

SYNTHESIS AND CHARACTERIZATION OF A NEW IRON (II)/4,4'-BIPYRIDINE COMPLEX

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ABSTRACT

The complex $[Fe(4,4'-bipy)_2(H_2O)_4](sac)_2 \cdot 2(4,4'-bipy)$ was obtained in an attempt to prepare a square grid polymer by reaction of tetraaquabis(saccharinato) iron(II) dihydrate with 4,4'-bipyridine. Its structure was determined by single crystal X-ray diffractometry. It belongs to the monoclinic space group $P2_1/c$ with $Z = 2$. The Fe(II) cation is in a slightly distorted octahedral coordination with two 4,4'-bipy and four water molecules as ligands. Its electronic and IR spectra, room temperature magnetic susceptibility and the thermal behavior were also investigated.

RESUMEN

Durante intentos para la generación de un polímero reticular cuadrado por reacción de tetraacuabis(sacarinato)hierro(II) dihidrato con 4,4'-bipridina (4,4'-bipy), se obtuvo el complejo simple $[Fe(4,4'-bipy)_2(H_2O)_4](sac)_2 \cdot 2(4,4'-bipy)$. Su estructura fue determinada por difracción de rayos X en monocristales. Perteneció al sistema cristalino monoclinico $P2_1/c$ con $Z = 2$. El catión Fe(II) presenta una coordinación octaédrica ligeramente distorsionada, estando ligado a dos moléculas de 4,4'-bipy y a cuatro moléculas de agua. También se investigaron sus espectros electrónicos y de IR, su susceptibilidad magnética a temperatura ambiente y su comportamiento térmico.

INTRODUCTION

Crystal engineering offers potential applications for the synthesis and development of new crystalline materials, in particular for those with functional properties as microporous solids for molecular absorption, ion exchange and heterogeneous catalysis [1]. For example, metal-organic networks can be designed through coordination chemistry methodologies and the obtained materials may mimic the properties of zeolites and clays. In this context, several coordination polymers containing 4,4'-bipyridine (4,4'-bipy) and other bridging ligands with transition metal cations, that form molecular binding blocks, have been synthesized [2-9]. The 4,4'-bipy has been selected because of its rod like rigidity and length. Some of these networks are square grid polymers, which have guest molecules, included in their pores.

As a part of our current studies with mixed metal saccharinate (saccharin = *o*-sulphobenzimide = $C_7H_5NO_3S$) complexes [10-14], we have attempted to prepare this type of polymeric complexes, containing this anion. In this context we have recently characterized the coordination square grid polymer $[Cu(4,4'-bipy)_2(H_2O)_2](sac)_2 \cdot DMF$ (DMF = *N,N'*-dimethylformamide) [15] which contains the saccharinate anions sandwiched between the complex layers and the DMF molecules filling the square holes.

Attempts to obtain a similar polymer using Fe(II) instead of Cu(II), failed leading to the simple $[Fe(4,4'-bipy)_2(H_2O)_4](sac)_2 \cdot 2(4,4'-bipy)$ coordination complex, which characteristics are reported herein.

EXPERIMENTAL

Synthesis of the complex

Tetraaquabis(saccharinato) iron(II) dihydrate, obtained by a standard procedure [16,17], was used as the starting material. 0.492 g (1 mmol) of this complex were dissolved in 20 mL of hot water. A solution of 0.386 g (2 mmol) of 4,4'-bipy in 10 mL of ethanol was dropwise added. After stirring during 30 min, a brown powder was generated which was filtered off and discarded. The resulting purple solution was concentrated by slow evaporation in air at room temperature. After a few hours, a purple precipitate was formed and was separated from the orange resulting solution. Upon slow evaporation of this solution, orange crystals suitable for X-ray diffraction studies were obtained.

Single crystal X-ray diffraction studies

Measurements were performed on a Kappa CCD diffractometer using graphite monochromated Mo- $K\alpha$ -radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal data, collection procedures, structure determination methods and refinement results are summarized in Table 1.

TABLE 1. Crystal data and details of refinement for $[Fe(4,4'-bipy)_2(H_2O)_4](sac)_2 \cdot 2(4,4'-bipy)$

Formula	$C_{54}H_{48}FeN_{10}O_{10}S_2$
M	1116.99
Crystal dimensions/mm	0.09 x 0.13 x 0.37
Temperature	293(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
<i>a</i> /Å	12.6101(2)
<i>b</i> /Å	14.8619(2)
<i>c</i> /Å	15.1793(3)
β (°)	114.4240(8)
Z	2
<i>D</i> /g cm ⁻³	1.432
F(000)	1160
μ /mm ⁻¹	0.442
θ range for data collect.(°)	3.06 – 25.00
No.reflections (total)	41349
unique	4516
observed [$I > 2\sigma(I)$]	4251
Refinement method	Full-matrix least-squares on F^2
Data/restr./parameters	4516/6/365
Final R indices [$I > 2\sigma(I)$]	R1=0.0448; wR2=0.1230
R indices (all data)	R1=0.0474; wR2=0.1265

All H-atoms but the ones of the loosely bound crystallization 4,4'-bipy molecule were located among the first 30 peaks of a difference Fourier map. However, the ligand and crystallization 4,4'-bipy and the saccharinate H-atoms were positioned stereochemically and refined with the riding model. The water H-atoms were refined with O-H and H...H distances restrained to target values of 0.86(1) and 1.40(1) Å, respectively.

Data reduction and correction have been performed using programs by Denzo and Scalepack [18], and SHELX-97 [19] for structure resolution.

Supplementary material available: Listings of atomic coordinates and equivalent isotropic displacement parameters, full intramolecular bond distances and angles, anisotropic thermal parameters, hydrogen coordinates and hydrogen bond distances and angles are available from the authors on request. They have also been deposited at the Cambridge Crystallographic Data Center, reference number, CCDC-188089.

Physicochemical measurements

Electronic UV/visible and diffuse reflectance spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer and a Shimadzu UV-300 spectrophotometer, respectively. Room temperature magnetic susceptibilities were determined with a Cahn-2000 balance, calibrated in the usual way with $\text{Hg}[\text{Co}(\text{SCN})_4]$, and working at a magnetic field strength of 6 kG. Infrared spectra were recorded on a Perkin Elmer 580 B spectrophotometer using the KBr pellet technique.

Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu thermoanalytical system (models TG-50 and DTA-50, respectively). Experiments were performed under an oxygen flow (60 mL/min) and at a heating rate of 10 °C/min. Sample quantities ranged between 10 and 20 mg. Al_2O_3 was used as a DTA standard.

RESULTS AND DISCUSSION

Structure of the complex

Intramolecular bond distances and angles around the Fe(II) cation are given in Table 2, and the ORTEP [20] drawing of the molecule is shown in Figure 1.

TABLE 2. Interatomic distances (Å) and bond angles (°) around iron (II) in $[\text{Fe}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 2(4,4'\text{-bipy})$ ^{a)}.

Fe-O(2w)	2.080(2)	Fe-O(1w)	2.135(2)
Fe-N(1)	2.237(2)		
O(2w)-Fe-O(1w')	89.83(8)	O(2w)-Fe-O(1w)	90.17(8)
O(2w)-Fe-N(1)	88.43(7)	O(1w')-Fe-N(1)	86.65(6)
O(1w)-Fe-N(1)	93.35(6)	O(2w)-Fe-N(1')	91.57(7)

^{a)} The primed atoms are obtained from the unprimed ones through the inversion symmetry transformation: $-x+2, -y, -z+2$.

The structure consists of distinct monomeric $[\text{Fe}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 2(4,4'\text{-bipy})$ complexes. The iron (II) ion is sited on a crystallographic inversion center in a slightly distorted octahedral (N_2FeOw_4) coordination with two 4,4'-bipy nitrogen atoms [$d(\text{Fe-N}) = 2.237(2)$ Å] and four water molecules [$d(\text{Fe-Ow}) = 2.082(2)$ and $2.135(2)$ Å].

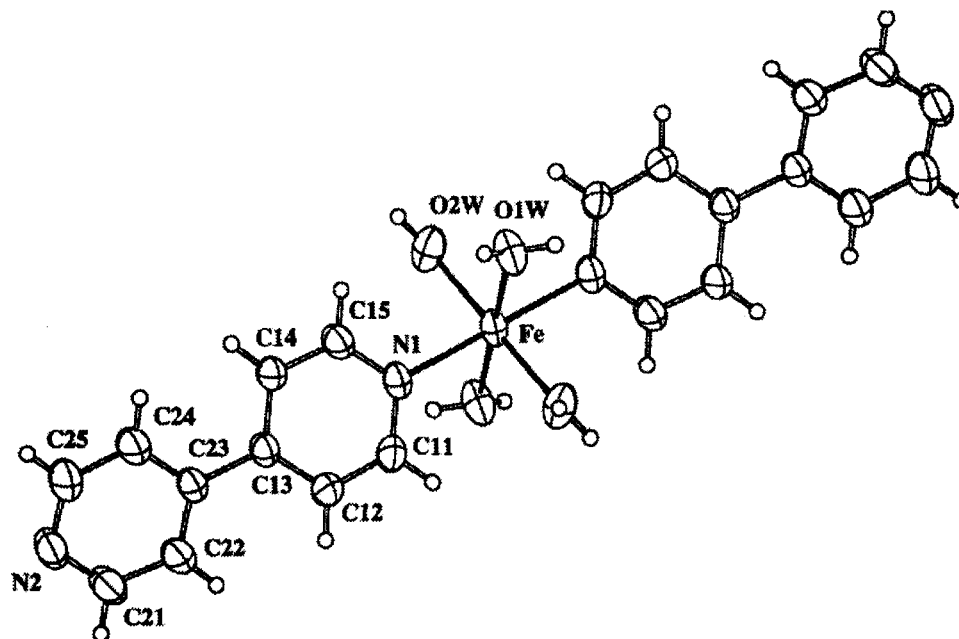


FIGURE 1. ORTEP plot showing the $[\text{Fe}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 2(4,4'\text{-bipy})$ complex, the labeling scheme for the non-H atoms and their displacement ellipsoids at 50% probability level. Full lines indicate iron-ligand bonds.

The pyridine rings of the 4,4'-bipy ligand are tilted in $18.82(6)^\circ$ from each other, and the 4,4'-bipy mean plane nearly bisects adjacent Fe-O(w) bonds. The corresponding tilt of the crystallization 4,4'-bipy molecules is $8.8(2)^\circ$. This molecule is more loosely bound to the lattice than the ligand molecules as shown by the relatively larger mean atomic displacement parameters of the crystallization molecule in comparison with the corresponding value for the ligand.

Although crystallographic data on other similar 4,4'-bipy/aquo complexes are not available for direct comparisons, it is interesting to mention that the Fe-O(w) distances found in the present case are similar to those reported in the simple $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ complex [21] whereas the Fe-N distances are comparable to those found in the Co(II) and Ni(II) pyridine (py) complexes of stoichiometry $[\text{M}(\text{py})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ [22] and in $[\text{Co}(\text{imidazole})_2(\text{H}_2\text{O})_4](\text{sac})_2$ [23]. Besides, the Fe-N distances are somewhat longer than the Cu-N distances (mean value = 2.011 \AA) found with the same ligand in $[\text{Cu}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot \text{DMF}$ [15] whereas the M-O(w) bonds are stronger in the Fe-complex.

The saccharinate C_6COSN molecular skeleton is nearly planar and parallel to the 4,4'-bipy ligand at van der Waals contact. The N-S and N-C bond lengths ($1.597(2)$ and $1.330(2) \text{ \AA}$, respectively) and the S-N-C angle ($111.3(2)^\circ$) are comparable to that found in the $[\text{Cu}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot \text{DMF}$ complex [15].

The structure is further stabilized by a net of medium to strong H-bonds involving the water molecules in three $\text{Ow-H} \cdots \text{N}$ and one $\text{Ow-H} \cdots \text{O}(\text{sac})$ interactions.

Electronic spectra and magnetic moment

The electronic absorption spectra in the UV region show the typical $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ ligand-based transitions (see Table 3). The band located at 460 nm has charge-transfer character. A weak band in the visible region around 885 nm can be assigned to the $d \rightarrow d$ transition of the FeN_2O_4 chromophore.

The major features of the diffuse reflectance spectra of the two complexes are similar to those in solution. The observed shifts between them are due to solvatochromic effects.

The value of the magnetic susceptibility, measured at room temperature (298 K) is also included in Table 3. It lies in the range usually expected for high spin Fe(II) complexes [24].

TABLE 3. Electronic spectra (band positions in nm) and room temperature magnetic moments (in Bohr magnetons) of $[\text{Fe}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 2(4,4'\text{-bipy})$. ^aDMF solution; in parenthesis: molar extinction coefficients ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)

Diffuse reflectance	450, 840
Absorption spectrum ^a	276 (8095), 284 (8090), 292 (7860), 460 (262), 885 (96)
Magnetic moment	5.40

Infrared spectrum

Table 4 shows an assignment of some of the most characteristic vibrational modes of the complex, compared with those of sodium saccharinate and free 4,4'-bipy. It exhibits the characteristic bands of 4,4'-bipy [25] and of the saccharinate anion [10-13, 26]. For 4,4'-bipy the band at 611 cm^{-1} can be assigned to a C-H bending motion. This band is very sensitive and shifts to higher frequency after coordination to the metal cation [5]. As expected, in the present case this band appears splitted. The two medium-intensity peaks, located at 619 and 601 cm^{-1} correspond to the coordinated and uncoordinated base, respectively. Metal-to-ligand vibrations are not easy to identify but we assign it, tentatively, by comparison with general literature data [27], in the following way: $\nu(\text{Fe-O}) = 536/528, 476\text{ cm}^{-1}$ and $\nu(\text{Fe-N}) = 394, 344\text{ cm}^{-1}$.

TABLE 4. Characteristic IR bands of the saccharinate anion, the free 4,4'-bipyridine molecule and the $[\text{Fe}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 2(4,4'\text{-bipy})$ complex. vs: very strong; s: strong; m: medium; w: weak; sh: shoulder

Na(sac).H ₂ O	4,4'-bipy	Complex	Assignments
1645 vs		1619 s	$\nu(\text{C=O})$
	1596 s	1596 s	$\nu(\text{C=C}) + \nu(\text{C=N})$, ring
1590 vs		1578 vs	$\nu(\text{C=C})$
	1533 m	1534 m	$\nu(\text{C=C}) + \nu(\text{C=N})$, ring
	1490 m	1490 m	$\nu(\text{C=C}) + \nu(\text{C=N})$, ring
	1407 m	1409 m	$\nu(\text{C=C}) + \nu(\text{C=N})$, ring + $\delta(\text{CH})$
1258 vs		1257 s	$\nu_{\text{as}}(\text{SO}_2)$
1150 vs		1149 vs	$\nu_{\text{s}}(\text{SO}_2)$
	807 s	805 s	$\delta(\text{CH})_{\text{oop}}$
677 m		669 m	$\delta(\text{CCC})$
	611 m	619m, 601m	$\delta(\text{CH})$

Thermal behavior

The complex was heated to 800°C in an oxygen atmosphere. The first weight loss occurs between 60 and 100°C (weak endothermic DTA signal at 73°C), corresponding to the four aqua ligands (observed loss, 6.53%; calculated 6.45%). After this step a continuous mass loss is observed up to 410°C, at which weight constancy is attained. This process is accompanied by a medium intensity exothermic DTA peak located at 376°C. The residue collected after heating up to 800 °C, was identified as Fe₂O₃ by IR spectroscopy (observed, 7.25%; calculated 7.17%).

CONCLUSIONS

The recrystallization in DMF of the product obtained by reaction of tetraaquabis (saccharinato) copper (II) dihydrate with 4,4'-bipy, leads to the generation of the square grid polymeric [Cu(4,4'-bipy)₂(H₂O)₂](sac)₂.DMF complex [15]. Attempts to obtain a similar polymeric species using Fe(II) instead of Cu(II) lead to a distorted FeN₂O₄ octahedral iron complex with the cation coordinated by two 4,4'-bipy and four water molecules, being the saccharinate anion the counter-anion. The unit cell is completed by two 4,4-bipy molecules.

The new complex could be thoroughly characterized by single crystal X-ray diffractometry and by electronic and infrared spectroscopy. Its magnetic and thermal behavior was also investigated. It constitutes a new example of a complex cation in which the saccharinate anion acts as a counter-anion, a type of compounds for which only a reduced number of examples are so far known [22, 23, 26, 28-31].

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