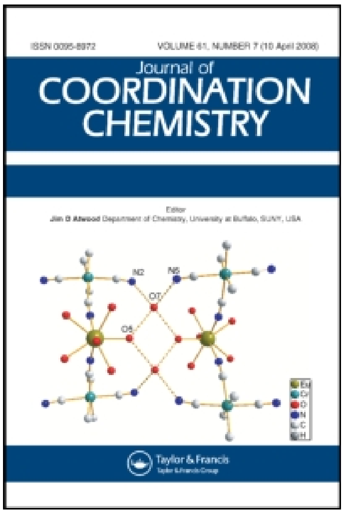

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Syntheses, characterization, spectroscopy, and quantum chemical calculation of two 2-(N-2'-aminopyridylo)pyridinium salts: observation of an acyclic water pentamer

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Syntheses, characterization, spectroscopy, and quantum chemical calculation of two 2-(N-2′-aminopyridylo)pyridinium salts: observation of an acyclic water pentamer

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Syntheses, characterization, and studies of two 2-(N-2′-aminopyridylo)pyridinium salts, $[\mathrm{DPA1HA}]_3^+[\mathrm{Fe(CN)_6}]^{3-}\cdot 5\mathrm{H_2O}$ (**1**) and $[\mathrm{DPA1HA}]^+\mathrm{Cl}^-\cdot 2\mathrm{H_2O}$ (**2**; DPA1HA = monoprotonated 2,2′-dipyridylamine (DPA) having one pyridine nitrogen protonated) are described. X-ray single crystal structure of **1** has been determined. This complex crystallizes in monoclinic $P2_1/\mathrm{n}$ space group with $a = 18.691(8)$ Å, $b = 11.685(6)$ Å, $c = 20.392(9)$ Å, $\beta = 117.03(3)°$, and $Z = 4$. Quantum chemical calculations on neutral, monoprotonated, and diprotonated 2,2′-dipyridylamine have been performed to understand the site of protonation in **1**. The water molecules in **1** are interlinked to result in the generation of the rare example of an acyclic water pentamer. The water pentamer is hydrogen bonded with the ferricyanide anion to generate a two-dimensional water-ferricyanide sheet. The overall supramolecular structure of **1** is three-dimensional due to hydrogen bonding interactions of the organic cations with both the ferricyanide anion and water cluster. Compound **2** has been characterized by elemental analyses and IR spectrum. Quantum chemical calculations in the gaseous state and the isolation of **1** and **2** in the solid state indicate that monoprotonation of DPA at one pyridine nitrogen is more favorable. However, spectrophotometric titration of DPA with acid indicates that di-(or tri-) protonation takes place in solution.

Keywords: Water cluster; Ferricyanide; Hydrogen-bond; 2,2′-Dipyridylamine; Quantum chemical calculation

1. Introduction

For chemical and biochemical reasons, experimental [1–6] and theoretical [7] studies of water clusters have attracted much attention. Water clusters of different nuclearities have been observed in crystal hydrates of organic and metal-organic compounds [1–6]. In most of the reported examples, basic units of a small number of water molecules are interconnected with each other to generate infinite polymeric networks like chain, tape, 2D layer, etc. [1–4]. Discrete water clusters that are not hydrogen bonded with the

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neighboring clusters but interact with organic or metal-organic moieties are less common [1, 5, 6]. In any case (discrete or polymeric), although there are a few examples of odd number members [1, 4, 6], the family of water clusters is dominated by even number examples [1, 3, 5]. As theoretically predicted [7], the observed structure of water clusters is cyclic or cage in most examples. Rare examples of acyclic clusters are, however, known in crystals where the required stabilization is achieved due to interaction between the acyclic cluster with the organic or metal-organic moieties [1, 6].

Cyanometalate compounds containing ferricyanide exhibit interesting magnetic and optical properties [8, 9] and are also appealing members [9] in the field of crystal engineering and development of novel topologies [10, 11]. Cyanometalate compounds usually crystallize with a number of solvent molecules [8, 9], which, in turn, may form hydrogen bonds with noncoordinated cyanide groups. For compounds containing hexacyanometalates as anion, the number of hydrogen bonding interactions and the probability of interesting topologies should be enhanced. At this point, it may be mentioned that we recently observed an example of strongly hydrogen-bonded interlocked infinite double helices in a gadolinium(III) hexacyanoferrate(III) supramolecule [11a].

With simple metal salts, ferricyanide usually forms amorphous precipitates (Prussian blues) [8]. Again, low symmetric crystalline systems that are deposited in the reaction of ferricyanide with coordinatively unsaturated metal complexes are usually cyano-bridged compounds [9]. Clearly, organic cations are the best choice to derive new compounds containing hexacyanometalates as anion. Although a few organic cation-ferricyanide compounds have been reported [12], supramolecular topologies in these examples have not been well explored. Herein, we report an easy synthesis and structural characterization of a new organic cation ferricyanide compound, $[\mathrm{DPA1HA}]_3^+[\mathrm{Fe(CN)_6}]^{3-}\cdot 5\mathrm{H_2O}$ (**1**; DPA1HA = monoprotonated 2,2′-dipyridylamine (DPA) having one pyridine nitrogen protonated). Interestingly, the water molecules in this compound form a rare example of an acyclic water pentamer. Synthesis and characterization of an analogous compound, $[\mathrm{DPA1HA}]^+\mathrm{Cl}^-\cdot 2\mathrm{H_2O}$ (**2**), as well as density functional calculations and UV-vis spectroscopic studies have been described in the present report to understand the site of protonation of 2,2′-dipyridylamine.

2. Experimental

2.1. *Materials and methods*

All reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Perkin–Elmer RXIFT spectrophotometer with samples as KBr disks. Density functional calculations were carried out with Gaussian 03 software [13].

2.2. *Syntheses and characterization*

$[\mathrm{DPA1HA}]_3^+[\mathrm{Fe(CN)_6}]^{3-}\cdot 5\mathrm{H_2O}$ (1). To an ethanol solution (3 mL) of 2,2′-dipyridylamine (DPA; 0.129 g, 0.75 mmol) was added 2 mL of 6N HCl and the resulting solution was treated with an aqueous solution (20 mL) of potassium hexacyanoferrate(III) (0.082 g, 0.25 mmol). The mixture was kept undisturbed. After a few minutes orange compound containing diffractable single crystals deposited, was isolated by filtration and washed with ethanol-water (5:2). Yield: 0.14 g (70%). Elemental analyses found: C, 52.65; H, 4.86; N, 25.75 (Calcd for $C_{36}H_{40}N_{15}O_5Fe$: C, 52.82; H, 4.93; N, 25.66). IR (KBr/cm^{-1}): 3390m (water); 2108m (cyanide); 1660s, 1600s, 1450m, 773m (monoprotonated 2,2′-dipyridylamine). UV-vis (methanol-water (1:1)/λ_{max}, nm (ε, M^{-1} cm^{-1}): 419 (933), 317 (43593), 292 sh (29279), 266 sh (22573), 254 (46082).

$[DPA1HA]^+Cl^- \cdot 2H_2O$ (2). To a HCl solution (6N, 20 mL), 2,2′-dipyridylamine (0.255 mg, 1.5 mmol) was added with stirring. After a few minutes, the mixture was filtered to remove any suspended particles and the clear colorless solution was evaporated on a water bath to *ca.* 5 mL. The solution was then kept in a desiccator. After one day, white crystalline compound that deposited was collected by filtration and washed with cold acetonitrile. Yield: 0.33 g (90%). The elemental analyses found: C, 49.50; H, 5.82; N, 16.92 (Calcd for $C_{10}H_{14}N_3O_2Cl$: C, 49.28; H, 5.79; N, 17.24). IR (KBr/cm^{-1}): 3353s (water); 1664s, 1597s, 1449s, 773m (monoprotonated 2,2′-dipyridylamine). UV-vis (methanol-water (1:1)/λ_{max}, nm (ε, M^{-1} cm^{-1}): 317 (14182), 292 sh (9527), 266 sh (8053), 254 (15239).

2.3. *Single-crystal X-ray diffraction of* $[DPA1HA]^+_3[Fe(CN)_6]^{3-} \cdot 5H_2O$ *(1)*

Diffraction data for **1** were collected on a Enraf – Nonius CAD4 diffractometer at 293 K in the $\omega - 2\vartheta$ scan mode using graphite-monochromated Mo-K$_\alpha$ radiation having $\lambda = 0.71069$ Å. Three standard reflections were periodically monitored and showed no significant variation over data collection. The accurate unit cell was obtained by means of least-squares fits of 25 centered reflections. The intensity data were corrected for Lorentz and polarization effects and semi-empirical multiscan absorption correction was made from ψ-scans using the program SADABS (1996) [14a]. A total of 13563 reflections were collected, of which 6953 ($R_{int} = 0.1163$) independent reflections were used for structure determination. The structure was solved by direct methods using SIR92 [14b] and was refined by full-matrix least-squares methods based on F^2 using the program SHELXL-97 [14c]. The nonhydrogen atoms, except the disordered nitrogen atoms, were refined anisotropically. During the development of the structure, it became evident that the nitrogen atoms N(17), N(37), and N(57) were each disordered over two sites. This was allowed for and the final occupancy parameters for these disordered atoms are 0.85, 0.82, and 0.74, respectively. The hydrogen atoms bonded to carbons were inserted at calculated positions with C–H distance of 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ and were refined in the riding model approximation. Coordinates for the hydrogen atoms of water molecules were also geometrically fixed and then allowed to ride using restrained refinement on C–H and H–H distances with independent U_{iso}. The hydrogen atoms attached to nitrogens could not be located. However, it became evident from quantum chemical calculations (vide infra) that one pyridine nitrogen of each organic moiety is protonated. Therefore, in addition to one hydrogen at each of the three amine nitrogens, three protons (H(14), H(34), and H(54)) at three pyridine nitrogens were adopted and refined accordingly to $R_1(I > 2\sigma(I)) = 0.0491$. All programs used in the structure refinement were incorporated in the WINGX package [14d]. The crystallographic data of **1** are summarized in table 1.

3. Results and discussions

3.1. *Description of the structure of [DPA1HA]$^+{}_3$[Fe(CN)$_6$]$^{3-}\cdot 5H_2O$ (1)*

The crystal structure of $[\mathrm{DPA1HA}]_3^+[\mathrm{Fe(CN)_6}]^{3-}\cdot 5\mathrm{H_2O}$ (**1**) is shown in figure 1. The structure consists of three monoprotonated 2,2′-dipyridylamine (having one pyridine nitrogen protonated), one ferricyanide anion, and five water molecules as solvent of crystallization. The coordination geometry of the metal center in the anion deviates only slightly from ideal octahedral as shown by the ranges of *cisoid* (88.00(17)°–92.23(18)°) and *transoid* (177.21(17)°–179.19(18)°) angles. The structural parameters of the organic moieties in **1** are discussed below and compared with optimized geometries of neutral, monoprotonated, and diprotonated 2,2′-dipyridylamine.

Five water molecules in **1** are interlinked to generate an acyclic $(H_2O)_5$ water cluster (figure 2). One of the terminal water molecules ($H_2O(2)$) in this cluster acts as a single acceptor and is hydrogen bonded with one hydrogen of $H_2O(5)$. Another terminal water molecule ($H_2O(4E)$) acts as a single donor, while other three water molecules in this

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{36}H_{40}N_{15}O_5Fe$
Formula weight	818.66
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	18.691(8)
b (Å)	11.685(6)
c (Å)	20.392(9)
β (°)	117.03(3)
V (Å^3)	3967(3)
Z	4
D (calculated, g cm^{-3})	1.371
λ (Mo-K$_\alpha$), Å	0.71073
μ (mm^{-1})	0.442
T (K)	293(2)
F(000)	1708
2θ range for data collection (°)	4 − 50
Index ranges	$-22\le h\le 22,\ 0\le k\le 13,\ -24\le l\le 24$
No. measured reflections	13563
No. independent reflections	6953
R_{int}	0.1163
No. refined parameters	553
No. observed reflections, $I\ge 2\sigma$ (I)	3025
Goodness-of-fit on F^2, S	0.88
Statistical weight, w	0.054
R_1^a, wR_2^b [$I\ge 2\sigma$ (I)]	0.0491, 0.1058
$R_1{}^a$, $wR_2{}^b$ [all data]	0.1783, 0.1414
Max., min. electron density (e Å^{-3})	0.816, −0.341

$^aR_1 = \left[\sum ||F_o| - |F_c|| / \sum |F_o|\right]$. $^bwR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

cluster behave as a single donor as well as a single acceptor. The O···O distances in the water cluster fall in the range 2.728(8)–2.986(8) Å (table 2).

The water pentamer is linked with the ferricyanide anion to self-assemble a two-dimensional sheet. The hydrogen bonds formed between the anion and the water cluster are illustrated in figure 3, while the geometries of the hydrogen bonds are summarized in table 2. As demonstrated in figure 3, the hydrogen bonds O(2)–H(W21)···N(3) and O(2)–H(W22)···N(5A) result in one-dimensional chains running parallel to the crystallographic *a* axis. Again, these one-dimensional chains are self-assembled in two-dimensions due to O(5)···O(2) and O(5)···N(6C) interactions. Evidently, $H_2O(5)$ acts as the bridge between the one-dimensional chains. There are two other hydrogen bonds, O(3F)–H(W32F)···N(1) and O(1F)–H(W12F)···N(5A), involving ferricyanide and water cluster. These hydrogen bonds, however, play no role in developing the extended structure. The extended views down the crystallographic *c* and *b* axes of the two-dimensional sheet are shown in figure 4.

The two-dimensional water···ferricyanide network in **1** is linked with the organic cations via C–H···O, C–H···N, N–H···O, and N–H···N hydrogen bonds to generate a three-dimensional supramolecular structure. Due to the disorder

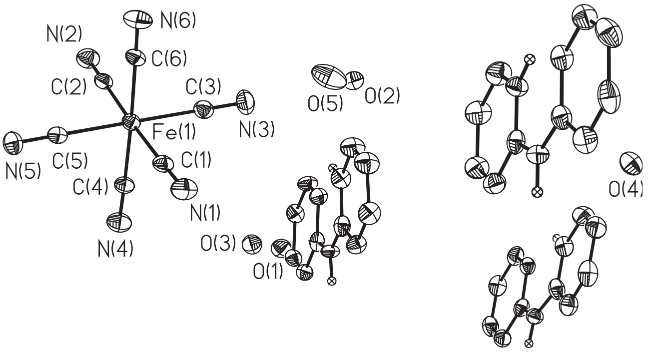


Figure 1. Crystal structure of $[DPA1HA]_3^+[Fe(CN)_6]^{3-} \cdot 5H_2O$ (**1**). Hydrogens attached to nitrogens are only shown.

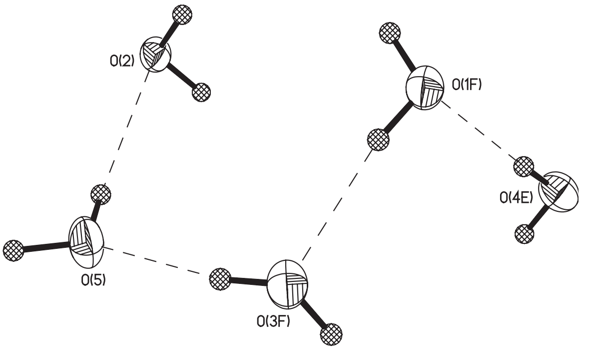


Figure 2. Acyclic water pentamer in **1**. Symmetry: see figure 3.

Table 2. Geometries of the major hydrogen bonds (H-bond distances (Å) and angles (°)) in **1**. Symmetry: as in Figure 3.

No.	D–H···A	H···A	D···A	D–H···A
1	O(2)–H(W21)···N(3)	2.01(3)	2.839(5)	172(3)
2	O(2)–H(W22)···N(5A)	2.03(3)	2.885(5)	175(3)
3	O(5)–H(W52)···O(2)	2.17(6)	2.986(8)	160(5)
4	O(5)–H(W51)···N(6C)	2.03(6)	2.866(8)	166(5)
5	O(3F)–H(W32F)···O(5)	1.93(2)	2.756(6)	171(2)
6	O(3F)–H(W31F)···N(1)	2.09(3)	2.928(5)	165(4)
7	O(1F)–H(W11F)···O(3F)	1.91(4)	2.728(8)	168(3)
8	O(1F)–H(W12F)···N(5A)	2.25(3)	3.129(5)	153(3)
9	O(4E)–H(W41E)···O(1F)	1.99(2)	2.820(6)	174(3)
10	N(54)–H(54)···N(59)	1.92	2.587(8)	134
11	N(34)–H(34)···N(39)	1.93	2.608(7)	136
12	N(14)–H(14)···N(19)	1.98	2.635(7)	133

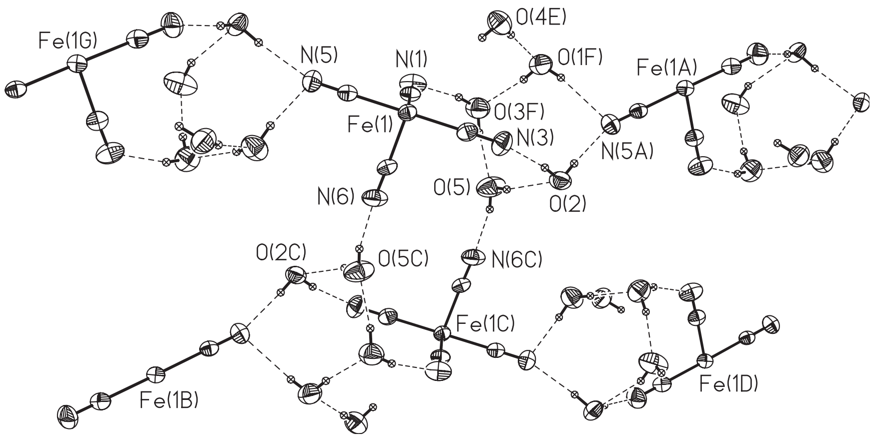


Figure 3. Perspective view to demonstrate the hydrogen bonds and generation of the two-dimensional structure in **1**. The organic cations as well as two cyanide groups (C(2), N(2), C(4), and N(4)) have been omitted for clarity. Symmetry: A, $0.5+x$, $0.5-y$, $0.5+z$; B, $0.5-x$, $y-0.5$, $-z-0.5$; C, $1-x$, $-y$, $-z$; D, $1.5-x$, $y-0.5$, $0.5-z$; E, $x-0.5$, $0.5-y$, $z-0.5$; F, $0.5+x$, $0.5-y$, $z-0.5$.

present in **1** (figure S1; vide infra), it is very difficult to comment on the geometric parameters of these N–H···O and N–H···N hydrogen bonds (table S1 in Supplementary materials). However, on placing the disordered atoms in one position, the nature of the supramolecular interactions can be understood from a simplified illustration (figure S2) indicating the linking of the two-dimensional water-ferricyanide sheet with the organic cations to result in an overall three-dimensional structure.

As mentioned earlier, the preferred geometry of water pentamer is cyclic. Acyclic structure may be possible if extra stabilization is achieved due to interactions of the water cluster with the organic or metal-organic moieties in the crystal. The organic moieties and the ferricyanide anion form several hydrogen bonds with the water pentamer. These interactions may be considered as the governing factor for the stabilization of the acyclic pentamer in **1**.

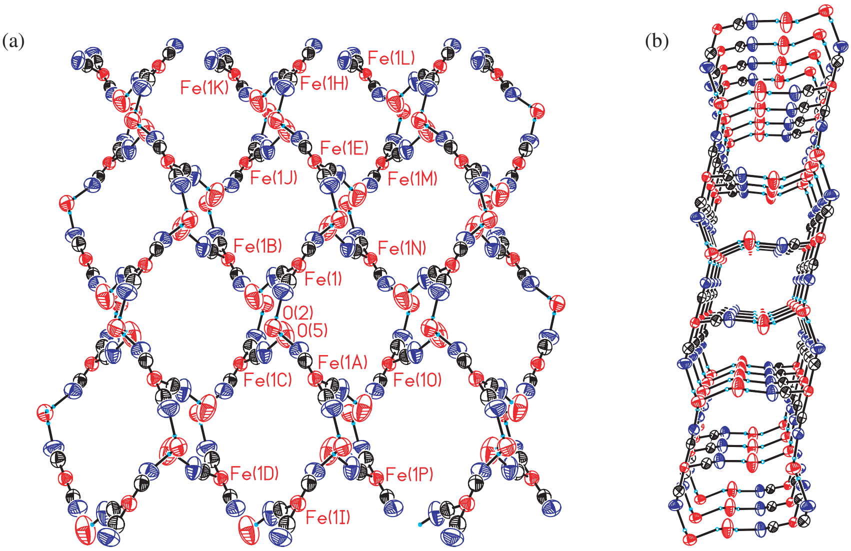
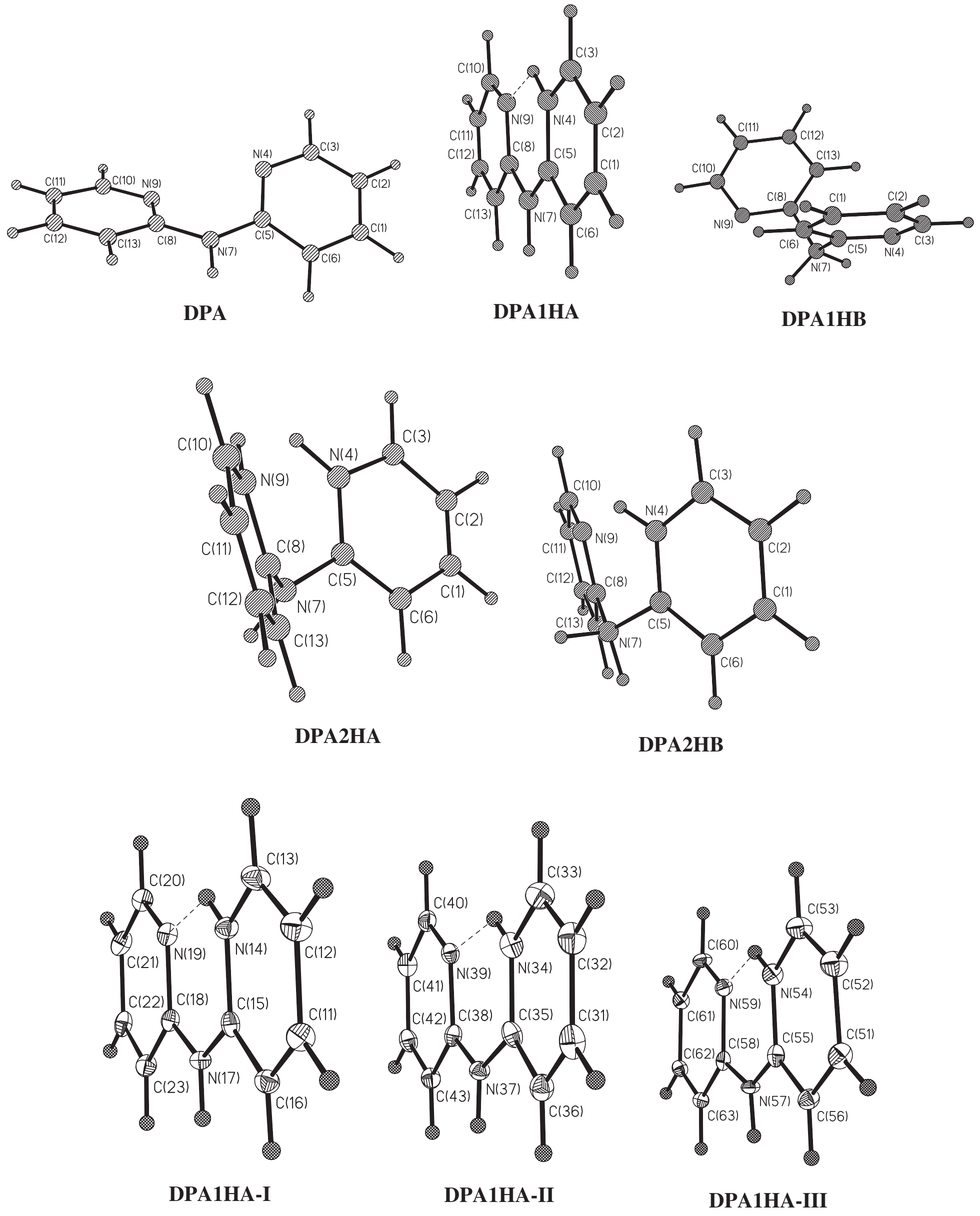


Figure 4. (a) Perspective view along crystallographic *c* axis to demonstrate the two-dimensional sheet formed due to strong hydrogen bonds involving ferricyanide and water molecules. The organic cations, two cyanide groups (C(2), N(2), C(4), and N(4)) and three water molecules ($H_2O(1)$, $H_2O(3)$, and $H_2O(4)$) have been omitted for clarity. Symmetry: A – E, as in figure 2; H, $x-1, y, z-1$; I, $1+x, y, 1+z$; J, $-x, -y, -z-1$; K, $x-1, y-0.5, -z-1.5$; L, $x-1, y+0.5, -z-1.5$; M, $-x, 1-y, -z-1.5$; N, $0.5-x, y+0.5, -z-0.5$; O, $1-x, 1-y, -z$; P, $1.5-x, y+0.5, 0.5-z$. (b) Perspective view of the hydrogen bonded ferricyanide—water sheet down the crystallographic *b* axis.

3.2. *Quantum chemical calculations*

It became difficult to judge the site of protonation in **1**. There are a number of possibilities: (a) at one pyridine nitrogen (DPA1HA); (b) at the amine nitrogen (DPA1HB); (c) at both the pyridine nitrogens (DPA2HA); (d) at one pyridine and the amine nitrogens (DPA2HB); (e) at all the three nitrogens (DPA3H). However, the existence of three DPA1HA or three DPA1HB should be more probable. To understand the site of protonation, geometry optimization and the energy calculation of neutral, monoprotonated, and diprotonated forms of 2,2′-dipyridylamine were carried out by the density functional method. Becke-style three parameter hybrid functional combined with Lee-Yang–Parr correlational functional (B3LYP) and split valence 6-31G basis set augmented with polarization functions, one d funtion for nonhydrogen atoms and one p function for hydrogen atoms, were used in these calculations [15]. The optimized geometries were compared with the structural parameters of the three moieties in **1**.

The similar orientations of the optimized geometries of DPA, DPA1HA, DPA1HB, DPA2HA, and DPA2HB as well as of the observed geometries of the three monoprotonated DPA (DPA1HA-I, DPA1HA-II and DPA1HA-III) are shown in figure 5, while similar structural parameters are compared in table 3. There arise some significant differences in C–N(central) bond distances (D1 and D2) and the dihedral angle (δ) between two cyclic C_5N moieties. In DPA and DPA1HB, D1 equals D2 (DPA: $D1 = D2 = 1.397$ Å. DPA1HB: $D1 = D2 = 1.497$ Å). In contrast, the values of D1 and D2 are not equal ($D1 = 1.364$ Å, $D2 = 1.410$ Å) for DPA1HA. Similar to those in



DPA **DPA1HA** **DPA1HB**

DPA2HA **DPA2HB**

DPA1HA-I **DPA1HA-II** **DPA1HA-III**

Figure 5. Optimized geometries of 2,2′-dipyridylamine (DPA) and its monoprotonated (DPA1HA and DPA1HB) and diprotonated (DPA2HA and DPA2HB) forms as well as the observed geometry (in **1**) of monoprotonated 2,2′-dipyridylamine (DPA1HA-I, DPA1HA-II, DPA1HA-III).

DPA1HA, D1 and D2 are unequal in the three units (DPA1HA-I, DPA1HA-II and DPA1HA-III): 1.361(5) Å, 1.384(5) Å; 1.345(5) Å, 1.408(6) Å; 1.349(6) Å, 1.362(6) Å) in the observed structure indicating that one pyridine nitrogen of each of the three DPA are protonated in **1**. However, as the amine nitrogen is disordered over two positions (figure S1), the site of protonation will be better understood from the comparison of

Table 3. Selected bond lengths (Å) and angles (°) of the optimized structures of neutral (DPA), monoprotonated (DPA1HA and DPA1HB), and diprotonated (DPA2HA and DPA2HB) forms as well as of the experimental structure (in **1**) of monoprotonated form (DPA1HA-I, DPA1HA-I1 and DPA1HA-III) of 2.2′-dipyridylamine.

	DPA	DPA1HA	DPA1HB	DPA2HA	DPA2HB	DPA1HA-I	DPA1HA-II	DPA1HA-III
C(l)–C(2)	1.397	1.411	1.396	1.404	1.395	C(ll)–C(12) = 1.382(6)	C(31)–C(32) = 1.382(7)	C(51)–C(52) = 1.385(7)
C(2)–C(3)	1.393	1.372	1.396	1.378	1.391	C(12)–C(13) = 1.356(6)	C(32)–C(33) = 1.359(7)	C(52)–C(53) = 1.355(6)
C(l)–C(6)	1.387	1.381	1.397	1.394	1.407	C(11)–(C16) = 1.357(6)	C(31)–C(36) = 1.363(7)	C(51)–C(56) = 1.357(6)
C(5)–C(6)	1.410	1.410	1.387	1.394	1.376	C(15)–C(16) = 1.387(6)	C(35)–C(36) = 1.371(6)	C(55)–C(56) = 1.373(6)
C(11)–C(12)	1.397	1.399	1.396	1.404	1.394	C(21)–C(22) = 1.376(7)	C(41)–C(42) = 1.377(7)	C(61)–C(62) = 1.380(6)
C(10)–C(11)	1.392	1.388	1.396	1.378	1.398	C(20)–C(21) = 1.360(6)	C(40)–C(41) = 1.349(6)	C(60)–C(61) = 1.370(6)
C(12)–C(13)	1.387	1.389	1.397	1.394	1.404	C(22)–C(23) = 1.371(7)	C(42)–C(43) = 1.370(6)	C(62)–C(63) = 1.371(6)
C(8)–C(13)	1.410	1.400	1.387	1.394	1.381	C(18)–C(23) = 1.379(6)	C(38)–C(43) = 1.380(6)	C(58)–C(63) = 1.359(6)
C(3)–N(4)	1.337	1.358	1.343	1.363	1.348	C(13)–N(14) = 1.342(5)	C(33)–N(34) = 1.344(6)	C(53)–N(54) = 1.342(6)
C(5)–N(4)	1.336	1.356	1.318	1.363	1.349	C(15)–N(14) = 1.347(5)	C(35)–N(34) = 1.328(6)	C(55)–N(54) = 1.358(6)
C(8)–N(9)	1.336	1.338	1.318	1.363	1.323	C(18)–N(19) = 1.341(6)	C(38)–N(39) = 1.359(6)	C(58)–N(59) = 1.361(6)
C(10)–N(9)	1.337	1.345	1.343	1.363	1.345	C(20)–N(19) = 1.329(5)	C(40)–N(39) = 1.351(6)	C(60)–N(59) = 1.349(5)
C(5)–N(7)	1.397	1.364	1.497	1.392	1.485	C(15) ~ N(17) = 1.361(5)	C(35)–N(37) = 1.408(6)	C(55)–N(57) = 1.349(6)
C(8)–N(7)	1.397	1.410	1.497	1.392	1.529	C(18)–N(17) = 1.384(5)	C(38)–N(37) = 1.345(5)	C(58)–N(57) = 1.362(6)
C(5)–N(7)–C(8)	129.5	128.6	115.6	129.5	117.7	C(15)–N(17)–C(18) = 131.0(5)	C(35)–N(37)–C(38) = 132.0(5)	C(55)–N(57)–C(58) = 136.3(5)
δ^a	39.5	0.0	74.4	63.2	39.3	3.4	2.0	5.0

[a] Dihedral angle between two cyclic moieties.

other structural parameters which are little affected by the disorder present in this crystal. As the central (amine) nitrogen is disordered over two sites, each of the two carbon atoms C(15) and C(18) as well as the two nitrogen atoms N(14) and N(19) are also disordered over two positions (figure S1). Clearly, the relative planarity of the two pyridine rings is not affected by the disorder. In the optimized geometry, two cyclic moieties are coplanar ($\delta = 0°$) in DPA1HA, while the two pyridine rings are appreciably twisted in DPA ($\delta = 39.5°$), DPA1HB ($\delta = 74.4°$), DPA2HA ($\delta = 63.2°$), and DPA2HB ($\delta = 39.3°$). If there are not some drastic influencing factors like coordination to metal ions, the geometries of these species in crystals should not deviate significantly from the optimized geometries. In **1**, the three organic moieties are not coordinated to metal ions. Therefore, as in the optimized geometry of DPA1HA, the coplanarity of the two cyclic moieties in each of the three organic moieties in **1** ($\delta = 3.4(3)$, 2.0(3), and 4.7(3)°) indicates that one pyridine nitrogen in each organic moiety is protonated.

It may be argued that protonation at one pyridine nitrogen can be modeled in a case where two pyridine nitrogens are equivalent. However, this is a general idea that the first protonation decreases the basicity of the remaining moiety. The calculated values of the proton affinities of the several cases discussed below also clearly indicate this. Similar monoprotonation at one pyridine nitrogen was adopted, without any explanation, in a previously reported example [16]. The extra proton in this previously reported example was also not found from diffraction data. The two C_5N rings in this previously reported example are coplanar. In our case, as discussed earlier, the dihedral angle between two C_5N rings are close to 0° indicating that protonation takes place similarly in the two compounds. However, we have concluded the site of protonation from quantum chemical calculations.

Between two possibilities, monoprotonation of DPA in **1** takes place at the pyridine nitrogen. This is in contrast to the general idea that the aliphatic amine nitrogen is more basic than the aromatic (pyridine) nitrogen. To understand the enhanced basicity of the pyridine nitrogen of DPA as well as the relative basicities of neutral and monoprotonated forms, the energies of DPA, DPA1HA, DPA1HB, DPA2HA, and DPA2HB have been calculated in the above mentioned density functional method. The energy values (in Kcal/mole) are as follows: DPA, –345601; DPA1HA, –345862; DPA1HB, –345833; DPA2HA, –346002; DPA2HB, –345973. Since the electronic energy of proton is zero, proton affinities can be calculated as the difference in energies between the protonated form and the deprotonated form [15b]. Therefore, the proton affinities (Kcal/mole) of the pyridine and amine nitrogens of DPA, pyridine and amine nitrogens of DPA1HA, and the pyridine nitrogen of DPA1HB are 261, 232, 140, 111, and 140, respectively. Clearly, the probability of diprotonation is much less than monoprotonation. Again, monoprotonation at the pyridine nitrogen is energetically more favorable. There should be some governing force for this apparent anomaly. In DPA1HA, the coplanarity of the two cyclic rings ($\delta = 0°$) stabilizes the system in two ways. First, a strong intramolecular N–H$\cdots$N hydrogen bond (N(4)$\cdots$N(9) = 2.75 Å, N(4)–H$\cdots$N(9) = 126.9°, H$\cdots$N(9) = 1.99 Å) is formed. Secondly, the π clouds are far apart so that the repulsive force between the two pyridine rings is minimized. In contrast, there is no possibility of hydrogen bonding interactions for DPA1HB. Moreover, as the two cyclic rings are almost perpendicular ($\delta = 74.4°$), the interaction between the π densities may destabilize the system. It may be noted that, as in optimized structures, there exists a similar strong intramolecular hydrogen bond in the monoprotonated 2,2′-dipyridylamine in **1** (figure 5, table 2). It may be argued that C–H···π hydrogen bonding interactions might be a stabilizing factor for DPA1HB, in which the two pyridine rings are almost perpendicular. However, as this stabilizing effect is very weak in comparison to the N–H···N hydrogen bonds, coplanar orientation of the two pyridine rings, i.e., protonation at pyridine nitrogen takes place.

Calculation by a few other methods (B3LYP-631G(d), HF-631G(d), and HF-631G(d,p)) were also carried out to check the optimizations. These calculations also result in similar geometries of the neutral and protonated DPA as well as similar trend of proton affinities (tables S2–S8, Supplementary material). In addition, no imaginary vibration has been obtained in the frequency calculation with the optimized structures indicating global minima in the optimization processes.

3.3. *Syntheses and electronic spectra*

To check whether the number (one, two or three) or the nature (pyridine or amine nitrogen) of protonation in the solid state is dependent on the ferricyanide anion, attempt was taken to derive another protonated compound on evaporating the aqueous solution of DPA in large excess of HCl. In this case, a white crystalline compound **2** was deposited. Elemental analyses of this compound correspond to the molecular formula $[DPA1HA]^+Cl^- \cdot 2H_2O$. The appearance of strong water vibration at 3353 cm^{-1} indicates that **2** contains water molecules.

The absorption spectrum of DPA in MeOH–H$_2$O exhibits two intense bands at 311 and 262 nm and a relatively weak band at 221 nm. As illustrated in figure 6, the absorption spectra of the organic moieties in **1**, **2**, and in the mixture of 1:1 DPA–HCl are of similar types. In these cases, the original bands of DPA at 311 and 262 nm are

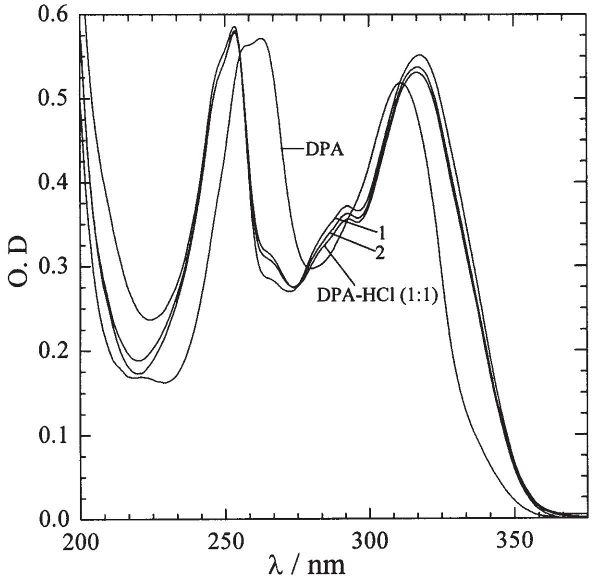


Figure 6. Absorption spectra of DPA (3.785 × 10^{-5} (M)), DPA–HCl (1:1; (3.785 × 10^{-5} (M)), **1** (3.7853 × 10^{-5} (M)), and **2** (3.785 × 10^{-5} (M)) in methanol-water (1:1).

slightly shifted to 317 and 254 nm, respectively, while the weak intensity band of DPA at 221 nm vanishes. In addition, each of these three systems (**1**, **2**, and 1:1 DPA–HCl) exhibits two shoulders at 292 and 266 nm. For **1**, an additional broad band appears at 419 nm (figure S3 in Supplementary material) which is due to the absorption of the ferricyanide anion.

Compositions of **1** and **2** indicate that monoprotonation of DPA at one pyridine nitrogen is more favorable in the solid state. As discussed earlier, the calculations in the gaseous state and the observed structure in the solid state indicate that N–H···N hydrogen bonding plays a key role for the favorable monoprotonation in these two states. To check the situation in solution, spectrophotometric titration of the methanol-water solution of DPA with HCl was carried out (figure 7). The gradual change of the spectra can be easily understood from the optical densities around 262 nm, the position of one band of neutral DPA. On addition of 0.5 mole ratio HCl, the peak of DPA at 262 nm is converted to a shoulder. In the case of 1:1 DPA–HCl, the intensity of the shoulder diminishes. On addition of increasing amounts of HCl, the intensity of this shoulder diminishes gradually and becomes a valley in the case of 1:1.5 DPA–HCl mixture. The valley becomes more prominent when more HCl is added and reaches the saturation in the case of 1:3 DPA–HCl. Clearly, if DPA is not di- (or tri-) protonated in solution, the spectra of the 1:1 DPA–HCl and the mixtures containing more HCl should be almost the same. Therefore, the observation is indicative that DPA is di- (or tri-) protonated in solution. However, isolation of the monoprotonated species, **2**, in presence of large excess of acid indicates that di- (or tri-) protonated species becomes monoprotonated during deposition as a solid. However, it is difficult to comment on the reason of this difference in protonation behavior.

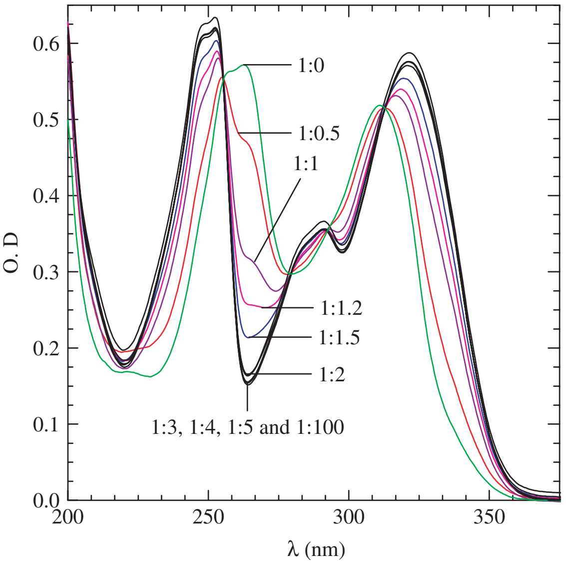


Figure 7. Absorption spectra of the titration of DPA (3.785 × 10^{-5} (M)) with HCl in methanol-water (1:1). DPA: HCl ratio has been indicated in the Figure.

4. Conclusions

An easy-route synthesis of 2-(N-2′-aminopyridylo)pyridinium ferricyanide, $[\mathrm{DPA1HA}]_3^+[\mathrm{Fe(CN)_6}]^{3-}\cdot 5\mathrm{H_2O}$ (**1**), has been described. As there are only few examples containing hexacyanometalate as anion, **1** may be considered an important addition in this family. The structural analyses of **1** reveal the existence of a rare example of acyclic water pentamer. The structure also consists of a hydrogen-bonded, two-dimensional water-ferricyanide sheet as well as overall three-dimensional supramolecular assembly. The site of protonation in 2,2′-dipyridylamine has been clearly explained by the quantum chemical calculations described in this report. The synthesis and characterization of an analogous compound, $[\mathrm{DPA1HA}]^+\mathrm{Cl}^-\cdot 2\mathrm{H_2O}$ (**2**), indicate that monoprotonation at one pyridine nitrogen of DPA is more favorable in the solid state. The absorption spectra of **1** and **2** as well as the spectrophotometric titration of DPA with acid indicate that, in contrast to gaseous (as evidenced by quantum chemical calculation) or solid (as evidenced by the composition of **1** and **2**) states, di- (or tri-) protonation takes place in solution.

Supplementary material

Crystallographic information for **1**, figures S1–S3, and tables S1–S8. Crystallographic data are available (CCDC no. 268412) from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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