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Unexpected cis-dioxido uranyl carboxylate compound: Synthesis, characterization and photocatalytic activity of uranyl-succinate complexes

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ABSTRACT

Two new complexes formed by uranyl ions with succinic acid and 4,4′-dipyridine have been investigated. Interestingly, the uranium(VI) coordination polymers possess two types dioxido unit, a cis-dioxido bond angle with 115.421(2)°and a trans-dioxido bond angle with 178.421(2)°, respectively. The complexes were characterized by elemental analysis, IR and UV–vis spectroscopy and X-ray crystal diffraction. In addition, the properties of luminescence and photocatalytic analysis were also investigated. The result revealed that the two complexes show different photocatalytic activity in the decomposition of RhB under visible light and UV light irradiation.

Uranium is a potentially carcinogenic metal of growing importance, especially with the increased use of depleted uranium in munitions and armor plating by the military [1]. In the meantime, it may also lead to internal contamination of people worldwide by various compounds of uranium through alpha particle decay [2]. This constitutes an occupational risk and has led to questions about its potential health effects since contamination with uranium compounds may induce radiological and chemical toxicity [3].

Nowadays, the class of uranyl polycarboxylate has been developed as an important member of the uranium organic coordination polymer family due to their fantastic structural diversities and excellent physicochemical properties in potential applications of ion exchange [4,5], proton conductivity [6], chiral materials [7], and materials [8,9].

This field has aroused great interest with increasingly attractive structural architectures resulting from various coordination modes of the uranium atom and the modification of the organic residues of polycarboxylate [10–12]. For these uranyl polycarboxylates, the template species (H_3O^+, NH_4^+, metalions, organic linkers etc.), dimensions, configurations, and the coordination abilities play important roles in structure directing for constructing new structures.

However, the aim of obtaining desirable architectures and functional properties of coordination polymers constructed by organic ligands and uranyl ions is still a long-term challenge to chemists due to the difficult prediction of either the compositions or the structures and properties of the reaction products. Therefore, it is necessary to (i) explore the fundamental chemistry of 5f-elements [13], reactivity and coordination behavior; (ii) understand the bonding interactions between the metal center and ligand (ionic or covalent bonding); (iii) explore possible applications of new complexes, such as in catalysis or as sensors, molecular adsorption, separation, drug delivery. From the chemical point of view, a large number of studies have reported the reactivity of organic polycarboxylates with uranium [14–16], since its crystal chemistry reveals a wide variety of coordination states, which give rise to a large diversity of topologies. In this course, uranium was found to be a good candidate element for the generation of mixed organic–inorganic extended networks [17]. When it is associated with multidentate O-donor ligands, such as carboxylate-based solids, uranium (especially with oxidation state VI) exhibits an interesting chemical ability to successfully form a wide variety of frameworks showing different dimensionalities. In case of uranyl cation UO_2^{2+}, the possible coordination environments (4 + 2, square bipyramid; 5 + 2, pentagonal bipyramid; 6 + 2, hexagonal bipyramid) also contribute to the richness of the structural topologies of such solids. The so-called uranyl – organic frameworks (UOF) have now been described in many contributions with the use of a large range of organic aliphatic or aromatic carboxylates [18]. The $[O = U = O]^{2+}$ moiety is typically unreactive and terminates bonding along the axial plane, resulting in the widely recognized two-dimensional sheets of uranyl polyhedra. The coordination chemistry of $[O = U = O]^{2+}$ is the most developed of the actinides, and the vast majority of complexes and solids exhibit the UO_2^{2+} uranyl ion.

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In some UO_2^{2+} uranyl complexes, it was found that there was cation–cation interaction (CCI) [19,20] through the oxo group and the two terminal oxygen atoms located in trans-position, which is an important feature in the chemistry of 5f elements. On the other hand, carboxylates and polycarboxylates are particularly suited for uranyl complexation [6], and they are very commonly used in this field. Among them, the simplest of these ligands is the linear, aliphatic dicarboxylates of the general formula $[OOC–(CH_2)_n–COO]^{2-}$, where Cn is denoted in the following. The coordination polymers formed by uranyl ions with malonate (C3), succinate (C4), glutarate (C5), adipate (C6), pimelate (C7), suberate (C8), azelate(C9), and sebacate (C10) have been frequently investigated [7–9], and compared with lanthanide ion complexes. Some one- to three-dimensional uranyl-organic assemblies were isolated, and the effect of additional N-heterocyclic small molecules, which can assume the different roles of ligand or structure-directing species, was also examined. But, we have found that two terminal oxygen atoms of UO_2^{2+} uranyl structures are both in trans-position (O = U = O). More recently, during an investigation of succinate (C4) as a ligand for uranyl ions, it is worthy to note that we have obtained two types of uranyl ions: one is trans-dioxido unit succ complex and the other one is cis-dioxido unit succinate complex, which is not reserved in common uranyl complexes so far. In particular, the discovery of the unexpected cis-dioxido uranyl compound is an exciting event and a milestone in the history of actinide chemistry. Although actinide is situated beneath the lanthanides within the f block of the periodic table, the lighter members of the actinide series (that is, Th–Am) retain a closer affinity in the ability to access higher formal oxidation states and engage in metal–ligand multiple bonding. These chemical properties are perhaps best exemplified by the dioxide cations MO_2^{n+} (n = 1, 2), which represent a group of considerable environmental importance for the actinides [21].

However, while the geometry of the dioxido unit (Fig. 1) in transition-metal complexes is highly dependent on the valence-electron count, this electronic distinction is not observed with the actinides, where, regardless of oxidation state or valence-electron count, the dioxido group always adopts a linear (trans) geometry, which imparts unique chemical behavior. Herein we describe the structures and spectroscopic characterization of the carboxylate-bridged uranium (VI) coordination polymers, $[(UO_2)(suc)(H_2O)]$ (1) and $[(UO_2)(suc)_{1.5}] \cdot (4,4'\text{-bipy})_{0.5} \cdot (suc)_{0.5} \cdot 3H_2O$ (2), in which complex 1 possesses a bent (cis) dioxido unit with an extraordinarily acute (115.421(2)°) bond angle and complex 2 is a trans-dioxido unit with an extraordinarily acute (178.421(2)°). The corresponding two uranyl (VI) complexes 1 and 2 were prepared by the reaction of $[UO_2(CH_3COO)_2]$ and succinate ligands in the system of aqueous at 100 °C [22]. The two complexes were fully characterized by elemental analysis, IR spectra, UV–vis spectroscopy, single-crystal X-ray diffraction, thermogravimetric analysis, luminescence and photocatalytic analysis.

X-ray single crystal analysis [23] indicates that complex 1 is crystallizing in orthorhombic, space group Ama2. The molecular structure contains one uranium atom, two terminal oxygen atoms, one succinate ligand, and one coordinated water molecule. The uranium (Fig. 2a) atom was seven-coordinated by two terminal oxygen atoms (O1, $O1^{\#}$ from uranyl unit, #1 = 0.5-x, y, z) with O = U = O angle of 115.421(2)° and bond length of 1.754(9)Å, four oxygen atoms (O3, $O3^{\#}$, O4, $O4^{\#}$) from the carboxyl group of four succinate ligands, respectively, with the corresponding bond distances in the range of 2.382(8)Å to 2.404(7) Å and one oxygen atom (O2) of from a water molecule with the bond length of 2.446(12)Å, forming a monocapped trigonal prismic geometry. The O = U = O bond angle is variously smaller from 178(1)° in $UO_2(CH_2COO)_2 \cdot H_2O$ (3) [24] and 178.4(4)° in $[UO_2(C_4H_4O_4)] \cdot H_2O$ (4) [25]. While, the bond length of U = O is slightly bigger than 1.74(2)Å of 3 [24] and 1.73(1)Å and 1.750(9)Å of 4 [25]. The adjacent uranium polyhedra were linked by two oxygen atoms from one carboxyl group of succinate acid ligand to form one-dimensional chain (Fig. 2b). These chains were linked by carbon atom of succinate acid ligand to form a two-dimensional layer (Fig. 2c). Furthermore, the three-dimensional network is formed by the bridging of the 2D layer through bidentate succinate groups (Fig. 2d). There is a kind of hydrogen bond in complex 1: O2–H2C---$O4^{\#1}$ (#1 = 1/2 − x, −1/2 + y, −1/2 + z), which enhance the molecular structural stability.

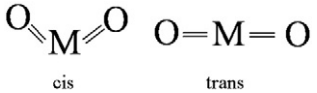

Fig. 1. Dioxido geometries of MO_2^{n+} complexes.

Structural analysis shows that complex 2 is crystallizing in monoclinic, space group C2/c. The molecular structure of complex 2 consist of one uranium atom, two terminal oxygen atoms, one and a half succinate ligand, half a lattice 4,4′-bipy molecule, half a lattice succinate acid molecular and three lattice water molecules. The uranium (Fig. 3a) atom was eight-coordinated by two oxygen atoms (O1, O2 from uranyl unit) with O = U = O angle of 178.942(6)° and U–O bond length in the range of 1.760(4) Å to 1.769(4) Å and six oxygen atoms (O3–O8) from the carboxyl group of three succinate ligands with the bond distances in the range of 2.443(4) Å to 2.470(4) Å, forming a hexagonal bipyramid. The adjacent uranium polyhedra were linked by oxygen atoms from two carboxyl group of succinate acid ligand to form an infinite one-dimensional chain (Fig. S4a). The uranium polyhedra form a layer in ab plane by the dicarboxylate group (Fig. S4b). There are two kinds of hydrogen bonds in complex 2: (i) hydrogen bond (O–H---O) between the oxygen (donor) and oxygen (acceptor); (ii) hydrogen bonds (C–H---O) of carbon (donor) and the oxygen (acceptor). The two adjacent layers were connected to form a 3D network supermolecular structure (Fig. S4) by the hydrogen bond of C6–H6A---O2.The interlayer region includes lattice 4,4′-dipy and water molecules which are connected also by the hydrogen bonds (Fig. 3b).

The structural analysis indicates that the complexes 1 and 2 contain different geometries of uranyl moiety, 1 is a cis-dioxo uranyl moiety (O = U = O band angle of 115.421(2)°) and bond length of 1.754(9)Å. The complex 2 is a trans-dioxido unit (O = U = O band angle of 178.942(6)°). Although the synthesis method is similar, the obtained results are different. And the particularly easy and reversible formation of this coordination polymeric product from uranyl acetate and succinate acid, occurring at 100 °C is comparable to those found in many uranyl(VI) complexes. It is surprising to find that the O–U–O angle (115.421(2)°) of complex 1 is much more than that reported ($[UO_2(fcdc)(thf) \cdot (Fc)]_n$, fcdc = 1,2-ferrocenedicarboxylate, Fc = ferrocene) by Duval et al.(70.8°), which was considerably the smallest than the O–M–O angles in cis-dioxido transition metal complexes, to be associated with U–O distances equal to those in trans-uranyl complexes. However, the result reported by Duval et al. is not confirmed furthermore so far and it failed to reproduce the product [21,26]. So, we think that the O–U–O angle (115.421(2)°) of the complex 1 should be more reasonable and reproducible.

It is worthy to note that in the synthetic process of complex 1, we introduced lanthanide element (Ln) and urea or thiourea to the reaction system, however, the reaction result did not contain the species, unexpectedly, a cis-dioxido uranyl succinate complex (1) was obtained. If in the reaction system, reagent of lanthanide element (Ln) and urea or thiourea was not added, reaction result is the same as that of reported in literature [24,25], namely, trans-dioxido uranyl succinate complex. So, we have thought that reagent of lanthanide element (Ln) and urea or thiourea plays important role probably in the directional synthesis course.

Fluorescence of uranyl complexes typically has a characteristic of six peak spectrum relating to the $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0\nu}$, where ν = 0–4, electronic transitions [27], and the most intense peak (S10 → S00) is positioned at 511 nm for $UO_2(CH_3COO)_2 \cdot 2H_2O$. Comparison of the