N_2O_2)(NO_3)(H_2O)]$, compound 4*

As this compound has been reported previously [103], we offer a brief structural description here as it pertains to these efforts. The crystal structure of **4** consists of copper (II) ions linked into one-dimensional chains by 2-pyrazinecarboxylate anions (see Scheme 2). Each copper (II) ion is surrounded by two 2-pyrazinecarboxylate anions; one is linked in a bidentate fashion, while the second in coordinated in a monodentate fashion to the metal center. A water molecule and a nitrate anion are also bound to each copper (II) center to complete the overall 6-coordinate local geometry.

4. Discussion

The synthesis of two novel thorium coordination polymers under hydrothermal conditions has been demonstrated using a pair of multifunctional ligands, H_3pdc and H_2pzdc. H_3pdc has been successful, as mentioned previously, in synthesizing coordination polymers owing to the various bridging modes of the ligand as described by Powell et al. [60]. Compound **1** is only the second example of an An–H_3pdc coordination polymer. Our group has previously synthesized a two-dimensional material, $[(UO_2)(C_5H_2N_2O_4)(H_2O)]$ [26], with similar binding modes to the organic linker as observed in **1**. Both of these coordination polymers contain metal centers bound to H_3pdc in a monodentate fashion through the carboxylate oxygen atoms and in a bidentate fashion through the pyrazole ring and the carboxylate group. The resulting bond lengths for these two compounds can furthermore be compared: within the bidentate bridging mode of the pyrazole ring and the carboxylate group the Th–O and U–O bond lengths (2.436 vs. 2.477 Å) are analogous, while the Th–N bond of 2.704 Å is slightly longer than 2.608 Å as seen for U–N.

In contrast to the actinide compounds just mentioned, numerous examples of lanthanide–H_3pdc coordination polymers have been synthesized. For instance, Li has synthesized a three-dimensional coordination polymer, $[Ce_2(C_5H_2N_2O_4)(C_5H_3N_2O_4)_4(H_2O)_6]$ [68], while Li et al. have produced a series of rare-earth metal compounds (Ln = La, Ce, Eu, Er, Lu) [70]. They found that the coordination numbers of the metal centers decrease from 9 (La, Ce) to either 9 or 8 (Eu) to finally only 8 (Er, Lu) as a result of the lanthanide contraction. Li et al. additionally found that the reaction pH affects the structure composition for the erbium compounds. All of the compounds synthesized by Li et al. have comparable metal to linker binding modes to **1**: binding via a single carboxylate oxygen atom along with a bidentate coordination through the pyrazole ring and the carboxylate group. However, $Ln_2(Hpdc)_3(H_2O)_4$ (Ln = La, Ce) illustrated an additional binding to the linker, coordination to a chelated carboxylate group.

Like H_3pdc, H_2pzdc is an attractive ligand to utilize in attempts to synthesize heterometallic coordination polymers by taking advantage of the distinct hard and soft functional groups within this linker. Moreover, we can theorize the various coordination modes of the metal centers to H_2pzdc by utilizing hard/soft acid/base distinctions [109,110]. A harder metal such as thorium will tend to

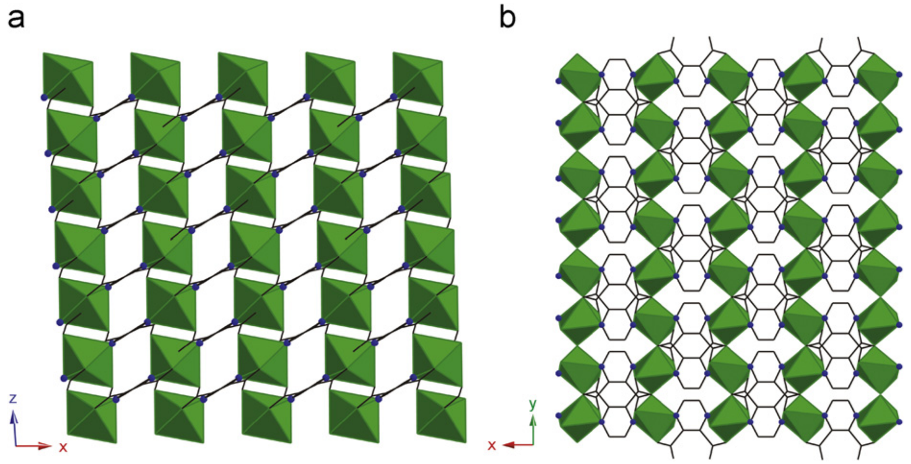
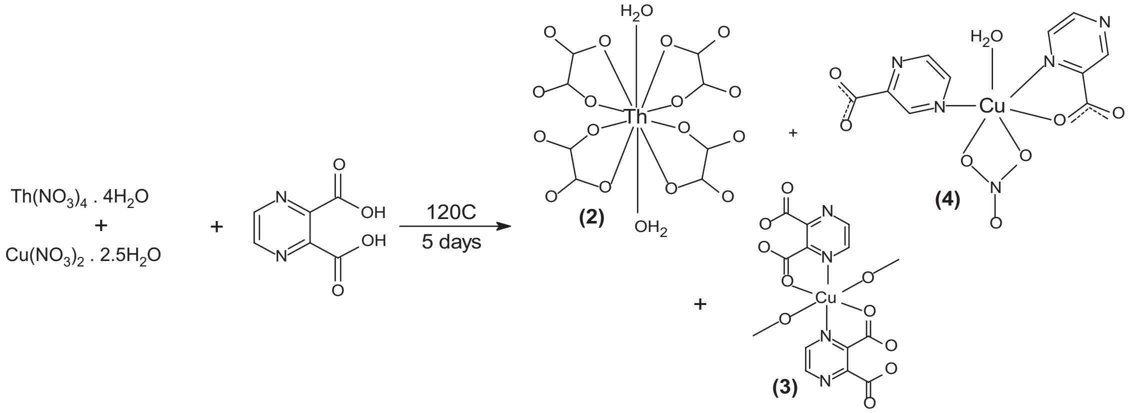


Fig. 6. View of compound **3**, $Cu(C_6H_2N_2O_4)$, down the (a) [010] direction and (b) [001] direction.



Scheme 2. Equation illustrating the various compounds and organic linkers in the hydrothermal reaction resulting in compounds **2**, **3** and **4**.

bind to the harder functional group such as a carboxylic acid, while a softer metal center will bind to a softer functional group, in this case the nitrogen of the pyrazine ring. In contrast, a triphasic product results wherein compounds, $Th(C_2O_4)_2(H_2O)_2 \cdot 2H_2O$ (**2**), $Cu(C_6H_2N_2O_4)$ (**3**) and, $Cu(C_5H_3N_2O_2)(NO_3)(H_2O)$ (**4**) [103], were synthesized upon combination of thorium (IV) nitrate, copper (II) nitrate and H_2pzdc under hydrothermal conditions (Scheme 2). Surprisingly, a bimetallic coordination polymer was not obtained, and only compound **3** contained *intact* H_2pzdc linker species. The Th(IV) metal centers in **2** are polymerized through oxalate ($C_2O_4^{2-}$) linkages, while the Cu(II) metal centers in compound **4** are coordinated to 2-pyrazinecarboxylate anions.

Other thorium (IV) oxalates have been reported [111–113]; yet this is likely the first observation of a thorium (IV) oxalate formed under hydrothermal conditions via *in situ* ligand synthesis. *In situ* oxalate formation has been observed in other systems via several proposed pathways including the reductive coupling of carbon dioxide and the decomposition or oxidation of an organic compound [82–92]. The formation of the oxalate linkages via *in situ* ligand synthesis in the structure of **2** could have formed from an alternative route—the decarboxylation of H_2pzdc followed by subsequent coupling to produce the ($C_2O_4^{2-}$) anions [35,79,93–102]. Oxalate and 2-pyrazinecarboxylate anions link the Th(IV) and Cu(II) metal centers in compounds **2** and **4** upon addition of copper (II) to the thorium (IV)–H_2pzdc system, whereas **3** contains the fully intact H_2pzdc connecting Cu(II) centers. The isolation of these three compounds is thus indicative for the *in situ* ligand formation of the oxalate anions through the proposed two-step process with the evidence for the decarboxylation of H_2pzdc captured in compound **4**. These results amount to the first account of a decomposition reaction wherein all of the intermediates are accounted for in the crystalline products.

As part of this investigation, a series of reactions were conducted to explore the factors that influence oxalate formation, including the role of the Cu(II) ions. Initially, Cu(II) was hypothesized to mediate the decarboxylation of H_2pzdc since this ion has been present in other systems where decarboxylation of the starting organic has been observed [114–119]. Whereas Cu(II) might *promote* oxalate formation in our system, it was proven to be non-essential as **2** can formed in the absence of Cu(II). For example, **2** can be obtained by reaction of $Th(NO_3)_4 \cdot 4H_2O$ and H_2pzdc at 120 °C for 1 day. Additionally, a temperature dependence for these reactions is noted: reactions at 70 °C (from 1 to 10 days) yielded no crystalline products containing oxalate anions implying no decarboxylation of the H_2pzdc. At the elevated temperatures of 120 and 150 °C (for 1 day), the oxalate containing compound **2** was produced at yields of 66–74%, respectively. Reaction of thorium (IV) nitrate with Hpzca ($C_5H_4N_2O_4$) also gives rise to **2**. The oxalate formation within the Th–Hpzca system appears to be influenced by reaction time wherein increased time (at 120 °C) improves the yield of **2** (2.9% for 1 day vs. 25.8% for 3 days vs. 35.7% for 6 days). Raising the reaction temperature to 150 °C did not influence oxalate formation; yet it did promote synthesis of another Th-oxalate phase, $Th(C_2O_4)_2(H_2O)_2$, at the expense of **2**. A preliminary structural evaluation of this material suggests it possesses a layered structure and a unit cell (orthorhombic, $a = 9.7533(9)$, $b = 10.3764(10)$ and $c = 8.4573(8)$ Å) consistent with that reported by Jenkins et al. [113] from a powder diffraction study. Further structural characterization is in progress and a complete refinement will be reported in the future.

In light of these observations, we can surmise that the decarboxylation and subsequent oxalate formation demonstrated with both the H_2pzdc and the Hpzca are metal mediated, either by Th(IV), Cu(II) or both. Considering the mixed phase nature of the products, distinguishing the influence of each metal individually (i.e. does Cu(II) promote additional oxalate formation beyond that of Th(IV)?) is clearly a challenge, which we leave for further consideration. However, to explore metal mediation in general, H_2pzdc and Hpzca were each dissolved (separately) in H_2O and heated to 150 °C for 2 days in Teflon-lined Parr bombs. NMR analysis on the resulting solution indicated no decomposition of the starting materials.

Oxalate anion formation has been observed in other systems where Hpzca is present. In the hydrothermal reaction of 2-pyrazinecarboxylic acid, Pr_6O_{11} (or Er_2O_3) and $FeCl_3$, a lanthanide coordination polymer, $[Ln_2(C_2O_4)_2(C_5H_3N_2O_4)_2(H_2O)_2]$, was obtained whereby the lanthanide metal centers (Pr^{3+} or Er^{3+}) were bridged through both 2-pyrazinecarboxylate and oxalate anions [97]. Liu et al. attempted to synthesize this compound in the absence of $FeCl_3$ or by adding sodium oxalate to the reaction mixture; yet they were unable to reproduce the compound of interest. With these findings, Liu et al. hypothesized that $FeCl_3$ took advantage of the degradation of the organic linker to aid in the formation of the oxalate anions. These authors synthesized another oxalate-containing coordination polymer, $[Nd_4(C_2O_4)_4(NO_3)_2(OH)_2(H_2O)_2] \cdot 5H_2O$, under hydrothermal conditions upon the combination of Nd_2O_3, $Fe(NO_3)_3$ and Hpzca [117]. Since no oxalic acid was in the starting materials, it was theorized that the oxalate anions were derived from the decomposition of Hpzca. Once again, the authors were unsuccessful at synthesizing the Nd(III)-oxalate compound through the direct assembly of neodymium nitrate and oxalic acid. These observations are consistent with some of the sentiments regarding *in situ* ligand synthesis mentioned above, notably the idea that some materials may be inaccessible by any other route.

5. Conclusions

Two novel thorium (IV) coordination polymers were synthesized under hydrothermal conditions utilizing two multi-functional ligands: 3,5-pyrazoledicarboxylic acid and 2,3-pyrazinedicarboxylic acid. Attempts to synthesize a Th–Cu bimetallic compound with 2,3-pyrazinedicarboxylic acid were unsuccessful and instead resulted in the triphasic mixture of a Th(IV) oxalate, a Cu(II) pyrazinedicarboxylate and a Cu(II) pyrazinecarboxylate (**2**, **3** and **4**, respectively). The oxalate anion linkers in compound **2** are proposed to result from decarboxylation of 2,3-pyrazinedicarboxylic acid followed by subsequent coupling of CO_2. The resulting decarboxylated species, 2-pyrazinecarboxylic acid, is observed as the organic linker in the structure of **4**. The isolation of these 3 compounds is an intriguing example of *in situ* ligand synthesis wherein mechanistic information may be implied based on the capture of all decomposition products in a single reaction.

6. Supplementary material

Crystallographic data (excluding structure factors) for compounds **1–3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 662198–662200. 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).

Acknowledgments

This work was supported by The National Science Foundation (DMR-0348982 and DMR-0419754) and the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Heavy Elements Program, US Department of Energy, under Grant DE-FG02-05ER15736 at GWU. KZ is grateful for NSF Research Experiences for Undergraduate (REU) support supplemental to DMR-0348982. We are grateful to Ms. Nausheena Baig (GWU) for assistance with the NMR studies.

References

[1] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319–330.

[2] G. Ferey, Chem. Mater. 10 (2001) 3084–3098.

[3] M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 369–378.
[4] R.J. Hill, D.-L. Long, P. Hubberstey, M. Schroeder, N.R. Champness, J. Solid State Chem. 8 (2005) 2414–2419.
[5] S.L. James, Chem. Soc. Rev. 32 (2003) 276–288.
[6] C. Janiak, Dalton Trans. 14 (2003) 2781–2804.
[7] J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 8239–8247.
[8] S. Kitagawa, K. Uemura, Chem. Soc. Rev. 34 (2005) 109–119.
[9] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629–1658.
[10] B. Moulton, M.J. Zaworotko, Curr. Opin. Solid State Mater. Sci. 6 (2002) 117–123.
[11] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466–1496.
[12] M.-L. Tong, S. Hu, J. Wang, S. Kitagawa, S.W. Ng, Cryst. Growth Des. 5 (2005) 837–839.
[13] P. Ayyappan, O.R. Evans, Y. Cui, K.A. Wheeler, W. Lin, Inorg. Chem. 41 (2002) 4978–4980.
[14] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, M. Yaghi Omar, Science 295 (2002) 469–472.
[15] L. Pan, K.M. Adams, H.E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, J. Am. Chem. Soc. 125 (2003) 3062–3067.
[16] B. Rather, B. Moulton, D.B. Walsh Rosa, M.J. Zaworotko, Chem. Commun. 7 (2002) 694–695.
[17] T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi, J. Am. Chem. Soc. 121 (1999) 1651–1657.
[18] N.L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O.M. Yaghi, Cryst. Eng. Commun. 4 (2002) 401–404.
[19] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, J. Am. Chem. Soc. 126 (2004) 5666–5667.
[20] O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (1998) 474–484.
[21] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705–714.
[22] L.A. Borkowski, C.L. Cahill, Inorg. Chem. 42 (2003) 7041–7045.
[23] C.L. Cahill, D.T. de Lill, M. Frisch, Cryst. Eng. Commun. 9 (2007) 15–26.
[24] W. Chen, H.-M. Yuan, J.-Y. Wang, Z.-Y. Liu, J.-J. Xu, M. Yang, J.-S. Chen, J. Am. Chem. Soc. 125 (2003) 9266–9267.
[25] M. Ephritikhine, Dalton Trans. (2006) 2501–2516.
[26] M. Frisch, C.L. Cahill, Dalton Trans. (2005) 1518–1523.
[27] M. Frisch, C.L. Cahill, Dalton Trans. (2006) 4679–4690.
[28] Y.B. Go, X. Wang, A.J. Jacobson, Inorg. Chem. 46 (2007) 6594–6600.
[29] Y.-S. Jiang, Z.-T. Yu, Z.-L. Liao, G.-H. Li, J.-S. Chen, Polyhedron 25 (2006) 1359–1366.
[30] J.-Y. Kim, A.J. Norquist, D. O'Hare, Dalton Trans. 14 (2003) 2813–2814.
[31] J.-Y. Kim, A.J. Norquist, D. O'Hare, Chem. Mater. 15 (2003) 1970–1975.
[32] J. Leciejewicz, N.W. Alcock, T.J. Kemp, Struct. Bonding 82 (1995) 43–84.
[33] B. Masci, P. Thuery, Polyhedron 24 (2005) 229–237.
[34] P. Thuery, Chem. Commun. 8 (2006) 853–855.
[35] P. Thuery, Polyhedron 26 (2007) 101–106.
[36] P. Thuery, Cryst. Eng. Commun. 9 (2007) 358–360.
[37] P. Thuery, Inorg. Chem. Commun. 10 (2007) 423–426.
[38] P. Thuery, Inorg. Chem. 46 (2007) 2307–2315.
[39] C.-M. Wang, C.-H. Liao, H.-M. Kao, K.-H. Lii, Inorg. Chem. 44 (2005) 6294–6298.
[40] Y.-R. Xie, H. Zhao, X.-S. Wang, Z.-R. Qu, R.-G. Xiong, X. Xue, Z. Xue, X.-Z. You, Eur. J. Inorg. Chem. 20 (2003) 3712–3715.
[41] Z.-T. Yu, G.-H. Li, Y.-S. Jiang, J.-J. Xu, J.-S. Chen, Dalton Trans. 22 (2003) 4219–4220.
[42] Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li, J.-S. Chen, Chem. Eur. J. 11 (2005) 2642–2650.
[43] Y.-Z. Zheng, M.-L. Tong, X.-M. Chen, Eur. J. Inorg. Chem. 20 (2005) 4109–4117.
[44] Y.-S. Jiang, G.-H. Li, Y. Tian, Z.-L. Liao, J.-S. Chen, Inorg. Chem. Commun. 9 (2006) 595–598.
[45] R.K. Agarwal, J. Prakash, Polyhedron 10 (1991) 2809–2812.
[46] D.M.L. Goodgame, D.J. Williams, R.E.P. Winpenny, Polyhedron 7 (1988) 1807–1811.
[47] J.-Y. Kim, A.J. Norquist, D. O'Hare, Chem. Commun. 19 (2002) 2198–2199.
[48] J.-Y. Kim, A.J. Norquist, D. O'Hare, J. Am. Chem. Soc. 125 (2003) 12688–12689.
[49] J. Xu, D.W. Whisenhunt, A.C. Veeck, L.C. Uhlir, K.N. Raymond, Inorg. Chem. 42 (2003) 2665–2674.
[50] D.L. Clark, S.D. Conradson, R.J. Donohoe, D.W. Keogh, D.E. Morris, P.D. Palmer, R.D. Rogers, C.D. Tait, Inorg. Chem. 38 (1999) 1456–1466.
[51] R.C. Ewing, Can. Mineral. 39 (2001) 697–715.
[52] J.J. Lenhart, S.E. Cabaniss, P. MacCarthy, B.D. Honeyman, Radiochim. Acta 88 (2000) 345–353.
[53] D.A. Palmer, C. Nguyen-Trung, J. Sol. Chem. 24 (1995) 1281–1291.
[54] L. Rao, J. Jiang, P. Zanonato, P. Di Bernardo, A. Bismondo, A.Y. Garnov, Radiochim. Acta 90 (2002) 581–588.
[55] E.L. Shock, D.C. Sassani, H. Betz, Geochim. Cosmochim. Acta 61 (1997) 4245–4266.
[56] P.C. Burns, Can. Mineral. 43 (2005) 1839–1894.
[57] J.C. Bayon, P. Esteban, G. Net, P.G. Rasmussen, K.N. Baker, C.W. Hahn, M.M. Gumz, Inorg. Chem. 30 (1991) 2572–2574.
[58] J.C. Bayon, G. Net, P. Esteban, P.G. Rasmussen, D.F. Bergstrom, Inorg. Chem. 30 (1991) 4771–4777.
[59] P. King, R. Clerac, C.E. Anson, C. Coulon, A.K. Powell, Inorg. Chem. 42 (2003) 3492–3500.
[60] P. King, R. Clerac, C.E. Anson, A.K. Powell, Dalton Trans. 6 (2004) 852–861.
[61] S. Konar, S.C. Manna, E. Zangrando, N.R. Chaudhuri, Inorg. Chim. Acta 357 (2004) 1593–1597.
[62] L. Pan, N. Ching, X. Huang, J. Li, Chem. Eur. J. 7 (2001) 4431–4437.
[63] L. Pan, T. Frydel, M.B. Sander, X. Huang, J. Li, Inorg. Chem. 40 (2001) 1271–1283.
[64] L. Pan, X. Huang, J. Li, J. Solid State Chem. 152 (2000) 236–246.
[65] P. Richard, D. Tran Qui, E.F. Bertaut, Acta. Crystallogr. Sect. B: Struct. Cryst. Cryst. Chem. 30 (1974) 628–633.
[66] J.-L. Tian, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, P. Cheng, Inorg. Chem. Commun. 6 (2003) 1025–1029.
[67] M.L. Hu, J.X. Yuan, F. Chen, Q. Shi, Acta. Crystallogr. Sect. C: Cryst. Struct. Commun. C 60 (2004) m186–m188.
[68] X.H. Li, Acta. Crystallogr. Sect. E: Struct. Rep. Online E 61 (2005) m2329–m2331.
[69] Y. Liang, M. Hong, R. Cao, W. Su, Y. Zhao, J. Weng, R. Xiong, Bull. Chem. Soc. Jpn. 75 (2002) 1521–1526.
[70] L. Pan, X. Huang, J. Li, Y. Wu, N. Zheng, Angew. Chem. Int. Ed. 39 (2000) 527–530.
[71] X.-J. Zheng, L.-P. Jin, S.-Z. Lu, Eur. J. Inorg. Chem. 12 (2002) 3356–3363.
[72] X.-M. Zhang, Coord. Chem. Rev. 249 (2005) 1201–1219.
[73] X.-M. Chen, M.-L. Tong, Acc. Chem. Res. 40 (2007) 162–170.
[74] J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin, Y.-H. Wen, J. Am. Chem. Soc. 126 (2004) 7796–7797.
[75] O.R. Evans, W. Lin, Chem. Mater. 13 (2001) 2705–2712.
[76] O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511–522.
[77] O.R. Evans, R.-G. Xiong, Z. Wang, G.K. Wong, W. Lin, Angew. Chem. Int. Ed. 38 (1999) 536–538.
[78] Z.B. Han, Y.K. He, Acta Crystallogr. Sect. E: Struct. Rep. Online E 62 (2006) m2374–m2376.
[79] Z.-B. Han, X.-N. Cheng, X.-F. Li, X.-M. Chen, Z. Anorg. Allg. Chem. 631 (2005) 937–942.
[80] X.-M. Zhang, M.-L. Tong, X.-M. Chen, Angew. Chem. Int. Ed. 41 (2002) 1029–1031.

[81] X.-M. Zhang, M.-L. Tong, M.-L. Gong, H.-K. Lee, L. Luo, K.-F. Li, Y.-X. Tong, X.-M. Chen, Chem. Eur. J. 8 (2002) 3187–3194.

[82] D.M.Y. Barrett Adams, I.A. Kahwa, J.T. Mague, New J. Chem. 22 (1998) 919–921.

[83] L.J. Farrugia, S. Lopinski, P.A. Lovatt, R.D. Peacock, Inorg. Chem. 40 (2001) 558–559.

[84] D.A. Morgenstern, R.E. Wittrig, P.E. Fanwick, C.P. Kubiak, J. Am. Chem. Soc. 115 (1993) 6470–6471.

[85] R.T. Stibrany, H.J. Schugar, J.A. Potenza, Acta Crystallogr. Sect. E: Struct. Rep. Online E 61 (2005) m1904–m1906.

[86] W.-K. Wong, L.-L. Zhang, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. 14 (2000) 2245–2246.

[87] B. Baruah, V.O. Golub, C.J. O'Connor, A. Chakravorty, Eur. J. Inorg. Chem. 12 (2003) 2299–2303.

[88] O.R. Evans, W. Lin, Cryst. Growth Des. 1 (2001) 9–11.

[89] R.W. Herbert, E.L. Hirst, E.G.V. Percival, R.J.W. Reynolds, F. Smith, J. Chem. Soc. (1933) 1270–1290.

[90] P. Orioli, B. Bruni, M. Di Vaira, L. Messori, F. Piccioli, Inorg. Chem. 41 (2002) 4312–4314.

[91] A.M. Thomas, G.C. Mandal, S.K. Tiwary, R.K. Rath, A.R. Chakravarty, J. Chem. Soc. Dalton Trans. 9 (2000) 1395–1396.

[92] C. Unaleroglu, B. Zumreoglu-Karan, Y. Zencir, T. Hokelek, Polyhedron 16 (1997) 2155–2161.

[93] A.J. Belsky, P.G. Maiella, T.B. Brill, J. Phys. Chem. A 103 (1999) 4253–4260.

[94] M. Frisch, C.L. Cahill, J. Solid State Chem. 180 (2007) 2597–2602.

[95] L. Hegedues, H.-D. Foersterling, M. Wittmann, Z. Noszticzius, J. Phys. Chem. A 104 (2000) 9914–9920.

[96] H.S. Huh, S.W. Lee, Bull. Korean Chem. Soc. 27 (2006) 1839–1843.

[97] B. Li, W. Gu, L.-Z. Zhang, J. Qu, Z.-P. Ma, X. Liu, D.-Z. Liao, Inorg. Chem. 45 (2006) 10425–10427.

[98] X. Li, R. Cao, D. Sun, Q. Shi, W. Bi, M. Hong, Inorg. Chem. Commun. 6 (2003) 815–818.

[99] X. Li, V.L. Pecoraro, Inorg. Chem. 28 (1989) 3403–3410.

[100] J.Y. Lu, J. Macias, J. Lu, J.E. Cmaidalka, Cryst. Growth Des. 2 (2002) 485–487.

[101] D. Min, S.W. Lee, Inorg. Chem. Commun. 5 (2002) 978–983.

[102] S. Neogi, G. Savitha, P.K. Bharadwaj, Inorg. Chem. 43 (2004) 3771–3773.

[103] B. Zheng, G. Liu, L. Gou, D.-Y. Wang, H.-M. Hu, Acta Crystallogr. Sect. E: Struct. Rep. Online E 61 (2005) m499–m501.

[104] SAINT, V 5.053 Program for Reduction of Data Collected on Bruker AXS CCD Area Detector Systems, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1998.

[105] G.M. Sheldrick, Acta Cryst. A 64 (2008) 112–122.

[106] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.

[107] A.L. Spek, Acta Crystallogr. Sect. A 46 (1990) C34.

[108] C. Janiak, J. Chem. Soc. Dalton Trans. 21 (2000) 3885–3896.

[109] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533–3539.

[110] R.G. Pearson, Coord. Chem. Rev. 100 (1990) 403–425.

[111] M.N. Akhtar, A.J. Smith, Acta Crystallogr. Sect. B: Struct. Cryst. Cryst. Chem. B 31 (1975) 1361–1366.

[112] R. Bressat, Y. Trambouze, B. Claudel, G. Lang, A. Navarro, Bull. Soc. Chim. Fr. 6 (1966) 2094–2099.

[113] I.L. Jenkins, F.H. Moore, M.J. Waterman, J. Inorg. Nucl. Chem. 27 (1965) 81–87.

[114] Y. Yan, C.-D. Wu, C.-Z. Lu, Z. Anorg. Allg. Chem. 629 (2003) 1991–1995.

[115] W. Yang, C. Lu, H. Zhuang, J. Chem. Soc. Dalton Trans. 14 (2002) 2879–2884.

[116] M.V. Yigit, Y. Wang, B. Moulton, J.C. MacDonald, Cryst. Growth Des. 6 (2006) 829–832.

[117] L.-Z. Zhang, W. Gu, B. Li, X. Liu, D.-Z. Liao, Inorg. Chem. 46 (2007) 622–624.

[118] X.-M. Zhang, R.-Q. Fang, Inorg. Chem. 44 (2005) 3955–3959.

[119] Y.-Z. Zheng, M.-L. Tong, X.-M. Chen, New J. Chem. 28 (2004) 1412–1415.