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Hydrothermal synthesis and characterization of a new iron phosphate structure of ladder-like chains and coordination directly by an organo-nitrogen ligand: $[Fe(phen)(HPO_4)(H_2PO_4)\cdot 0.5H_2O]$ (phen = 1,10-phenanthroline)

He Meng, Guanghua Li, Yunling Liu, Li Liu, Yanjie Cui, Wenqin Pang*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Number 10, Changchun 130012, P.R. China

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Abstract

A coordination iron phosphate, $Fe(phen)(HPO_4)(H_2PO_4)\cdot 0.5H_2O$ (**I**), has been hydrothermally synthesized and characterized by elemental analysis, IR spectral analysis, thermogravimetric analysis, and single-crystal X-ray diffraction. The title compound crystallizes in the monoclinic system, space group $C2/m$ (No. 12), with cell parameters $M = 438.03$, $a = 21.421(5)$ Å, $b = 6.4292(1)$ Å, $c = 12.190(3)$ Å, $\beta = 105.964(9)^\circ$, $V = 1614.1(6)$ Å^3, $Z = 4$, $R_1[I > 2\sigma(I)] = 0.0545$, $wR_2[I > 2\sigma(I)] = 0.1186$. This compound displays a new structure of ladder-like chains, in which each one-dimensional chain is constituted by the distorted octahedral units of Fe^{3+} bridged through PO_4 tetrahedron. The phen ligands in the compound bind in a bidentate fashion to the metal atoms and the ladder-like structure of the compound extends into a three-dimensional supramolecular array via $\pi-\pi$ stacking interactions of phen ligands. Mössbauer spectroscopy shows the presence of Fe^{3+} in the octahedral coordination. Magnetic susceptibility measurement studies show that this material may model as anti-ferromagnetic.

Keywords: Iron-phosphate; Hydrothermal synthesis; Inorganic–organic hybrid; Ladder-like chains

1. Introduction

New types of organically templated framework solids are being intensively studied because of their potential uses in catalysis, selective sorption and other applications [1]. Amongst the huge variety of phases prepared, organically templated iron phosphates (FePOs) show great structural diversity. In the last decade, a large number of new one-dimensional (1-D) [2], two-dimensional (2-D) [3] and three-dimensional (3-D) [4] structures have been synthesized successfully in hydrothermal or solvothermal conditions. The variable oxidation state and coordination preferences of iron mean that the structural chemistry of these materials is complex, and the field promises a wider range of materials. It is proposed that in most cases the amine, when bound weakly to a wholly inorganic framework by intermolecular interactions or hydrogen bonding, acts as a structure-directing and charge-balancing agent and/or space filler in the structure. On the other hand, the organic components can greatly affect the connecting patterns of inorganic polyhedra, thus providing a method for the synthesis of new organic–inorganic hybrid materials. Up to now, there are few reports on inorganic–organic hybrid iron phosphate frameworks with organic amines acting as ligands. Lii reported a 2-D fluorinated iron phosphate incorporating 2,2′-bipyridine (2,2′-bpy) ligands [3d]. In this structure the 2,2′-bpy ligands bind in a bidentate fashion to the metal atoms in

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*Corresponding author. Fax.: +86 431 516 8624.
E-mail address: wqpang@mail.jlu.edu.cn (W. Pang).

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the interlamellar region of 2-D sheets. We were interested in synthesizing a new iron phosphate with an open-framework all the while [5] for its special properties of electromagnetism and catalysis [6]. 1,10-phen may act as a bidentate ligand, much like 2,2′-bpy, and passivate coordinated points of the metal atom center to form low-dimension architecture which has the desired anisotropic physical and chemical properties. Here we report the synthesis, crystal structure, Mössbauer spectroscopy, and magnetic susceptibility measurement of a new 1-D inorganic–organic hybrid iron phosphate $Fe(phen)(HPO_4)(H_2PO_4) \cdot 0.5H_2O$ (**I**).

2. Experimental

2.1. Synthesis and characterization

The title compound was prepared from a mixture of iron **(II)** chloride tetrahydrate (⩾99.7%, Shantou Xilong Chemical factory of Guangdong), phosphoric acid (85 wt%, Beijing Chemical Plant), 1,10-phen (⩾99.0%, Shanghai Shanpu Chemical Ltd.), and deionized water. In a typical synthesis, the solution was prepared by dissolving 0.2 g of $FeCl_2 \cdot 4H_2O$ into 10.0 mL deionized water under constant stirring, then 0.4 mL of phosphoric acid (85 wt%) was slowly added dropwise, followed by addition of 0.2 g phen with constant stirring. The resulting mixture, with a molar ratio of $1.0FeCl_2 \cdot 4H_2O{:}6.0H_3PO_4{:}1.0phen{:}556H_2O$, was transferred into a 15 mL Teflon-lined stainless-steel autoclave and heated at 453 K for 7 days. The resulting yellow block-like crystal product as a single phase (in about 20% yield based on the Fe source) was recovered by filtration, washed with distilled water and dried at room temperature.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu*K*α radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count time was 4 s. The element analyses were performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer optima 3300 DV ICP spectrometer. The infrared (IR) spectrum was recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. A NETZSCH STA 449C unit was used to carry out the TGA analyses under nitrogen atmosphere with a heating rate of 10 °C/min. Magnetic susceptibility data were obtained on polycrystalline samples from ca. 2 to 300 K in a magnetic field of 5 k Oe after zero-field cooling using a Quantum Design MPMS-7 SQUID magnetometer. The ^{57}Fe Mössbauer measurements were made on a OXFORD-500 instrument at room temperature. Isomer shifts are reported with respect to an iron foil standard at 300 K.

2.2. Determination of crystal structure

A suitable single crystal of the title compound **I** ($0.20 \times 0.20 \times 0.16$ mm^3) was selected and mounted on a thin glass fiber. The intensity data were collected on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (graphite-monochromated Mo*K*α radiation, λ(Mo-*K*α) = 0.71073 Å). The numbers of collected reflections and independent reflections were 4353 and 1509 for **I**. Data processing was accomplished with the SAINT processing program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1 [7]. The iron and phosphorus atoms were first located. The carbon, nitrogen and oxygen atoms were found in the final difference Fourier maps. It is noteworthy that the P(2) atoms of (H_2PO_4) show disorder and occupy two positions with occupancy factors 0.5 in the structure of compound **I**, as shown in Fig. 1. All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. Further details of the X-ray structural analysis are given in Table 1.

3. Results and discussion

3.1. Characterization

The ICP analysis shows that the compound contains 12.45 wt% Fe and 14.33 wt% P, in good agreement with the values (12.68 wt% Fe, 14.85 wt% P) based on the single-crystal structure analysis. The elemental analysis

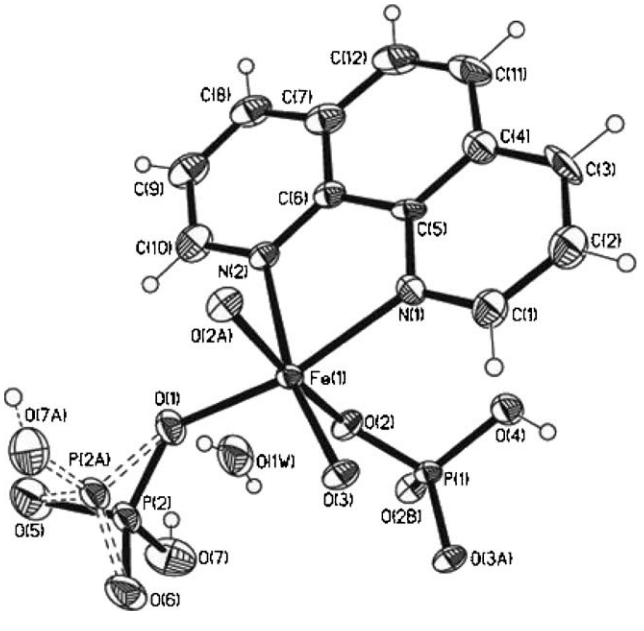

Fig. 1. ORTEP view of $Fe(phen)(HPO_4)(H_2PO_4) \cdot 0.5H_2O$ showing the atom labeling scheme (50% thermal ellipsoids).

shows that the C, H, and N contents are 32.92, 2.76, and 6.35 wt%, respectively (calculated: C, 32.87 wt%; H, 2.74 wt%; N, 6.39 wt%), corresponding to an empirical molar ratio of C:H:N = 6.05:6.08:1.00. These results are in accordance with the formula Fe(phen)(HPO_4)(H_2PO_4) · 0.5H_2O obtained from the single-crystal analysis.

The IR absorption spectrum of **I** can be assigned as follows: a band at ca. 527 cm^{-1} is attributed to the Fe–N stretching vibrations. The bands at 3300–3000 cm^{-1} are typically assigned to contributions from hydrogen bonding and N–H bonding. The bands at 3390 and 3502 cm^{-1} may be due to P–OH groups. The bands at 1180, 1075, 1037, 973 and 933 cm^{-1} are associated with the asymmetric stretching vibrations of PO_4 units, whereas the band at 723 cm^{-1} corresponds to the symmetric stretching vibrations of PO_4 groups. The bands at 1640, 1519, 1424, and 1257 cm^{-1} are assigned to frequencies of δ_{N-H}, ν_{C-H}, ν_{C-C}, and ν_{C-N}, which are related to the organic parts.

Table 1
Crystal data and structure refinement for Fe(phen)(HPO_4)(H_2PO_4) · 0.5H_2O

Empirical formula	$C_{12}H_{12}FeN_2O_{8.5}P_2$
Formula weight	438.03
Temperature	293(2) K
λ (Mo$K\alpha$)	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/m$
Unit cell dimensions	a = 21.421(5) Å b = 6.4292(1) Å c = 12.190(3) Å β = 105.964(9)°
Volume	1614.1(6) Å^3
Z	4
Density (Calculated)	1.803 mg/m^3
Absorption coefficient	3.396 mm^{-1}
θ range for data collection	1.98–25.05°
Completeness to θ = 25.05	96.1%
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0545, wR_2 = 0.1186

The powder X-ray diffraction pattern of the as-synthesized Fe(phen)(HPO_4)(H_2PO_4) · 0.5H_2O and the pattern simulated based on the single-crystal structure are presented. The diffraction peaks on both patterns correspond well in position, indicating the phase purity of the as-synthesized sample.

Thermogravimetric analysis shows that the weight loss of the compound is ca. 8.23% from 100 °C to 405 °C corresponding to the loss of the dehydrate between molecules (calc. 8.22%). There is a constant weight loss in the range from 405 to ca. 806 °C (obs = 41.16%, calc. = 41.09%) due to the decomposition of 1,10-phen molecules. We also analyzed the corresponding phases in different calcined temperature. The structure collapses and converts into an amorphous phase after calcinations at 600 °C for 2 h. The powder X-ray diffraction pattern of the sample heated at 900 °C for 2 h corresponds to $FePO_4$ (JCPDS file card No. 17-0837) and Fe(PO_3)$_3$ (JCPDS file card No. 44-0772).

Table 2
Selected bond lengths (Å) for Fe(phen)(HPO_4)(H_2PO_4) · 0.5H_2O

Fe(1)–O(3)	1.905(5)	N(1)–C(5)	1.366(9)
Fe(1)–O(1)	1.985(5)	N(2)–C(10)	1.332(1)
Fe(1)–O(2)	1.994(3)	N(2)–C(6)	1.350(1)
Fe(1)–O(3)	1.905(5)	C(1)–C(2)	1.381(1)
Fe(1)–N(1)	2.152(6)	C(2)–C(3)	1.373(1)
Fe(1)–N(2)	2.215(6)	C(3)–C(4)	1.420(1)
P(1)–O(3)#2	1.520(5)	C(4)–C(5)	1.393(1)
P(1)–O(2)	1.527(3)	C(4)–C(11)	1.427(1)
P(1)–O(2)#3	1.527(3)	C(5)–C(6)	1.432(1)
P(1)–O(4)	1.560(6)	C(6)–C(7)	1.417(1)
P(2)–O(1)	1.504(6)	C(7)–C(8)	1.410(1)
P(2)–O(6)	1.515(6)	C(7)–C(12)	1.421(1)
P(2)–O(5)	1.517(6)	C(8)–C(9)	1.359(1)
P(2)–O(7)	1.556(9)	C(9)–C(10)	1.406(1)
N(1)–C(1)	1.325(1)	C(11)–C(12)	1.346(1)
O(3)–Fe(1)–O(1)	103.6(2)	O(3)#2–P(1)–O(2)	112.36(2)
O(3)–Fe(1)–O(2)	93.88(1)	O(2)–P(1)–O(2)#3	106.7(3)
O(1)–Fe(1)–O(2)	90.42(1)	O(3)#2–P(1)–O(4)	109.1(3)
O(2)#1–Fe(1)–O(2)	171.8(2)	O(2)–P(1)–O(4)	108.10(2)
O(3)–Fe(1)–N(1)	91.5(2)	O(2)#3–P(1)–O(4)	108.10(2)
O(1)–Fe(1)–N(1)	165.0(2)	O(1)–P(2)–O(6)	115.3(3)
O(2)–Fe(1)–N(1)	88.53(1)	O(1)–P(2)–O(5)	107.9(3)
O(3)–Fe(1)–N(2)	167.0(2)	O(6)–P(2)–O(5)	111.1(3)
O(1)–Fe(1)–N(2)	89.4(2)	O(1)–P(2)–O(7)	110.1(4)
O(2)–Fe(1)–N(2)	85.91(1)	O(6)–P(2)–O(7)	108.6(4)
N(1)–Fe(1)–N(2)	75.6(2)	O(5)–P(2)–O(7)	103.1(4)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1, z$ #2 $-x+1/2, -y+1/2, -z$ #3 $x, -y, z$.

3.2. Description of the structure

The final selected bond lengths and bond angles are listed in Table 2. The crystal structure of **I** is constructed from neutral ladder-like 1-D chains consisting of [Fe(phen)(HPO_4)(H_2PO_4)] entities. Fig. 1 shows a perspective view of the entity with the atomic numbering scheme. Each Fe^{3+} ion adopts a distorted octahedral coordination geometry of $\{FeO_4N_2\}$, defined by two *cis*-nitrogen donors from the one phen molecule, three oxygen donors from three [HP(1)O_4] groups and one oxygen donor from the [H_2P(2)O_4] group. In each octahedral $\{FeO_4N_2\}$ unit, the Fe–N bonds are 2.152(6) and 2.215(6) Å. The Fe–O bonds are in the range of 1.905(5)–1.994(3) Å. Taking into account the irregular bond angles (O–Fe–O angles are in the range of 90.42(11)–171.8(2)°, O–Fe–N angles are in the range of 85.91(10)–167.0(2)°, N(1)–Fe–N(2) angel is 75.6(2)°) and a short Fe–O distances (Fe–O(3) = 1.905(5) Å), the geometry of each iron center in **I** is best described as a distorted octahedron.

The most interesting feature of **I** is its ladder-like 1-D chain structures. [HP(1)O_4] and $\{FeO_4N_2\}$ units, by corner-sharing, connect with O(2) atoms to form one sidepiece of the ladder (Fig. 2a), then two sidepieces connect each other by corner-sharing O(3) atoms to form the entity of the ladder-like chain. The oxygen bridge acts as the crosspiece of the ladder. Therefore, a four-membered ring (4-MR), $\{Fe_2P_2O_4\}$, is formed from two [HP(1)O_4] and two $\{FeO_4N_2\}$ via a corner-sharing mode. The [H_2P(2)O_4], corner-sharing, connect the Fe^{3+} center atom by the O(1) atom and are "hung" on the ladder chain. Such "hanging" H_2PO_4 units attached to each of metal centers on the framework are also reported by Yang in CdPO [8]. It is a notable similarity that two chain-like compounds are neutral and do not contain extra-framework cationic amines. This structural feature is quite different from other chain-like metal phosphates observed previously, most of which contain cationic amines as charge-balancing agents and/or space fillers in their structures [2,9].

The planar phen molecules are located nearly parallel to the equatorial plane of the Fe^{3+} center and perpendicular to the chain extension direction. It is of note that there are π–π stacking interactions between interchain phen groups. Adjacent phen groups in **I** are generally parallel and separated by 3.21 Å, which indicates strong π–π stacking interactions (Fig. 2b). The conjugated interaction is between a phen molecule of a chain and four phen molecules of another two chains. Therefore, the ladder-like chain of the title compound is further extended into interesting 3-D supramolecular arrays [3d,10]. Furthermore, strong multi-point hydrogen bonds also exist between P(1)–O(4)H and P(2)–O(6) with the distance O(4)–H···O(6) = 2.590(7) Å, O(1W)H and P(2)–O(1) with the distance O(1W)–H···O(1) = 3.462(5) Å, O(1W) and P(2)–O(7)H with the distance O(1W)···H–O(7) = 2.529(15) Å, O(1W)H and P(2)–O(7) with the distance O(1W)···H–O(7) = 2.529(15) Å. Detailed information about the hydrogen bonding is summarized in Table 3. We may thus conclude that the hydrogen bonding and π–π stacking interactions of phen groups play an important role in the stability of whole structure of compound **I**.

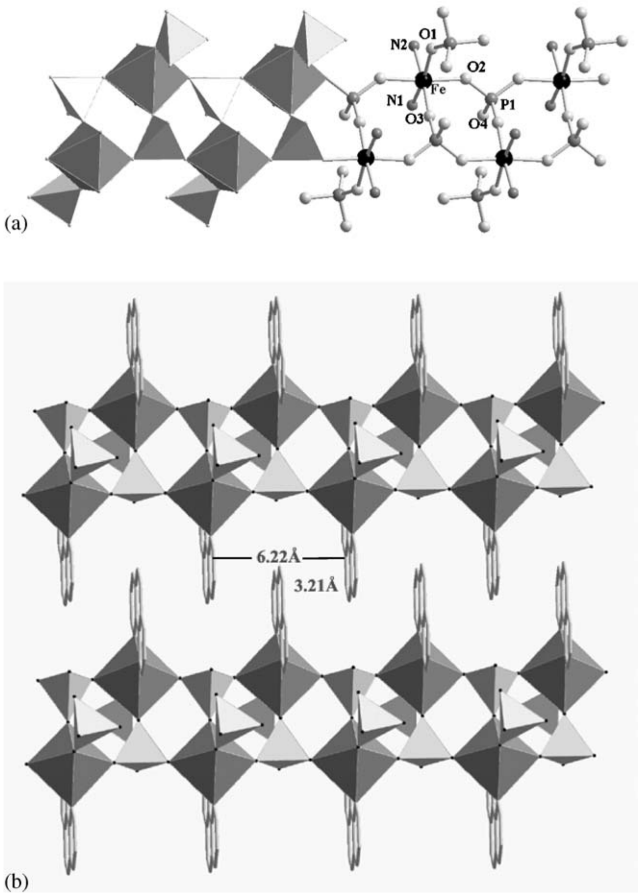

Fig. 2. (a) Polyhedral and ball-stick model of the ladder-like chain structure of compound **I**. (b) View of π–π stacking interaction between interchain or intermolecular phen groups of compound **I**.

3.3. Magnetic and Mössbauer spectrum measurements

Magnetic measurement of compound **I** was on powdered samples from room temperature to 2.0 K. Plots of χ_m and χ_m^{-1} for the compound are shown in Fig. 3, where χ_m is molar magnetic susceptibility. The molar magnetic susceptibility of this phase increases with decreasing temperature and reaches a maximum at ca. 20 K, indicating a long magnetic ordering in the temperature range studied. The observed magnetic moment $\mu_{eff} = 5.43\,\mu_B$ at 300 K derived from $\mu_{eff} = (8\chi_m T)^{1/2}$ is in good agreement with the calculated spin-only value for a magnetically uncoupled system of

Table 3
Hydrogen bonds for compound I (Å and deg)

D–H···A	*d*(D–H)	*D*(H···A)	*d*(D···A)	Angle (D–H···A)
O(4)–H(4)…O(6)#2	0.82	1.80	2.590(7)	160.3
O(7)–H(7)…O(1W)	0.82	1.81	2.529(15)	145.5
O(1W)–H(1A)…O(7)#3	0.88(4)	2.08(16)	2.529(15)	110(12)
O(1W)–H(1A)…O(1)#4	0.88(4)	2.65(10)	3.462(5)	154(13)

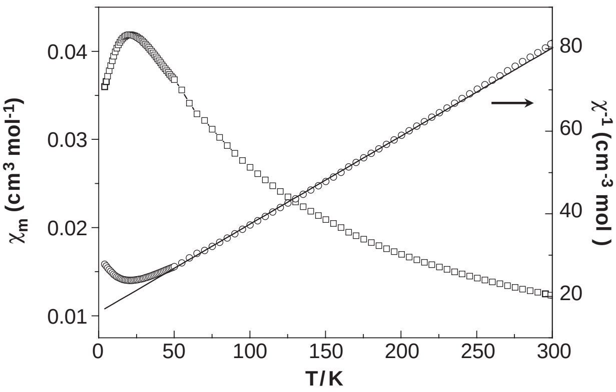

Fig. 3. Temperature variation of the magnetic susceptibility of compound **I**.

$\mu_{\text{eff}} = 5.92\,\mu_B$ [$\mu_{\text{eff}} = (\sum 4S_i(S_i+1))^{1/2}\,\mu_B$ with $S_i = 5/2$ for Fe^{3+}]. The thermal evolution of χ_m follows the Curie–Weiss law at a temperature higher than ca. 20 K, with $C_m = 4.69\,cm^3\,K/mol$ and $\theta = -75.74\,K$. The larger negative value of θ suggests a predominantly antiferromagnetic interaction. As described above, compound **I** exhibits a chain structure with the Fe(**III**) ions connected by the O–P–O bridges to form the 4-MR ring. The shortest Fe…Fe distance is 5.119 Å along the diagonal of 4-MR. The magnetic interaction could be due to the superexchange coupling between two Fe(**III**) mediated through the O–P–O bridge.

The room temperature ^{57}Fe Mössbauer spectrum of **I** was least-squares fit by one doublet (Fig. 4). The obtained parameters are δ(isomer shift) = 0.41 mm s^{-1}, ΔE_Q(quadrupole splitting) = 0.22 mm s^{-1}, and Γ(full-width at half-height) = 0.17 mm s^{-1}. The isomer shift is characteristic of high-spin Fe^{3+}. According to Menil [11], the usual range of isomer shifts in oxides is 0.29–0.50 mm s^{-1} for Fe^{3+} with six-coordination. Therefore, the valence of the iron atoms in **I** is confirmed by Mössbauer spectroscopy.

4. Concluding remarks

A new organic amine-coordinated iron phosphate compound, $Fe(phen)(HPO_4)(H_2PO_4) \cdot 0.5H_2O$, has been prepared by using hydrothermal conditions. This mechanism provided the possibility of preparing iron-containing inorganic–organic hybrid materials in a wide range of systems. It also would be of interest to investigate the role of the amines in the formation of open-framework structures more closely and explore other structures where the amine plays different roles.

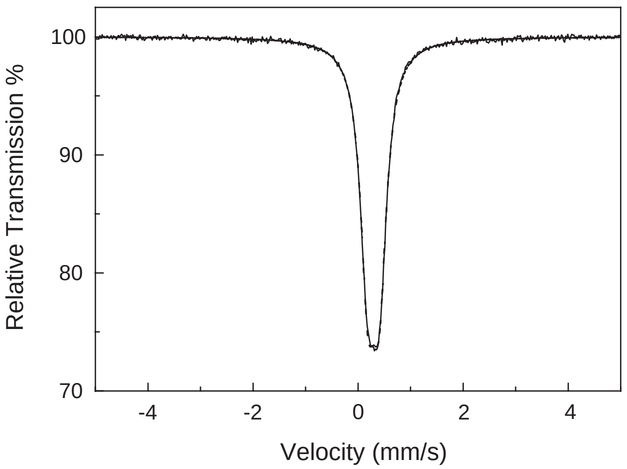

Fig. 4. Mössbauer spectroscopy of compound **I** at 300 K.

Acknowledgments

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