Ice-like $(H_2O)_{12}$ and $(H_2O)_{14}$ clusters in the crystal structures of alkali metal–ethyl viologen hexacyanometallates

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The $(H_2O)_{12}$ and $(H_2O)_{14}$ water clusters found in the crystal structures of alkali metal–ethyl viologen hexacyanometallates are similar to analogous structural units in ice I_h and ice XI.

The structures of gas hydrates with three-dimensional frameworks of water molecules the tunnels or polyhedral cavities of which contain solute molecules (clathrates)[1,2] were adequately characterised. Hydrates with water molecules arranged in channels or cavities within a rigid framework, such as an aluminosilicate framework of zeolites, are also well known. The most widespread crystal hydrates in which cations and anions are packed together with water molecules occupy an intermediate position between the above limiting structures.[1] In this case, compact water clusters may be formed. For example, clusters containing eight[3] and ten[4] water molecules were detected. In this work, the crystal structure of the lithium ethyl viologen hexacyanoferrate $EV_{1.5}Li[Fe(CN)_6]\cdot 14H_2O$† **1** ($EV^{2+}$ is *N*,*N*′-diethyl-4,4′-bipyridinium) containing a cluster of 14 water molecules was studied. The results were compared with previous data[5] on isostructural compounds $EV_{1.5}K[M(CN)_6]\cdot 12.5H_2O$ **2** (M = Fe or Ru), in which $(H_2O)_{12}$ structural units were detected (Figures 1 and 2).

We found that O(3) and O(4) water molecules in **2** (Figure 2) occupy spherical cavities 11 Å in diameter formed by ethyl viologen cations and form ice-like $(H_2O)_{12}$ clusters. The replacement of potassium with lithium dramatically increased parameter *c* [20.853, 20.956 and 21.586 Å for **2** (Fe), **2** (Ru) and **1**, respectively]. This is due to the fact that the alkali metal coordination changed from octahedral to tetrahedral and this change was accompanied by the incorporation of an additional water molecule [O(6)] into the chain $A(H_2O)_x[M(CN)_6]$ (A = K, *x* = 3; A = Li, *x* = 4) (Figure 1). An increase in parameter *c* is a reflection of the ordering of water molecules O(5). Thus, the formula unit of **1** contains 1.5 additional water molecules as compared with that of **2**; however, the main structural motif remained unchanged. The ordering of water molecules O(5) makes it possible to recognise a $(H_2O)_{14}$ cluster in **1**.

The $(H_2O)_{12}$ and $(H_2O)_{14}$ clusters form $(H_2O)_{18}$ and $(H_2O)_{20}$ units in the structures of **2** and **1**, respectively, *via* six hydrogen bonds with crystal water molecules O(2). Taking into account water molecules O(1) coordinated to alkali metal atoms, the dimensionality of the units increases to $(H_2O)_{24}$ and $(H_2O)_{26}$, respectively. The geometry parameters of the $(H_2O)_{18}$ unit are similar to those of ice I_h[6] and ice XI.[7] Two types of six-membered rings can be recognised in this unit: three O(3)–O(4)–O(3E)–O(3C)–O(4C)–O(3B) with boat conformations and two O(3)–O(4)–O(3E)–O(4E)–O(3D)–O(4D) with chair conformations. The orientation of hydrogen bonds in the structure of ice I_h is disordered, whereas these bonds in the structure of ice XI are oriented along oxygen–oxygen bonds. We localised all hydrogen atoms in the test $(H_2O)_{12}$ clusters from difference Fourier syntheses. However, the number of short O···O contacts is greater than the number of hydrogen atoms that participate in the formation of hydrogen bonds, and hydrogen atoms are located at not all O···O lines (Figure 2). Note that in the structure of **2** (Fe) hydrogen atoms of molecule O(4) form hydrogen bonds O(4)···O(3), O(4)···O(51, 52), and in **2** (Ru) and **1**, O(4)···O(3) and

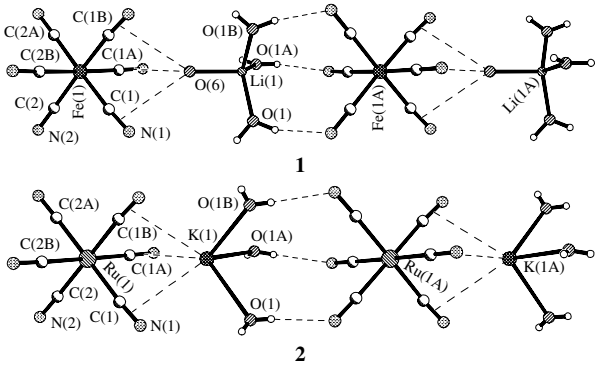

Figure 1 Chains of the $A(H_2O)_x[M(CN)_6]$ ion pairs in the structures of **1** and **2** (Ru).

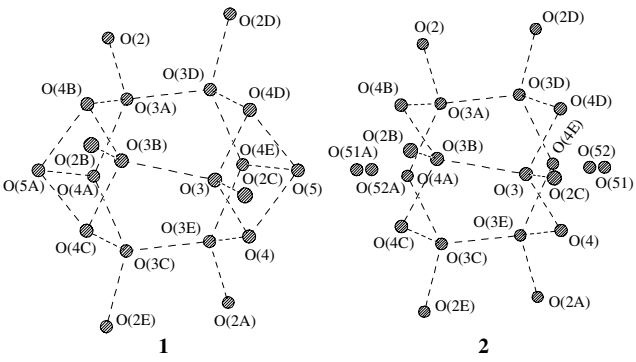

Figure 2 Structural units of **1** and **2** (Ru). The geometry of O···O···O contacts (° and Å) in **1**: O(3)···O(2C) 2.881, O(3)···O(3B) 2.777, O(3)···O(4) 2.826, O(3)···O(4D) 2.871, O(4)···O(5) 2.755, O(2C)–O(3)–O(3B) 105.4, O(2C)–O(3)–O(4) 118.0, O(2C)–O(3)–O(4D) 122.3, O(3B)–O(3)–O(4) 121.0, O(3B)–O(3)–O(4D) 103.5, O(4)–O(3)–O(4D) 85.9, O(3)–O(4)–O(3E) 122.0, O(3)–O(4)–O(5) 90.4, O(3E)–O(4)–O(5) 89.5, O(4)–O(5)–O(4E) 89.6.

† The compound $EV_{1.5}Li[Fe(CN)_6]\cdot 14H_2O$ **1** was isolated by the mixing (*T* = 277 K) of solutions of ethyl viologen diiodide (Aldrich) and lithium hexacyanoferrate (pure) in the 1:1 molar ratio.

Crystal structure data for **1**: $C_{27}H_{55}FeLiN_9O_{14}$, *M* 792.59, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 14.6690(10)$ Å, $c = 21.586(5)$ Å, $V = 4022.6(10)$ Å^3, $Z = 4$, $d_{calc} = 1.309$ g cm^{-3}, F(000) = 1684. Crystal size 0.4×0.3×0.3 mm. Experiments were performed on a Smart 1000 CCD diffractometer using MoKα-radiation ($\lambda = 0.71073$ Å, ω-scans with a 0.3° step and 10 s per frame exposure, $2\theta < 60°$) at 110 K. The intensities of 24136 reflections were measured within the range $1.89 < \theta < 30.05°$; 3884 independent reflections were used in the calculations ($R_{int} = 0.0622$). The model of **2** (without oxygen atoms of the crystal water and without a potassium atom) was used as an initial approximation in refining. The structure was refined by the least-squares technique in an anisotropic–isotropic approximation (H atoms). The final refinement parameters: $wR_2 = 0.1764$, $R_1 = 0.1037$ (all reflections), $wR_2 = 0.1598$, $R_1 = 0.0683$ [2229 reflections with $I > 2\sigma(I)$], GOF = 0.923 (225 refinement parameters). All calculations were performed using the SHELXL 97 program.[8] Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/100.

O(4)···O(3E), respectively. This fact suggests partial disordering of the hydrogen atoms of water molecules in compounds **1** and **2**. Unfortunately, disordered hydrogen atoms cannot be reliably localised even at 110 K because of the mosaic structure of crystals.

References

1 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1986.

2 Yu. A. Dyadin, I. S. Terekhova, T. V. Rodionova and D. V. Soldatov, *Zh. Strukt. Khim*., 1999, **40**, 797 [*J. Struct. Chem.* (*Engl. Transl.*), 1999, **40**, 645].

3 (*a*) W. B. Blanton, S. W. Gordon-Wylie, G. R. Clark, K. D. Jordan, J. T. Wood, U. Geiser and T. J. Collins, *J. Am. Chem. Soc*., 1999, **121**, 3551; (*b*) J. L. Atwood, L. J. Barbour, T. J. Ness, C. L. Raston and P. L. Raston, *J. Am. Chem. Soc.*, 2001, **123**, 7192.

4 (*a*) L. J. Barbour, G. W. Orr and J. L. Atwood, *Nature*, 1998, **393**, 671; (*b*) L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 2000, 859.

5 S. A. Kostina, A. B. Ilyukhin, B. V. Lokshin and V. Yu. Kotov, *Mendeleev Commun*., 2001, 12.

6 A. Goto, T. Hondoh and S. Mae, *J. Chem. Phys*., 1990, **93**, 1412.

7 R. Howe and R. W. Whitworth, *J. Chem. Phys*., 1989, **90**, 4451.

8 G. M. Sheldrick, *SHELXL-97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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