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Crystal structure, magnetic property and Mössbauer spectra of bis(pyridine-2,6-dicarboxylato) iron(III) dihydrate

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Abstract

Crystal structure, magnetic property and Mössbauer spectra studies of bis(pyridine-2,6-dicarboxylato) iron(III) dihydrate indicate a structure consisting of $H_5O_2^+$ and $[Fe(dipic)_2]^-$ ions, and Fe(III) in the complexes in a high-spin state. Temperature-dependent magnetic susceptibility shows a smooth curvature with Curie–Weiss behavior characteristic of appreciable weak ferromagnetic interaction.

Introduction

Several examples of iron(II) and iron(III) complexes of pyridine-2,6-dicarboxylic acid (dipicolinic acid) have been reported [1–4]. Ou *et al.* have reported that the complex of 4-chlorodipicolinic acid with Fe(III) exhibits an oxo-bridged binuclear with antiferromagnetic superexchange coupling [4]. In the present paper, we wish to report the results of structural, Mössbauer spectral and magnetic studies of the first example of $H_5O_2^+$ in an iron(III) complex with pyridine-2,6-dicarboxylate (or dipicolinic acid, $dipicH_2$), $(H_5O_2)[Fe(dipic)_2]$. Although a number of structural studies on diaquahydrogenium, $H_5O_2^+$, in transition-metal complexes have been reported [5–14], no examples of $H_5O_2^+$ in iron(III) complexes have been found in the literature.

Experimental

The compound $(H_5O_2)[Fe(dipic)_2]$ (m.p. 328 °C) was prepared by dissolving the iron(III) sulfate in a hot dilute sulfuric acid added aqueous solution of pyridine-2,6-dicarboxylic acid (dipicolinic acid, abbreviated $dipicH_2$), in which the metal to ligand ratio was 1:2. After several days a light green single crystal had grown; it was filtered off and washed with ethanol without recrystallization. The crystal size and quality were suitable for X-ray analysis. *Anal.* Calc. for $FeC_{14}H_{11}O_{10}N_2$: C, 39.7; H, 2.62; N, 6.62. Found: C, 39.6; H, 2.63; N, 6.78%.

The crystal data were measured on a CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. A total of 2263 reflections was measured up to 2θ of 50° in the $+h$, $+k$, $+l$ octant, among which 1191 are observed with $I_{net} \geqslant 2.5\sigma(I)$. An experimental absorption correction according to the Ψ curve was applied to the intensity data; the range of normalized transmission factors is 0.93–1.00 ($\mu = 18.6$ cm^{-1}). The structure was solved by the heavy atom method and subsequent difference Fourier maps followed by full-matrix least-squares refinement; the final agreement indices are $R(F) = 0.035$, $R_w(F) = 0.047$ including the secondary extinction correction ($g = 1.3 \times 10^{-3}$). In addition, the hydrogen atoms were then included in the refinement with isotropic thermal parameters. The atomic scattering factors and anomalous scattering factors ($\Delta f'$, $\Delta f''$) were taken from the International Tables for X-ray Crystallography, Vols. III and IV. The computer programs used for processing data were from NRC VAX. Relevant crystallographic data are given in Table 1.

The Raman spectra of the sample at 298 K were measured with a Spectra Physics model 2000 spectrometer using the 5145 Å line of an argon ion laser

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TABLE 1. Crystallographic data for $(H_5O_2)[Fe(dipic)_2]$

Empirical formula	$C_{14}H_{11}N_2O_{10}Fe$
Molecular weight	423.09
Colour	light green
Space group	*Pnna*
a (Å)	8.863(1)
b (Å)	11.018(3)
c (Å)	16.315
$\alpha=\beta=\gamma$ (°)	90
Cell volume (Å^3)	1593.20
Z	4
ρ (g/cm^3)	1.76
Diffractometer	Nicolet R3m/V
Radiation	Mo Kα ($\lambda=0.71073$ Å)
Temperature (K)	298
2θ max (°)	50.0
Reflections collected	2263
Reflections observed ($I > 2.5\sigma I$)	1191
R	0.035
R_w	0.047

as the exciting source.

The temperature-dependent magnetic susceptibility measurements in solid state were performed by the VSM system. Mössbauer spectra were recorded at 30, 90 and 295 K using a ASA-S-600 Mössbauer spectrometer. An iron foil was used as the standard of the isomer shift.

Results and discussion

$(H_5O_2)[Fe(dipic)_2]$ crystallizes in the orthorhombic space group *Pnna* with $a=8.863(1)$, $b=11.018(3)$, $c=16.315(4)$ Å and $Z=4$. The cation $(H_5O_2)^+$ (as shown in Fig. 1) is of C_2 symmetry. The central hydrogen atom is symmetrically bonded to two water molecules. The O····O distance is 2.439(6) Å and the bond angle of $H_2O\cdots H^+\cdots OH_2$ is 168.8(1)°. The four terminal hydrogen atoms in $H_2O\cdots H^+\cdots OH_2$ participated in intra- and intermolecular hydrogen bonds with oxygen atoms of the dipic ligand in the $Fe(dipic)_2^-$ anion. The selected interatomic distances and angles in $(H_5O_2)[Fe(dipic)_2]$ are listed in Table 2. The anion $[Fe(dipic)_2]^-$ is a distorted octahedral with respect to the ligand field symmetry of iron(III) and has an imposed two fold axis passing through C_6–N_1–Fe–$N_{11}C_{16}$ (as shown in Fig. 2). The bond length of Fe–$N_1=2.037(3)$ Å is shorter than that of Fe–$N_{11}=2.076(3)$ Å.

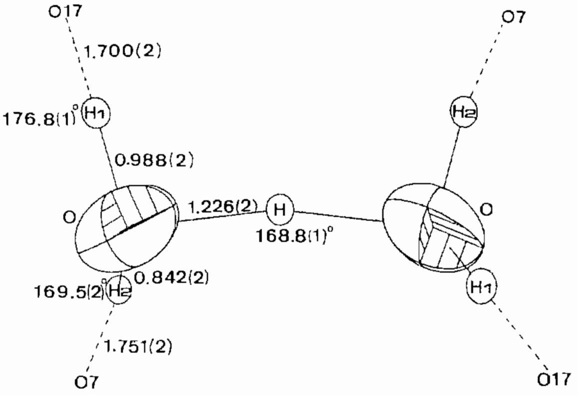

Fig. 1. The diaquohydrogen ion $(H_2O$–H–$OH_2)^+$. Hydrogen bonds to O(7) and O(17) atoms of the dipic anion are also shown.

TABLE 2. Select bond distances (Å) and bond angles (Å) of $(H_5O_2)[Fe(dipic)_2]$

distances			
Fe–N(1)	2.037(3)		
Fe–O(4)	2.0350(20)		
Fe–N(11)	2.076(3)	C(12)–C(13)	1.507(4)
Fe–O(14)	2.0056(19)	C(12)–C(15)	1.371(4)
N(1)–C(2)	1.323(3)	C(13)–O(14)	1.284(3)
C(2)–C(3)	1.501(4)	C(13)–O(17)	1.223(3)
C(2)–C(5)	1.385(4)	C(15)–C(16)	1.395(4)
C(3)–O(4)	1.273(4)	O–OH	1.226(3)[b]
C(3)–O(7)	1.223(4)	O–OH(1)′	0.990(3)[b]
C(5)–C(6)	1.377(4)	O–OH(2)′	0.840(5)[b]
N(11)–C(12)	1.328(3)	O·····O	2.439(4)
Angles			
N(1)–Fe–O(4)	75.80(6)		
N(1)–Fe–O(14)	104.51(5)		
O(4)–Fe–O(4)′	151.61(8)		
O(4)–Fe–N(11)	104.20(6)		
O(4)–Fe–O(14)	92.10(9)		
O(4)–Fe–O(14)′	94.95(9)		
N(11)–Fe–O(14)	75.49(5)		
O(14)–Fe–O(14)′	150.99(8)		
H(1)′–H(2)′	105.95(20)		
O–H–O′	168.8(1)		

[a] Primes indicate a two-fold symmetry related atom. [b] The hydrogen atoms H(1), H(2) were located from the difference map.

The nature of the $H_5O_2^+$ bonding in the present complex was also determined on the basis of the Raman spectra. The bonds assigned to the $H_5O_2^+$ ion occur in frequency regions which have been cited as characteristic of $H_5O_2^+$ ion from previous studies [8, 10]. It has been shown that the most notable $H_5O_2^+$ stretching and deformation vibration for $H_5O_2^+SbCl_6^-$ [10] fall into the following bands: 3425(vs) cm^{-1} for the OH_2 stretching vibration, 1675(s) cm^{-1} for the deformation vibration of OH_2 and 1015(s) cm^{-1} for the stretching vibration of OHO. Inspection of the Raman spectra for the present $(H_5O_2)[Fe(dipic)_2]$ complex reveals that the OH_2 and OHO stretching frequencies are observed

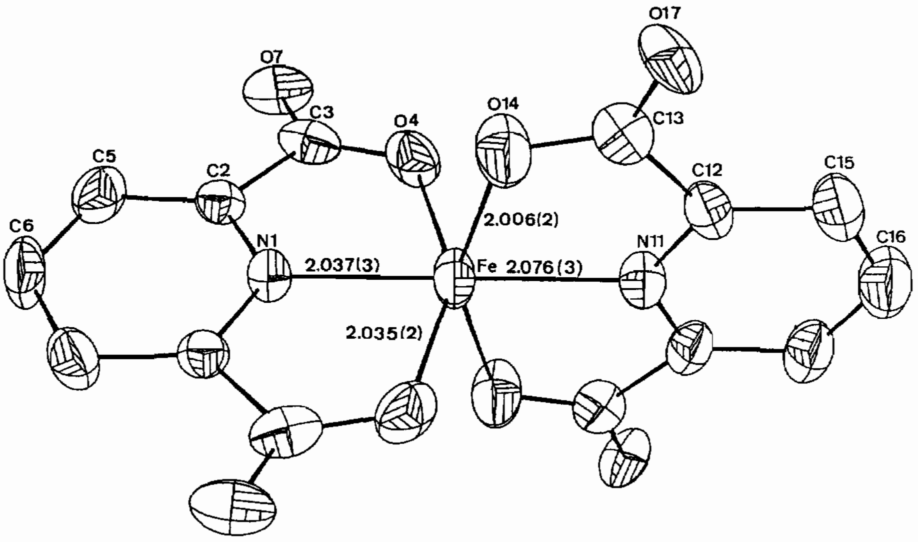

Fig. 2. ORTEP drawing and atomic labelling of $[Fe(dipic)_2]^-$ with 50% probability.

at 3422(vs) and 1040(vs) cm^{-1}, respectively and the OH_2 deformation frequency is observed at 1648(w) cm^{-1}.

The magnetic moment of 5.91 BM at 293 K indicates that the Fe(III) complex has a value in agreement with the spin-only value expected for a paramagnetic compound with Fe^{3+} in the $^6S_{5/2}$ high-spin state. Nevertheless, the temperature-dependent magnetic moment shows (Fig. 3) that the effective moment μ_{eff} value regularly rises with decreasing temperature; as the temperature decreases to 30 K, the μ_{eff} value is increased to about 7.5 BM. Furthermore, from the plot of magnetic susceptibility and reciprocal susceptibility against absolute temperature (Fig. 4) we found a smooth curvature with Curie–Weiss behavior ($\theta \approx 20$ K). It is apparent that this magnetic behavior is characteristic of appreciable weak ferromagnetic ordering between Fe(III) atoms. It is best to interpret the ferromagnetic magnetic behavior of the present iron(III) complex by assuming that the complex has a pseudo-polynuclear iron complex chain with $H_5O_2^+$ linkage; the magnetic coupling between the spin $^6S_{5/2}$ of the neighbor iron(III) ions (the shortest iron–iron distance is estimated from unit cell to be about 6 Å) could be brought about by the pathway of $H_5O_2^+$ linkage.

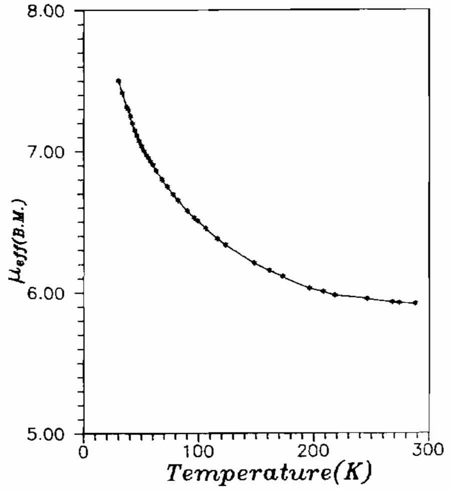

Fig. 4. Experimental magnetic moment vs. temperature for $(H_5O_2)[Fe(dipic)_2]$.

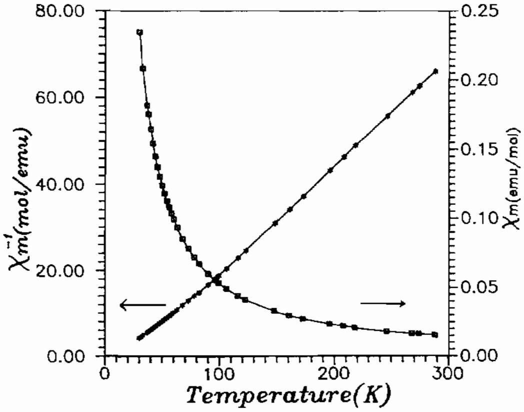

Fig. 3. Experimental molar paramagnetic susceptibility vs. temperature for $(H_5O_2)[Fe(dipic)_2]$.

The Mössbauer spectra obtained at 30, 90 and 295 K of the polycrystalline sample are shown in Fig. 5. The Mössbauer spectra observed at 295 K consist of an asymmetric quadrupole pattern consisting of two lines of different shapes. The quadrupole splitting is 0.76 mm/s, and the center of the lines indicates an isomer shift of 0.35 mm/s with respect to α-iron. Both values are characteristic for high-spin ($^6S_{5/2}$) Fe(III) compounds. This asymmetric

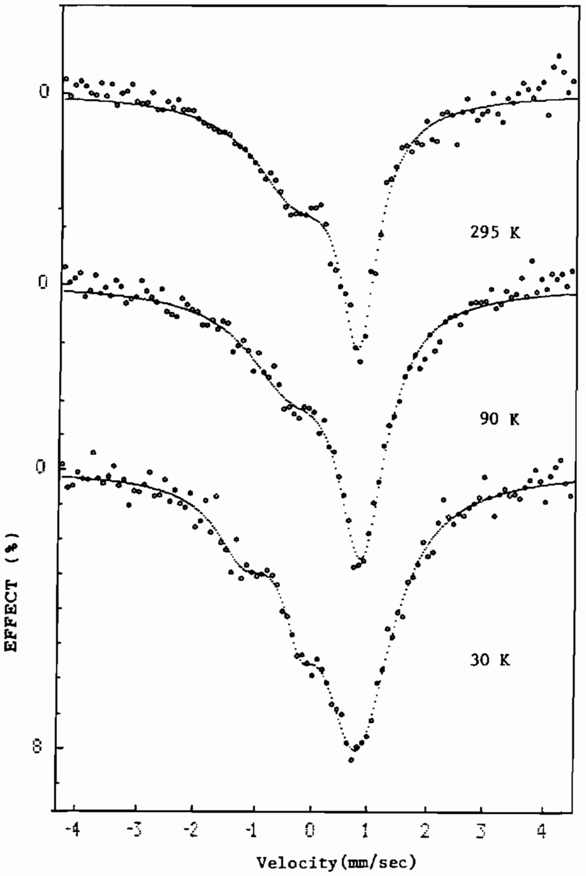

Fig. 5. Temperature dependent Mössbauer spectra of $(H_5O_2)[Fe(dipic)_2]$. The temperature is given beside each spectrum.

spectra, similar to that of $FeCl_3 \cdot 6H_2O$ [14, 15] in which above 78 K the spectra show the high-velocity component (right-hand peak), has kept a sharp line whilst the low-velocity component (left-hand peak) is broad. A Mössbauer spectrum obtained at 4.2 K, in an external magnetic field of 3 wb/m^2, showed a six-line pattern from which it was found that the nuclear quadrupole coupling constant e^2qQ is negative [14].

A quadrupole-split Mössbauer spectrum of polycrystalline isotropic samples is asymmetric because of the Karyagin–Goldanskii effect and the relaxation of paramagnetic ions causing a fluctuating magnetic field [14–18]. The former effect is based on the anisotropy of the Debye–Waller factor (recoil-free fraction). In the present result, both effects dominate the absorption spectra of $(H_5O_2)[Fe(dipic)_2]$.

The asymmetry results from the anisotropy of the recoil-free fraction of the iron nucleus in the reduced symmetry site and is predicted to decrease with decreasing temperature. Indeed, one might expect the recoil-free fraction for the present complex to be anisotropic because the bond length of the iron to the coordinated nitrogen and oxygen atoms of the ligands is different (as shown in Fig. 2). In other words, an anisotropic recoil-free fraction should produce an asymmetry in the $\pm 3/2 \rightarrow \pm 1/2$ nuclear quadrupole doublet of the present complex.

It is found that without an external field the linewidth of the spectra increases with decreasing temperature, up to 30 K (cf. Fig. 5). Although the line will never become solved, a doublet splitting is slightly observed at the left-hand side of the spectrum (the low-velocity side), while the width of the right-hand line remains constant. This indicates that a magnetic relaxation effect between iron(III) ions exists in the sample. In general, in the presence of a magnetic field, one line of the quadrupole doublet splits into a triplet and the other splits into a doublet. If the doublet is of higher energy (higher velocity) than the triplet, the sign of the nuclear quadrupole coupling constant e^2qQ is positive. If the doublet is of lower energy, e^2qQ is negative [15, 19, 20]. In the present case the magnetic field produced by ferromagnetic ordering of the iron(III)–iron(III) interaction is too weak to split the asymmetric quadrupole doublet. Therefore, to determine the sign of e^2qQ, it is necessary to apply a stronger external magnetic field to the sample. The detailed results of this external field application will be reported in the near future.

Supplementary material

Table SI listing the atomic positional and thermal parameters (2 pages), Table SII giving a complete list of bond lengths and angles (2 pages), and Table SIII listing calculated and observed structure factors (5 pages) are available from the authors on request.

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