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# 1. Introduction

Uranium is the most abundant actinide element in the uranium-based nuclear fuel cycle and large quantities of uranium exist in nuclear waste, presenting an enormous challenge in the environmental management of nuclear waste. Safe treatment and proper disposal of uranium-bearing wastes require the knowledge of the chemical behavior of uranium in the waste stream and in the environment. Also, ligands that could form complexes with uranium and have the potential of being used as separation agents need to be developed.

Among the organic ligands, mixed N- and O-donor ligands have been studied in recent years due to their potential application in the GANEX process (Group ActiNides EXtraction) for

# A structural and thermodynamic study of the complexes of U(vi) with azinecarboxylates†

Lina Lv,<sup>a</sup> Baihua Chen,<sup>a</sup> Jun Liu,<sup>a</sup> Jing Chen,<sup>b</sup> Chao Xu 🕩 \*<sup>b</sup> and Yanqiu Yang 🕩 \*<sup>a</sup>

Complexation of U(v) with pyridazine-3-carboxylate (PDZ) and pyrazine-2-carboxylate (PAZ) was studied by spectrophotometry, potentiometry and microcalorimetry in 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub>. Three complexes,  $[UO_2L]^+$ ,  $UO_2L_2(aq)$  and  $[UO_2L_3]^-$ , were identified and their stability constants (log  $\beta$ ) and the corresponding formation enthalpies were determined. The thermodynamic parameters indicate that the formation of the three complexes is endothermic and driven exclusively by entropy. <sup>1</sup>H and <sup>13</sup>C-NMR data provide insight into the coordination modes of the complexes which corroborate with the thermodynamic data. Ligands chelate to U(vi) via  $\kappa^2(N,O)$  coordination mode in complexes [UO<sub>2</sub>L]<sup>+</sup> and  $UO_2L_2(aq)$ . The crystal structures of four U(vi) complexes, [(UO\_2)(PAZ)\_2(H\_2O)]·H\_2O(i), [(UO\_2)(PDZ)\_2(H\_2O)](ii), (UO\_2)(PDZ)\_2(H\_2O)](ii), (UO\_2)(H\_2O)](ii), (UO\_2)(H\_2O)](  $[(UO_2)(PDZ)_3Na_2ClO_4] \cdot 2H_2O(III)$ , and  $[(UO_2)_2(PDZ)_4(H_2O)_2] \cdot 2H_2O(IV)$ , were determined by single-crystal X-ray diffraction and compared with the  $U(v_1)$  complex with picolinate (PA) (CH<sub>6</sub>N<sub>3</sub>)[UO<sub>2</sub>(PA)<sub>3</sub>] in the literature. The structure data suggest that the carboxylates coordinate with uranium in O=C-O-U mode. The strengths of the U–O–C–C–N chelate cycles in the  $U(v_i)/L$  complexes decrease with the trend of PA > PDZ > PAZ, which is in great agreement with the trend of thermodynamic parameters in aqueous solutions. It is interesting that in compound II two PDZ molecules coordinate with U(v) in cis-planar positions via  $\kappa^2(N,O)$  mode, but in other metal complexes of the three ligands having the same  $\kappa^2(N,O)$  coordination mode the two ligand molecules are all in trans-arrangement. In the dimeric complex IV, one ligand coordinate with U(v) in  $\kappa^2(N,O)$  mode, while the other does it in  $\mu_2$ -L- $\kappa^2(O;O')$  mode respectively.

> an advanced nuclear fuel cycle.<sup>1-4</sup> For example, complexation of uranium and other actinides with the amide derivatives of azine carboxylic acids, such as picolinic acid, pyrazinecarboxylic acid, dipicolinic acid (DPA), 2,2'-bipyridine-6,6'acid 1,10-phenanthroline-2,9-didicarboxylic (BiPDA), carboxylic acid, etc., has been intensively investigated. The thermodynamic and structural properties of actinide complexes with these aza-heterocyclic carboxylic acids and their amide derivatives were obtained by techniques including solution chemistry and crystallography.<sup>3,5-15</sup> Most studies have so far focused on exploring the influence of the amide moieties of aza-heterocyclic carboxylic acids on the complexation with metals, while very few studies have been conducted to investigate the influence of the changes in the heterocyclic aza-structure on the binding strength and coordination modes. For example, complexation of U(vi) with picolinic acid (denoted as PA in this paper), the simplest aza-heterocyclic carboxylic acid, was studied previously.<sup>16</sup> In acidic aqueous solution (pH  $\leq$  4), three successive mononuclear U(vi)/PA complexes (1:1, 1:2, and 1:3) were identified and the corresponding stability constants and enthalpy of complexation were determined.<sup>16</sup> The thermodynamic parameters suggest that the first and the second ligand molecules coordinate with UO2<sup>2+</sup> via the N and a carboxylate O atom via the



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<sup>&</sup>lt;sup>a</sup>Institute of Nuclear Physics and Chemistry, Chinese Academy of Engineering Physics, Mianyang, Sichuan 621900, China. E-mail: yan.qiu.yang@163.com <sup>b</sup>Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China. E-mail: chaoXu@tinghua.edu.cn

<sup>†</sup> Electronic supplementary information (ESI) available: Composition and speciation of samples for the NMR analysis, hydrolysis and speciation of ligands in a typical sample for microcalorimetric titration, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of U(v1)/PDZ/H solutions, and the CIF files for the crystal structures from this work. CCDC 1586814, 1865674, 1586812 and 1865676. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04099k

 $\kappa^2$ (N,O) mode in the equatorial plane,<sup>16</sup> in agreement with the single crystal structures.<sup>17,18</sup>

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Aza-ligands that contain multiple nitrogen atoms in the cvclic aza-moiety are more resistant to radiolysis and therefore could be more applicable in the treatment of nuclear wastes, but only limited studies have been conducted on these ligands.<sup>19</sup> As a result, fundamental questions remain to be answered, such as (1) how the total basicity of the ligand is affected by the presence of multiple nitrogen atoms in the cyclic aza-moiety, and (2) what kinds of coordination modes are present in the ligand complex(es) with metal ions like U(vi). To help answer these fundamental questions and provide support for the development of more efficient separation ligands, complexation of U(vi) with an aza-heterocyclic carboxylate ligand, pyridazine-3-carboxylate (PDZ) and pyrazine-2-carboxylate (PAZ) (see Fig. 1) where the cyclic aza-moiety contains two nitrogen atoms in different positions was studied in this work. Multiple thermodynamic techniques, including potentiometry, spectrophotometry, and microcalorimetry, were used to determine the equilibrium constants and enthalpy for the U(vi) complexes over a pH range of 1.0-4.0. Structural information on the U(vi) complexes in the solution and solid states was obtained by NMR and crystallography.

Structural information on the coordination mode in  $U(v_1)$  complexes with aza-heterocyclic monocarboxylates is scarce.



**Fig. 1** Picolinic acid (PA), pyridazine-3-carboxylic acid (PDZ) and pyrazine-2-carboxylic acid (PAZ). For all ligands, the deprotonated, singlyprotonated, and doubly-protonated forms are donated in this paper as  $L^-$ , HL, and  $H_2L^+$ , respectively.

Only limited structural data in crystals have been reported. In the crystal structures of the 1:2 complexes of U(v1) with picolinate<sup>17</sup> and pyrazinecarboxylate,<sup>19</sup> two ligand molecules chelate with U(v1) *via* the equatorial plane in the  $\kappa^2(N,O)$  mode. For pyridazine-3-carboxylic acid (PDZ), 1:2 complexes with Mn<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> in the  $\kappa^2(N,O)$  mode were reported.<sup>20</sup> In addition, Resul Leciejewicz<sup>21</sup> obtained a binuclear U(v1) complex,  $[(UO_2)_2(PDZ)_4(H_2O)_2]\cdot 2H_2O$ , by stirring a mixture of HL and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2:1) under the condition of boiling. Each UO<sub>2</sub><sup>2+</sup> ion is coordinated by two ligand molecules: one coordinates with U(v1) by the N,O-bonding group ( $\kappa^2(N,O)$  mode) and the other by both carboxylate O atoms bridging adjacent uranyl ions ( $\mu_2$ -L- $\kappa^2(O:O')$  mode).

In contrast to the structural data for crystals, very little structural information on aza-complexes with  $U(v_I)$  in solution is available. In the present study, while new crystal structures of  $U(v_I)$ /aza-carboxylate complexes were explored, we conducted <sup>1</sup>H and <sup>13</sup>C-NMR studies to obtain the structural information of  $U(v_I)$ /PDZ complexes in solution and corroborated with the thermodynamic data, providing a fundamental understanding of the coordination behavior of  $U(v_I)$  with heterocyclic N- and O-donor ligands.

# 2. Results

#### 2.1 Thermodynamic parameters

**2.1.1. Protonation constants of ligands.** The protonation constants of the two ligands were determined by potentiometry. The experiments were conducted in two different directions (from basic to acidic or in reverse) with perchloric acid or sodium hydroxide. Fig. 2 shows the representative potentiometric titrations to determine the protonation constants of PDZ and PAZ. The calculated protonation constants are listed in Table 1. In this work the second protonated species of PDZ



**Fig. 2** Representative potentiometric titrations for the protonation of PDZ (a) and PAZ (b) at 298 K ( $I = 1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$ ,  $pK_w = 13.78$ ). Initial solution in the cup  $[V^0(\text{mL})/C_L^0(\text{mmol dm}^{-3})/C_H^0(\text{mmol dm}^{-3})]$ : (a) 20.0/2.06/2.06, and (b) 21.5/7.35/3.26; titrant: (a)  $C_{\text{HCIO}_4} = 1.00 \text{ mol dm}^{-3}$ , and (b)  $C_{\text{HCIO}_4} = 0.10 \text{ mol dm}^{-3}$ . Left *y*-axis:  $\diamond$ , observed  $pC_H$ ; red dashed line, calculated  $pC_H$ . Right *y*-axis (ligand speciation): black, L<sup>-</sup>; red, HL; green, H\_2L^+.

Table 1 Thermodynamic parameters for the complexation of U(vi) with PDZ and PAZ (298 K, / = 1.0 M NaClO<sub>4</sub>)

Reaction		Method	$\log \beta_{\rm M}$	$\Delta H \left( \text{kJ mol}^{-1} \right)$	$\Delta S \left( J \mod^{-1} K^{-1} \right)$	Ref.
$L^- + H^+ = HL$	PAZ	pot, cal	$2.78 \pm 0.01$	$-(0.20 \pm 0.01)$	$60.4 \pm 0.3$	pw
	PDZ	pot, cal	$2.86 \pm 0.01$	$-(1.36 \pm 0.02)$	$50.2 \pm 0.1$	pw
	PA	pot, cal	$5.38 \pm 0.02$	$-(13.9 \pm 0.6)$	$56.3 \pm 2.0$	16
$L^{-} + 2H^{+} = H_{2}L^{+}$	PDZ	pot	$3.86 \pm 0.06$	$-(0.82 \pm 0.03)$	$71 \pm 1$	pw
	PA	pot	6.33			23
$L^{-} + UO_{2}^{2+} = [UO_{2}L]^{+}$	PAZ	sp, cal	$2.76\pm0.01$	$4.35\pm0.04$	$67 \pm 1$	pw
		pot	$2.79\pm0.02$			pw
	PDZ	sp, cal	$2.84\pm0.01$	$5.19\pm0.09$	$71.8 \pm 0.5$	pw
	PA	pot, cal	$4.35\pm0.04$	$-(3.6 \pm 0.1)$	$71 \pm 1$	16
$2L^{-} + UO_2^{2+} = UO_2L_2(aq)$	PAZ	sp, cal	$4.43\pm0.03$	$11.7 \pm 0.1$	$124 \pm 2$	pw
		pot	$4.86\pm0.03$			pw
	PDZ	Sp	$5.19\pm0.04$	$9.56 \pm 0.06$	$135 \pm 3$	pw
	PA	pot, cal	$7.68 \pm 0.03$	$-(8.3 \pm 0.1)$	$119 \pm 1$	16
$3L^{-} + UO_2^{2+} = [UO_2L_3]^{-}$	PAZ	sp, cal	$5.59 \pm 0.03$	$14.8 \pm 0.2$	$157 \pm 3$	pw
		pot	$6.70\pm0.04$			pw
	PDZ	sp, cal	$6.71\pm0.08$	$17.0 \pm 0.2$	$185 \pm 2$	pw
	PA	pot, cal	$10.29\pm0.05$	$2.0 \pm 0.2$	$203 \pm 1$	16

 $(H_2L^+)$  was successfully detected, while that of PAZ was not detected even when 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub> was used as the titrant. There are two contributions to this: the lone pairs on the two adjacent nitrogen atoms in pyridazine making the protonation of PDZ easier than PAZ, and the mesomeric interaction between the protonated and neutral nitrogen atoms in pyrazine probably destabilising the cation.<sup>22</sup>

**2.1.2.** Stability constants of  $U(v_1)$  complexes. The stability constants of  $U(v_1)$  complexes with PDZ and PAZ were determined by spectrophotometry. In addition, the stability constants of  $U(v_1)$ /PAZ complexes were also determined by potentiometry. Preliminary experiments showed that precipitation occurred when the pH of the titration system was above 4.0, probably due to the hydrolysis of  $U(v_1)$  and the poor solubility of the neutral complexes of  $U(v_1)$  with ligands. To avoid precipitation, titrations were conducted with a large ratio of L/M and the pH was controlled below 4.

Fig. 3 shows the representative spectrophotometric titrations of U(vi) solutions with neutralized PDZ and PAZ. As shown in the upper pictures of Fig. 3, absorption bands of  $UO_2^{2^+}$  in the range of 380–500 nm exhibit a systematic red shift and an increase in intensity with the addition of ligands, indicating the successive formation of U(vi) complexes. Factor analysis with the program HypSpec 2009 suggested that three U(vi) complexes formed. A number of models including different U(vi)/L complexes were tested to fit the data, including monomeric and dimeric complexes (*e.g.*,  $[UO_2L_2]_2$ suggested by the crystal structure in the literature<sup>21</sup>), and the best fit was achieved with the model containing only monomeric complexes  $[UO_2L]^+$ ,  $UO_2L_2(aq)$ , and  $[UO_2L_3]^-$ , as represented by eqn (1), (2), and (3).

$$UO_2^{2+} + L^- = [UO_2L_n]^+ \beta_{101}$$
(1)

$$UO_2^{2+} + 2L^- = UO_2L_2(aq) \beta_{102}$$
(2)

$$UO_2^{2+} + 3L^- = [UO_2L_3]^- \beta_{103}$$
(3)

The calculated stability constants of the complexes are summarized in Table 1, and the molar absorptivities of the complexes are shown in Fig. 3 (bottom row).

In addition, the complexation of U(v1) with PAZ was investigated by potentiometric titration, as shown in Fig. 4. The best model to fit the data includes three successive mononuclear U(v1)/PAZ complexes. As shown in Table 1, the stability constants of the U(v1)/PAZ complexes measured by spectrophotometry and by potentiometry are in good agreement, suggesting that the dinuclear complex that was found to exist in the crystal form,<sup>21</sup> [UO<sub>2</sub>L<sub>2</sub>]<sub>2</sub>, may not be present or is insignificant in aqueous solutions under the experimental conditions in this work.

2.1.3. Enthalpies. Enthalpies for the protonation of ligands and the formation of U(vi) complexes were determined by microcalorimetry. Fig. 5 shows the representative calorimetric titrations of PDZ and PAZ with perchloric acid at 298 K to determine their protonation enthalpies. Multiple titrations were performed with different concentrations of the ligand  $(C_{\rm L}^0)$  in a vessel and the same titrant (0.100 mol dm<sup>-3</sup> HClO<sub>4</sub>). The enthalpies of protonation of ligands were calculated with HypDeltaH<sup>24</sup> in conjunction with the protonation constants which were determined by potentiometry in this work, and are listed in Table 1. The enthalpies of PDZ protonation were determined in two steps. The enthalpy for HL was determined by the titration of NaL with 0.1 M HClO<sub>4</sub>, controlling the  $H_2L^{\dagger}$ species less than 3% throughout the titration. The enthalpy for  $[H_2L]^+$  was determined simultaneously along with the enthalpy of U(vi)/PDZ complexation, because the U(vi)/PDZ complexation experiments were carried out in high acidic solutions (pH 1.29–2.92, see Fig. S1 of the ESI<sup>†</sup>) containing sufficient  $[H_2L]^+$ .

Fig. 6 shows the representative calorimetric titrations of  $U(v_I)$  with PDZ and PAZ respectively. The enthalpies for the all  $U(v_I)/L$  complexes were calculated with HypDeltaH in conjunction with the thermodynamic parameters of the stability constants of the  $U(v_I)/L$  complexes, and are summarized in Table 1.

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**Fig. 3** Representative spectrophotometric titration of U(v)/PDZ (a) and U(v)/PAZ complexation at 298 K. Initial solution in a cuvette [ $V^0$ (mL)/ $C_U^0$ (mmol dm<sup>-3</sup>)/ $C_H^0$ (mmol dm<sup>-3</sup>)]: (a) 2.00/5.18/32.8, and (b) 2.00/5.50/10.6; titrant: (a)  $C_L = 0.18 \text{ mol dm}^{-3}$ , (b)  $C_L = 1.00 \text{ mol dm}^{-3}$ . (Top) absorption spectra (normalized to  $C_U^0$ ). (Bottom) calculated molar absorptivity of U(v) species; black: UO<sub>2</sub><sup>2+</sup>, red: UO<sub>2</sub>L<sup>+</sup>, blue: UO<sub>2</sub>L<sub>2</sub>(aq), and purple: [UO<sub>2</sub>L<sub>3</sub>]<sup>-</sup>.



**Fig. 4** Potentiometric titration of U(vI) with PAZ at 298 K (I = 1.0 M NaClO<sub>4</sub>). Initial condition [ $V^0$ (mL)/ $C_U^0$ (mmol dm<sup>-3</sup>)/ $C_H^0$ (mmol dm<sup>-3</sup>)]: 20.39/3.23/6.08; titrant:  $C_L = 0.18 \text{ mol dm}^{-3}$ . Left *y*-axis: pC<sub>H</sub>, ( $\Diamond$ ) experimental; red short dashed line, fitted. Right *y*-axis: speciation of U(vI). Black solid line, free UO<sub>2</sub><sup>2+</sup>; red line, UO<sub>2</sub>L<sup>+</sup>; green line, UO<sub>2</sub>L<sub>2</sub>(aq); blue line, UO<sub>2</sub>L<sub>3</sub><sup>-</sup>.

#### 2.2. Crystal structures of U(vi) complexes

Structures of the U(vi) complexes in solid compounds,  $[(UO_2)(PAZ)_2H_2O]$ ·H<sub>2</sub>O(i),  $[(UO_2)(PDZ)_2H_2O](II)$ ,  $[(UO_2)(PDZ)_3Na_2CIO_4]$ · 2H<sub>2</sub>O(III) and  $[(UO_2)_2(PDZ)_4(H_2O)_2]$ ·H<sub>2</sub>O(IV), are shown in Fig. 7. Selected bond lengths of compounds **I**, **II**, **III**, and **IV**, and those of  $(CH_6N_3)[UO_2(PA)_3]$  from the literature<sup>25</sup> for comparison are listed in Table 2.

**2.2.1.**  $[(UO_2)(PAZ)_2(H_2O)] \cdot H_2O$  (I). Compound I is a new crystal of the uranyl complex with PAZ in the triclinic space group  $P\overline{1} - p1$ . A uranyl(vI) ion is at the centre of symmetry coordinated by two PAZ molecules in *trans*-planar positions and a water molecule; both ligands chelate to  $UO_2^{2^+}$  via  $\kappa^2(N,O)$  mode, which is in agreement with the reported coordination mode in the literature.<sup>19</sup> Both PAZ molecules are almost planar with only a small tension angle between them (2.9°). The least-squares plane of both PAZ molecules passes through the central U-atom and is almost perpendicular to O=U=O (89.6° in angle). The O=U=O moiety is slightly distorted, being imperfectly linear (177.1(2)° angle) but almost symmetrical (bond length: U1–O5, 1.762(6) Å; U1–O6, 1.757(6) Å).

**2.2.2.**  $[(UO_2)(PDZ)_2(H_2O)]$  (II).  $[(UO_2)(PDZ)_2(H_2O)]$  is a new U(v1) complex with PDZ, crystallized in the orthorhombic space group *Pna* 21 (33). A uranyl(v1) ion is at the centre of symmetry



**Fig. 5** Microcalorimetric titrations of the protonation of PDZ (a) and PAZ (b) ( $t = 25 \,^{\circ}$ C,  $I = 1.0 \,\text{M}$  NaClO<sub>4</sub>). (Top) Thermogram of the protonation of ligands; (bottom) total reaction heat (left *y* axis, ( $\diamond$ ) experimental; (- -) calculated) and speciation of ligands (right *y* axis; black line, L<sup>-</sup>; red line, HL; green line, H<sub>2</sub>L<sup>+</sup>). Initial solution [ $V^0$ (mL)/ $C_L^0$ (mmol dm<sup>-3</sup>)]: (a) 0.75/20.0, and (b) 0.70/28.6. Titrant: (a)  $C_{\text{HClO}_4} = 0.100 \,\text{mol dm}^{-3}$ , 0.005 mL × 43 additions; (b)  $C_{\text{HClO}_4} = 0.100 \,\text{mol dm}^{-3}$ , 0.010 mL × 22 additions.

coordinated by two PDZ molecules in cis-planar positions and a water molecule, both ligands chelating via  $\kappa^2(N,O)$  mode. To our knowledge, the *cis*-arrangement of ligands in  $[(UO_2)]$  $(PDZ)_2(H_2O)$  is the only example of mononuclear U(vi) complexes with two aza-heterocyclic carboxylate molecules. In all the reported U(vi) complexes having two aza-heterocyclic carboxylates chelating via  $\kappa^2(N,O)$  mode in the CSD database (about 10 structures),<sup>20</sup> including in complex UO<sub>2</sub>(PDZ)<sub>3</sub>Na<sub>2</sub>ClO<sub>4</sub>·2H<sub>2</sub>O(III) from this work and in the 1:2 (M/L) complexes of PDZ with other metal ions (such as Mn<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup> etc.),<sup>20</sup> ligands are all in trans-arrangement. Both PDZ molecules are almost planar with only a small tension angle between them  $(4.4^{\circ})$ . The least-squares plane of both PDZ molecules passes through the central U-atom and is almost perpendicular to O=U=O (89.1° in angle). The O=U=O moiety is distorted greater than that in compound I, being imperfectly linear (179.2(4)° angle) and asymmetrical (bond length: U1-O5, 1.68(3) Å; U1-O6, 1.84(2) Å).

**2.2.3.**  $[UO_2(PDZ)_3Na_2CIO_4] \cdot 2H_2O.$   $[UO_2(PDZ)_3Na_2CIO_4] \cdot 2H_2O$  is a multinuclear 1:3:2 U(vi)/PDZ/Na(i) complex, crystallized in the monoclinic space group P12/n1(13). The O=U=O moiety in the complex is slightly distorted, being imperfectly

linear (176.43(16)° angle) and unsymmetrical (bond length: U1–O7, 1.723(5) Å; U1–O8, 1.764(4) Å). U(v1) is equatorially fivecoordinated and chelated by three PDZ units. Two of the three PDZ molecules coordinate with U(v1) in  $\kappa^2$ (N,O) mode *via* the N-atom on the 2-position and one carboxylate O-atom, and the other carboxylate O-atoms coordinate with Na1 and Na2 respectively (Fig. 7). The third PDZ molecule bridges U1 and Na1 in  $\mu_2$ -L- $\kappa^2$ (O:O') coordination mode.

**2.2.4.** [(UO<sub>2</sub>)<sub>2</sub>(PDZ)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (IV). [(UO<sub>2</sub>)<sub>2</sub>(PDZ)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]· 2H<sub>2</sub>O(IV) is a dinuclear 1:2 U(v1)/PDZ complex crystallized in the monoclinic space group *C*12/*c*1 (15), which is in agreement with that reported in the literature.<sup>21</sup> Four PDZ molecules coordinate with two uranyl(v1) through two modes:  $\kappa^2$ (N1,O1) and  $\mu_2$ -L- $\kappa^2$ (O3:O6).

# 3. Discussion

#### 3.1 Comparison of structures

As shown in Fig. 7, compounds I and II are of the same coordination mode between ligands and central  $U(v_I)$ , and those of



**Fig. 6** Microcalorimetric titrations of U(v) complexation with PDZ (a) and PAZ (b) (t = 25 °C,  $I = 1.0 \text{ mol } dm^{-3} \text{ NaClO}_4$ ). (Top) Thermograms; (bottom) total reaction heat (left *y* axis; ( $\diamond$ ) experimental; (- -) calculated) and speciation of U(v) (right *y* axis; black line, U(v); red line, [UO<sub>2</sub>L]<sup>+</sup>; green line, UO<sub>2</sub>L<sub>2</sub>(aq); blue line, [UO<sub>2</sub>L<sub>3</sub>]<sup>-</sup>). Initial solution [ $V^0$ (mL)/ $C_U^0$ (mmol  $dm^{-3}$ )/ $C_H^0$ (mmol  $dm^{-3}$ )]: (a) 0.75/5.28/51.9, and (b) 0.70/6.29/11.6. Titrant: (a)  $C_L = 0.40 \text{ mol } dm^{-3}$ , 0.008 mL × 45 additions; (b)  $C_L = 0.40 \text{ mol } dm^{-3}$ , 0.008 mL × 30 additions.



**Fig. 7** Crystal structures of  $U(v_1)$  complexes  $[(UO_2)(PAZ)_2(H_2O)] \cdot H_2O(1)$ ,  $[UO_2(PDZ)_2(H_2O)](1)$ ,  $[UO_2(PDZ)_3Na_2CIO_4] \cdot 2H_2O(10)$  and  $[(UO_2)_2(PDZ)_4(H_2O)_2] \cdot 2H_2O(1v)$ . Element colour: green (U), red (O), pink (Cl), plum (Na), and grey (C); hydrogen atoms and uncoordinated water molecules are not shown for clarity.

compound III and  $(CH_6N_3)[UO_2(PA)_3]$  are the same. Average distances of some selected bonds are listed in Table 3. For all the complexes, C–O(carboxylate) bonds are much longer than C–O(free), indicating that the carboxylate groups coordinate with the U-atom in O=C–O–U mode. The average distance of

U–O(carboxylate) bonds in compounds I and II (2.31(2) Å) is shorter than the normal U–O(carboxylate) bond with simple carboxylate ligands (2.37 Å),<sup>26,27</sup> while those in compound III and (CH<sub>6</sub>N<sub>3</sub>)[UO<sub>2</sub>(PA)<sub>3</sub>] (2.36(1) Å) are of equivalent lengths to the normal U–O bond with simple carboxylate ligands.

Table 2 Selected bond lengths (Å) and angles (°)

$[UO_2(PAZ)_2H_2O]{\cdot}H_2O$	$[UO_2(PDZ)_2H_2O]$	$[UO_2(PDZ)_3Na_2ClO_4]\cdot 2H_2O$	$[UO_2(PDZ)_2H_2O]_2{\cdot}H_2O$	$(CH_6N_3)[UO_2(PA)_3]^{25}$
U1-O1 2.329(5)	U1-O1 2.30(1)	U1-O1 2.366(4)	U1-O1 2.345(3)	U1-O3 2.366(3)
U1–O3 2.292(5)	U1-O3 2.318(9)	U1–O5 2.351(4)	U1-O3 2.346(3)	U1-O5 2.362(3)
		U1-O3 2.286(4)	U1-O6 2.334(3)	U1-O7 2.269(2)
U1-N1 2.628(6)	U1-N1 2.624(11)	U1-N1 2.630(5)	U1-N1 2.616(3)	U1-N1 2.631(4)
U1–N3 2.623(6)	U1-N5 2.541(11)	U1-N5 2.666(5)		U1-N2 2.609(4)
U1–O5 1.762(6)	U1-O5 1.68(3)	U1–O7 1.723(5)	U1-O4 1.748(3)	U1–O1 1.762(4)
U1–O6 1.757(6)	U1-O6 1.84(2)	U1-O8 1.764(4)	U1–O5 1.756(3)	U1–O2 1.766(4)
C5-O1 1.255(9)	C5-O1 1.311(16)	C5–O1 1.270(7)	C5-O1 1.283(5)	C11-O3 1.288(5)
C10-O3 1.274(9)	C10-O3 1.271(16)	C15–O5 1.261(7)	C10-O3 1.233(5)	C31–O7 1.287(6)
		C10-O3 1.291(6)	C10-O6 1.244(5)	C21–O5 1.298(6)
C5-O2 1.219(9)	C5-O2 1.231(18)	C5-O2 1.235(7)	C5-O2 1.225(5)	C11-O4 1.218(5)
C10-O4 1.206(9)	C10-O4 1.223(16)	C15-O6 1.220(6)		C31-O8 1.221(6)
		C10-O4 1.223(6)		C21–O6 1.217(6)
O1-U1-N1 63.45(18)	O1-U1-N1 63.1(3)	O1-U1-N1 62.70(14)	O1-U1-N1 63.13(11)	O3-U1-N1 63.45(12)
O3–U1–N3 63.64(19)	O3-U1-N3 64.2(3)	O5–U1–N5 62.67(13)	O3-U1-O6 79.20(11)	O5-U1-N2 63.64(12)
O5-U1-O6 177.1(2)	O5–U1–O6 179.2(4)	07-U1-O8 176.43	O4-U1-O5 178.62(15)	O1-U1-O2 178.53(16)

Table 3 Average distances (Å) of some bonds involving the coordination groups around U  $% \left( {{{\rm{D}}_{\rm{B}}}} \right)$ 

	U–O (carboxylate) <sup>a</sup>	U–N	C–O (carboxylate)	C–O (free)
$ \begin{bmatrix} UO_2(PAZ)_2 ] (I) \\ [UO_2(PDZ)_2 ] (II) \\ [UO_2(PDZ)_3 ]^{-} (III) \\ [UO_2(PA)_3 ]^{-b} \end{bmatrix} $	$2.31(2) \\ 2.31(2) \\ 2.36(1) \\ 2.36(1)$	$2.63(1) \\ 2.58(2) \\ 2.65(2) \\ 2.62(2)$	1.26(2) 1.29(4) 1.27(1) 1.29(1)	$1.21(2) \\ 1.23(2) \\ 1.23(1) \\ 1.22(1)$

 $^a$  O(carboxylate) denotes the O-atoms in the carboxylate groups which coordinate with U-atoms in crystal structures, and O(free) denotes those which don't coordinate with U-atoms.  $^b$  Calculated using the data from the literature.<sup>25</sup>

The difference in the U–O(carboxylate) bond lengths between compounds I and II is within the uncertainty range, while the average U–N distance in compound I is longer than that in compound II, suggesting that the interaction of U(vI) with PAZ is weaker than that with PDZ. For the comparison of the structural data between compound III and (CH<sub>6</sub>N<sub>3</sub>) [UO<sub>2</sub>(PA)<sub>3</sub>], the average U–O(carboxylate) bonds are of the same value  $(2.36 \pm 0.1 \text{ Å})$ , while the longer U–N bond length in  $[UO_2(PDZ)_3]^-$  suggests that the chelating rings of U–O–C–C–N in  $[UO_2(PDZ)_3]^-$  are weaker than those in  $[UO_2(PA)_3]^-$ . In addition, the interaction of the third ligand with U(vI) in  $[UO_2(PDZ)_3]^-$  is also weaker than that in  $[UO_2(PA)_3]^-$ , because the U–O bond (2.286(4) Å) in compound III is longer than that in  $(CH_6N_3)[UO_2(PA)_3]$  (2.269(3) Å).

In brief, the structural data show that ligands PDZ and PAZ interact with  $U(v_I)$  in similar coordination modes to the ligand PA, and the interaction strengths of the three ligands with  $U(v_I)$  decrease as the trend: PA > PDZ > PAZ, which is consistent with the thermodynamic parameters in Table 1.

# 3.2 Possible coordination modes of the $[UO_2L]^+$ complex in solution

Single crystal structures of compounds I, II, III, and IV in this work and others in the CSD database<sup>20</sup> have shown that  $\alpha$ -N-aro-

matic carboxylates could bind UO<sub>2</sub><sup>2+</sup> in three coordination modes: (1)  $\kappa^1(O)$  monodentate coordination with the oxygen of the carboxylate group without the participation of the heterocyclic group in bonding, (2)  $\kappa^2(N,O)$  coordination by the nitrogen atom of the heterocyclic group and the oxygen atom of the carboxylate group, and (3)  $\mu_2$ -L- $\kappa^2(O;O')$  coordination by the two oxygen atoms of the carboxylate group bridging two UO<sub>2</sub><sup>2+</sup> ions. Besides, a bidentate  $\kappa^2(O,O')$  coordination mode by two carboxylate oxygen atoms is also observed with other simple monocarboxylate ligands such as benzoate.<sup>28,29</sup> Possible coordination modes for the U(vI)/PDZ complexes in solution are shown in Fig. 8.

Keeping in mind that the structures of complexes observed in the solid state may not be identical to those in solution, in this work, we rely on the analysis of the thermodynamic data, the comparison with related ligands, and the structural information obtained by techniques applicable to solution samples (such as NMR) to gain insight into the coordination modes of the  $U(v_I)/L$  complexes in solution. These are discussed in the following sections.

#### 3.3 Thermodynamic trends

The thermodynamic parameters for the protonation of PA and the  $U(v_I)/PA$  complexes from previous work<sup>16</sup> are listed in Table 1 for comparison with  $U(v_I)/L$  complexation of this work.



Fig. 8 Possible coordination modes.

The protonation constants of three analogue ligands follows  $PA \gg PDZ > PAZ$ , indicating that the basicity of ligands follows the same trend. Evidently, the cyclic aza-moiety of PDZ/PAZ containing two nitrogen atoms in an *ortho/para*-position has a stronger electron-withdrawing effect than that of PA.

Data in Table 1 show that the entropy of protonation and the entropies of complexation of U(v1) complexes are all very similar to the three ligands, PAZ, PDZ and PA, which is a strong indication that the modes of protonation and coordination with U(v1) of the three ligands are probably identical. The previous study on PA has revealed that the proton in HL and the uranium in the complexes are shared by the carboxy-late O and N in a  $\kappa^2(N,O)$  mode. By analogy, it is very likely that the protonation of PDZ and PAZ and the complexation of them with U(v1) take the same coordination mode.

Complexation of carboxylic acids with actinide ions is dominantly electrostatic interactions in nature<sup>30</sup> so that the stability constants of the complexes usually correlate with the protonation constants of the ligand.<sup>16,30</sup> A linear relationship is expected for the complexes with the same coordination mode.

Fig. 9 shows the plot of the stability constants of the 1:1 complexes  $(\log \beta_{101})$  of  $U(v_1)$  with some monocarboxylates as a function of the protonation constants of these ligands. The ligands complexing with  $U(v_1)$  in Fig. 9 are classified into two groups: (A) simple monocarboxylates (number 1 to 8) which coordinate with  $U(v_1)$  through two carboxylate O-donors in  $\kappa^2(O,O')$  mode, and (B)  $\alpha$ -aminocarboxylates (number 12 to 16) and PA (number 11) which chelate with  $U(v_1)$  through one carboxylate O- and the  $\alpha$ -N-donor in  $\kappa^2(N,O)$  mode. As shown in Fig. 9, two different linear correlations are observed and the interactions of  $U(v_1)$  with  $\alpha$ -N-donor-monocarboxylates are always stronger than those with simple monocarboxylates in



**Fig. 9** Relationship of the stability constants of the 1:1 complexes between uranyl(v) and various monocarboxylate ligands. 1: aminoacetate, <sup>31</sup> 2: 3-aminopropanoate, <sup>32</sup> 3: benzoate, <sup>29</sup> 4: phenylacetate, <sup>33</sup> 5: 4-aminobutanoate, <sup>32</sup> 6: acetate, <sup>34</sup> 7: propanoate, <sup>23</sup> 8: nicotinate, <sup>35</sup> 9: pyrazine-2-carboxylate, 10: pyridazine-3-carboxylate, 11: picolinate, 12: D-methionine, <sup>36,37</sup> 13: D-threonine, <sup>36</sup> 14: DL-phenylalanine, <sup>36</sup> 15: L-leucine, <sup>36,37</sup> and 16: L-isoleucine. <sup>36,37</sup>

terms of the same p*K*<sub>a</sub>. If the value of p*K*<sub>a</sub> is considered a measure of the basicity of the ligand, the two different linear correlations in Fig. 9 indicate that the complexation is enhanced by the presence of the α-N-donor atom due to the chelating in the  $\kappa^2$ (N,O) mode. For the 1:1 complex UO<sub>2</sub>(PDZ)<sup>+</sup> and UO<sub>2</sub>(PAZ)<sup>+</sup> studied in this work, the values of log  $\beta_{101}$  = (2.85 ± 0.01) for UO<sub>2</sub>(PDZ)<sup>+</sup> (number 9) and log  $\beta_{101}$  = (2.76 ± 0.01) for UO<sub>2</sub>(PAZ)<sup>+</sup> (number 10) fall perfectly on the line with other α-N-donor-monocarboxylates including picolinic acid. Based on the above comparison, we conclude that the α-N-donor in PDZ/PAZ participates in coordination with U(v) and the chelating  $\kappa^2$ (N,O) mode is the dominating coordination mode between U(v) and PDZ/PAZ in solution.

### 3.4 Analysis of NMR data

The <sup>1</sup>H and <sup>13</sup>C NMR data of the U(v1)/PDZ solution samples are shown in Fig. S2 of the ESI.† NMR is a technique that is applicable to solution samples and capable of revealing structural information of complexes in solution. As listed in Table S1,† solution sample A contains the ligand PDZ only, while the others (B, C, D, and E) contain U(v1) and PDZ at different acidities. The speciation of these samples is provided in Table S2 of the ESI.† The <sup>1</sup>H–<sup>13</sup>C COSY spectrum of solution A is shown in Fig. S3 of the ESI† to help assign the chemical shifts.

As the speciation shows, under the experimental conditions, the free ligand species (L<sup>-</sup>, HL, HL<sup>+</sup>) are dominant in all samples containing U(v<sub>1</sub>) (up to 85%) and the U(v<sub>1</sub>)/PDZ complexes are minor (<15%). As a result, the NMR data are not very informative of providing insight into the coordination modes in the U(v<sub>1</sub>)/PDZ complexes. Only a very limited discussion can be made below.

Because the species in the solution exchange rapidly, only the average spectra of all species were observed. The three signals in the <sup>1</sup>H NMR spectra (Fig. S2<sup>†</sup>) are straightforward to assign to the hydrogens on pyridazine. The shift of the <sup>1</sup>H NMR signals seems to correlate well with the change in pH, reflecting the change in the degree of protonation of the ligand in the solution samples.

From Samples B, to C, D, and E, the degree of complexation with U(vi) gradually increased. Samples B and C contained appreciable amounts of the 1:1 and 1:2 complexes (about 58% in B and 66% in C in terms of total U(vi)). For samples B and C, the <sup>13</sup>C NMR spectra show that the signals for C3 and C7 nearly disappeared due to significant line broadening. Based on the previous data in the literature that show that the <sup>13</sup>C NMR peaks of the carbons in the chelating ring could shift downfield and broaden into the baseline due to the chelation with  $U(v_1)$ ,<sup>38</sup> we postulate that the disappearance of <sup>13</sup>C NMR signals for C3 and C7 suggests that the chelating  $\kappa^2$ (N,O) mode is the major coordination mode in the 1:1 and 1:2 U(vI)/PDZ complexes. For samples D and E, the <sup>13</sup>C NMR signals for C3 and C7 re-appeared, which could probably be due to the  $\kappa^{1}(O)$ coordination of U(vi) with a single O on the carboxylate of the third PDZ ligand as shown by the crystal structure of  $[UO_2(PDZ)_3Na_2ClO_4]$ ·2H<sub>2</sub>O. It should be pointed out that the

disappearance and re-appearance of the signals for C3 and C7 could also be due to the change in pH that affects the degree of protonation of the PDZ ligand, since it is very likely that the proton in HL is shared by the carboxylate O and the N in a chelating  $\kappa^2(N,O)$  mode similar to that in the U(v1)/PDZ complexes.

The good agreement between the thermodynamic and NMR results implies that only mononuclear U(vi) complexes are formed in solution, although a dimeric 1:2 U(vi)/PDZ complex with two bridging PDZ molecules in a  $[(UO_2)_2(PDZ)_4(H_2O)_2]\cdot 2H_2O$  crystal is identified in this work and literature.<sup>21</sup> In fact, this is not the only example of U(vi) complexes. A dimeric 1:2 U(vi)/Ac complex ( $[UO_2(Ac)_2(DMSO)]_2$ , Ac = acetate) was isolated from DMSO media, while only the mononuclear complexes were formed in solution.<sup>39</sup>

# 4. Conclusion

Complexation of U(v1) with pyridazine-3-carboxylic acid (PDZ) and pyrazine-2-carboxylic acid (PAZ) was studied in both solution and in the solid state. 1:1, 1:2, and 1:3 U(v1)/L complexes were identified and the thermodynamics for them were determined in 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub>. The stability constants for the corresponding complexes decrease in the following order: PA > PDZ > PAZ, which is consistent with the changing trend of ligands' basicity. The formation of U(v1) complexes with PDZ and PAZ is all endothermic and driven exclusively by entropy.

Single-crystal structural data of the novel complexes  $[UO_2(PAZ)_2H_2O] \cdot H_2O$ ,  $[UO_2(PDZ)_2H_2O]$ , and  $[UO_2(PDZ)_3Na_2ClO_4] \cdot 2H_2O$ , and a previously reported dimeric 1:2 complex,  $[(UO_2)_2L_4(H_2O)_2] \cdot 2H_2O$ , indicate that different coordination modes of  $\kappa^2(N,O)$  and  $\mu_2$ -L- $\kappa^2(O:O')$  exist in the U(vI) complexes in the solid state. Spectrophotometric and potentiometric titrations, NMR analysis of the U(vI)/PDZ solutions, and the thermodynamic comparisons with a series of related ligands suggest that in solution, there is no stable dimeric 1:2 U(vI)/L complex, and  $\kappa^2(N,O)$  is the dominant coordination mode in the 1:1 and 1:2 U(vI)/L complexes.

# 5. Experimental section

### 5.1 Chemicals

All chemicals are reagent grade or higher, and used without further purification. Boiled/cooled Milli-Q water was used in the preparations of all solutions. The stock solution of U(v1) in perchloric acid was prepared by dissolving  $U_3O_8$  in 2 mol dm<sup>-3</sup> HNO<sub>3</sub> (prepared from 70% HNO<sub>3</sub>, Sigma-Aldrich), followed by precipitation with NH<sub>4</sub>OH (Sigma-Aldrich). Then the precipitate was washed with water to pH 7–8 and then dissolved in 0.2 mol dm<sup>-3</sup> HClO<sub>4</sub> (from 70% HClO<sub>4</sub>, Sigma-Aldrich). The concentration of U(v1) and the acidity in the stock solution were determined, respectively, by fluorimetry<sup>40</sup> using standard solutions of U(v1) in 1 mol dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub> and by the Gran titration.<sup>41</sup>

The stock solutions of ligands were prepared by neutralizing the weighed amounts of solid pyridazine-3-carboxylic acid (HL, 98%, Sigma-Aldrich) or pyrazine-2-carboxylic acid (HL, 98%, Sigma-Aldrich) with an equivalent amount of NaOH (1.0 mol dm<sup>-1</sup>, Sigma-Aldrich). The ionic strength of all working solutions was maintained at 1.00 mol dm<sup>-3</sup> NaClO<sub>4</sub> (298 K).

#### 5.2 Potentiometry

Potentiometric titrations were performed to determine the protonation constants of PDZ and the stability constants of the U(vI)/PAZ complexes, using an autotitration unit consisting of a glass cell with a lid and a Metrohm dosimat (907 Titrando) connected with a glass pH electrode (Metrohm, 6.0229.100). Both the cell and the lid were water-jacketed and maintained at (298.2 ± 0.1) K by circulating water from a constant temperature bath. An inert atmosphere was maintained in the cell by passing Ar gas to prevent the sorption of CO<sub>2</sub> in the solution during titration. The original electrode filling solution (3 mol dm<sup>-3</sup> KCl) was replaced with 1.0 mol dm<sup>-3</sup> NaCl to prevent the clogging of the electrode junction due to the low solubility of KClO<sub>4</sub>.

In the potentiometric titrations, the proton concentration in the cup was determined from the measured electromotive force (EMF). Titration experiments were conducted in the acidic regions, and the EMF can be expressed using eqn (4).

$$E = E^{\circ} + \frac{RT}{F} \ln[\mathrm{H}^+] + \gamma_{\mathrm{H}}[\mathrm{H}^+]$$
(4)

where *R* is the gas constant, *F* is the Faraday constant, and *T* is the temperature in kelvin. The last term is the electrode junction potential for the hydrogen ion  $(\Delta E_{j,H^+})$ , assumed to be proportional to the concentration of the proton. Prior to each titration, an acid/base titration with standard perchloric acid and sodium hydroxide was performed to obtain the electrode parameters  $E^\circ$  and  $\gamma_{H}$ . These parameters allow the calculation of proton concentrations from the EMF in the subsequent titration. Corrections for the electrode junction potential of the hydroxide ion were not necessary in these experiments.

In a typical titration, the EMF data were collected at time intervals determined by the data collection criterion, that is, the drift of EMF ( $\Delta E$ ) was less than 0.1 mV for 180 s. Forty to seventy data points were collected in each titration. Multiple titrations were performed with different initial concentrations of solutes (L<sup>-</sup>/H<sup>+</sup> in the protonation titrations, and U(vi)/H<sup>+</sup> for the U(vi)/PAZ complexation titrations) and the same titrant (NaOH for the protonation titrations, and L<sup>-</sup> for the U(vi)/PAZ complexation titration data were analyzed to obtain the stability constants of the U(vi)/PAZ complexes or the protonation constants of ligands by the program Hyperquad.<sup>42</sup>

#### 5.3 Spectrophotometry

Spectrophotometric titrations were performed to determine the stability constants of the  $U(v_1)/L$  complexes. Absorption spectra of  $U(v_1)$  from 380 to 500 nm (0.5 nm interval) were collected on a spectrophotometer (Lambda-650, PerkinElmer, USA). Suprasil quartz cuvettes of 1 cm path length were used and maintained at (298.2  $\pm$  0.1) K by circulating water from a constant temperature bath through the jackets of the sample holders and their lids. In a typical titration, appropriate aliquots of the titrant solution were successively added into the sample cuvette by an injection pump (Havard 11EX) driven by a computer program. Usually 15–20 additions were made, thus generating a set of 16–21 spectra in each titration. Multiple titrations were performed with different initial concentrations of U(vi). The stability constants of complexes were calculated by non-linear least-squares regression using the HypSpec program.<sup>42</sup>

#### 5.4 NMR spectroscopy

5.4.1 Preparation of solutions for NMR analysis. 10.0 mg pyridazine-3-carboxylic acid was put in a 2.0 mL glass bottle, and certain volumes of 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub> (or 1.0 mol dm<sup>-3</sup> NaOH) and uranium stock solution ([U] = 0.259 mol dm<sup>-3</sup>, [H] = 0.120 mol dm<sup>-3</sup>) were transferred into the bottle, and then D<sub>2</sub>O was added to bring the volume to 1.0 mL. Detailed conditions are provided in Table S3 of the ESI.<sup>†</sup>

**5.4.2 NMR experiments.** <sup>1</sup>H- and <sup>13</sup>C-NMR data were collected on a Bruker Ascend 600 Spectrometer. The spectrometer was operated at 600.17 and 150.91 MHz for the measurements of <sup>1</sup>H and <sup>13</sup>C signals, respectively. NMR spectra were collected at a calibrated probe temperature of 298.2 K using the method described in the literature.<sup>43</sup> <sup>1</sup>H NMR spectra were recorded by averaging 16 scans for each spectrum. <sup>13</sup>C NMR spectra were

recorded by averaging  $\sim 14\,000$  scans for each spectrum with continuous decoupling of the protons using WALTZ16 decoupling. All spectra were referenced with TMS (tetramethyl silane).

#### 5.5 Microcalorimetry

Calorimetric titrations were conducted at 298.2 K with an isothermal microcalorimeter (TAM III, TA Instruments-Waters LLC, USA) to determine the enthalpy of complexation. The performance of the calorimeter was tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The value,  $(-47.7 \pm 0.3)$  kJ mol<sup>-1</sup>, was obtained at 298 K and is in excellent agreement with the literature.44 0.750 mL of a solution containing U(vi)/HClO<sub>4</sub> was placed in the calorimetric cell, and titrated with a solution of PDZ/ HClO<sub>4</sub>. Multiple titrations with different concentrations of the reagents were performed to reduce the uncertainty. In a typical titration, *n* additions of 0.005 mL titrant were made (n = 40-50) through a 0.250 mL syringe, resulting in n experimental values of the heat generated in the titration cell  $(Q_{ex,j}, j = 1 - n)$ . These values were corrected for the heats of titrant dilution  $(Q_{\text{dil},i})$  that were measured in a separate run. The net reaction heat at the  $j^{\text{th}}$  point  $(Q_{r,j})$  was obtained from the difference:  $Q_{r,j}$ =  $Q_{\text{ex,j}} - Q_{\text{dil,j}}$ . The value of  $Q_{r,j}$  is a function of the concentrations of the reactants ( $C_{\rm M}$  and  $C_{\rm L}$ ), the equilibrium constants, and the enthalpies of the reactions that occurred in the titration. A least-squares minimization program, HypDeltaH,<sup>24</sup> was used to calculate the reaction enthalpies ( $\Delta H$ ). The corres-

 Table 4
 Crystallographic data and structure refinement for the U(vi)/PDZ complexes

	(I)	(II)	(III)	( <b>IV</b> )
Empirical formula	$C_{10}H_8N_4O_7U, H_2O$	$C_{10}H_8N_4O_7U$	$C_{15}H_{13}ClN_6Na_2O_{14}U$	$C_{10}H_{10}N_4O_8U$
Formula weight	730.19	534.23	820.77	552.25
Temperature	293	293	293	293
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	Pna 21	P12/n1	C12/C1
Hall group	<i>-p</i> 1	P2C-2n	-p2yac	-C2yc
Unit cell dimensions (Å)	a = 7.8240(5)	a = 26.1101(17)	a = 15.1242(3)	a = 25.7342(9)
	b = 8.0617(6)	b = 7.7452(5)	b = 7.0651(1)	b = 6.8614(3)
	c = 11.9538(7)	c = 6.8023(5)	c = 23.2973(5)	c = 16.7222(6)
	$\alpha = 87.484^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 75.764^{\circ}$	$\beta = 90^{\circ}$	$\beta = 104.600(2)^{\circ}$	$\beta = 96.750(3)^{\circ}$
	$\gamma = 88.380^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Cell ratio	a/b = 0.9705	a/b = 3.3711	a/b = 2.1407	a/b = 3.7506
	b/c = 0.6744	b/c = 1.1386	b/c = 0.3033	b/c = 0.4103
	c/a = 1.5278	c/a = 0.2605	c/a = 1.5404	c/a = 0.6498
Volume (Å <sup>3</sup> )	730.01(9)	1375.61(16)	2409.02(8)	2932.2(2)
Z	1	4	4	8
Calculated density (g cm $^{-3}$ )	2.512	2.580	2.263	2.502
$Mu (mm^{-1})$	11.167	11.842	6.968	11.121
F(000)	508.0	976.0	1552.0	2032.0
$h, k, l_{\max}$	9, 10, 14	32, 9, 8	18, 8, 29	32, 8, 20
N <sub>ref</sub>	2982	2244	4931	3000
$T_{\min}, T_{\max}$	0.195, 1.000	0.373, 1.000	0.604, 1.000	0.624, 1.000
Data completeness	0.997	1.46/0.80	0.997	0.999
Theta (max)	26.370	26.372	26.373	26.370
R (reflections)	0.0400(2676)	0.0437(1862)	0.0334(4089)	0.0233(2524)
$wR_2$ (reflections)	0.0806(2982)	0.0960(2244)	0.0768(4917)	0.426(3000)
S	1.043	1.102	1.063	0.996
$N_{ m par}$	217	128	363	220

ponding entropies of complexation ( $\Delta S$ ) were calculated from the expression  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta G = -RT \ln \beta$ .

## 5.6 Single-crystal X-ray diffractometry

5.6.1 Crystallization. [UO<sub>2</sub>(PAZ)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O (I): 12.4 mg of pyrazine-2-carboxylic acid were dissolved in 1.0 mL water in a 4 mL glass sample bottle with a cap, and then 192  $\mu$ L U(v) solutions ([U] = 0.22 M,  $[HClO_4] = 0.12$  M) were added into it. After refluxing for 1 hour on an electric hot plate at 150°, the mixture solutions were put aside at ambient temperature. Green crystals were obtained 3 days later. [UO<sub>2</sub>(PDZ)<sub>2</sub>(H<sub>2</sub>O)] (II): 1.00 mL of an aqueous solution containing 40.0 mmol U(vi), 80.7 mmol sodium pyridazine-3-carboxylate, and 99.3 mmol HClO<sub>4</sub> was refluxed for 2 h on an electric hot plate, and then evaporated at room temperature. Yellowish green crystals appeared in about one day. [UO<sub>2</sub>(PDZ)<sub>3</sub>Na<sub>2</sub>ClO<sub>4</sub>]·2H<sub>2</sub>O (III): 2.0 mL of a 1.0 M NaClO<sub>4</sub> solution containing 0.01 mmol U(vi), 0.31 mmol sodium pyridazine-3-carboxylate, and 0.07 mmol HClO<sub>4</sub> was evaporated at room temperature. Yellowish green crystals were deposited in about one month.  $[(UO_2)_2(PDZ)_4(H_2O)_2] \cdot 2H_2O$  (IV): 0.61 mL of an aqueous solution containing 11 mmol U(vi), 24 mmol sodium pyridazine-3carboxylate, and 6 mmol HClO<sub>4</sub> was evaporated at room temperature. Yellowish green crystals appeared in about one day.

**5.6.2 X-ray diffraction.** Representative crystals were mounted on a goniometer and crystallographic data were collected on an Xcalibur E X-ray single-crystal diffractometer at 293 K. The XRD data indicate that compound I is a mononuclear 1:2 U(v1)/PAZ complex,  $[\text{UO}_2(\text{PAZ})_2(\text{H}_2\text{O})]$ ·H<sub>2</sub>O, compound II is a mononuclear 1:2 U(v1)/PDZ complex,  $[\text{UO}_2(\text{PDZ})_2(\text{H}_2\text{O})]$ , compound III is a 1:3:2 U(v1)/PDZ/Na complex,  $[\text{UO}_2(\text{PDZ})_3(\text{H}_2\text{O})]$ , compound III is a 1:3:2 U(v1)/PDZ/Na complex,  $[\text{UO}_2(\text{PDZ})_3(\text{H}_2\text{O})_3]$ ·ClO<sub>4</sub>]·2H<sub>2</sub>O, and compound IV is a dinuclear 1:2 U(v1)/PDZ complex,  $[(\text{UO}_2)_2(\text{PDZ})_4(\text{H}_2\text{O})_2]$ ·2H<sub>2</sub>O, with a structure identical to that in the literature.<sup>21</sup> Detailed crystallographic data and structural refinement for the U(v1) complexes I, II, III, and IV are given in Table 4, and details of their structural information have been deposited with the Cambridge Structural Database (CCDC 1586814, 1865674, 1586812, and 1865676†).<sup>20</sup>

# Conflicts of interest

There are no conflicts to declare.

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