异金属膦酸铀的合成、晶体结构和荧光性质

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摘要:构建异金属膦酸铀仍然具有挑战性。在本工作中,从苯磺酰甲基膦酸二乙酯(Et₂L)出发,成功合成了一系列同构的异金 属膦酸铀化合物[UO₂M(L)₂(H₂O)₄],其中 M=Mn (1)、Co (2)、Ni (3)、Zn (4)、Cd (5)。晶体结构研究表明,磺酰基团没有与金属离子配 位,而膦酸基团完全去质子化,连接2个铀酰离子和1个过渡金属离子,形成了二维层状晶体结构。荧光研究表明,在Mn(II)、 Co(II)和Ni(II)离子存在时,铀酰离子的特征荧光发射被猝灭,而在Zn(II)和Cd(II)离子存在时,显示出强的特征荧光发射。

关键词:铀酰;膦酸盐;晶体结构;荧光 中图分类号:0614.71⁺1;0614.81⁺2;0614.81⁺3;0614.24⁺1;0614.24⁺2 文献标识码:A 文章编号:1001-4861(2023)04-0746-07 DOI:10.11862/CJIC.2023.034

Heterometallic uranyl sulfophosphonates: Synthesis, crystal structures, and fluorescence properties

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Abstract: It is still a great challenge to construct heterometallic uranyl phosphonates. In this work, a series of isostructural heterometallic uranyl sulfophosphonates, namely $[UO_2M(L)_2(H_2O)_4]$, where M=Mn (1), Co (2), Ni (3), Zn (4), Cd (5) and Et₂L=diethyl ((phenylsulfonyl)methyl)phosphonate, have been successfully synthesized and systematically characterized. The sulfonyl group is not involved in coordination with the metal centers, whereas the phosphonate group is fully deprotonated and connects with two uranyl cations and one transition metal ion, affording a 2D layered crystal structure. It was found that the luminescent emission was almost totally quenched in the presence of Mn(II), Co(II), and Ni(II), whereas showed strong emissions in the presence of Zn(II) and Cd(II). CCDC: 2210686, 1; 2210687, 2; 2210688, 3; 2210689, 4; 2210690, 5.

Keywords: uranyl; phosphonates; crystal structures; fluorescence

Uranyl organic frameworks (UOFs) have gained more and more attention not only because of their exquisite crystal structures but also because of their close relation to nuclear waste disposal^[1-2]. In recent years, many new UOFs with interesting properties and potential applications have been reported^[3-5]. It is reasonable to believe that UOFs can be developed into functional materials^[6-7] in the further since the half-life of uranium is very long and mainly emits α radiation^[8]. The photophysical properties of UOFs are very interest-

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ing and have found many potential applications, such as chemical sensors^[9], adsorption/separation^[10], and proton conduction^[11-12].

Currently, UOFs are mainly constructed from carboxylate - based ligands and have been extensively researched. Compared with the carboxylate group, the phosphonate group possesses an additional binding oxygen atom, showing higher affinity toward metal centers and leading to better thermal and chemical stability which is beneficial to their applications. However, the study on phosphonate-based UOFs is still limited, probably due to their poor crystallinity^[13]. In recent years, some new methods have been developed and more and more new uranyl phosphonates have been synthesized. To enhance the crystallinity of uranyl phosphonates, new phosphonate ligands decorated with additional functional groups, including carboxylic^[14] and hydroxyl^[15], etc., have been employed. Additionally, incorporating s - block^[16], d - block^[17-19], and f - block^[20] metal ions into the crystal structure to prepare heterometallic uranyl phosphonates has also been proven to be an effective approach. Through this approach, the crystal structure of uranyl phosphonates can be greatly enriched and the physiochemical properties altered to meet a specific application^[19,21-22]. In addition to the above strategies, using phosphonate ester as raw material is also an effective strategy for preparing uranyl phosphonates^[23-24]. The phosphonate ester ligand would hydrolyze slowly in the reaction process, which reduces the rates of crystal nucleus formation and is conducive to the growth of single crystals.

Combining the above two methods, namely introducing additional functional groups and using esters as ligands, is a very promising strategy for the construction of heterometallic uranyl phosphonates. In our previous work, a sulfophosphonate ester ligand, diethyl ((phenylsulfonyl)methyl)phosphonate (Et₂L), has been successfully employed for the construction of a series of lanthanide-uranyl phosphonates^[25]. These heterometallic uranyl phosphonates display very interesting luminescence properties. To further explore new heterometallic uranyl phosphonates, recently we used this ligand to react with *d*-block metal salts and uranyl sulfate by a hydrothermal method and successfully obtained a series of new d-f heterometallic uranyl phosphonates: $[UO_2M(L)_2(H_2O)_4]$, where M=Mn (1), Co (2), Ni (3), Zn (4), Cd (5). Their crystal structures and luminescent properties have been systematically investigated.

1 Experimental

Caution: Uranium-bearing materials are radioactive and toxic, and necessary protection shall be taken during use.

1.1 Materials and instruments

All chemicals were purchased from Aladdin or Energy chemical incorporations and used without purification. The elemental analyses were performed on a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded in a 2θ range of 5°-50° on a TD-3000 diffractometer using Cu $K\alpha$ radiation (tube voltage: 35 kV; tube current: 25 mA; λ = 0.154 056 2 nm). IR spectra were recorded on a Thermo Fisher Nicolet iS-10 FTIR Spectrometer using KBr pellets in a range of 4 000-400 cm⁻¹. Thermogravimetric analyses (TGA) were carried out in a temperature range of 50-1 000 °C on a TA SDT 650 analyzer at a heating rate of 10 $^{\circ}$ C ·min⁻¹ under a nitrogen atmosphere. The fluorescent spectra of compounds 1-5 were measured on a HITACHI F - 7000 FL spectrophotometer. The UV-Vis spectra of compounds 1-5 were recorded on a HITACHI U-3900 spectrophotometer using BaSO₄ as background.

1.2 Synthesis of compound 1

0.029 3 g Et₂L (0.1 mmol), 0.021 0 g uranyl sulfate (0.05 mmol), 0.016 9 g manganese sulfate monohydrate (0.1 mmol), 10 mL deionized water, and two drops of 0.9 mol·L⁻¹ H₂SO₄ were mixed in a 50 mL Teflon-lined autoclave and reacted at 180 °C for 4 d. Yellow block crystals could be obtained by filtration (Yield: 78%). Elemental analysis (%) found for C₁₄H₂₂MnO₁₆P₂S₂U (Calcd.): C 19.49 (19.43), H 2.63 (2.56). IR(KBr, cm⁻¹): 3 455 (b, m), 2 974 (w), 2 921 (w), 2 358 (vw), 1 635 (m), 1 448 (w), 1 402 (w), 1 294 (m), 1 209 (m), 1 158 (s), 1 115 (m, sh), 1 087 (m), 1 051 (s), 1 025 (s), 929 (w), 911 (m), 810 (w), 796 (m), 764 (w), 725 (w), 685 (w), 617 (w), 544 (m), 458 (m) (Fig.S1, Supporting information).

1.3 Syntheses of compounds 2-5

Compounds 2-5 were synthesized using the same method as compound 1 except the displacement of $MnSO_4 \cdot H_2O$ with $CoSO_4 \cdot 7H_2O$ for 2, $NiSO_4 \cdot 6H_2O$ for **3**, $ZnSO_4 \cdot 7H_2O$ for **4**, and $2CdSO_4 \cdot 0.5H_2O$ for **5**. Elemental analysis (%) found for 2 (Calcd.): C 19.36 (19.34), H 2.65 (2.55); IR(KBr, cm⁻¹): 3 493 (b, m), 3 062 (w), 2 974 (m), 2 922 (m), 1 683 (w), 1 651 (m), 1 634 (m), 1 583 (w), 1 558 (w), 1 480 (w), 1 448 (m), 1 370 (m), 1 292 (s), 1 211 (m), 1 162 (m), 1 113 (w), 1 086 (w), 1 022 (s), 929 (w), 911 (s), 852 (w), 810 (m), 769 (s), 763 (m), 725 (m), 684 (m), 606 (m), 546 (m), 510 (m), 457 (m). Elemental analysis (%) found for 3 (Calcd.): C 19.42 (19.35), H 2.60 (2.55); IR(KBr, cm⁻¹): 3 446 (b, m), 2 973 (m), 2 921 (m), 1 644 (m), 1 558 (vw), 1 480 (vw), 1 448 (w), 1 402 (m), 1 371 (w), 1 291 (m), 1 210 (m), 1 158 (s), 1 115 (m, sh), 1 086 (m), 1 050 (m), 1 020 (s), 929 (w), 912 (s), 811 (w), 797 (m), 763 (w), 725 (m), 684 (m), 608 (w), 545 (m), 511 (w), 460 (w). Elemental analysis (%) found for 4 (Calcd.): C 19.26 (19.20), H 2.61 (2.53); IR(KBr, cm⁻¹): 3 449 (b, s), 2 974 (m), 2 922 (m), 1 637 (m), 1 479 (w), 1 448 (m), 1 402 (m), 1 370 (w), 1 292 (s), 1 210 (s, sh), 1 158 (s), 1 116 (s, sh), 1 086 (s), 1 051 (s), 1 023 (s), 929 (m, sh), 911 (s), 859 (w), 810 (w), 796 (m), 763 (w), 725 (m), 684 (m), 545 (m), 460 (w). Elemental analysis (%) found for **5** (Calcd.): C 18.28 (18.22), H 2.45 (2.40); IR (KBr, cm⁻¹): 3 445 (b, m), 2 974 (w), 2 922 (w), 1 635 (w), 1 479 (w), 1 448 (m), 1 370 (w), 1 293 (m), 1 206 (w), 1 190 (w), 1 148 (s), 1 107 (m), 1 086 (m), 1 047 (m), 1 007 (s), 942 (m), 929 (m), 908 (s), 852 (w), 809 (w), 788 (w), 763 (w), 722 (s), 684 (m), 608 (m) (Fig.S1).

1.4 Single-crystal structure determination

The intensity data were collected on a Bruker SMART APEX II CCD diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.071\ 073\ nm$) at room temperature. The integration of intensity and scaling was performed using SAINT. Absorption corrections were carried out with the SADABS program. The crystal structures were solved by direct methods using SHELXS and refined by least-square methods with SHELXL-2013. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically using a riding model. The crystallographic details are summarized in Table 1.

CCDC: 2210686, **1**; 2210687, **2**; 2210688, **3**; 2210689, **4**; 2210690, **5**.

Parameter	1	2	3	4	5
Formula	${\rm C}_{14}{\rm H}_{22}{\rm MnO}_{16}{\rm P}_2{\rm S}_2{\rm U}$	${\rm C}_{14}{\rm H}_{22}{\rm CoO}_{16}{\rm P}_2{\rm S}_2{\rm U}$	$\mathrm{C_{14}H_{22}NiO_{16}P_2S_2U}$	$\mathrm{C}_{14}\mathrm{H}_{22}\mathrm{ZnO}_{16}\mathrm{P}_{2}\mathrm{S}_{2}\mathrm{U}$	$C_{14}H_{22}CdO_{16}P_2S_2U$
Formula weight	865.34	869.33	869.11	875.77	922.80
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	I2/a	I2/a	I2/a	I2/a	I2/a
<i>a</i> / nm	2.135 38(17)	2.131 04(15)	2.152 21(13)	2.160 52(16)	2.146 38(11)
<i>b</i> / nm	0.558 51(3)	0.556 16(4)	0.554 92(2)	0.556 44(3)	0.560 10(2)
<i>c</i> / nm	2.183 16(10)	2.151 21(15)	2.134 90(8)	2.137 76(10)	2.208 63(7)
β/(°)	98.435(5)	98.417(6)	98.097 0(10)	98.200 0(10)	98.387(3)
V / nm^3	2.575 5(3)	2.522 1(3)	2.524 3(2)	2.543 7(3)	2.626 79(19)
Ζ	4	4	4	4	4
$D_{\rm c} /({\rm g}{\cdot}{\rm cm}^{-3})$	2.232	2.289	2.287	2.287	2.333
μ / mm $^{-1}$	7.128	7.436	7.519	7.664	7.318
<i>F</i> (000)	1 652	1 660	1 664	1 672	1 744
heta range / (°)	3.768-24.993	2.913-25.000	2.900-24.999	3.784-24.998	3.730-24.998
Completeness / %	97.5	97.2	96.9	97.1	97.1
Reflection collected	21 671	13 744	16 163	15 725	16 407
Independent reflection (R_{int})	2 274 (0.077 4)	2 225 (0.083 1)	2 224 (0.044 7)	2 242 (0.045 9)	2 312 (0.035 3)

Table 1 Crystal parameters of compounds 1-5

Continued Table 1					
GOF on F^2	1.041	1.022	1.052	1.037	1.058
Final R indices $[I\!\!>\!\!2\sigma(I)]R_1,wR_2*$	0.029 3, 0.055 8	0.042 8, 0.075 0	0.021 0, 0.043 4	0.023 0, 0.048 2	0.020 0, 0.044 8
R indices (all data) $R_{\rm 1}, wR_{\rm 2}$	0.038 0, 0.058 1	0.058 3, 0.079 7	0.024 5, 0.044 3	0.027 2, 0.049 3	0.022 7, 0.045 6

 $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}.$

2 **Results and discussion**

2.1 Synthesis

These heterometallic uranyl sulfophosphonates can be hydrothermally synthesized from metal chlorides and acetates in a temperature range of 120 -200 °C with the yields varying from 20% to 80 %. The purity of the bulk samples has been confirmed by PXRD techniques (Fig.S2-S6).

2.2 Structural description of compounds 1-5

Compounds 1-5 are isostructural and possess 2D layered crystal structures. Compound 1 is taken as an example and its crystal structure is described in detail. It crystallizes in monoclinic space group I2/a (Table 1). In the asymmetric unit, there is half uranyl cation (U1), half manganese (II) ion (Mn1), two coordinated water molecules, and one fully deprotonated sulfophosphonate ligand (L²⁻), suggesting a formula of [UO₂Mn(L)₂(H₂O)₄] (Fig. 1). U1 and Mn1 are located at special positions at 0.25, 0.466 956, 0.5, and 0.25, -0.25, 0.25, respectively. The uranyl cation is connected by four symmetry-related phosphonate oxygen atoms (O4 and O5) with the U—O bond lengths in a range of 0.225 4(3) - 0.229 8(3) nm (Table S1) and O-U-O bond angles in a range of 86.31(13)°-96.97(17)° (Table S2), which are comparable with other reported uranyl compounds^[26-28]. The manganese ion is octahedrally coordinated by four symmetry-related water molecules (O1w and O2w) and two symmetry-related phosphonate oxygen atoms (O3) with the Mn-O bond lengths in a range of 0.212 9(3)-0.218 4(4) nm. As for the sulfophosphonate ligand, the sulfonyl group is not involved in the coordination, whereas the phosphonate group is fully deprotonated and connects two uranyl cations and one manganese ion. These uranyl cations and manganese ions are connected by these sulfophosphonate ligands into a 2D layered crystal structure parallel to the *bc*-plane (Fig. 2a) with the phenyl groups dangling on both sides. $\pi \cdots \pi$ stacking interactions are formed between the phenyl rings of the sulfophosphonate ligands (6-membered π plane: C1-C2-C3-C4-C5-C6, centroid coordinates: -0.038 14, 1.068 22, 1.398 20; distance between ring centroids: 0.456 69 and 0.558 51 nm; dihedral angle: 0°) (Table S3). Additionally, O- $H\cdots \pi$ (Table S4) and hydrogen bonds (Table S5) are



Thermal ellipsoids are given at 30% probability; Symmetry codes: A: 0.5-x, y, 1-z; B: x, 1+y, z; C: 0.5-x, 1+y, 1-z; D: 0.5-*x*, -0.5-*y*, 0.5-*z*; E: *x*, -1+*y*, *z*

Fig.1 Coordination environments of the metal centers and phosphonate ligand in compound 1



 UO_6 , MnO_6 , and CPO_3 polyhedrons are shaded in yellow, pink, and cyan, respectively; The $\pi \cdots \pi$ interactions are shown as green dotted lines; Symmetry codes: A: 0.5-*x*, *y*, 1-*z*; B: *x*, 1+*y*, *z*; C: 0.5-*x*, 1+*y*, 1-*z*; D: 0.5-*x*, -0.5-*y*, 0.5-*z*; E: *x*, -1+*y*, *z*

Fig.2 Two-dimensional layer parallel to bc-plane (a) and 3D supramolecular structure (b) of compound 1 viewed along the b-axis

also formed between the sulfophosphonate ligands and the water molecules. These weak interactions further assemble these layers into a 3D supramolecular structure (Fig.2b).

2.3 Thermal stability

The TGA curves of compounds 1-5 were similar which is expected for isostructural compounds. Taking compound **1** as an example, the TGA curve showed two consecutive weight losses in a temperature range of 50-800 °C (Fig. 3). The first weight loss was about 8.3%, occurring in a temperature range of 80-160 °C and corresponds to the removal of coordinated water molecules (Calcd. 8.3%). There was a plateau before 400 °C, then compound **1** lost weight dramatically until 485 °C, suggesting the decomposition of the compound.



Fig.3 TGA curves of compounds 1-5

2.4 Spectroscopy

The FT-IR spectra of compounds **1-5** are shown in Fig. S6. At the low wavenumber region, the O—P—O

bending and C—P stretching vibration bands could be found at 685 and 725 cm⁻¹, respectively. In a range of 900-1 200 cm⁻¹, a series of characteristic absorption peaks could also be observed, indicating the existence of phosphonate groups. The strong peaks at 1 157 and 1 087 cm⁻¹ correspond to the stretching vibration bands of P=O and P—O bonds, whereas the peak around 1 020 cm⁻¹ can be ascribed to the P—O—M vibrations, suggesting the coordination of phosphonate groups to the metal centers.

The solid-state UV-Vis absorption spectra of compounds 1-5 were recorded on the powdered crystalline samples (Fig. 4). The strong broad bands in a range of 200-350 nm can be assigned to the intraligand $\pi \rightarrow \pi^*$ transitions or ligand to metal charge transfer^[29], whereas the weak bands in a range of 385-550 nm correspond to the vibrational and electronic transitions^[30].



Fig.4 Solid-state UV-Vis adsorption spectra of compounds 1-5

Uranyl-bearing compounds have interesting photophysical properties. They usually show characteristic emissions in the green region. The fluorescence properties of compounds 1-5 were investigated at room temperature on the powdery samples by exciting at 365 nm. As shown in Fig.5, compounds 1-3 were not fluorescent, and the characteristic emissions originated from the electronic and vibronic coupling between S_{11} - S_{00} and S_{10} - S_{0i} transitions $(j=0-4)^{[31-32]}$ were absent, indicating their fluorescence is almost totally quenched by the incorporated transition metals, probably due to the special electronic configurations of these transition metals (Mn(II): d^5 , Co(II): d^7 , Ni(II): d^8) which may have energy transfer to the d - d excited state and provide non - radiation energy transfer pathways^[33]. Different from compounds 1-3, strong emission peaks could be found for compounds 4 and 5 because Zn(II) and Cd(II) ions have d^{10} electronic configuration and $d \cdot d$ transitions cannot occur. For compound 4, four prominent peaks appeared at about 510, 532, 556, and 582 nm showing an obvious red shift (25 nm) compared with the benchmark UO₂(NO₃)₂·6H₂O. Four well - resolved emission peaks could be found at about 498, 520, 544, 570, and 599 nm in the emission spectrum of compound 5, which were about 13 nm red-shifted compared with $UO_2(NO_3)_2 \cdot 6H_2O$.



Fig.5 Solid-state emission spectra of compounds 1-5

3 Conclusions

In this work, a series of 3d-5f heterometallic uranyl sulfophosphonates have been hydrothermally synthesized from a sulfophosphonate ester ligand, diethyl ((phenylsulfonyl)methyl)phosphonate (Et₂L). Et₂L hydrolyzes during the hydrothermal reactions and functions as tridentate linking ligands, leading to the formation of 2D layered crystal structures. The sulfonyl group is not involved in the coordination with the metal centers but forms weak interactions with neighboring ligands. It is found that the incorporation of Mn (II), Co(II), and Ni(II) ions can lead to luminescence quenching whereas Zn(II) and Cd(II) can contribute to the luminescence.

Supporting information is available at http://www.wjhxxb.cn

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