Inorg. Chem. **2006**, *45*, 1168–1172

Inorganic Chemistry

Article

Structure of an $I^{-}\cdot(H_2O)_6$ Anion Cluster in a 3D Anion Crystal Host $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$

Wen Dong,[†,‡] Yan Ou-Yang,[†] Hai-Bin Song,[†] Dai-Zheng Liao,*[,†] Zong-Hui Jiang,[†] Shi-Ping Yan,[†] and Peng Cheng[†]

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China, and
Department of Chemistry, Guangzhou University, Guangzhou, 510045, People's Republic of China

Received September 26, 2005

A planar structure of an anion cluster $I^{-}\cdot(H_2O)_6$ in a 3D supramolecular complex $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$ has been determined by single-crystal X-ray analysis. In the supramolecule, the anion cluster $I^{-}\cdot(H_2O)_6$, together with the anion $[Fe(CN)_6\cdot H_2O]^{2-}$, acts as a 3D crystal host, and the $[Ru(bpy)_3]^{2+}$ cations, as the guest molecules, occupy the vacancies of the 3D host framework. This is the first crystal example of the anion cluster $I^{-}\cdot(H_2O)_6$.

Introduction

It is not surpising how much scientific attention has been paid to the apparently simple water molecule.[1] Water is of fundamental importantance for human life and plays a very important role in many biological and chemical processes.[2−6] The water molecule exhibits an enormous complexity of interactions with other molecules, including other water molecules.[1−6] Structural information of small water clusters is the first step toward understanding the behavor of bulk water.[7] In the past decade, various hydrogen-bonded water or ice clusters of $(H_2O)_n$ ($n = 3-18$) and 1D−3D water polymers in different supramolecular systems have been extensively investigated both experimentally and theoretically.[8−21] In recent years, the anion water clusters of $X^{-}\cdot(H_2O)_n$ ($X = F^{-}, Cl^{-}, Br^{-}, I^{-}, OH^{-}$, $n = 1-6$) have also been an important subject of interest in both solution chemistry and biochemistry.[22−28] The anion water clusters of $X^{-}\cdot(H_2O)_n$ have also been extensively investigated both experimentally and theoretically due to their suitable simplified model systems for aerosol study and molecular recognition study to design the X receptors.[29,30] The $X^{-}\cdot(H_2O)_n$ cluster shows a clear distinction from that of alkali metal

---

* To whom correspondence should be addressed. Fax: +86-22-23502779. E-mail: coord@nankai.edu.cn.

† Nankai University.

‡ Guangzhou University.

(1) Soper, A. K. *Science* **2002**, *297*, 1288.
(2) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808.
(3) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501.
(4) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671.
(5) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293.
(6) Ugalde, J. M.; Alkorta, I.; Elguero, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 717.
(7) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1374.
(8) Gregory, J. K.; Clary, D. C.; Liu, K.; Brown M. G.; Saykally, R. J. *Science* **1997**, *275*, 814.
(9) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.
(10) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192.
(11) Blanton, W. B.; Gordon-Wylie, S. W.; Clark, G. R.; Jordan, K. D.; Wood, J. T.; Geiser U.; Collins, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3551.
(12) Gruenloh, C. J.; Carney, J. R.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Jordan, K. D. *Science* **1997**, *276*, 1678.
(13) Matsumoto, M.; Saito, S.; Ohmine, I. *Nature* **2002**, *416*, 409.
(14) Koga, K.; Gao, G. T.; Tanaka, H.; Zeng, X. C. *Nature* **2001**, *412*, 802.
(15) Luzar, A.; Chandler, D. *Nature* **1996**, 379, 55.
(16) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094.
(17) Park, K.-M.; Kuroda, R.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 884.
(18) Janiak, C.; Scharmann, T. G. *J. Am. Chem. Soc.* **2002**, *124*, 14010.
(19) Pal, S.; Sankaran, N. B.; Sananta, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1741.
(20) Raghuraman, K.; Katti, K. K.; Barbour, L. J.; Pillarsetty, N.; Barnes, C. L.; Katti, K. V. *J. Am. Chem. Soc.* **2003**, *125*, 6955.
(21) (a) Kim, K. S.; Dupuis, M.; Lie, G. C.; Clementi, E. *Chem. Phys. Lett.* **1986,** *131*, 451. (b) Lee, H. M.; Suh, S. B.; Lee, J. Y.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys*, **2000**, *112*, 9759.
(22) Marcus, Y. *Ion Solvation*; Wiley-Interscience: New York, 1985. Kirk, K. L. *Biochemistry of Halogens and Inorganic Halides*; Plenum: NewYork, 1991. *Chemisensors of Ion and Molecular Recognition*; Desevergne, J.-P., Czarnik, A. W., Eds.; NATO Series, Series C; Kluwer Academic: Dordrecht, The Netherlands, 1997; Vol. 492. Coe, J. V. *Int. Rev. Phys. Chem.* **2001** *20*, 33.
(23) Tuckerman, M. E.; Marx, D.; Parrinello, M. *Nature* **2002**, *417*, 925.
(24) Bakker, H. J.; Nienhuys, H.-K. *Science* **2002**, *297*, 587.
(25) Chen, B.; Park, J. M.; Iavnov, I.; Tabacchi, G.; Klein, M. L.; Parrinello, M. *J. Am. Chem. Soc.* **2002**, *124*, 8534.
(26) Baik, J.; Kim, J.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9116.
(27) Lehr, L.; Zanni, M. T.; Frischkorn, C.; Weinkauf, R.; Neumark, D. M. *Science* **1999**, *284*, 63638.
(28) Robertson, W. H.; Diken, E. G.; Price, E. A.; Shin, J.-W.; Ohnson, M. *Science* **2003**, *299*, 1367.

10.1021/ic051657u CCC: $33.50

ions because the anion hydration tends to favor surface states, while the cation hydration favors internal states.[31−35] The study of the $X^-\cdot(H_2O)_n$ cluster is essential for understanding the solvation and molecular recognition phenomena of the anionic systems.[36] In anion water clusters of $X^-\cdot(H_2O)_n$, the iodine anion water cluster is of particular interest because it has large polarizability and a large ionic radius.[37] Another particularly interesting aspect in the iodine anion water cluster is in the molecular recognition study to design the I receptors. Currently, the hotly discussed topics in halogen hydration are whether the halide is inside the clusters or on their surface and how many water molecules are necessary for its complete solvation.[36] So far, various models for the $I^-\cdot(H_2O)_n$ anion cluster have been theoretically predicted.[36−38] However, precise crystal data for the $I^-\cdot(H_2O)_n$ anion cluster, to our knowledge, are very limited. The key to understanding the behavior of water is precise structural data of various hydrogen-bonded water clusters and water polymers in diverse environments. Thus, studies of small water clusters in crystal hydrates have the ultimate goal(s) of underestanding the role(s) played by small water clusters in stabilization and functioning of biomolecules, as well as in designing of new materials.[39] For this, we report a planar topological structure of an $I^-\cdot(H_2O)_6$ anion cluster in a 3D supramolecular complex $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$.[40]

Experimental Section

X-ray Crystallography and Struction Solution. For the complex $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$, determination of the unit cell and data collection were performed on a Bruker Smart 1000 area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Its structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).[41] Crystal data are given in Table 1.

Table 1. Crystal Data and Structure Refinement for Supramolecular $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$

formula	$C_{66}H_{60}FeIN_{18}O_7Ru$
fw	1602.1
cryst syst	monoclinic
space group	*Cc*
a/Å	12.922(4)
b/Å	23.713(7)
c/Å	21.776(6)
β/°	90.705(5)
V/Å^3	6672(3)
Z	4
D_c/gcm^{-3}	1.597
absorption coeff/ mm^{-1}	1.192
F(000)	3228
θ range/°	1.96−26.43
reflns collected/unique	19 315/11 045 [*R*(int) = 0.0362]
completeness to θ = 24.91	99.7%
absorption correction	semiempirical from equivalents
max and min transmission	1.000000 and 0.828680
refinement method	full-matrix least-squares on F^2
data/restraints/params	11045/2/857
GOF on F^2	1.015
final R indices [$I > 2\sigma(I)$]	R1 = 0.0411, wR2 = 0.0686
R indices (all data)	R1 = 0.0686, wR2 = 0.0768
absolute structure param	0.184(18)
largest diff. peak and hole/e.Å^{-3}	0.505 and −0.511

Physical Measurements. Elemental analyses were carried out using a Perkin-Elmer analyzer model 240. The IR spectra were recorded as KBr disks on a Shimadzu IR-408 infrared spectrophotometer in the 4000−600 cm^{-1} region.

Synthesis. The red crystals of $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$ were obtained by slow diffusion of an aqueous solution of $K_3[Fe(CN)_6]$ into a solution of $[Ru(bpy)_3]I_2\cdot 6H_2O$ dissolved in a mixed solvent of $CH_3CN/CH_3CHOHCH_3$ (5:1) in an H-shaped tube.

Results and Discussion

Figure 1shows the perspective diagram of the $I^-\cdot(H_2O)_6$ anion cluster viewed along the crystallographic *c* axis. The $I^-\cdot(H_2O)_6$ anion cluster does not show a surface structure predicted by theoretical calculation. The I^- anion and $(H_2O)_6$ water molecules are located in a plane. In the anion cluster $I^-\cdot(H_2O)_6$, each I^- anion connects to two water molecules through I···O hydrogen bonds forming a V-shaped structure. The $(H_2O)_6$ water molecules are divided into two groups. One is water monomer ($H_2O(3)$) connected with an I^- anion and a nitrile nitrogen atom through O···I and O···N hydrogen bonds. Other $(H_2O)_5$ water molecules form a pentamer water cluster through O···O hydrogen bonds. In the $(H_2O)_5$ water cluster, five water molecules locate in a plane and do not show a cyclic cluster. Five water molecules show different connected manners. Each O(2) atom connects to the I(1) anion and the O(5) and N(15) atoms through I···O, O···O,

---

(29) Achatz, U.; Fox, B. S.; Beyer, M. K.; Bondybey, V. E. *J. Am. Chem. Soc.* **2001,** *123*, 6151; Fox, B. S.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Phys. Chem. A.* **2000**, *104*, 1147.

(30) Cho, S. J.; Hwang, H. S.; Park, J. M.; Oh, K. S.; Kim, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 485; Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399; Choi H. S.; Kim, K. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 2256; Lee, C.-W.; Jung, E. J.; Lee, S. J.; Ahn, K. H.; Kim, K. S. *J. Org. Chem.* **2000**, *65*, 7225.

(31) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1993**, *99*, 4222. Sremaniak, L. S.; Perera, L.; Berkowitz, M. L. *Chem. Phys. Lett.* **1994**, *218*, 377. Thompson W. H.; Hynes, J. T. *J. Am. Chem. Soc.* **2000**, *122*, 6278. Chen H. Y.; Shen, W.-S. *Chem. Phys. Lett.* **2001**, *335*, 475.

(32) Combariza, J. E.; Kestner, N. R.; Jortner, J. *J. Chem. Phys.* **1994**, *100*, 2851.

(33) Kim, J.; Lee, H.M.; Suh, S. B.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **2000**, *113*, 5259.

(34) Lee, H. M.; Kim, K. S. *J. Chem. Phys.* **2001**, *114*, 4461.

(35) Perera, L; Berkowitz, M. L. *J. Chem. Phys.* **1991**, *95*, 1954. Caldwell, J.; Dang, L. X.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 9144−1990. Lee, H. M.; Kim, J.; Lee, S.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1999**, *111*, 3995.

(36) Lee, H. M.; Kim, D.; Kim, K. S. *J. Phys. Chem.* **2002**, *116*, 5509.

(37) Lee, H. M.; Kim, D.; Kim, K. S. *J. Phys. Chem.* **2001**, *114*, 4461.

(38) Achatz, U.; Fox, B. S.; Beyer, M. K.; Bondybey, V. E. *J. Am. Chem. Soc.* **2001**, *123*, 6151

(39) Joannopoulous, J. D. *Nature* **2001**, *414*, 257.

(40) Crystal data for supramolecular $[Ru(bpy)_3]_2[Fe(CN)_6][I]\cdot 7H_2O$, M_r = 1604.23, *T* = 293 K, monoclinic, space group *Cc*, *a* = 11.178(3) Å, *b* = 14.824(4) Å, *c* = 23.166(6) Å, β= 91.429(5)°, α = 90°, *V* = 6672(3)Å^3, *Z* = 4, ρ = 1.597 Mg m^{-3}, μ(Mo Kα) = 1.192 mm^{-1}, *F*(000) = 3228, R1 = 0.0411 (11 045 obsvd). Though the supramolecular data were reported in our previous paper (Dong, W.; Liao, D.-Z. *J. Coord. Chem.* **2003**, 531), the crystal structures of the $I^-\cdot(H_2O)_6$ anion cluster and the 3D host framework $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$ have been not previously found and discussed. The good crystal of supramolecular $[Ru(bpy)_3]_2[Fe(CN)_6][I]\cdot 7H_2O$ was prepared and characterized by X-ray crystallography again.

(41) (a) Sheldrick, G. M. *SHELXS-97, Program for solution of crystal structures*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M *SHELXL-97, Program for refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

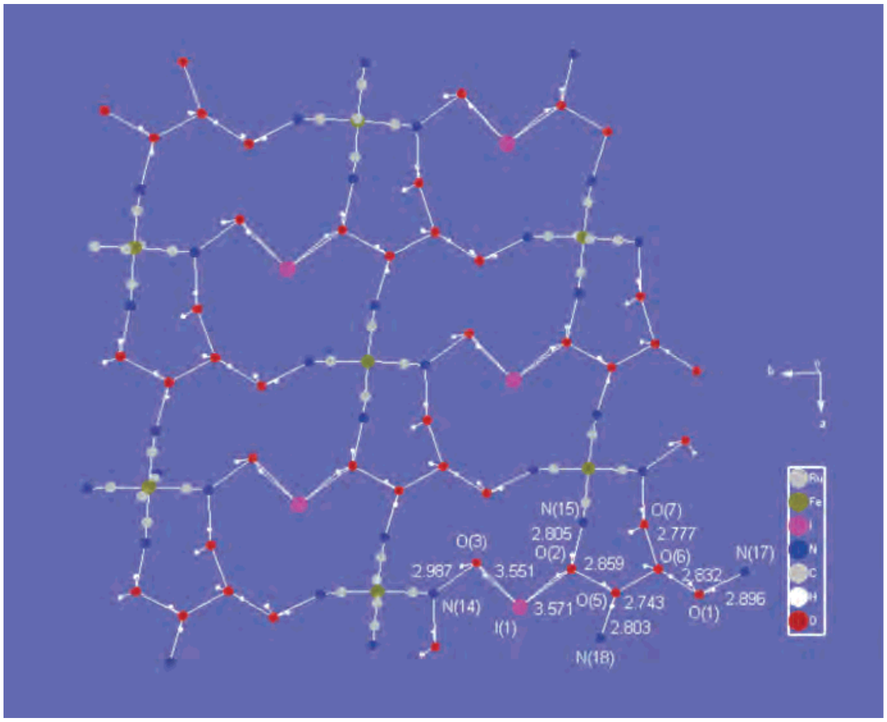

Figure 1. The perspective diagram of the $I^{-}{\cdot}(H_2O)_6$ anion cluster viewed along the crystallographic *c* axis.

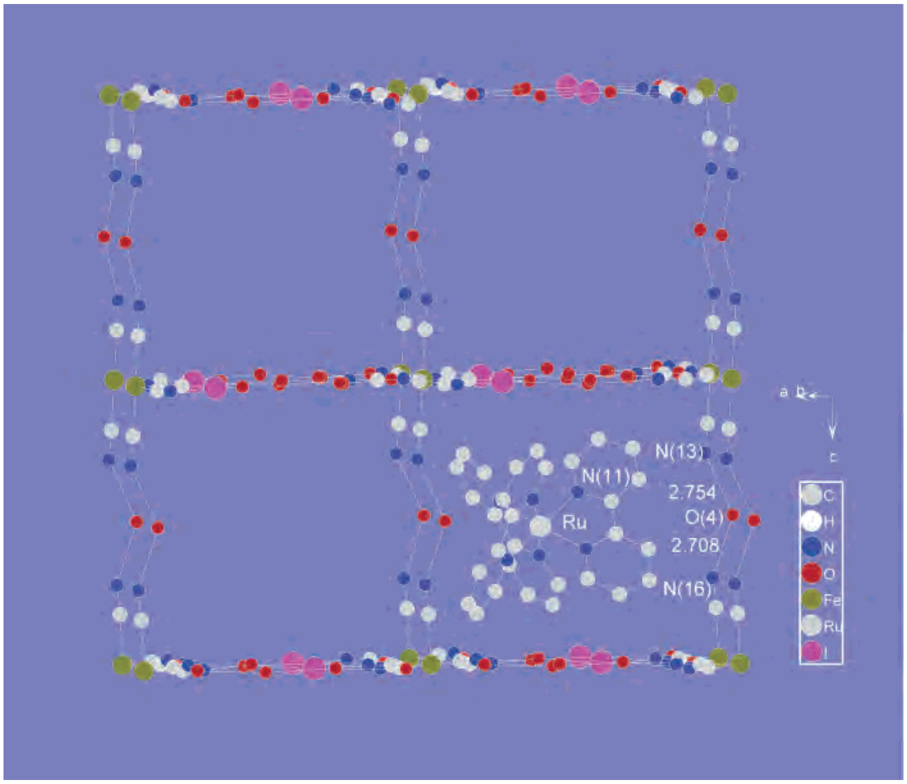

Figure 2. The perspective diagram of the 3D host framework $[I{\cdot}(H_2O)_6Fe(CN)_6{\cdot}H_2O]^{4-}$ and the guest molecule of $[Ru(bpy)_3]^{2+}$ viewed along the crystallographic *b* axis.

O···N hydrogen bonds, respectively; each O(5) atom connects to O(6), O(2), and N(18) atoms through O···O and O···N hydrogen bonds; each O(6) atom connects to three different oxygen atoms O(1), O(7), and O(5) through O···O hydrogen bonds. The O(7) and O(1) atoms show similar connectivity. Each O(7) or O(1) atom connects to the O(6) atom and a nitrile nitrogen atom through O···O and O···N hydrogen bonds, respectively. Obviously, the coplanar $(H_2O)_5$ water cluster is a new conformer different from the cyclic pentamer water cluster. In the $I^{-}{\cdot}(H_2O)_6$ anion cluster, the I···O distances are O(3)···I(1) = 3.551 Å and O(2)···I(1) = 3.571 Å and the bond angle is O(3)···I(1)···O(2) = 96°. The

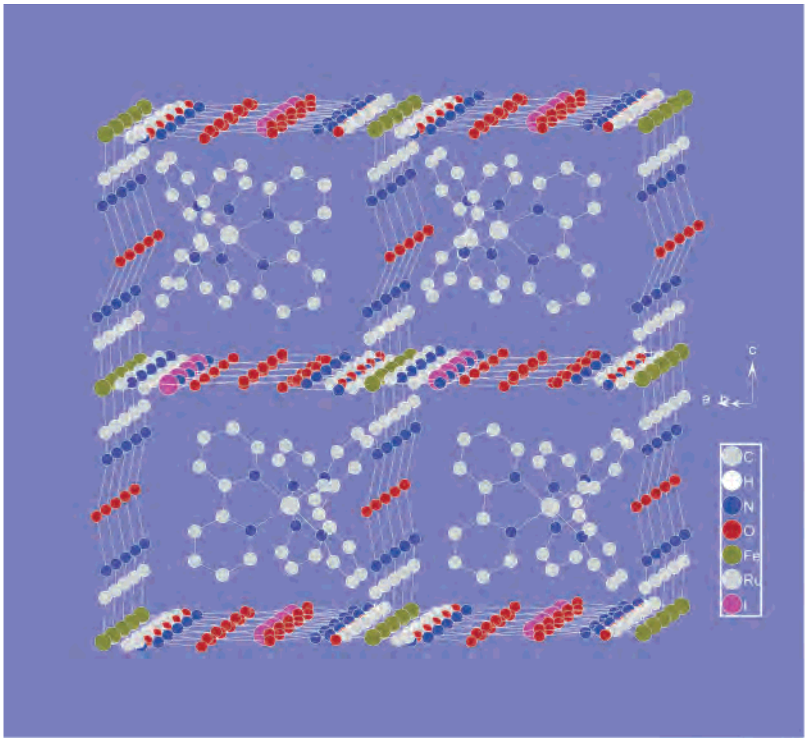

Figure 3. The packing diagram of the supramolecule $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$ viewed along the crystallographic *b* axis.

shortest O···O and N···N distances are O(6)···O(7) = 2.777 Å and O(4)···N(16) = 2.708 Å, respectively. The I···O distances are shorter than the averaged theoretical value of 3.67 Å for the lowest-energy Bd′ conformer.[37] The shorter I···O distances show stronger interactions between the I^- anion and water molecules through I···O hydrogen bonds in this supramolecular complex.

Figure 2 shows the perspective diagram of the 3D host framework $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$ and the guest molecule of $[Ru(bpy)_3]^{2+}$ viewed along the crystallographic *b* axis. Each $I^-\cdot(H_2O)_6$ anion cluster connects four $[Fe(CN)_6]^{3-}$ anions through O···N hydrogen bonds. Each $[Fe(CN)_6]^{3-}$ anion links to four $I^-\cdot(H_2O)_6$ anion clusters through O···N hydrogen bonds and two other $[Fe(CN)_6]^{3-}$ anions through two bridging water molecules, resulting in an elaborate 3D porous host framework. The $[Ru(bpy)_3]^{2+}$ cations as the guest molecules occupy the vacancies of the 3D cubic framework (Figure 3). The O···N distances are O(4)···N(13) = 2.754 Å and O(4)···N(16) = 2.708 Å, and the N(16)···O(4)···N(13) bond angle is ~122°. The shortest Fe···Fe distance is 10.915 Å. Generally, the repulsion between $I^-$and $[Fe(CN)_6]^{3-}$, as well as between two $[Fe(CN)_6]^{3-}$ anions, dominates in the 3D anionic host framework $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$. It is very interesting that not only the $[Fe(CN)_6]^{3-}$ and $I^-\cdot(H_2O)_6$ anions but also two different $[Fe(CN)_6]^{3-}$ anions connect together through O···N hydrogen bonds in the 3D anionic host framework $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$. Obviously, the guest cation $[Ru(bpy)_3]^{2+}$ located at the vacancies of the 3D cubic framework plays an important role in stabilizing the 3D anionic host framework $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$. Selected bond distances (Å) and bond angles (deg) of the crystal host $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$ are given in Table 2.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of Crystal Host $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$

I(1)−O(2)	3.571	O(5)−N(6)	2.7463
I(1)−O(3)	3.551	O(6)−O(7)	2.777
O(3)−N(14)	2.987	O(6)−O(1)	2.832
O(2)−N(15)	2.805	O(1)−N(17)	2.896
O(5)−N(18)	2.803	O(4)−N(13)	2.754
O(2)−O(5)	2.859	O(4) −N(16)	2.708
O(3)−I(1)−O(2)	96	O(5)−)O(6)−O(7)	100
N(14)−O(3)−I(1)	96	O(1)−O(6)−O(7)	140
I(1)−O(2)−O(5)	115	O(2)−O(5)−N(18)	101
I(1)−O(2)−N(15)	138	O(6)−O(5)−N(18)	134
O(5)−O(2)−N(15)	105	O(6)−O(1)−N(17)	120
O(2)−O(5)−O(6)	122	N(13)−O(4)−N(16)	122
O(1)−O(6)−O(5)	118		

IR Spectra and Elemental Analyses. IR spectra of the complex $[Ru(bpy)_3]_2[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$ exhibit the bands expected for terminal CN stretching (2112, 2052 cm^{-1}) and the bands for 2,2,-bipy stretching (1631, 1603, 1461, and 1422 cm^{-1}). The results of the elemental analyses of **1** are as follows. Anal. Found: C, 49.56; H, 3.61; N, 15.88%; Calcd for $C_{66}H_{60}FeN_{18}O_7Ru$: C, 49.43, H, 3.74; N, 15.72%.

Conclusions

In conclusion, a planar topological structure of an $I^-\cdot(H_2O)_6$ anion cluster in a 3D supramolecular complex $[Ru(bpy)_3]_2$-$[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]$ has been determined by single-crystal X-ray analysis. The novel planar topological model of an $I^-\cdot(H_2O)_6$ anion cluster has been not theoretically predicted. The $I^-\cdot(H_2O)_6$ anion cluster favors internal states in the supramolecular environment. In the supramolecule, the anion cluster $I^-\cdot(H_2O)_6$, together with the anion $[Fe(CN)_6\cdot H_2O]^{2-}$, acts as a 3D crystal host and the [Ru-

$(bpy)_3]^{2+}$ cations, as the guest molecules, occupy the vacancies of the 3D host framework. The guest cations, $[Ru(bpy)_3]^{2+}$, play an important role in stabilizing the 3D anionic host framework $[I\cdot(H_2O)_6Fe(CN)_6\cdot H_2O]^{4-}$. The precise structural information of an $I^-\cdot(H_2O)_6$ anion cluster demonstrated herein are helpful for improving the modeling of some of the unexplained properties of water and understanding better the structure and behavior of water molecules in chemical and biological processes.

Acknowledgment. This work is supported by the National Natural Science Foundation of China (No. 20471031, 20331010, 90501002 and the Natural Science Key Foundation of Tianjin).

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051657U