

КРАТКИЕ СООБЩЕНИЯ

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IN SITU SYNTHESIS AND STRUCTURE OF $\text{FeCl}_4(4,4\text{-DIETHYL-4,4'-BIPYH})$ (BIPY = BIPYRIDINE)W.-T. Chen¹, Z.-G. Luo, D.-S. Liu, Y.-P. Xu, Q.-Y. Luo

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A novel viologen(4,4'-bipyridinium)-based compound $\text{FeCl}_4(4,4\text{-diethyl-4,4'-bipyH})$ (**1**) (bipy = bipyridine), in which 4,4'-diethyl-4,4'-bipyH (MQ^+) was generated *in situ*, is synthesized via the hydrothermal reaction and structurally characterized by single crystal X-ray diffraction. The crystal structure analysis reveals that the title compound features an isolated structure based on 4,4'-diethyl-4,4'-bipyH moieties and an iron atom terminally bound by four chlorine atoms. The 4,4'-diethyl-4,4'-bipyH moieties and $(\text{FeCl}_4)^-$ anions are interconnected by hydrogen bonds to form a 3D supramolecular framework.

Keywords: bipyridine, hydrothermal reaction, *in situ*, viologen.

Nowadays, increasing attention is being attracted by *in situ* reactions under hydro(solvo)thermal conditions, due to that the *in situ* reactions can lead to the formation of new compounds with interesting structures or novel properties for variously potential applications [1, 2]. Supramolecular chemistry has gained in interest due to the design of new crystalline materials because it takes advantage of self-assembly to prepare new compounds by virtue of weak cooperative interactions, such as hydrogen bondings, aromatic π — π stacking interactions, ion-ion interactions, dipole-dipole interactions, and ion-dipole interactions, to link different subunits together and, up to date, many supramolecular compounds have been documented [3, 4]. The 4,4'-bipyridine (bipy) moiety has delocalized π -electrons of pyridyl rings, which makes bipy an excellent candidate in preparing light emitting compounds with potential in several technical applications, such as sensitizers in solar energy conversion [5], chemical sensors [6], and emitting materials for organic light emitting diodes [7]. Recently, we have focused on supramolecular systems containing both magnetically active metal centers (as the Fe^{3+} ion) and bi-functional moieties such as 4,4'-bipy. Herein, we report the hydrothermal synthesis and crystal structure of $\text{FeCl}_4(4,4\text{-diethyl-4,4'-bipyH})$ (**1**) that possesses a 3D supramolecular framework, and 4,4'-diethyl-4,4'-bipyH was generated *in situ*. To our knowledge, it is the first report on MQ^+ -containing chlorometallate, although many chlorometallates with bipyridinium cations have been documented thus far [8—11].

Experimental. Instrumentation. All reactants of analytical grade were obtained commercially and used without further purification. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario EL III microanalyzer. Infrared spectra were recorded on a Thermo Nicolet NEXUS 870 FT-IR spectrophotometer over the frequency range 4000—400 cm^{-1} using the KBr pellet technique.

X-ray diffraction data were collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. The CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by

Table 1

<i>Crystal data</i>	
Empirical formula	C ₁₄ H ₁₉ Cl ₄ FeN ₂
Formula weight	412.96
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å; γ , deg.	14.148(6), 9.667(4), 13.836(9); 104.59(2)
<i>Z</i>	4
<i>V</i> , Å ³	1831(2)
<i>D_c</i> , mg/m ³	1.498
Absorption coefficient, mm ⁻¹	1.401
Crystal size, mm	0.35×0.30×0.10
No. of reflections collected / unique	5279/1558 [<i>R</i> _(int) = 0.0338]
Goodness-of-fit on <i>F</i> ²	0.991
Final <i>R</i> indices	<i>R</i> ₁ = 0.0506, <i>wR</i> ₂ = 0.1137
Index ranges	-16 ≤ <i>h</i> ≤ 16, -11 ≤ <i>k</i> ≤ 11, -16 ≤ <i>l</i> ≤ 16
(Δ/σ) _{max}	0
Largest difference peak, e/Å ³)	0.493, -0.327

Table 2

Selected bond lengths and bond angles of 1

Bond	Dist. (Å)	Angle	(deg.)	Angle	(deg.)
Fe(1)—Cl(1)	2.260(1)	Cl(2)#1—Fe(1)—Cl(2)	98.24(7)	Cl(2)#1—Fe(1)—Cl(1)	130.39(5)
Fe(1)—Cl(1)#1	2.260(1)	Cl(2)#1—Fe(1)—Cl(1)#1	102.23(5)	Cl(2)—Fe(1)—Cl(1)	102.23(5)
Fe(1)—Cl(2)	2.209(1)	Cl(2)—Fe(1)—Cl(1)#1	130.39(5)	Cl(1)#1—Fe(1)—Cl(1)	97.88(6)
Fe(1)—Cl(2)#1	2.209(1)				

Symmetry code: #1 $-x+1, y, -z+1/2$.

direct methods using the Siemens SHELXTLTM Version 5 package of crystallographic software. Difference Fourier maps based on the atomic positions yielded all non-hydrogen atoms. Hydrogen atom positions were generated theoretically and allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters, but were not refined. The structure was refined using a full-matrix least-squares refinement on *F*². All non-hydrogen atoms were refined anisotropically. The summary of the crystallographic data and structure analysis is given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Synthesis. FeCl₄(4,4'-diethyl-4,4'-bipyH) (1). The title compound was prepared by mixing FeCl₃ (1 mmol, 162.2 mg), 4,4'-bipyridine (1 mmol, 156.2 mg), concentrated HCl acid (1 ml), ethanol (2 ml), and distilled water (10 ml) in a 23 ml Teflon-lined stainless steel autoclave and heated at 180 °C for 10 days. After being slowly cooled to room temperature at 6 °C/h, yellow crystals suitable for the X-ray analysis were obtained. The yield was 72 %. Anal. Calcd. for C₁₄H₁₉Cl₄FeN₂: C, 40.72; H, 4.64; N, 6.78. Found: C, 40.55; H, 4.57; N, 6.89. Fourier transform IR (KBr, cm⁻¹): 3435(m), 2980(s), 2943(w), 2134(vs), 2112(s), 1483 (vs), 1452(m), 1436(s), 1388(vs), 1362(m), 1171(s), 1055(m), 997(vs), 901(w), 791(s) and 421(w).

Results and discussion. The hydro(solvo)thermal method has been known as a powerful technique in the synthesis of solid state compounds, and this method is also well-known for its effective-

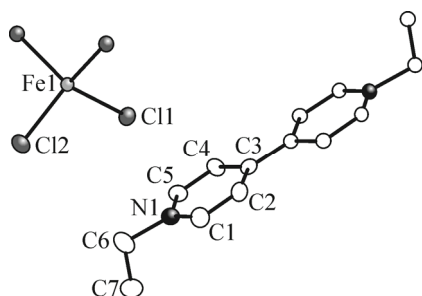


Fig. 1. ORTEP drawing of **1** with 10 % thermal ellipsoids. Hydrogen atoms were omitted for clarity

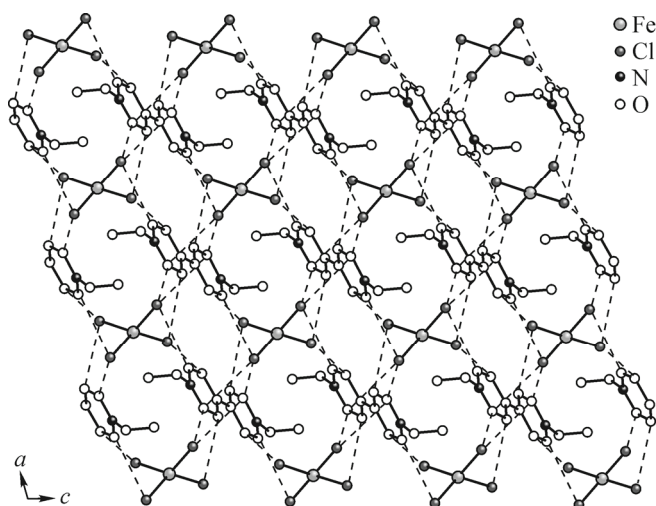


Fig. 2. Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): C(1)—H(1A)...Cl(1) 3.529(5), C(5)—H(5A)...Cl(1) 3.580(4) and C(2)—H(2A)...Cl(2) 3.496(5)

ness in *in situ* reactions. When superheated, water shows large difference from what is observed under normal conditions. The drastically lowered viscosity, for example, increases the solubility as well as the diffusion rate of the reagents, therefore possibly leading to *in situ* reactions. Many novel compounds synthesized *in situ* have been reported up to now [12–14]. However, viologen (4,4'-bipyridinium)-containing *in situ* reactions are relatively rare [15].

Compound **1** was prepared from the reaction of FeCl₃, 4,4'-bipyridine, ethanol, and concentrated HCl acid by the hydrothermal method. The X-ray diffraction analysis reveals that the structure of **1** is characterized as isolated, based on 4,4'-diethyl-4,4'-bipyH moieties and an iron atom terminally bound by four chlorine atoms, as shown in Fig. 1. All the crystallographically independent atoms, except for Fe1, are in general positions. The Fe1 atoms have a distorted tetrahedral geometry, coordinating with four terminal chlorine atoms. The bond lengths of Fe1—Cl11 and Fe2—Cl12 are 2.260(1) Å and 2.209(1) Å respectively, which is comparable with those reported [16, 17]. The Cl—Fe—Cl bond angles are in a wide range between 97.88(6)° and 130.39(5)°. The result of bond valence calculations indicates that the iron atom is in the +3 oxidation state (Fe1: 2.713) [18]. Due to that iron and chlorine atoms are in +3 and –1 oxidation states respectively, for the requirement of charge balance the MQ moieties should have one positive charge derived from the methylation of the N atom, as in the cases found in other compounds [19, 20]. The pyridyl rings in each MQ⁺ moieties are well coplanar with a dihedral angle of 0°. There is no π···π stacking interaction found between the pyridyl rings of the MQ⁺ moieties in the title compound. However, some C—H···Cl hydrogen bondings interconnect the MQ⁺ moieties and (FeCl₄)[–] anions to yield a 3D supramolecular framework. Therefore, the hydrogen bondings and the electrostatic interactions between the MQ⁺ moieties and (FeCl₄)[–] anions contribute to the stabilization of the crystal packing of **1** (Fig. 2). To our knowledge, compound **1** is the first MQ⁺-containing chlorometallate, although dozens of MV²⁺-containing chlorometallates have been documented (MQ⁺ = 4,4'-diethyl-4,4'-bipyH; MV²⁺ = 4,4'-dimethyl-4,4'-bipyH₂) [21–23].

Unlike the preparation of other viologen-containing compounds, in which viologen cations were brought from the starting materials [24, 25], the synthesis of **1** led to the *in situ* generation of the MQ⁺ cation. This provides a methodology for the preparation of viologen-based compounds and makes the synthesis of viologen relatively less toxic and more efficient. To our knowledge, this is the first example of the *in situ* generation of the MQ⁺ cation (MQ⁺ = 4,4'-diethyl-4,4'-bipyH), although an unprecedented *in situ* generation of the MV²⁺ dication (MV²⁺ = 4,4'-dimethyl-4,4'-bipyH₂) was reported before [15].

A search from the Cambridge Crystallographic Data Centre (CCDC) shows that there are hundreds of $(\text{FeCl}_4)^-$ -containing compounds [26, 27]. However, in these compounds, the counterpart cations are various, but none of them is the 4,4'-diethyl-4,4'-bipyH cation. Therefore, compound **1** is the first example containing both $(\text{FeCl}_4)^-$ and 4,4'-diethyl-4,4'-bipyH moieties.

In summary, by using the hydrothermal reactions of FeCl_3 , 4,4'-bipyridine, and concentrated HCl acid, a novel compound was obtained. It is the first example of the *in situ* generation of the MQ^+ cation ($\text{MQ}^+ = 4,4'$ -diethyl-4,4'-bipyH). The *in situ* formation of MQ^+ in the title compound may serve as a more efficient approach for the synthesis of viologen-based compounds. The scope for the syntheses of new viologen-based compounds with novel structures and properties appears to be very large, and further systematically experimental and theoretical investigations on this system are in progress.

Supplementary material. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 729436. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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