



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



Preliminary communication/Communication

Unusual case of a polar copper(II) uranyl phosphonate that fluoresces

Anna-Gay D. Nelson, Thomas E. Albrecht-Schmitt*

Department of Civil Engineering and Geological Sciences and Department of Chemistry and Biochemistry, 156 Fitzpatrick Hall, University of Notre Dame, Notre Dame, Indiana 46556, USA

ARTICLE INFO

Article history:

Received 4 December 2009

Accepted after revision 16 March 2010

Available online 5 May 2010

Keywords:

Uranyl

Noncentrosymmetric

Fluorescence

Phosphonate

ABSTRACT

A polar Cu(II) uranyl diphosphonate, $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$, has been prepared under mild hydrothermal conditions. This compound has direct linkages between the oxo atoms of the uranyl moieties and the Cu(II) centers. Despite the presence of Cu(II) in the structure, vibronically-coupled emission is still observed, most likely because there are two crystallographically unique uranyl moieties, only one of which bonds to Cu(II).

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

The structural chemistry of U(VI) is dominated by the formation of an uranyl, UO_2^{2+} , cation, and subsequent ligation of this moiety by four to six donor atoms yielding tetragonal, pentagonal, and hexagonal bipyramids [1]. The UO_7 pentagonal bipyramidal geometry is the most common of these, occurring in approximately 85% of known uranyl structures [2]. At first glance, one might think that because a pentagon cannot be placed on an inversion center without subsequent disorder, many uranyl compounds will adopt noncentrosymmetric structures. This is not the case. The linear nature of the uranyl cations allows these units to be crystallographically related through nearby inversion centers without placing them directly on one. This can be easily visualized by edge-sharing two UO_7 units, and placing an inversion center in the center of the edge that is shared. Methods that might induce the adoption of acentric structures, such as the incorporation of anions with a stereochemically-active lone pair of electrons, typically fail. For example, approximately 60% of typical inorganic compounds with such polar anions are noncentrosymmetric [3], whereas this

number falls to approximately 3% when the compounds contain an uranyl unit [4]. Nevertheless, rare noncentrosymmetric, or more specifically, polar, structures have been found in diverse uranyl compounds such as $\text{K}_2[(\text{UO}_2)_2(\text{VO})_2(\text{IO}_6)_2\text{O}] \cdot \text{H}_2\text{O}$ [5], $[\text{NH}_4]_4[(\text{UO}_2)_5(\text{MoO}_4)_7] \cdot 5\text{H}_2\text{O}$ [6], and $\text{Cs}(\text{UO}_2)\text{F}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ [7].

A second feature of the uranyl unit that has long been of interest is its luminescence [8]. The majority of uranyl compounds exhibit charge-transfer vibronically-coupled emission at room temperature. This emission, however, can be quenched in ways that are not always well-understood. For example, large variances in the luminescent properties of two closely related uranyl phosphonates, $[\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ and $\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$, were reported [9]. While not quenching in a formal sense, the addition of Cu(II) also normally eliminates emission from uranyl, because the emission overlaps directly with the d-d absorption band of Cu(II) leading to energy-transfer followed by non-radiative decay [10]. Herein we disclose the details of an unusual Cu(II) uranyl phosphonate that both crystallizes in a polar space group, and fluoresces despite the presence of Cu(II).

Clusters of large green crystals of $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$ (**1**) can be grown from common

* Corresponding author.

E-mail address: talbrecl@nd.edu (T.E. Albrecht-Schmitt).

starting materials under mild hydrothermal conditions.¹ Single crystal X-ray diffraction experiments reveal that the compound crystallizes in the polar tetragonal space group $P4bm$ (crystal class 4mm).² These data yield a layered structure constructed from two crystallographically unique uranyl units, one of which is bound by four oxygen atoms from the methylenediphosphonate anion to yield a tetragonal bipyramidal geometry. The second uranyl moiety is also bound by four oxygen atoms from the methylenediphosphonate anion, but also has a fifth atom in its equatorial plane from a coordinating water molecule creating a pentagonal bipyramidal environment. The bridging of the uranyl cations by the methylenediphosphonate anions creates layers that extend in the $[ab]$ plane as shown in Fig. 1a. Hydrated Cu(II) cations are directly bound to the layers via the “yl” oxo atoms of the UO_6 units as depicted in Fig. 1b. The polarity of the structure, which is along the c axis, is best identified by viewing both the coordination around Cu(II), which is asymmetric (*vide infra*), and the methylene units that are all located on one side of the layers.

The important bonding metrics for this compound center around the uranium polyhedra. The UO_6 unit possesses two short $\text{U}=\text{O}$ bonds with distances of 1.776(14) and 1.796(12) Å making up the uranyl core. The uranium atom resides on a four-fold site yielding one unique equatorial $\text{U}-\text{O}$ bond of 2.273(4) Å ($\times 4$). The formal oxidation state of the uranium is +6 with a bond-valence sum of 5.94 [11]. The uranyl core of the UO_7 units has $\text{U}=\text{O}$ bond distances of 1.754(10) and 1.764(10) Å, with the remaining five $\text{U}-\text{O}$ bonds in equatorial plane ranging from 2.319(4) to 2.696(3) Å. Again the formal oxidation state of the uranyl center is +6 with a bond-valence sum of 6.08 [11]. As can be seen in Fig. 1a, the UO_7 polyhedra share a corner. This corner is a rare example of a bridging water molecule. Typical $\text{U}-\text{O}$ bonds with water are on the order of 2.5 Å [12]. The bridging nature of this water molecule lengthens this interaction by an additional 0.2 Å.

The $\text{Cu}-\text{O}$ bonds vary dramatically as expected for a Jahn-Teller ion, particularly one with weakly bound

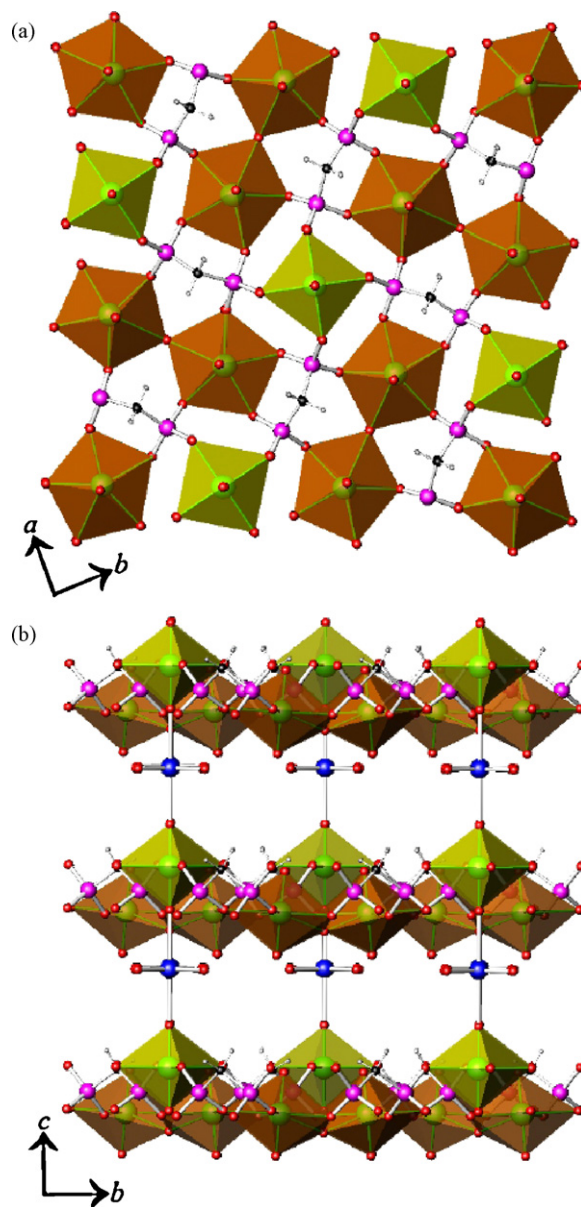


Fig. 1. (a) A view of the $\infty \{(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2\}^{2-}$ layers in $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$ in the $[ab]$ plane showing UO_6 (yellow) and UO_7 (orange) building units linked by methylenediphosphonate anions. (b) A depiction of the stacking of the layers with interlayer $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ cations bound directly to the uranyl oxo atoms of the UO_6 units. Cu = blue.

ligands along z . The four equatorial bond distances to water that yield a square plane are at 1.960(5) Å ($\times 4$). The axial distances to the uranyl oxo atoms are asymmetric at 2.350(14) and 2.471(14) Å. It should be noted that the z axis of the CuO_6 distorted octahedron is aligned along the polar c axis of the structure.

During the X-ray diffraction data collection, a total of 847 Friedel pairs were collected, and these data suggest a noncentrosymmetric space group. Furthermore, we were unable to find a reasonable solution in a centrosymmetric setting. The polarity of the structure can be viewed in

¹ $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$ was prepared by loading $[\text{UO}_2]$ (0.292 g, 1.019 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.241 g, 1.037 mmol), methylenediphosphonic acid (0.178 g, 1.011 mmol), and 2 mL of Millipore filtered water in a 23 mL PTFE-lined autoclave. The autoclave was heated at 200 °C for 3 days and then cooled to room temperature at 9 °C/hr. Clusters of green block crystals of $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$ were isolated, washed with methanol, and then allowed to dry. Yield 83.3 mg, (18% yield based on U). The crystals are large enough that they can be manually isolated leading to a pure sample.

² X-ray structural analyses: $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$: green block, tetragonal, $P4bm$, $Z=2$, $a=12.8681(8)$, $b=12.8681(8)$, $c=8.3935(5)$ Å, $V=1389.86(12)$ Å³ ($T=193$ K), $\mu=185.18$ cm⁻¹, $R_1=0.0251$, $wR_2=0.0578$. Bruker APEX CCD diffractometer: $\theta_{\text{max}}=28.29^\circ$, $\text{MoK}\alpha$, $\lambda=0.71073$ Å, 0.3° ω scans, 11929 reflections measured, 1579 independent reflections, all of which were included in the refinement. The data were corrected for Lorentz-polarization effects and for absorption, solution was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 92 parameters. Flack parameter: 0.016(11). b) Sheldrick, G. M. SHELXTL PC, Version 6.12, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI 2001.

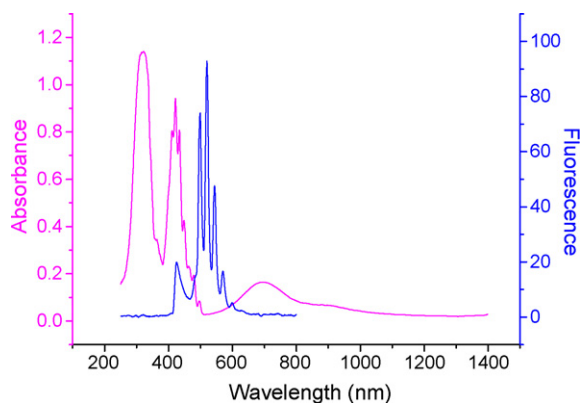


Fig. 2. Absorption and emission spectra of $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$ showing the charge-transfer vibronically-coupled features.

Fig. 1b. The CuO_6 octahedra are distorted along the polar c axis (*vide supra*), but more obviously the UO_6 units lie in a different plane than the UO_7 units, and they are all disposed on the same side of each layer.

The absorption and fluorescence spectra of this compound are shown in Fig. 2. These data were acquired from a single crystal using a UV-vis-NIR microspectrophotometer with a fluorescence attachment.³ The key absorption feature of the uranyl cations is centered at 421 nm, the most intense emission feature is at 519 nm. Vibronic fine structure is clearly defined. Broader absorption bands are also found at longer wavelengths (681 and 833 nm). These features are ascribed to d-d transitions from the Cu(II) ions. It should be noted that there is some overlaps between the edge of the absorption band at 592 nm and the emission from uranyl. However, the overlap is not sufficient to allow for complete energy transfer to the d-d band, and fluoresce is still observed. One explanation that might account for the emission from this compound is that the UO_6 units that are directly bound to the Cu(II) centers do not emit whereas the UO_7 units,

which are not bound to Cu(II), might be responsible for the observed emission.

In conclusion, $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$ represents an example of an uranyl compound that fluoresces despite the presence of Cu(II) in the compound. Cu(II) is known to quench fluorescence through both energy-transfer and paramagnetic quenching. This compound is also a rare example of a polar uranyl compound that is constructed from building units that could have quite easily yielded a centrosymmetric structure given the linear nature of the uranyl units.

Supporting information available

X-ray crystallographic files for $\text{Cu}(\text{H}_2\text{O})_4(\text{UO}_2)_3(\text{H}_2\text{O})_2[\text{CH}_2(\text{PO}_3)_2]_2 \cdot 5\text{H}_2\text{O}$.

Acknowledgements

We are grateful for support provided by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Heavy Elements Program, U.S. Department of Energy, under grants DE-FG02-01ER15187 and DE-FG02-01ER16026.

References

- [1] P.C. Burns, *Can. Mineral.* 43 (2005) 1839.
- [2] P.C. Burns, M.L. Miller, R.C. Ewing, *Can. Mineral.* 34 (1996) 845.
- [3] P.S. Halasyamani, K.R. Poeppelmeier, *Chem. Mater.* 10 (1998) 2753.
- [4] R.E. Sykora, T.Y. Shvareva, T.E. Albrecht-Schmitt, *Structural Chemistry of Inorganic Actinide Compounds*, Elsevier, 2007.
- [5] R.E. Sykora, T.E. Albrecht-Schmitt, *Inorg. Chem.* 47 (2003) 2179.
- [6] S.V. Krivovichev, C.L. Cahill, P.C. Burns, *Inorg. Chem.* 42 (2003) 2459.
- [7] K.M. Ok, J. Baek, P.S. Halasyamani, *Inorg. Chem.* 45 (2006) 10207.
- [8] R.G. Denning, J.O.W. Norris, I.G. Short, T.R. Snellgrove, D.R. Woodwark, *Lanthanide and Actinide Chemistry and Spectroscopy (ACS Symp. Ser. no. 131)*, in: N.M. Edelstein (Ed.), Ch. 15, American Chemical Society, Washington, DC, 1980.
- [9] D. Grohol, A. Clearfield, *J. Am. Chem. Soc.* 119 (1997) 4662.
- [10] M. Frisch, C.L. Cahill, *Dalton Trans.* (2005) 1518.
- [11] P.C. Burns, R.C. Ewing, F.C. Hawthorne, *Can. Mineral.* 35 (1997) 1551.
- [12] A.C. Bean, S.M. Peper, T.E. Albrecht-Schmitt, *Chem. Mater.* 13 (2001) 1266.

³ UV-vis-NIR data were acquired from a single crystal using a Craic Technologies UV-vis-NIR microspectrophotometer with a fluorescence attachment. Excitation was achieved with 365 nm light.