

Two-Dimensional Hybrid Germanium Zeotype Formed by Selective Coordination of the *trans*-1,2-Diaminocyclohexane Isomer to the Ge Atom: Heterogeneous Acid–Base Bifunctional Catalyst

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[C₆H₁₀(NH₂)₂Ge₃O₆] **ICMM9** is a two-dimensional germanate in which the metallic atoms are covalently bonded to chelating diamines. Its layered structure having some similitude with that of the pyroxene mineral, presents a totally new topology with two 4-c nodes. The solvothermal synthesis reaction allows the separation in situ of the two 1,2-diaminocyclohexane isomers by selective coordination of the *trans* isomer to octahedral Ge atoms of the **ICMM9** framework. This material behaves as an active and selective heterogeneous acid–base bifunctional catalyst.

Introduction

In open-framework germanates, germanium analogues of zeolites in contrast to the usually tetrahedrally coordinated silicon, the secondary building unit (SBU) can be formed by Ge atoms in tetrahedral, trigonal bipyramidal, and octahedral coordination. These polyhedrons being connected by sharing vertices, edges, or faces can form variable and expanded coordination environments because of the large Ge/O radius ratio. Anions (oxygen atoms or hydroxyl groups) are also frequently found in 1-, 2-, or 3-coordination, and so a great number of novel structures can be potentially obtained. During the past decade, a number of new porous germanates has been obtained whose structures consist of pure tetrahedral or mixed polyhedra,^{1–4} most of them templated by amines. There exist also some germanates templated by amino-complexes of different metals.^{5–8} Although several zeotypes brought about by diamine have

been reported^{9–12} not many have lamellar structure^{13–16} being, in general, an alternation of inorganic anionic germanate sheets and protonated diamines that give rise to the 2D-structures. In them, amines are bonded to the inorganic framework through more or less strong hydrogen bonds. Recently, one silico-germanate¹⁷ in which 1,2-diaminopropane molecules are monocoordinated to the Ge atoms has also appeared. In our previous work on the synthesis of chiral germanates¹⁸ we had observed the formation of diverse

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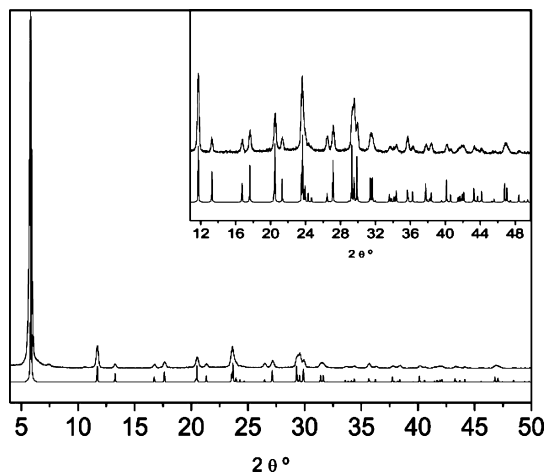


Figure 1. Comparative simulated (bottom) and experimental (top) powder pattern.

aminocomplexes¹⁹ of germanium in the course of the zeotypes formation reaction. Working in this direction here, we present **ICMM9**, a new germanate, in which 1,2-diaminocyclohexane molecules are directly coordinated in a chelating way to germanium atoms resulting in a neutral inorganic–organic hybrid two-dimensional (2D) framework. Its ability to act as a heterogeneous catalyst has been examined by using it in different reactions known to be catalyzed by acid sites (acetalization of aldehydes) and basic sites (Knovenagel condensation, Michael reaction).

Experimental Section

Synthesis. The germanate **ICMM9**, $[\text{C}_6\text{H}_{10}(\text{NH}_2)_2\text{Ge}_3\text{O}_6]$, was prepared under hydro/solvothermal conditions. The synthesis procedure was as follows: 1 g of GeO_2 (99.999%, Sigma-Aldrich) was added to a mixture of 5.0 mL of H_2O and 40.0 mL of 1,2-diaminocyclohexane (99%, mixture of cis- and trans-isomers, Sigma-Aldrich) under continuous stirring. The molar ratio was $\text{GeO}_2/\text{C}_6\text{H}_{10}(\text{NH}_2)_2/\text{H}_2\text{O} \approx 1:34:29$. The final mixture (pH 12) was sealed in a Teflon-lined autoclave and heated at 180 °C for 5 days under autogenous pressure. A fine powder with a few crystals was obtained. The resulting product was washed first with abundant water, then with acetone, and finally dried in open air at room temperature. The maximum yield of **ICMM9** was 48 wt % based on GeO_2 . The product was obtained as a single phase, as was confirmed by the comparison of the experimental X-ray powder pattern with that simulated from the single crystal data (Figure 1). The **ICMM9** compound is stable in air and is insoluble in most organic solvents.

IR spectra obtained for the **ICMM9** compound shows peaks of medium intensity between 3435 and 3135 cm^{-1} that correspond to $\nu(\text{NH}_2)$. In the range 945–740 cm^{-1} is where the most intense bands of the spectra are observed, which can be assigned to Ge–O vibrations of the tetrahedral and octahedral germanium polyhedra. The absorption bands at 573, 542, 513, and 466 cm^{-1} are due to vibrations of Ge–O and Ge–N.

Thermogravimetric Analysis (TGA). **ICMM9** is stable up to ~260 °C. TGA was performed on crystalline samples in the range

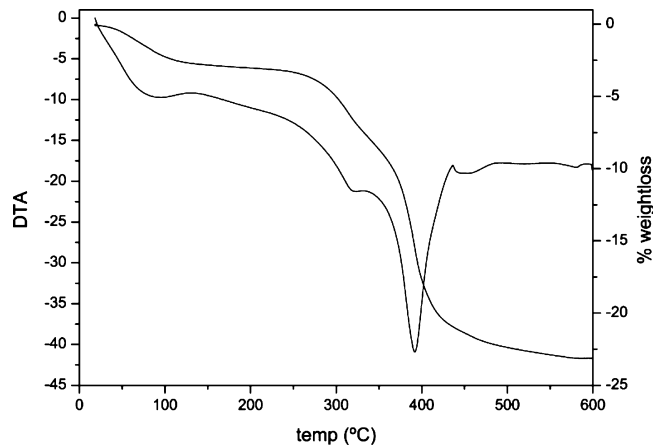


Figure 2. TGA data for **ICMM9**.

20–600 °C in N_2 flow. Below 120 °C there is a weight loss of 2.7%, corresponding to adsorbed water molecules. At 265 °C the compound starts to gradually decompose. The maximum exothermic peak in the DTA curve appears at 390 °C (Figure 2). At this temperature, fragments from the decomposition of the organic part are found in the mass detector.

X-ray Structure. The main crystallographic and refinement data for **ICMM9** and the two complexes are given in Table 1. Colorless parallelepiped-shaped crystals were selected under a polarizing optical microscope and glued on a glass fiber for a single-crystal X-ray diffraction experiment. X-ray intensity data were collected in a Bruker SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo $\text{K}\alpha$ radiation = 0.71073 Å). Data were collected at room temperature over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each exposure of 20 s covered 0.3° in ω . Unit cell dimensions were determined by a least-squares fit of 60 reflections with $I > 20\sigma(I)$. The structures were solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were geometrically situated. Calculations were carried out with the SMART software for data collection and data reduction and with SHELXTL.²⁰

The spectra of the two complexes are poor because only a few crystals were extracted from different stages of the zeolitic reaction. They are very small crystals and do not diffract at higher angles; this is the reason why the completeness is not very high but enough to determine and refine both structures.

Catalytic Experiments. Acetalization of Benzaldehyde with Trimethyl Orthoformate (TMOF). A 20 mg portion of **ICMM9** was added to a solution of benzaldehyde (1 mmol) and TMOF (5 mmol) in tetrachloromethane (3 mL). The resulting suspension was magnetically stirred at 313 K. Samples of the reaction were periodically withdrawn and analyzed by gas chromatography (GC).

Knovenagel Condensation. In a typical experiment, 25 mg (10%) of the catalyst was added to a solution of ethyl cyanoacetate or malononitrile (2 mmol) in dichloromethane while being stirred under an inert atmosphere (N_2). After temperature adjustment to reflux, 2 mmol of benzaldehyde was added, with the reaction periodically monitored by gas chromatography.

Michael Addition of Nitro Ethane to But-3-en-2-one. A mixture of catalyst (10%), 1 mmol of methylvinylketone (MVK),

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Table 1. Main Refinement and Crystallographic Data

compound	[C ₆ H ₁₀ (NH ₂) ₂ Ge ₃ O ₆] ICMM9	[Ge(IV)(OH) ₆]	[Ge(II)(en) ₃][Ge(IV)(en)(OH) ₄]
empirical formula	C ₆ H ₁₄ Ge ₃ N ₂ O ₆	C ₃ H ₁₅ Ge N ₃ O ₃	C ₂ H ₁₂ Ge N ₂ O ₄
formula weight	427.96	213.77	200.73
crystal system	orthorhombic	trigonal	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 312	<i>C</i> 2/ <i>c</i>
unit cell dimensions	<i>a</i> = 5.3321(9) Å <i>b</i> = 7.4268(12) Å <i>c</i> = 15.101(2) Å	<i>a</i> = 9.2324(7) Å <i>b</i> = 9.2324(7) Å <i>c</i> = 4.9209(5) Å	<i>a</i> = 8.9151(11) Å <i>b</i> = 7.2710(9) Å; β = 109.012(3)° <i>c</i> = 9.6826(12) Å
volume	598.01(16) Å ³	363.25(5) Å ³	593.40(13) Å ³
<i>Z</i>	2	2	4
calculated density	2.377 Mg/m ³	1.954 Mg/m ³	2.247 Mg/m ³
absorption coefficient	7.509 mm ⁻¹	4.174 mm ⁻¹	5.109 mm ⁻¹
crystal size	0.10 × 0.05 × 0.02 mm	0.10 × 0.10 × 0.05 mm	0.16 × 0.16 × 0.16 mm
independent reflections	1103, <i>R</i> (int) = 0.0813	590, <i>R</i> (int) = 0.0751	464, <i>R</i> (int) = 0.0265
data/restraints/parameters	1103/0/74	590/0/36	464/0/39
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0583, <i>wR</i> 2 = 0.1317	<i>R</i> 1 = 0.0575, <i>wR</i> 2 = 0.1405	<i>R</i> 1 = 0.0451, <i>wR</i> 2 = 0.1217
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0837, <i>wR</i> 2 = 0.1418	<i>R</i> 1 = 0.0697, <i>wR</i> 2 = 0.1456	<i>R</i> 1 = 0.0453, <i>wR</i> 2 = 0.1219

and 1 mmol of nitroethane in toluene (3 mL) were stirred for 24 h at 373 K. Samples of the reaction were periodically withdrawn and analyzed by GC.

Condensation of Benzaldehyde with Heptanal. All reactions were carried out under a nitrogen atmosphere. A mixture of previously distilled benzaldehyde (5 mmol) and heptanal (1 mmol) was placed in a flask immersed in a thermostated silicone oil bath. Once the mixture reached a temperature of 398 K, 25 mg (10%) of catalyst was added. Samples of the reaction were periodically withdrawn and analyzed by GC. Each reaction product was identified by GC–mass spectrometry.

Results

From our previous work on the synthesis of germanates templated by diamines we had observed the formation of diverse chelating ethylenediamine complexes (Table 1, Figure 3) of germanium in the course of zeotype formation reactions, specially when synthesizing **ICMM6**.¹¹ [Ge(IV)(OH)₆]²⁻[Ge(II)(en)₃]²⁺ is a cation anion complex in which the tetravalent germanium atom is coordinated to six crystallographically equivalent hydroxyl groups at a distance Ge–O of 1.913(8) Å and the divalent one to three chelating ethylene-diamines (distance Ge–N = 1.925(8) Å).

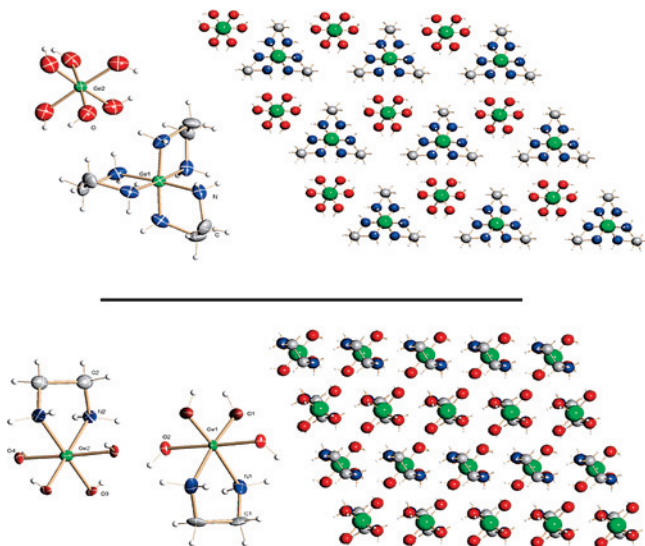


Figure 3. ORTEP (Oak Ridge Thermal Ellipsoid Plot) and packing views of the germanium amino-complexes obtained with ethylenediamine. Top, [Ge(IV)(OH)₆][Ge(II)(en)₃]; bottom, [Ge(IV)(en)(OH)₄].

Table 2. Interatomic Distances in **ICMM9** (Å)

Ge(1)–O(1)	1.752(6)
Ge(1)–O(2)	1.720(8)
Ge(1)–O(3)	1.717(10)
Ge(1)–O(4)	1.749(5)
Ge(2)–O(2) (×2)	1.875(10)
Ge(2)–O(3) (×2)	1.815(9)
Ge(2)–N(1) (×2)	2.084(11)
N(1)–C(1)	1.481(19)
C(1)–C(2)	1.51(2)
C(1)–C(1) ^a	1.54(3)
C(2)–C(3)	1.48(2)
C(3)–C(3) ^a	1.53(3)

^a Symmetry operator: $-x, -y + 1, z$.

[Ge(IV)(en)(OH)₄] is a Ge(IV) neutral complex with the metallic atom bonded to four OH anions (average Ge–O distance = 1.784(4) Å) and one chelating ethylene-diamine molecule (distance Ge–N = 1.977(6) Å, Table 2).

For the current **ICMM9** we selected a cyclic amine (1,2-diaminocyclohexane) with two conformations, so that it plays a role in the structural building formation. The synthesis procedure was tuned by changing the reaction time and the amine concentration up to the obtainment of the extended net (under the optimized conditions given in the Experimental Section). **ICMM9** is to our knowledge the first germanium zeotype in which the Ge atoms are covalently bonded to chelating diamine.

Upon determination of the crystal structure, the composition was found to be C₆H₁₀(NH₂)₂Ge₃O₆ (**ICMM9**). Its asymmetric unit comprises one-half of the formula, with one germanium atom (Ge1) in tetrahedral coordination and the other (Ge2), situated in a 2-fold axis, in octahedral coordination (Figure 4). Tetrahedra are formed sharing a vertex (GeO₃)_∞ of 2T metagermanate chains, which give rise, also by sharing vertices with the octahedral germanium atom, to GeO₂ infinite eight-R containing layers (Figure 5); every two of them are connected in a double one, which is a new 2D binodal 4-c net, with Schläfli symbol (3.5³.6²)₂(3.5⁴.8). As Ge2 is surrounded by four active oxygen atoms (each belonging only to a tetrahedron) with two position blocked by the coordinated chelating amine, the octahedral germanium atom is also considered as a 4 connected node in this net (Figure 6).

The distance Ge–N (2.084 Å) shows the covalent nature of this bond and makes the cyclic organic amine part of the framework structure. The reason of the formation of the

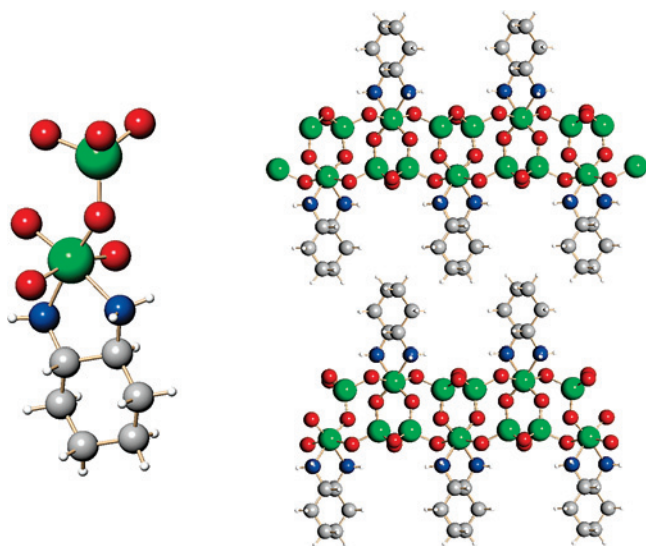


Figure 4. Structure of ICMM-9. Color scheme: green, germanium; red, oxygen; blue, nitrogen; gray, carbon; white, hydrogen.

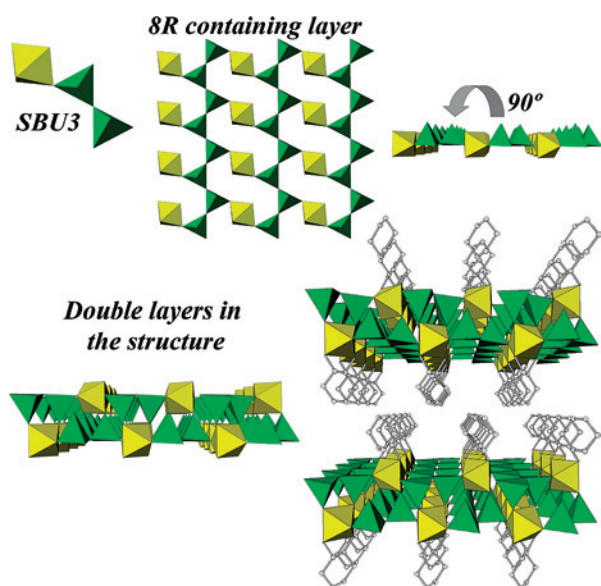


Figure 5. Polyhedral representation of the SBU3 (top left), single layer (top middle and right), double layer (bottom left), and perspective view of the ICMM9 structure (bottom right).

stable ICMM9 compound with a covalent Ge–N bond is probably due to special solvothermal conditions of the synthesis with a high molar proportion of the amine used. The structure could be depicted as a 2D Ge–MOF in which the M–M links are made via oxygen atoms and the organic part is pendent from the inorganic layer.

Looking at the inorganic part, a correlation can be established among ICMM9, pyroxene, and amphibole structure types: the chains of ICMM9 are present in the pyroxene group of minerals (2T metasilicates chains) as single chains and in the amphibole minerals (3T chains) as double ones forming 6-member-rings. They run, in both families, along the [0 0 1] direction, giving (in their orthorhombic form) a *c* parameter that corresponds to the distance across two tetrahedra (5.34 Å in pyroxene and 5.28 Å in amphibole).²¹ In our ICMM9, chains run along the [1 0 0] direction, and thus, the value of 5.33 Å corresponds to

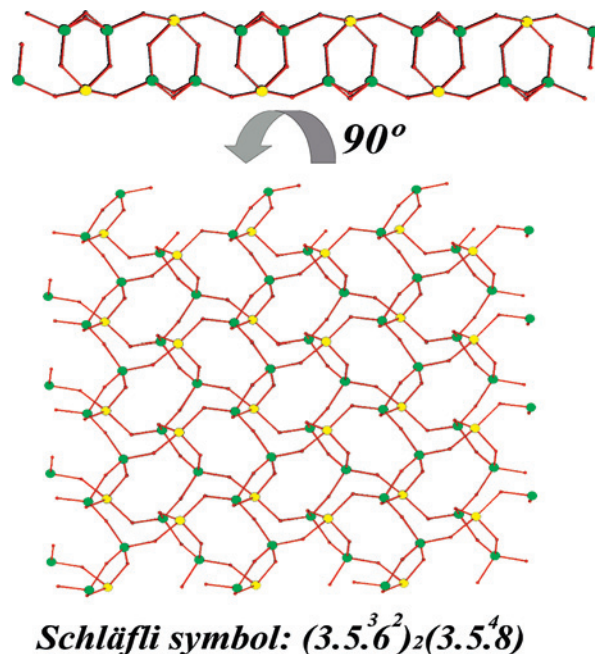


Figure 6. Topology of the new binodal 4c net.

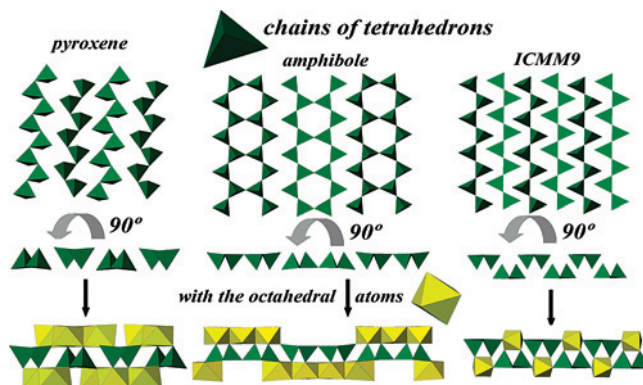


Figure 7. Comparison of the chains formed by tetrahedrons in pyroxene, amphibole, and ICMM9, and position of the octahedral atoms.

the *a* parameter. While in the two minerals the chains of tetrahedra lie in the same plane (with the octahedral atoms above and below them), in the structure of ICMM9 the chains run alternated in two planes (Figure 7).

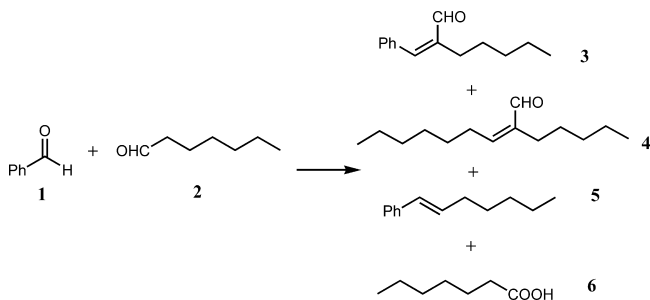
Even though a mixture of *cis/trans*-1,2-diaminocyclohexane is used in the synthesis of ICMM9, only the *trans* molecule is present in its structure. The filtrate from the reaction mixture becomes enriched in the *cis* isomer as confirmed by ¹HNMR analysis.

Catalytic Activity. The ability of ICMM9 to act as an heterogeneous catalyst has been examined by using it in different reactions known to be catalyzed by acid sites (acetalization of aldehydes) and basic sites (Knoevenagel condensation, Michael reaction).

Indeed, the new compound is able to catalyze the reaction of benzaldehyde with trimethyl orthoformate to form the benzaldehyde dimethyl acetal with 100% yield after 2 h.

Knoevenagel condensation between benzaldehyde and compounds containing activated methylenic groups can be

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Scheme 1. Products of the Condensation of Benzaldehyde with Heptanal

catalyzed by a wide variety of bases from weak to strong basicities. As it is known, the different pK_a values of the methylenic groups to be deprotonated allows an estimation of the catalyst basic strength.²²

ICMM9 has proven to possess basic activity in the condensation of benzaldehyde with ethyl cyanoacetate ($pK_a \leq 9$) and also with a substrate with a medium pK_a value such as malononitrile ($pK_a \leq 11$). In the reaction with ethyl cyanoacetate, the E and Z isomers of α -ethyl-2-cyanocinnamate in an E/Z ratio > 150 were obtained with a selectivity of 100%. In the condensation with malononitrile, a yield of 66% after 48 h was achieved.

Additionally, the basic character of this material was proved in the Michael addition of nitroethane to methylvinylketone with a yield of 45% after 48 h.

Because of the acid–base bifunctional character of **ICMM9**, its activity has been examined in the synthesis of α -n-aminocinnamaldehyde (jasminaldehyde)²³ (**3**, Scheme 1), a compound with a violet scent that provides this substance of commercial interest in the fragrance industry. This compound is usually obtained by the condensation of heptanal with benzaldehyde (Scheme 1), in the presence of alkali or acid catalyst, but in those conditions different byproducts are obtained that reduce significantly the yield. Improved selectivity has been achieved by using acid–base bifunctional catalysts, in which the weak acid sites proceed

activating the benzaldehyde, favoring the subsequent attack of the enolate heptanal intermediate generated at the basic sites.²⁴

The condensation reaction between benzaldehyde (**1**) and heptanal (**2**) was carried out with heterogeneous acid–base **ICMM9**. A molar ratio of benzaldehyde/heptanal of 5 was chosen to minimize heptanal self-condensation. **ICMM9** behaves as an active and selective catalyst for this reaction, achieving 85% conversion after 24 h of reaction time with selectivity to jasminaldehyde (**3**) of $> 75\%$. Moreover, only traces of product **5** were detected. **ICMM9** shows a selectivity comparable to that found when AlPO (Al/P = 1) was used as catalyst. After completing the reaction, the filtrate was used in a new reaction and no catalytic activity was found. On the other hand, the solid heterogeneous catalysts were routinely checked by X-ray powder diffraction before and after reactions showing no alteration.

Conclusions

In sum, **ICMM9** is a thermally stable 2D hybrid germanate that combines the following features: (i) it is formed by selective coordination of the *trans*-1,2-diaminocyclohexane isomer to the Ge atom, (ii) to our knowledge, it is the first pure germanium zeotype in which the metallic atoms are covalently bonded to chelating diamine, and (iii) it behaves as an active and selective heterogeneous acid–base bifunctional catalyst for the synthesis of jasminaldehyde.

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Supporting Information Available: X-ray crystallographic information in.cif files for **ICMM9** and Ge-En complexes (CCDC numbers 655684, 670288, and 670289). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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