

Synthesis and Characterization of Organically Templated Metal Arsenates with a Layer Structure: $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{M}(\text{OH})\text{AsO}_4]$ ($M = \text{Ga}, \text{Fe}$)

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Two organically templated metal arsenates, $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{M}(\text{OH})\text{AsO}_4]$ ($M = \text{Ga}, \text{Fe}$), have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction and ⁷¹Ga NMR spectroscopy. The two compounds are isostructural and crystallize in the orthorhombic space group *Fdd2* (No. 43) with $a = 9.5584(7) \text{ \AA}$, $b = 41.593(3) \text{ \AA}$, $c = 5.6438(4) \text{ \AA}$, $V = 2243.8(3) \text{ \AA}^3$, and $Z = 16$ with $R_1 = 0.0302$ for the Ga compound, and $a = 9.7301(2) \text{ \AA}$, $b = 41.5035(2) \text{ \AA}$, $c = 5.7411(1) \text{ \AA}$, $V = 2318.45(8) \text{ \AA}^3$, and $Z = 16$ with $R_1 = 0.0228$ for the Fe compound. The structure consists of two-dimensional anionic sheets of metal arsenate in the *ac* plane with charge-compensating propanediammonium cations between the sheets. The sheets are constructed from infinite chains of *cis*-corner-sharing MO_6 octahedra, which are joined by arsenate ligands. This work is one of the few studies concerning organically templated metal arsenates. © 2000

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INTRODUCTION

The synthesis of open-framework metal phosphates is a subject of intense research because of their interesting structural chemistry and potential applications as solid catalysts (1). A wide range of metals including group 13 elements and transition metals have been incorporated into the phosphates, particularly in the presence of organic amine templates. Within group 13, the research emphasis has focused on the phosphates of aluminum and gallium. The first transition metal phosphates were prepared with molybdenum and vanadium (2, 3). A large number of iron phosphates and fluorophosphates have also been reported (4, 5). Since phosphorus and arsenic belong to the same group in the periodic table, it is of interest to prepare metal arsenates occluding organic amines. Little work however

has been carried out on the arsenates as compared to the phosphates, and to date only several arsenates of gallium, molybdenum, vanadium, and iron have been reported in the literature (6–10). We therefore extended our research to the arsenate system. By using 1,3-diaminopropane as a structure-directing agent under hydrothermal synthesis conditions, we synthesized two isostructural layered metal arsenates described below.

EXPERIMENTAL

Synthesis and Initial Characterization

The compounds were synthesized hydrothermally in a 23-mL Teflon-lined autoclave under autogenous pressure. Reaction of 1,3-diaminopropane (5 mmol), $\text{Ga}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (1 mmol), H_3AsO_4 (5 mmol), oxalic acid (4 mmol), *n*-butanol (5 mL), and H_2O (5 mL) at 180°C for 3 days followed by slow cooling at 6°C/h to room temperature produced $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Ga}(\text{OH})\text{AsO}_4]$, **1**, as colorless plate crystals in 79% yield. An energy-dispersive X-ray (EDX) analysis of a colorless plate crystal confirmed the presence of As and Ga. A plate crystal was selected for structure determination by single-crystal X-ray diffraction. The bulk product was monophasic as indicated by good agreement of its powder pattern with that simulated from the atomic coordinates derived from the single-crystal X-ray study. Elemental analysis confirmed the stoichiometry. Analysis found C, 7.00%; H, 2.76%; and N, 5.29%. Calculations determined C, 6.83%; H, 2.68%; and N, 5.31%. We have also carried out retrosyntheses excluding oxalic acid from the reactants; the resulting products are always a mixture of **1** and unidentified side products. The iron analogue $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Fe}(\text{OH})\text{AsO}_4]$, **2**, was prepared by heating a mixture of 1,3-diaminopropane (7.5 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.5 mmol), H_3AsO_4 (7.5 mmol), *n*-butanol (7 mL), and H_2O (3 mL) at 180°C for 3 days. Green plate crystals of **2** as the major product and a small amount of

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unidentified side product, as indicated from powder X-ray diffraction, were obtained. An EDX analysis of a green plate crystal confirmed the presence of As and Fe. An optimum set of reaction conditions to prepare a single-phase product of **2** was not found. Ion-exchange experiments were performed by stirring **1** with 4 M $\text{NH}_4\text{Cl}_{(\text{aq})}$ at room temperature and 50°C overnight. Elemental analysis of the ion-exchanged products showed that the propanediammonium cations were not replaced by NH_4^+ in a significant amount.

Structure Determination

A suitable single crystal of each compound was selected for indexing and intensity data collection on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected at room temperature in 1200 frames with increasing ω (width of 0.3° per frame). Empirical absorption corrections were applied. The structures were solved by direct methods and difference Fourier syntheses. Bond-valence calculations indicated that the Ga and Fe atoms are trivalent and O(5) is a hydroxo oxygen atom (11). All of the seven hydrogen atoms in **1** were found in difference Fourier

TABLE 1
Crystal Data and Structure Refinement Parameters for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Ga}(\text{OH})(\text{AsO}_4)]$ (**1**) and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Fe}(\text{OH})(\text{AsO}_4)]$ (**2**)

	1	2
Empirical formula	$\text{GaAsO}_5\text{C}_{1.5}\text{NH}_7$	$\text{FeAsO}_5\text{C}_{1.5}\text{NH}_7$
Formula weight	263.72	249.85
Crystal color, habit	Colorless, plate	Green, plate
Crystal size, mm	$0.20 \times 0.15 \times 0.02$	$0.21 \times 0.15 \times 0.02$
Crystal system	Orthorhombic	Orthorhombic
Space group	$Fdd2$ (No. 43)	$Fdd2$ (No. 43)
Unit cell dimensions	$a = 9.5584(7) \text{ \AA}$ $b = 41.593(3) \text{ \AA}$ $c = 5.6438(4) \text{ \AA}$ $V = 2243.8(3) \text{ \AA}^3$	$a = 9.7301(2) \text{ \AA}$ $b = 41.5035(2) \text{ \AA}$ $c = 5.7411(1) \text{ \AA}$ $V = 2318.45(8) \text{ \AA}^3$
Z	16	16
D_{calcld} , $\text{g} \cdot \text{cm}^{-3}$	3.111	2.863
T, K	295(2)	295(2)
λ (MoK α), \AA	0.71073	0.71073
μ , mm^{-1}	10.71	8.22
$2\theta_{\text{max}}$, $^\circ$	56.55	57.10
Index ranges	$-12 \leq h \leq 8$, $-36 \leq k \leq 54$, $-7 \leq l \leq 7$	$-12 \leq h \leq 12$, $-45 \leq k \leq 53$, $-7 \leq l \leq 6$
Data collected	2686	3250
Unique data	1230, $R(\text{int}) = 0.0437$	1131, $R(\text{int}) = 0.0365$
Number of variables	88	88
Goodness-of-fit	1.103	1.104
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0302$, $wR_2 = 0.0758$	$R_1 = 0.0228$, $wR_2 = 0.0651$
R indices (all data)	$R_1 = 0.0316$, $wR_2 = 0.0766$	$R_1 = 0.0230$, $wR_2 = 0.0654$
Flack x parameter	0.03(3)	0.01(2)
Extinction coefficient	0.00137(13)	0.00125(11)
$(\Delta\rho)_{\text{max, min}}$, $\text{e} \cdot \text{ \AA}^{-3}$	0.79, -0.89	0.55, -0.67

Note. $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$. $wR_2 = \{[\sum (w(F_o^2 - F_c^2))^2] / \sum [w(F_o^2)^2]\}^{1/2}$, $w = 1 / [\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\text{Max}(F_o, 0) + 2(F_c)^2] / 3$, where $a = 0.0472$ and $b = 8.87$ for **1** and $a = 0.0347$ and $b = 24.15$ for **2**.

TABLE 2
Atomic Coordinates and Temperature Factors (\AA^2) for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Ga}(\text{OH})(\text{AsO}_4)]$ (**1**) and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Fe}(\text{OH})(\text{AsO}_4)]$ (**2**)

Atom	x	y	z	U_{eq}^a
Compound 1				
As(1)	0.73610(5)	0.08480(1)	0.20507(9)	0.0079(2)
Ga(1)	0.57241(6)	0.09828(1)	$-0.2820(1)$	0.0088(2)
O(1)	0.6650(4)	0.07090(9)	0.462(1)	0.0115(7)
O(2)	0.7334(4)	0.12495(9)	0.217(1)	0.0080(7)
O(3)	0.6428(4)	0.06868(9)	$-0.023(1)$	0.0105(8)
O(4)	0.9024(4)	0.07021(9)	0.188(1)	0.0109(8)
O(5)	0.7466(4)	0.1220(1)	$-0.2595(8)$	0.0120(9)
N(1)	0.3997(5)	0.0463(1)	0.215(1)	0.017(1)
C(1)	0.3779(7)	0.0119(2)	0.286(1)	0.024(2)
C(2)	0.5	0	0.434(3)	0.025(2)
H(1)	0.3794	-0.0012	0.1614	0.05
H(2)	0.2859	0.0097	0.3893	0.05
H(3)	0.5266	0.0158	0.5154	0.05
H(4)	0.4764	0.0509	0.1311	0.05
H(5)	0.3334	0.0564	0.1422	0.05
H(6)	0.4610	0.0433	0.3915	0.05
H(7)	0.7838	0.1281	-0.4032	0.05
Compound 2				
As(1)	0.73581(4)	0.08387(1)	0.20515(6)	0.0110(1)
Fe(1)	0.57245(6)	0.09758(1)	$-0.2830(1)$	0.0116(2)
O(1)	0.6662(3)	0.07018(7)	0.4604(9)	0.0150(6)
O(2)	0.7332(3)	0.12449(7)	0.2099(8)	0.0130(6)
O(3)	0.6424(3)	0.06793(7)	$-0.0172(8)$	0.0131(7)
O(4)	0.8992(3)	0.06947(7)	0.1867(8)	0.0140(6)
O(5)	0.7483(4)	0.12190(8)	$-0.2634(7)$	0.0172(7)
N(1)	0.3994(4)	0.04672(9)	0.212(1)	0.0200(7)
C(1)	0.3792(6)	0.0116(1)	0.281(1)	0.026(1)
C(2)	0.5	0	0.426(2)	0.027(2)
H(1)	0.7838	0.1203	-0.3964	0.05
H(2)	0.5200	0.0156	0.5185	0.05

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

maps, while only two hydrogen atoms in **2** could be located. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The atomic positions and isotropic thermal parameters for all hydrogen atoms were fixed. All calculations were performed using SHELXTL Version 5.0 software package. The crystal data and structure refinement parameters are given in Table 1, the atomic coordinates are in Table 2, and selected bond distances are in Table 3.

⁷¹Ga NMR

⁷¹Ga magic angle spinning (MAS) NMR experiments were carried out at room temperature on a Bruker AVANCE-400 spectrometer at ⁷¹Ga resonance frequency of 121.84 MHz. ⁷¹Ga MAS NMR spectra were acquired by using a solid-echo pulse sequence, i.e., $\pi/2 - \tau - \pi/2$ -acquisition, where τ was set to be the rotor period. To avoid any

TABLE 3
Selected Bond Lengths (Å) for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Ga}(\text{OH})(\text{AsO}_4)]$ (1) and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Fe}(\text{OH})(\text{AsO}_4)]$ (2)

Compound 1			
As(1)–O(2)	1.671(4)	As(1)–O(1)	1.701(6)
As(1)–O(4)	1.704(4)	As(1)–O(3)	1.706(6)
Ga(1)–O(5)	1.924(4)	Ga(1)–O(5)	1.939(4)
Ga(1)–O(2)	1.984(5)	Ga(1)–O(4)	2.008(4)
Ga(1)–O(3)	2.024(6)	Ga(1)–O(1)	2.043(6)
N(1)–C(1)	1.500(8)	C(1)–C(2) (2 ×)	1.52(1)
O(5)–H(7)	0.92	N(1)–H(4)	0.89
N(1)–H(5)	0.86	N(1)–H(6)	1.16
C(1)–H(1)	0.89	C(1)–H(2)	1.06
C(2)–H(3) (2 ×)	0.84		
Compound 2			
As(1)–O(2)	1.686(3)	As(1)–O(3)	1.701(4)
As(1)–O(4)	1.702(3)	As(1)–O(1)	1.711(5)
Fe(1)–O(5)	1.969(4)	Fe(1)–O(5)	1.990(4)
Fe(1)–O(2)	2.011(4)	Fe(1)–O(4)	2.057(3)
Fe(1)–O(1)	2.073(4)	Fe(1)–O(3)	2.075(4)
N(1)–C(1)	1.500(8)	C(1)–C(2) (2 ×)	1.52(1)
O(5)–H(1)	0.84	C(2)–H(2) (2 ×)	0.86

overlap of the spinning sidebands, a high-speed 2.5-mm probehead for acquiring ^{71}Ga MAS NMR spectra at a spinning speed of 30 kHz was used. The applied rf field strength was carefully chosen to be well within the fictitious spin-1/2 approximation ($\nu \ll \nu_Q$). This was measured on a 1 M gallium nitrate solution that was also used as a reference. The simulation of a ^{71}Ga MAS NMR spectrum was performed with the WINFIT program of the Bruker WINNMR software package.

RESULTS AND DISCUSSION

Structural Description

The two compounds are isostructural; therefore, only the structure of **1** is discussed. The structure consists of two-dimensional anionic sheets of gallium arsenate in the *ac* plane with charge-compensating propylenediammonium cations between the sheets (Fig. 1). Each sheet sits on a *d* glide plane and is constructed from infinite zig-zag chains of *cis*-corner-sharing GaO_6 octahedra, which are joined by arsenate ligands (Fig. 2). The bond angle at the bridging hydroxo oxygen atom, O(5), is 134° . Each arsenate tetrahedron shares its three corners with three gallium atoms within a chain with the fourth corner being shared with a gallium atom in a neighboring chain. An alternative description of the sheet is three oxygen layers in the stacking sequence ABA. The central layer is a close packed layer where every oxygen atom is surrounded by six others, while the other two layers are only three-quarters occupied. One-eighth of the tetrahedral sites and a quarter of the octahedral sites between two adjacent layers of oxygen atoms are

filled with arsenic and gallium atoms, respectively, which amount to 20 oxygen, 4 arsenic, and 4 gallium atoms within a sheet per unit cell. All the hydroxo oxygen atoms are in the central layer. The propylenediammonium cations form a two-dimensional six-coordinate lattice between adjacent sheets of gallium arsenate. The central carbon atom of each organic molecule sits on a twofold rotational axis. The molecule lies in a direction at an angle of 26° between the $\text{N} \cdots \text{N}$ vector

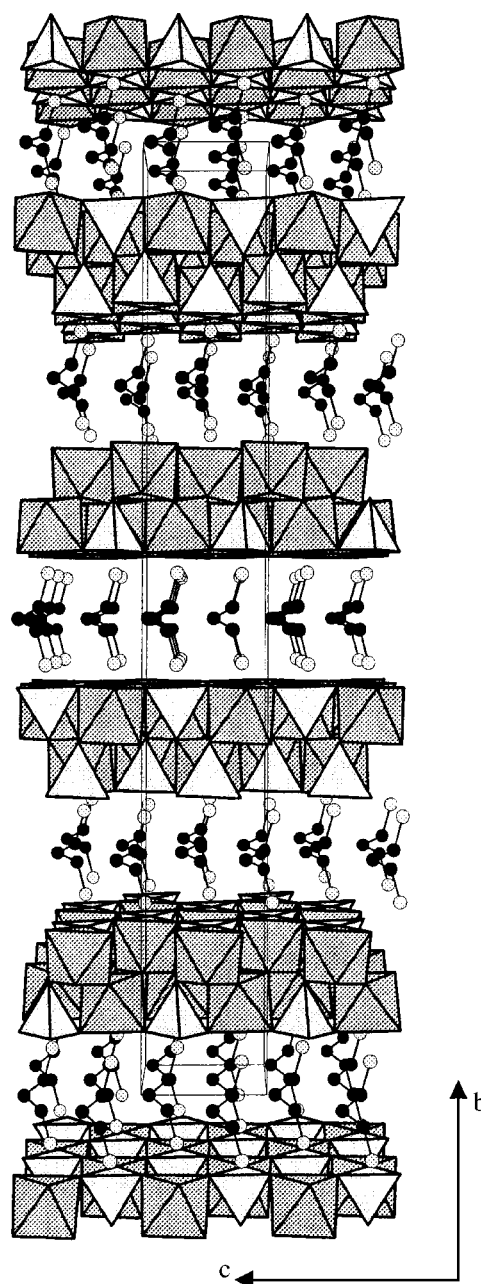


FIG. 1. Polyhedral plot of the structure of **1** along the *a* axis. GaO_6 octahedra are dark gray and PO_4 tetrahedra are light gray. Solid circles and stippled circles are C and N atoms of propylenediammonium cations, respectively.

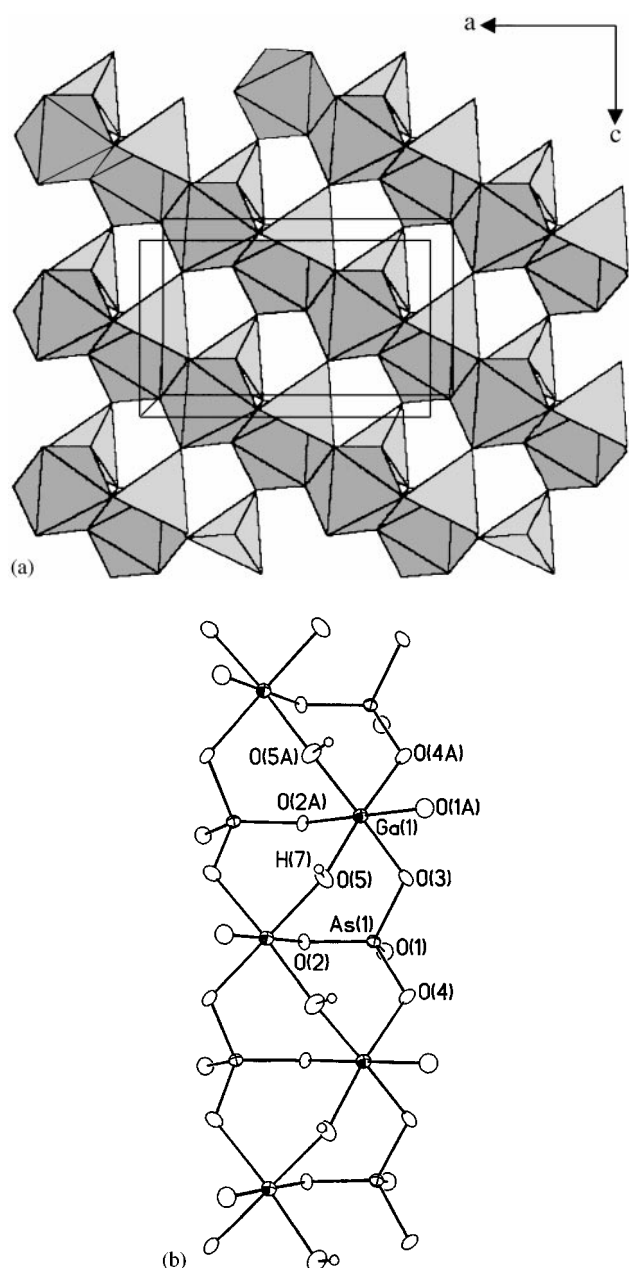


FIG. 2. (a) Section of a sheet in **1**. (b) Section of an infinite chain in a sheet (60% thermal ellipsoids) showing the atom-labeling scheme. The small open circles are H atoms.

and the *b* axis. The molecules are stabilized via hydrogen bonds to the arsenate oxygen atoms as indicated by the short NH...O and N...O distances [H(4)...O(3), 1.96; N(1)...O(3), 2.84; H(5)...O(1), 2.00; N(1)...O(1), 2.85; H(6)...O(4), 2.09; N(1)...O(4), 2.85 Å].

The structure of **1** is reminiscent of $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]_{0.5}[\text{Fe}(\text{OH})\text{PO}_4]$ (12), which exhibits a layered structure consisting of infinite chains of edge-sharing FeO_6 octahedra linked into 2-D sheets by PO_4 tetrahedra that possess

terminal P–O groups that protrude into the interlamellar space. Each sheet can be considered as four oxygen layers in the packing sequence ABAB. The central two layers are fully occupied by oxygen atoms, while the outer two are only a quarter occupied. Half of the octahedral sites between central layers are filled with iron atoms, and every oxygen atom in the outer layers corresponds to a terminal P–O group, which amounts to a total of 10 oxygen, 2 phosphorus, and 2 iron atoms within a sheet per unit cell. The hexagonal layers of oxygen atoms are strongly distorted because of edge-sharing octahedra, in contrast to the regular layers in **1**.

^{71}Ga MAS NMR

^{71}Ga NMR spectra are often affected by the quadrupolar broadening, which arises from the interaction of the nuclear quadrupolar momentum with the electric field gradient (EFG) tensor at the nucleus position. The quadrupolar interaction can easily become so large that the satellite transitions become unobservable while only the central transition $\langle -1/2 \leftrightarrow 1/2 \rangle$ is visible but suffers severe second-order quadrupolar interaction, which is only partially averaged by MAS. Recently, Massiot *et al.* studied a series of gallium-containing compounds, and summarized three types of NMR acquisition conditions for obtaining ^{71}Ga NMR spectra, depending on the size of quadrupolar coupling constants (C_Q) of ^{71}Ga nuclei (13). In the case of large quadrupolar interaction (typically $C_Q < 10$ MHz), the central transition of the quadrupolar spin system behaves as an isolated fictitious spin-1/2 system, and it can still be possible to perform echo or whole-echo experiments to acquire the whole spectrum in the acquisition bandwidth.

Figure 3 shows the experimental ^{71}Ga MAS NMR spectrum of **1** at 9.4 T, together with the simulation. The observed ^{71}Ga NMR lineshape can be fitted with these parameters: $\delta_{\text{CS}} = -82 \pm 2$ ppm, $C_Q = 7.7 \pm 0.2$ MHz, and $\eta = 0.63 \pm 0.02$, by assuming that the spectrum is only influenced by second-order quadrupolar broadening since chemical shift anisotropy (CSA) is averaged by very fast sample spinning. The result not only confirms the presence of six-coordinated Ga atoms in **1**, but also provides the EFG tensor that characterizes the asymmetry of the local environment.

Although a large number of organically templated metal phosphates have been reported, only very few arsenates are known. The synthesis conditions are analogous to those for phosphates. Metal chlorides or nitrates have been used as the reactants. Iron metal in its elemental form has also been used for the synthesis of mixed-valence iron arsenates (10). The use of HF as a mineralizer appears helpful to the crystal growth and thus leads to several new arsenates and fluoroarsenates. The use of HF may produce novel frameworks that do not form in a fluoride-free medium. We have

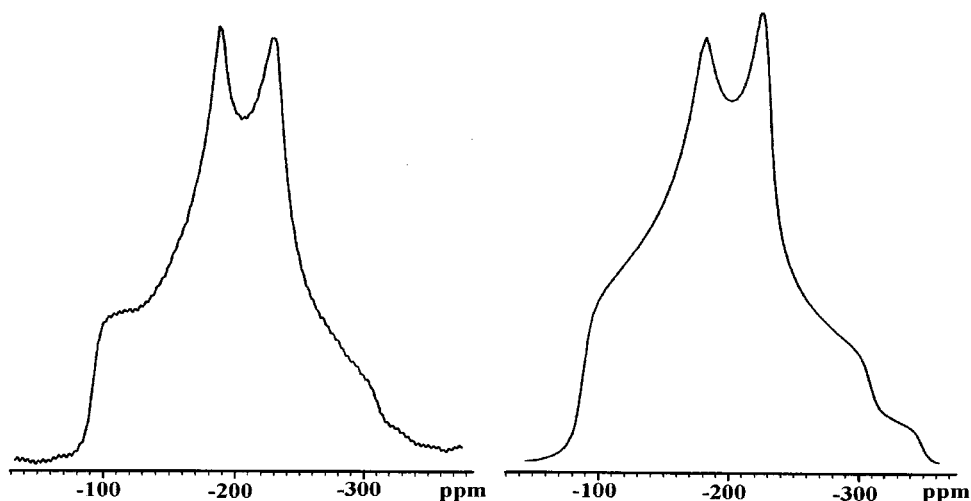


FIG. 3. Experimental ^{71}Ga MAS NMR spectrum of **1** (left) and simulated spectrum with second-order quadrupolar broadened lineshape (right).

also found that the structure is sensitive not only to the nature of the organic template incorporated but also to reaction conditions. To this end, we will shortly report on the synthesis and characterization of two polymorphs obtained from different solvent systems.

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