Flexible Diphosphonic Acids for the Isolation of Uranyl Hybrids with Heterometallic U^{VI}=O—Zn^{II} Cation–Cation Interactions

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S *Supporting Information*

ABSTRACT: A family of uranyl diphosphonates have been hydrothermally synthesized using various flexible diphosphonic acids and $Zn(UO_2)(OAc)_4 \cdot 7H_2O$ in the presence of bipy or phen. Single-crystal X-ray analyses indicate that these compounds represent the first examples of uranyl phosphonates with heterometallic U^{VI}=O—Zn^{II} cation–cation interactions.

Uranyl phosphonates have received increasing attention because of not only their versatile intriguing architectures in structure chemistry but also their real applications in nuclear waste management and separation processes.[1] So far, a large number of uranyl phosphonates with various structures have been isolated, including 1D assemblies,[2] 2D layers,[3] and 3D frameworks.[4] Some of the cases have shown potential applications in ion exchange,[5,6] proton conductivity,[2] chiral materials,[4] and biomaterials.[7] It is known that organic ligands play a pivotal role in the construction of coordination polymers and further affect their properties.[8] To the best of our knowledge, diphosphonic acids used for the construction of uranyl materials are limited to rigid centered organics, such as methylenediphosphonic acid,[4] 1-hydroxyethylidene-1,1-diphosphonic acid,[9] phenylphosphonic acid,[10] benzenediphosphonic acid,[5] and 4,4′-biphenylenebis(phosphonic acid).[6] So far, no phosphonate ligands featuring flexible structures have been exploited to synthesize uranyl complexes. It is challenging to isolate versatile uranyl phosphonates using varied flexible ligands with different alkyl chains.

Cation–cation interactions (CCIs) refer to the interaction of an inert "yl" oxygen atom of one actinyl ion with an adjacent actinyl ion. This character usually increases the dimensionality of the complexes, leading to framework structures and impacting their physical and chemical properties. Such CCIs, first discovered in solutions,[11] are often observed in An^V complexes (An = Np, U, Pu, Am), while they rather rarely occur for U^{VI} species. In recent studies, this designation of CCIs has been extended to common parlance for actinyl ions and other metal ions. For example, the interactions of uranyl dications with alkali- or alkaline-earth-metal ions appeared in condensed phases and some discrete molecules.[12] Very recently, new CCIs were observed in heterometallic uranyl compounds in the form of penta- and hexavalent uranyl cations with lanthanide elements.[13] As to CCIs between UO_2^{2+} dications and transition metals, examples are still limited.[14,15] As far as we know, only a few

compounds featuring U=O—Zn interactions have been isolated, such as Schiff-base calixpyrrole macrocycle complexes, carboxylates, and arsonates.[15] The occurrence of phosphonate with U=O—Zn interactions has never been reported. In this communication, we choose ethane-1,2-diyldiphosphonic acid (H_4EDP), propane-1,3-diyldiphosphonic acid (H_4PDP), and butane-1,4-diyldiphosphonic acid (H_4BDP) as the ligands (Figure 1a), and three new uranyl diphosphonates, Zn(bipy)-
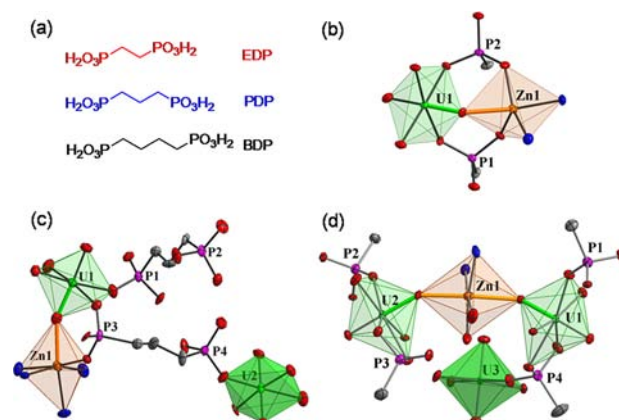

Figure 1. Diphosphonate ligands (a) and the connection modes of uranium and zinc atoms in ZnUEDP (b), ZnUPDP (c), and ZnUBDP (d).

$(UO_2)(EDP)$ (ZnUEDP), $Zn(phen)_2(UO_2)_2(HPDP)_2 \cdot 2H_2O$ (ZnUPDP), and $Zn(phen)(H_2O)_2(UO_2)_3(BDP)_2$ (ZnUBDP), were obtained under hydrothermal conditions,[16] all of which comprise the heterometallic U^{VI}=O—Zn^{II} CCIs.

ZnUEDP crystallizes in monoclinic space group $P2_1/c$ and possesses a 2D layered structure. The uranium atom is in a square-planar-bipyramidal environment and shares oxygen atoms with four EDP ligands in the equatorial plane and one zinc atom on the axis (Figure 1b). The bond valence sum at the U1 site, calculated using coordination-specific parameters,[17] is 5.88, which corresponds well with the formal valence of U^{VI}. Every phosphonate group adopts a η_3-coordination mode, connecting two uranyl centers and one zinc atom. The zinc atom is five-coordinated by three μ-oxygen atoms and two nitrogen atoms of one bipy, forming a square pyramid. The UO_6

tetragonal bipyramids are connected by parallel EDP ligands through corner-sharing to form a layered arrangement. Zn(bipy) groups link to both sides of such a layer via the sharing of μ-oxygen atoms with uranyl centers and PO_3 groups, resulting in a 2D heterometallic structure of ZnUEDP (Figures 2a and S1 in the Supporting Information, SI). A 3D supramolecualr structure is produced through $\pi\cdots\pi$ interactions between bipy molecules (Figure S2 in the SI).
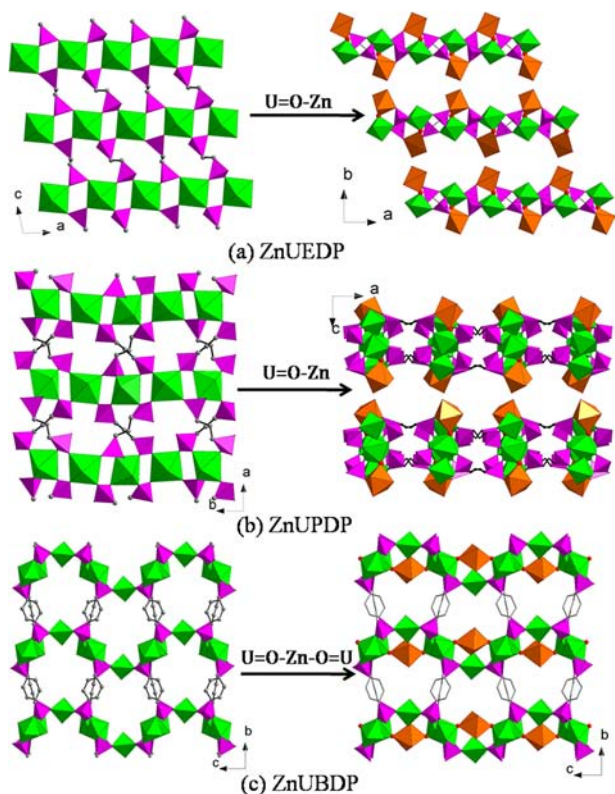

Figure 2. Uranyl phosphonate partial structures connected by zinc-centered polyhedra via CCIs to form the whole structures of ZnUEDP (a), ZnUPDP (b), and ZnUBDP (c).

ZnUPDP also comprises a layered structure. Similar to ZnUEDP, the uranyl centers are equatorially connected by four PDP groups, generating a layered uranyl phosphonate partial structure, but the PDP ligands are arranged in a crossed way as the linkage. The calculated bond valence sums for the uranium atoms are 5.87 for U1 and 6.02 for U2. The zinc atom is coordinated by four nitrogen atoms of two phen and two μ-oxygen atoms from one PDP and one U1 "yl" oxygen atom (Figure 1c), respectively, forming a tetragonal bipyramid. On both sides of this uranyl phosphonate layer, $Zn(phen)_2$ groups are decorated through the sharing of oxygen atoms with U1- and P3-centered polyhedra (Figures 2b and S3 in the SI). Such heterometallic phosphonate layers interact via $\pi\cdots\pi$ interaction between phen molecules to generate a supramolecular architecture (Figure S4 in the SI).

ZnUBDP exhibits a 3D framework structure with rare U═O—Zn—O═U CCIs. Two crystallographically distinct uranium atoms, U1 and U2, are seven-coordinated by five oxygen atoms from four distinct BDP ligands and two terminal oxygen atoms, forming pentagonal bipyramids. Two such pentagonal bipyramids connect to each other through edge-sharing to produce a dimer. U3 is equatorially coordinated by four μ-oxygen

atoms from four unique BDP groups, leaving two oxo atoms on the axis. The calculated valence states of U1, U2, and U3 are 6.01, 6.08, and 6.13, respectively. The zinc atom is in a distorted octahedral geometry defined by two nitrogen atoms of one phen, two aqua ligands, and two oxygen atoms from two distinct uranyl centers (Figure 1d). Two of the BDP ligands disorder over two positions. All of the PO_3 groups of four unique BDP ligands adopt η_3-coordination modes, which connect three distinct uranyl centers. The uranyl dimers are linked by BDP to generate a layered arrangement, which is further connected by U3-centered polyhedra to form a 3D framework (Figure S5 in the SI). The ZnO_4N_2 octahedra are bridged between two UO_7 pentagonal bipyramids via the sharing of uranyl oxo atoms (Figures 2c and S6 in the SI). It is worth noting here that such a U═O—Zn—O═U connection has never been reported before.

It is interesting that heterometallic U^{VI}═O—Zn^{II} CCIs are displayed for the first time in all of the synthesized uranyl phosphonates (Figure 1). In ZnUEDP, the U═O(μ) distance [1.807(5) Å] is slightly longer than the terminal U═O distance [1.785(5) Å], which is caused by the heterometallic CCI. Similarly, the zinc-bound U═O distance of 1.832(10) Å in ZnUPDP is longer than that of the terminal U═O length with 1.774(10) Å. Besides, there is a unique uranyl center (U2) with no CCIs in ZnUPDP. Differently, in ZnUBDP, the zinc-centered polyhedra connect two distinct uranyl centers through CCIs, leaving one unique U3 atom. Such CCIs between UO_2^{2+} and Zn^{2+} ions are also reflected in the difference of the U═O bond lengths of ZnUBDP. The zinc-bound U═O distances are 1.795(5) and 1.800(5) Å, which are longer than 1.761(5) and 1.754(5) Å of the terminal U═O distances. The layered uranyl phosphonate partial structures of ZnUEDP and ZnUPDP, which are different in their arrangement of the diphosphonate groups, are connected by ZnO_3N_2 square pyramids and ZnO_2N_4 octahedra via CCIs on both sides, respectively, to form 2D assemblies of ZnUEDP and ZnUPDP (Figure 2a,b). It is noted that, upon further extension of the flexibility of the diphosphonate ligand, a framework architecture of the uranyl phosphonate partial structure of ZnUBDP is formed, which is further connected by ZnO_4N_2 octahedra via U═O—Zn—O═U CCIs (Figure 2c).

IR and Raman spectra show the vibrations of UO_2^{2+} in the region of 760−950 cm^{-1} (Figures S7 and S8 in the SI). The antisymmetric stretching modes v_3 are observed in the area 942−866 cm^{-1} in IR spectra, while the symmetric stretching vibrations v_1 are displayed in the range of 841−735 cm^{-1} in both IR and Raman spectra. The bond lengths related to the antisymmetric vibrations v_3 for UO_2^{2+} in these title complexes based on Bartlett's and Veal's empirical equations[18] are calculated, respectively. As shown in Table 1, the predicted U═O lengths well agreed with that obtained from the single-crystal X-ray diffraction (XRD) data, and Bartlett's expression leads to values closer to the real distances.

The solid-state UV−vis absorption spectra of these compounds display the characteristic absorptions of hexavalent uranium species in the region of 320−500 nm (Figure S9 in the SI). The characteristic fine structures with maxima at 430 nm for ZnUEDP and ZnUPDP are clearly indicated. For ZnUBDP, only a broad adsorption centered at 430 nm is observed. Besides, the broad adsorption centered at 320 nm for ZnUEDP is due to the equatorial U−O charge-transfer bands of UO_2^{2+}. The photoluminescent properties of these uranyl phosphonates have also been investigated (Figure S10 in the SI). All of the title

Table 1. Comparison between Calculated and Experimental U═O Lengths for the Synthesized Uranyl Diphosphonates

	ν_3 of UO_2^{2+} (cm^{-1})	Bartlett's law (pm)	Veal's law (pm)	exptl (pm)
ZnUEDP	880	179.9	177.9	180.7
	897	178.7	176.8	178.5
ZnUPDP	852	182.1	179.9	183.2
	896	178.7	176.9	177.4
	927	176.5	175.0	176.1
ZnUBDP	866	181.0	178.9	180/179.5
	927	176.5	175.0	176.1
	942	175.5	174.0	175.5/175.4/174.7

complexes exhibit typical green light ranging from 480 to 580 nm with well-structured emission bands (480, 496, 506, 517, 528, 539, 551, and 564 nm for ZnUEDP, 510, 531, and 554 nm for ZnUPDP, and 486, 503, 524, 547, and 572 nm for ZnUBDP). These emission peaks are related to the symmetric and antisymmetric vibrational modes of the uranyl cation.

In summary, we have synthesized the first examples of uranyl phosphonates with heterometallic U^{VI}═O—Zn^{II} CCIs. These compounds are constructed of flexible alkyl-based diphosphonate ligands. With an increase in the alkyl chain, the framework structure of ZnUBDP is formed, instead of layered assemblies of ZnUEDP and ZnUPDP. This work demonstrates that uranyl phosphonates with novel structural arrangements will be achieved by using flexible phosphonate ligands. Future work will be focused on the expansion and modification of the phosphonate ligands to isolate new uranyl complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for phosphonic acids, X-ray crystallographic files in CIF format (CCDC 931846−931848), crystal data and structure refinement, selected bond length and angles, powder XRD patterns, thermogravimentric analysis curves, structural pictures, IR, Raman, UV−vis, and photoluminescent spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Burns, P. C.; Ewing, R. C.; Navrotsky, A. *Science* **2012**, *335*, 1184.
(2) Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264.
(3) (a) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2010**, *49*, 5701. (b) Knope, K. E.; Cahill, C. L. *Eur. J. Inorg. Chem.* **2010**, 1177.
(4) Diwu, J.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2012**, *48*, 3827.
(5) Adelani, P. O.; Albrecht-Schmitt, T. E. *Angew. Chem., Int. Ed.* **2010**, *49*, 8909.
(6) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2011**, *50*, 12184.
(7) (a) Wang, L.; Yang, Z. M.; Gao, J. H.; Xu, K. M.; Gu, H. W.; Zhang, B.; Zhang, X. X.; Xu, B. *J. Am. Chem. Soc.* **2006**, *128*, 13358. (b) Yang, Z. M.; Xu, K. M.; Wang, L.; Gu, H. W.; Wei, H.; Zhang, M. J.; Xu, B. *Chem. Commun.* **2005**, 4414.
(8) Mao, J. G. *Coord. Chem. Rev.* **2007**, *251*, 1493.
(9) (a) Yang, W. T.; Wu, H. Y.; Wang, R. X.; Pan, Q. J.; Sun, Z. M.; Zhang, H. J. *Inorg. Chem.* **2012**, *51*, 11458. (b) Wu, H. Y.; Yang, W. T.; Sun, Z. M. *Cryst. Growth Des.* **2012**, *12*, 4669.
(10) Yang, W. T.; Tian, T.; Wu, H. Y.; Pan, Q. J.; Dang, S.; Sun, Z. M. *Inorg. Chem.* **2013**, *52*, 2736.
(11) Sullivan, J. C.; Hindman, J. C.; Zielen, A. J. *J. Am. Chem. Soc.* **1961**, *83*, 3373.
(12) (a) Burns, P. C. *Can. Mineral.* **2005**, *43*, 1839. (b) Krot, N. N.; Grigoriev, M. S. *Russ. Chem. Rev.* **2004**, *73*, 89. (c) Tian, G.; Rao, L.; Oliver, A. *Chem. Commun.* **2007**, *40*, 4119. (d) Wang, S.; Diwu, J.; Alekseev, E. V.; Jouffret, L. J.; Depmeier, W.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2012**, *51*, 7016. (e) Arnold, P. L.; Pécharman, A.-F.; Hollis, E.; Yahia, A.; Maron, L.; Parsons, S.; Love, J. B. *Nat. Chem.* **2010**, *2*, 1056.
(13) (a) Liu, S. P.; Chen, M. L.; Chang, B. C.; Lii, K. H. *Inorg. Chem.* **2013**, *52*, 3390. (b) Fortier, S.; Hayton, T. W. *Coord. Chem. Rev.* **2010**, *254*, 197. (c) Arnold, P. L.; Hollis, E.; White, F. J.; Magnani, N.; Caciuffo, R.; Love, J. B. *Angew. Chem., Int. Ed.* **2011**, *50*, 887. (d) Volkringer, C.; Henry, N.; Grandjean, S.; Loiseau, T. *J. Am. Chem. Soc.* **2012**, *134*, 1275.
(14) (a) Arnold, P. L.; Patel, D.; Blake, A. J.; Wilson, C.; Love, J. B. *J. Am. Chem. Soc.* **2006**, *128*, 9610. (b) Thuéry, P. *Inorg. Chem. Commun.* **2009**, *12*, 800. (c) Shvareva, T. Y.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2006**, *45*, 1900. (d) Olchowka, J.; Falaise, C.; Volkringer, C.; Henry, N.; Loiseau, T. *Chem.—Eur. J.* **2013**, *19*, 2012.
(15) (a) Arnold, P. L.; Patel, D.; Wilson, C.; Love, J. B. *Nature* **2008**, *451*, 315. (b) Chen, W.; Yuan, H. M.; Wang, J. Y.; Liu, Z. Y.; Xu, J. J.; Yang, M.; Chen, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 9266. (c) Tian, T.; Yang, W. T.; Pan, Q. J.; Sun, Z. M. *Inorg. Chem.* **2012**, *51*, 1150.
(16) Synthesis details: A mixture of Zn(UO$_2$)(OAc)$_4$·7H$_2$O (40 mg), diphosphonic acid (40 mg), bipy (20 mg for ZnUEDP) or phen (20 mg for ZnUPDP and ZnUBDP), and deionized water (3.0 mL) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160 °C for 2 days and then cooled to room temperature. Yellow blocklike crystals were isolated. Yield: 20 mg (72.1% based on uranium) for ZnUEDP. Anal. Calcd for C$_{12}$H$_{12}$N$_2$O$_8$P$_2$UZn: C, 21.27; H, 1.79; N, 4.13. Found: C, 20.66; H, 1.75; N, 3.98. Yield: 18 mg (64.3% based on uranium) for ZnUPDP. Anal. Calcd for C$_{30}$H$_{32}$N$_4$O$_{18}$P$_4$U$_2$Zn: C, 25.74; H, 2.16; N, 4.00. Found: C, 25.81; H, 2.22; N, 4.09. Yield: 15 mg (59.8% based on uranium) for ZnUBDP. Anal. Calcd for C$_{20}$H$_{16}$N$_2$O$_{20}$P$_4$U$_3$Zn: C, 15.93; H, 1.07; N, 1.86. Found: C, 15.87; H, 1.01; N, 1.83. Powder XRD has been characterized to confirm the phase purity (Figure S11 in the SI), and thermogravimetric analysis curves (Figure S12 in the SI) were used to study the thermal stability and water content of the title compounds.
(17) (a) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.
(18) (a) Veal, B. W.; Lam, D. J.; Carnall, W. T.; Hestra, H. R. *Phys. Rev. B* **1975**, 5651. (b) Bartlett, J. R.; Cooney, R. P. *J. Mol. Struct.* **1989**, *193*, 295.

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dx.doi.org/10.1021/ic4009834 | *Inorg. Chem.* 2013, 52, 8288−8290