A cyclic supramolecular $(H_2O)_4$ cluster in an unusual Fe_3 complex that aggregates to $\{Fe_3\}_n$ with a zig-zag chainlike structure

Sabbani Supriya, Sathi Manikumari, Pallepogu Raghavaiah and Samar K. Das*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.
E-mail: skdsc@uohyd.ernet.in

Received (in Montpellier, France) 12th June 2002, Accepted 2nd October 2002
First published as an Advance Article on the web 3rd December 2002

An aqueous solution containing ferric chloride, acetic acid and 2-hydroxypyridine results in the solid-state isolation of an unusual mixed-ligand trinuclear iron(III) complex $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]ClO_4{\cdot}4H_2O$, 1, where the iron-coordinated water ligand forms a hydrogen-bonded water tetramer with three other solvent water molecules; the Fe_3 clusters aggregate to $\{Fe_3\}_n$ *via* N–H···O type hydrogen bonds, forming a zig-zag chainlike structure.

Information about small hydrogen-bonded water clusters, $(H_2O)_n$, can provide not only a key for understanding bulk water but also help to understand the water structuring associated with many proteins.[1,2] There is clearly a need to have more insight into how such aggregates influence the transition from small clusters to bulk water and the role of water in the active site of proteins. Small water clusters have been characterized spectroscopically[3,4] using liquid water (or D_2O) and clusters with n = 4, 6, 8 and 10 have been observed crystallographically in crystalline hydrates.[5–8] Among these, the hydrogen-bonded cyclic water tetramer, $(H_2O)_4$, has received considerable attention. We wish to present here the synthesis and characterization of an unusual Fe_3 cluster-containing compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]ClO_4{\cdot}4H_2O$, **1**, emphasizing the supramolecular $(H_2O)_4$ tetramer with a quasi-planar cyclic arrangement of the water molecules. The Fe_3 cluster is unusual in the sense that, unlike symmetric oxo-bridged trinuclear basic iron carboxylates $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}RCOO)_6L_3]^{1+}$ (where L is H_2O or pyridine and R is an alkyl or aryl group),[9] the present trinuclear cluster is asymmetric with respect to monodentate ligands: one iron centre has water coordination while the other two are bonded to two 2-pyridone ligands (Fig. 1). There are two other examples of such a mixed (monodentate) ligand Fe_3 cluster in the literature, which are structurally characterized.[10,11] Taking advantage of the ability of iron-coordinated 2-pyridone ligands to form N–H···O hydrogen bonds, we are further able to show here that the Fe_3 cluster undergoes linking into a zig-zag chainlike structure, providing thereby a novel example of supramolecular aggregation from Fe_3 to $(Fe_3)_n$.

Compound **1** was prepared from an aqueous solution containing acetic acid, ferric chloride and 2-hydroxypyridine. It was characterized by single crystal X-ray structural analysis, elemental analysis, infrared spectroscopy, thermogravimetry (to determine the amount of crystal water) and room temperature magnetic moment measurement.

The complex is trinuclear (overall "basic carboxylate" structure) with the central oxygen atom O(1) lying approximately in the plane (deviation 0.003 Å) of the three irons (Fig. 1). However, unlike symmetric μ_3-oxotriiron(III) clusters in basic iron carboxylates, one of the iron centres, Fe(1) in **1**, has water coordination with other two iron atoms, Fe(2) and Fe(3), coordinating 2-pyridone ligands through neutral oxo donor atoms (Fig. 1). Elemental analysis supports the presence of two 2-pyridones instead of the usual three such neutral ligands for symmetric μ_3-oxotriiron(III) clusters in basic iron carboxylates. Bond lengths and angles within the trinuclear cluster are consistent with values found for other iron basic carboxylate structures.[9,12] The geometrical parameters within the 2-pyridone ligand are in agreement with those found in monomeric Fe(III)-2-pyridone complexes.[13]

The most striking feature of the present system is that the iron-coordinated water O(2) and three other crystal water molecules [O(21), O(22) and O(23)] together form a cyclic hydrogen-bonded water tetramer (Figs. 1 and 2). The O···O distances in the supramolecular water tetramer are O(2)···O(21) = 2.675(11), O(2)···O(22) = 2.647(13), O(21)···O(23) = 3.01(3) and O(22)···O(23) = 2.74(3) Å. According to the crystal structure analysis, there are four crystal water molecules per formula unit of **1**. Among these, three are involved in forming the water tetramer with the iron-coordinated water. The fourth crystal water molecule [O(24)] is within hydrogen-bonding distance of the perchlorate anion and also

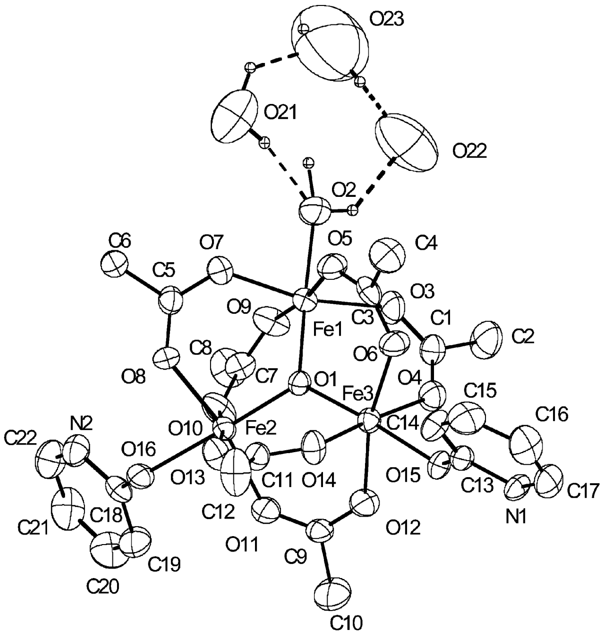

Fig. 1 Thermal ellipsoid plot of the unusual Fe_3 complex featuring a supramolecular water tetramer at one of the iron centres, whereas the other two iron centres are coordinated to two neutral 2-pyridone ligands.

DOI: 10.1039/b205695j

with one water [O(22)] of the $(H_2O)_4$ cluster (Fig. 2). In terms of the connectivity of hydrogen bonds in the ring system of the $(H_2O)_4$ cluster (Figs. 1 and 2), it has C_s symmetry with a quasi-planar ring structure (when the water tetramer is considered separately from the Fe_3 complex).

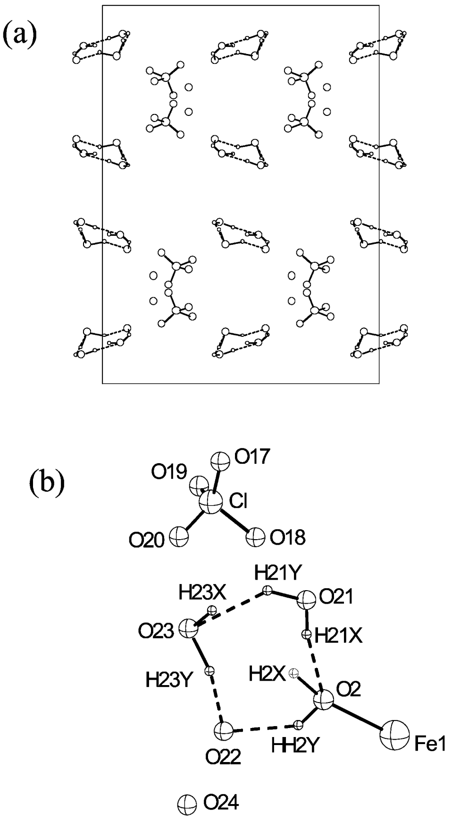

Fig. 2 (a) The unit cell packing of water clusters, perchlorate anions and other crystal waters (excluding Fe_3 complexes). (b) The molecular surrounding of an $(H_2O)_4$ cluster. Covalent chemical bonds are shown as solid lines and H bonds as dashed lines.

The packing diagram of the water tetramers, other crystal waters [O(24) type] and perchlorate anions, but excluding the Fe_3 clusters, is shown in Fig. 2(a). The molecular surrounding of an $(H_2O)_4$ cluster is presented in Fig. 2(b). O(2) water is covalently bonded to Fe(1) iron. The O(22)···O(24) distance of 2.422 Å suggests strong hydrogen bonding between these oxygen atoms. However, the hydrogen atoms of both these waters [O(22) and O(24) waters] could not be located in the crystal structure. Although the O(18)···O(21) distance of 2.99 Å and the O(20)···O(23) distance of 3.00 Å suggest hydrogen bonding interactions between perchlorate anion and water tetramer, the positions of the hydrogen atoms on O(21) and O(23) do not allow such interactions. These findings are not surprising, because the perchlorate ion has a relatively low surface charge and hydrophobic character. As a consequence the water molecules may come close to the hydrophobic particle but none of the hydrogens interact with the perchlorate anions.

The abundance of water molecules in **1** is further corroborated by thermogravimetric analysis, where the total loss of water corresponds to one coordinated and four crystal water molecules. Mass loss starts at ambient temperature and a sharp mass loss occurs at ~100 °C. The room temperature magnetic moment, 5.84 μ_B (3.37 μ_B per Fe atom), of a solid sample of **1** indicates that high spin Fe^{3+} ions are antiferromagnetically coupled and this is consistent with other iron basic carboxylates.[9c]

Interestingly, each Fe_3 cluster is connected to two other clusters (from opposite sides) by N–H···O type hydrogen bonds, forming chains that run along the crystallographic *b* axis [Fig. 3(a)]. There are two N–H···O hydrogen bonds in each linkage, which involves two 2-pyridone rings from two different Fe_3 clusters [Fig. 3(b)]. The chain is of the zig-zag type with respect to the positions of the water tetramers present in each Fe_3 cluster. The relevant hydrogen bonding distances are N(1)···O(16) = 2.852(19) Å and N(2)···O(15) = 3.086(18) Å [Fig. 3(b)].

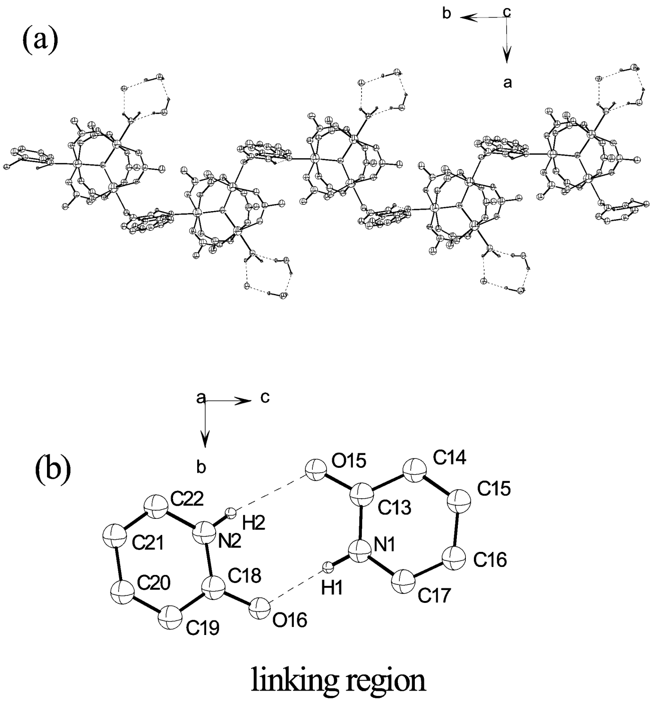

Fig. 3 (a) Ball-and-stick representation of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)_4]^+$ showing a zig-zag chain running along the crystallographic *b* axis. (b) The linkage region, which involves two 2-pyridone rings from two Fe_3 clusters, is highlighted and it is shown that the rings are linked by two N–H···O bonds.

In conclusion, we have reported a cyclic supramolecular $(H_20)_4$ cluster in the solid state in a crystal host. Extended structures based on the Fe_3O building unit showing chain or layerlike networks are very scarce. We have achieved the extended supramolecular aggregation from a Fe_3 discrete building unit to a $(Fe_3)_n$ zig-zag chain.

Experimental

Synthesis

Compound **1** was prepared in the following manner. To a stirred solution containing 2.0 g (12.33 mmol) of $FeCl_3$ in 25 mL of water were added 10 mL of CH_3COOH (100%) and 0.9 g (9.46 mmol) of 2-hydroxypyridine. $NaClO_4$ (4.5 g, 36.75 mmol) was subsequently dissolved in this solution, followed by the dropwise addition of an aqueous NaOH solution (29 mL, 1 M). From the final red-brown solution, which was filtered and kept in an open flask at room temperature for 7 days, block-shaped brown crystals of **1** were obtained in 65% yield (based on Fe). X-Ray quality crystals were obtained from a comparatively dilute solution. IR (KBr, cm^{-1}): 3510s, 3260s, 3108s, 2940s, 2528w, 2467w, 2382w, 1576s, 1445s, 1267m, 1222m, 1161m, 1088s, 999m, 902m, 860m, 825w, 796m, 773m, 731m, 661m, 590s, 525m, 498m, 464w. Calcd anal. for $C_{22}H_{38}ClFe_3N_2O_{24}$ (M 917.54): C, 28.79; H, 4.17; N, 3.05; found: C, 29.03; H, 4.01; N, 3.11.

X-Ray crystallography

Data were collected on an Enraf–Nonius CAD4 diffractometer at 20 °C in the range $1.68 < \theta < 24.96°$. Based on 3133 reflections (observed) with $I > 2\sigma(I)$ and 475 parameters gave R (wR) = 0.0550 (0.1306). The structure was solved by direct method (SHELXS-97)[14] and refined using SHELXL-97 programs.[15] All non-hydrogen atoms were refined anisotropically. The ring hydrogens of 2-pyridone ligands and acetate hydrogens were assigned positions on the basis of geometrical considerations and were allowed to ride upon their respective carbon and nitrogen atoms. Among the four lattice water molecules, the hydrogens of two [O(22) and O(24)] waters could not be located. The hydrogen atoms of other two crystal waters [O(21) and O(23)] and the iron-coordinated water [O(2)] were located from difference Fourier maps and their positions were refined. Bond length constraints were applied to these water hydrogens.

Crystal data for **1**: $C_{22}H_{38}ClFe_3N_2O_{24}$, orthorhombic, *Pbca*, $a = 16.810$ (3), $b = 17.682$ (3), $c = 24.199$ (4) Å, $U = 7193$ (2) Å^3, $Z = 8$, $\mu = 1.362$ mm^{-1}.

CCDC reference number 178947. See http://www.rsc.org/suppdata/nj/b2/b205695j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank Professor N. Ray Chaudhuri and his group of IACS, Kolkata for the thermogravimetric analysis. The National X-ray Diffractometer facility at University of Hyderabad by the Department of Science and Technology, Government of India, is gratefully acknowledged. We thank the Council of Scientific and Industrial Research, New Delhi for financial support.

References

1 R. Ludwig, *Angew. Chem., Int. Ed.*, 2001, **40**, 1808.

2 (*a*) W. F. Royer, A. Pardanani, Q. H. Gibson, E. S. Peterson and J. M. Feldman, *Proc. Natl. Acad Sci. U. S. A.*, 1996, **93**, 14 526; (*b*) M. M. Teeter, *Proc. Natl. Acad. Sci. U. S. A.*, 1984, **81**, 6014; (*c*) E. N. Baker, *J. Mol. Biol.*, 1980, **141**, 441.

3 (*a*) J. D. Cruzan, L. B. Braly, K. Liu, M. G. Brown, J. G. Loeser and R. J. Saykally, *Science*, 1996, **271**, 59; (*b*) M. G. Brown, F. N. Keutsch, L. B. Braly and R. J. Saykally, *J. Chem. Phys.*, 1999, **111**, 7801; (*c*) J. D. Cruzan, M. G. Brown, K. Liu, L. B. Braly and R. J. Saykally, *J. Chem. Phys.*, 1996, **105**, 6634.

4 F. Huisken, M. Kaloudis and A. Kulcke, *J. Chem. Phys.*, 1996, **104**, 17.

5 (*a*) K. K. Chacko and W. Saenger, *J. Am. Chem. Soc.*, 1981, **103**, 1708; (*b*) V. Zabel, W. Saenger and S. A. Mason, *J. Am. Chem. Soc.*, 1986, **108**, 3664; (*c*) F. C. Stephens and R. S. Vagg, *Inorg. Chim. Acta.*, 1982, **57**, 43; (*d*) J. Xu, E. Radkov, M. Ziegler and K. N. Raymond, *Inorg. Chem.*, 2000, **39**, 4156; (*e*) M. C. Favas, D. L. Kepert, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1980, 454.

6 (*a*) R. Custelcean, C. Afloroaei, M. Vlassa and M. Polverejan, *Angew. Chem., Int. Ed.*, 2000, **39**, 3094; (*b*) C. Foces-Foces, F. H. Cano, M. Martinez-Ripoll, R. Faure, C. Roussel, R. M. Claramunt, C. Lopez, D. Sanz and J. Elguero, *Tetrahedron: Asymmetry*, 1990, **1**, 65; (*c*) R. J. Doedens, E. Yohannes and M. I. Khan, *Chem. Commun.*, 2002, 62.

7 (*a*) W. B. Blanton, S. W. Gordon-Wylie, G. R. Clark, K. D. Jordon, 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.

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

9 (*a*) F. A. Cotton, *Advanced Inorganic Chemistry*, Wiley, New York, 1980, pp 154–155; (*b*) J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291; (*c*) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195.

10 P. Poganiuch, S. Lui, G. C. Papaefthymiou and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 4645.

11 V. M. Lynch, J. W. Sibert, J. L. Sessler and B. E. Davis, *Acta Crystallogr., Sect. C*, 1991, **47**, 866.

12 A. B. Blake and L. R. Frazer, *J. Chem. Soc., Dalton Trans.*, 1975, 193.

13 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *Inorg. Chim. Acta*, 1989, **166**, 159.

14 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Göttingen University, Göttingen, Germany, 1997.

15 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Göttingen University, Göttingen, Germany, 1997.