the *R* absolute configuration,[36] but after X-ray analyses it was revised as *S*.[37]

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[38] For instance, the eudismic ratio shown by the volatile anesthetic halotane (1-bromo-1-chloro-2,2,2-trifluoroethane[39]) has been attributed to the binding with a proteinaceous receptor site.[5] The enantioselective recognition involving the bromine atoms of **2** in cocrystal **3** is consistent with an involvement of the bromine atom of halothane as the electron-acceptor site in a complex with a peptide-donor site.

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A Germanium Zeotype Containing Intratunnel Transition Metal Complexes[**]

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Crystalline microporous materials are widely used in the fields of catalysis, ion exchange, and adsorption. Since the first discovery of zeolite, numerous natural and synthetic zeolites,[1–4] silica polymorphs, aluminophosphate-based molecular sieves, and microporous compounds built from MO_4 units ($M \neq Al, Si$)[5–8] have been synthesized.

Like silicon, germanium tends to be surrounded by a tetrahedron of oxygen atoms, which may join with other tetrahedra through shared corners to form larger units; in fact, some compounds of the two elements are isomorphous. However, in Ge zeotypes the structure of the framework can be formed by GeO_4 tetrahedra, GeO_6 octahedra, and sometimes GeO_5 trigonal bipyramids. Therefore, it is surprising that there are so few reports on microporous germanates. To our knowledge, the only fully characterized systems are those based on the pharmacosiderite structure[8–16] and those in which some of the Ge atoms are five-coordinate.[17, 18] Nevertheless, during the last year the interest in these materials seems to be increasing. We reported the new $(NH_4)_2Ge_7O_{15}$ (ICMM-1),[19] which is the first microporous material containing nine-rings. More recently, papers on new microporous germanates[20, 21] and gallogermanates[22–24] have appeared. All these new compounds have a framework structure and show many of the properties of zeolites.

We followed our synthesis strategy for preparing novel zeolite-like germanates by changing the ratio of GeO_6 octahedra to GeO_4 tetrahedra to obtain differently charged frameworks without introducing a trivalent cation. Here we report the novel $(NH_4)^+[M(NH_3)_2]^+(Ge_9O_{19})^{2-}$ (M = Cu, Ag; ICMM-2). These compounds are, to our knowledge, the first microporous germanates containing a transition metal complex in their channels. Furthermore, they are the result of our attempts to incorporate metals during the hydrothermal synthesis of the zeotype. As in the case of ICMM-1, a new group of zeolite-type structures arises since compounds of type ICMM-2 had not yet been prepared, neither as a silicate nor as a phosphate.

The relative stabilities of copper(I) and copper(II) in aqueous solution depend very strongly on the nature of the anions and other ligands present, and vary considerably with solvent or identity of the neighboring atoms in the crystal. In the following synthesis, the amines present in the reaction media reduce Cu^{II} to Cu^{I} and the ammonia simultaneously prevents disproportionation to Cu^0 and Cu^{II}. Thus the $[Cu(NH_3)_2]^+$ cation is stabilized and incorporated into the crystal to partially compensate for the charge of the anionic framework.

Both the Cu and Ag compounds were synthesized hydrothermally from reaction mixtures containing GeO_2, $Cu(NO_3)_2 \cdot 3H_2O$ or $Ag(NO_3)$, ammonia, water, and, in order to obtain larger crystals, ethylene glycol in a molar ratio of 1:0.1:2:2:0.1; in the case of the Cu compound propylamine and pyridine (0.3:1) were also added. The mixtures were heated at 180 °C for six days. Variations of the procedure were explored, in particular the effects of changing the temperature and duration of the reaction. The cubic and platelike crystals observed in the resulting solid product were identified as the title compound (approximate yield 70 %) and the known cubic phase whit pharmacosiderite-type structure; the latter compound was easily eliminated upon heating at 250 °C for three hours.

A suitable single crystal of each compound with platelike features was selected and mounted in a diffractometer equipped with a CCD detector. According to the crystal structure determination[25] the composition is $(NH_4)^+[M(NH_3)_2]^+(Ge_9O_{19})^{2-}$ (M = Cu, Ag), in which eight Ge atoms are tetrahedrically coordinated by oxygen and the remaining Ge atom forms a GeO_6 octahedron (Table 1).

The framework structure of ICMM-2 (Figure 1) is constructed from a secondary structural building unit denoted 4 = 1, which is present in several natural zeolites such as edingtonite, natrolite, and thomsonite. These 4 = 1 units are joined by three-tetrahedra rings into an infinite sheet of composition $[Ge_4O_9]^{2-}_{\infty}$ containing nine-tetrahedra rings. This arrangement has recently been reported in the gallogermanate UCSB-9[23] and is also present in ICMM-1;[19] in the latter GeO_6 octahedra were involved in both three- and nine-rings.

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Table 1. Selected crystallographic data for the ICMM-2 structure type.

	ICMM-2Cu	ICMM-2Ag	ICMM-2H
formula	$NH_4[Cu(NH_3)_2]Ge_9O_{19}$	$NH_4[Ag(NH_3)_2]Ge_9O_{19}$	$NH_4(H)Ge_9O_{19}\cdot 2H_2O$
a [Å]	12.284(1)	12.203(1)	12.273(2)
b [Å]	23.256(2)	23.115(3)	23.249(3)
c [Å]	7.2272(8)	7.1890(8)	7.2267(9)
V [Å^3]	2064.7(4)	2027.8(4)	2053.7(5)
T [K]	295	170	295
$R(F^2)$ [$I > 2\sigma(I)$]	0.042	0.057	0.073
Ge_t–O [Å][a]	1.702(8) – 1.781(8)	1.679(9) – 1.777(9)	1.69(1) – 1.79(1)
Ge_o–O [Å][b]	1.858(9) – 1.889(8)	1.857(9) – 1.875(9)	1.85(1) – 1.90(1)
O-Ge_t-O [°][a]	102.3(4) – 118.0(5)	102.3(4) – 119.4(4)	101.7(6) – 118.8(6)
O-Ge_o-O [°][b]	83.7(4) – 96.0(5)	83.9(4) – 94.5(4)	84.1(5) – 96.8(9)
Ge_t-O-Ge_t [°][a]	119.6(5) – 156.9(9)	121.5(5) – 160.0(11)	121.6(7) – 156.8(12)
Ge_t-O-Ge_o [°][a,b]	124.6(4) – 130.9(4)	123.9(6) – 131.8(6)	124.4(9) – 131.3(7)
M–N [Å]	1.94(2)	2.18(2)	
N-M-N [°]	175.8(9)	169.8(9)	

[a] Ge_t = tetrahedral Ge center. [b] Ge_o = octahedral Ge center.

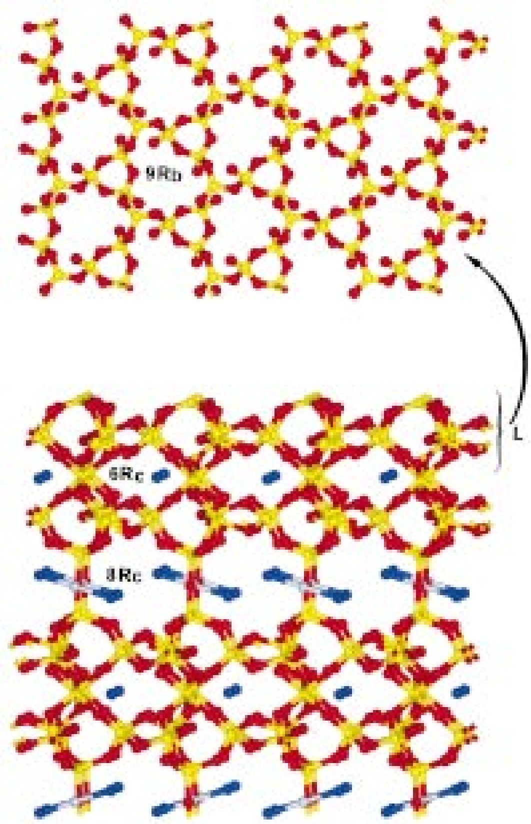

Figure 1. Bottom: View of the structure of ICMM-2 along the [001] direction (Ge: yellow, O: red, N: blue, M: white). Top: Detail of the three- and nine-ring layer (L) constructed from 4 = 1 secondary structural building units.

In ICMM-2 two adjacent sheets of nine-rings are joined through GeO_6 octahedra in an eclipsed configuration, creating sandwiches or blocks perpendicular to the *b* direction that are mutually shifted in the (110) direction, in accordance with the symmetry of the *Pnna* space group. Along *b*, the cohesion among sandwiches is established through O(9), the only oxygen atom that is not involved in connectivity within the layers (Figure 2).

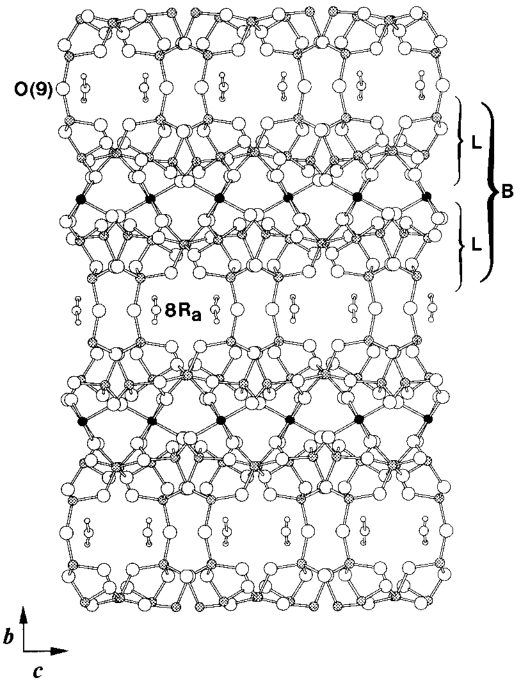

Figure 2. View of the structure of ICMM-2 along the [100] direction, showing the layers (L) and blocks (B) and the connectivity between them through O(9). Black and dotted spheres are Ge atoms in octahedral and tetrahedral environments, respectively.

This three-dimensional structure contains intersecting tunnels along the three directions: One set of tunnels runs in a zigzag fashion along the *b* direction as a consequence of the shifted pillaring of the $9R_b$ nine-rings. In the *a* direction there are tunnels of eight- and four-rings ($8R_a$ and $4R_a$); the latter are too small to allow the passage of any adsorbants. Parallel to *c* there are two kinds of tunnels, one ($6R_c$) centered at (0,1/4,*z*)—that is, inside the sandwiches—and built up from four tetrahedra- and two octahedra-rings, and the other ($8R_c$) outside the sandwiches at (0,0,*z*) and formed by eight-tetrahedra rings. Cages are formed at the intersection of the $9R_b$ and $6R_c$ channels. The NH_4^+ template cations are situated on twofold rotation axes inside the cages, thus compensating for one-half of the negative charges of the framework, and are bonded to different oxygen atoms of the framework through the four hydrogen atoms. For the Cu and Ag compounds the following bond lengths are in the ranges: N–H 0.78(7)/0.80(9)) – 1.05(9)/1.10(9), N $\cdots$ O 2.94(1)/2.94(1) – 2.96(1)/2.95(1), and O $\cdots$ H 2.24(7)/2.01(7) – 2.55(9)/2.40(9) Å.

The structure can also be thought of in terms of blocks, two-dimensional arrays of cages which repeat by vertical translation along the stacking direction *b* to generate the full three-dimensional structure. Owing to this quasi-bidimensionality of the structure, the channels (with the exception of $6R_c$) are all interconnected in the interblock spaces.

Along the $8R_a$ helical channel a row of linear $[M(NH_3)_2]^+$ complex cations is hosted. This arrangement allows an unhindered access of reactants to the active metallic sites through the uniformly sized $8R_c$ channels. The M atoms are situated on twofold rotation axes and bonded to two NH_3 molecules (see Table 1 for bond distances and angles; the asymmetric unit in the Ag compound (ICMM-2Ag) is shown in Figure 3). The $[M(NH_3)_2]^+$ complex cations are isolated inside the channels, and the distance between the M atom and the nearest oxygen atom of the framework is 2.99 Å. The shortest M–M distances in the *a* and *c* directions, respectively, are 6.87 and 7.22 Å for M = Cu and 6.82 and 7.22 Å for M = Ag; all of these distances are inside the interblock space. This separation between metal centers should favor catalytic activity in ICMM-2. There is no hydrogen bond between the coordinated NH_3 molecules and the framework, since the shortest N(1)–O distances are 3.34 Å (M = Cu) and 3.28 Å (M = Ag). As expected, thermal parameters involving $[M(NH_3)_2]^+$ show a directional anisotropy along the *a* axis.

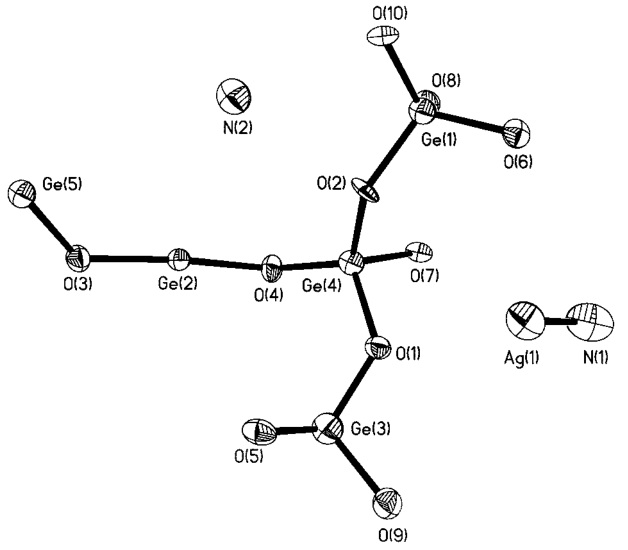

Figure 3. Labeled ORTEP plot of the asymmetric unit in ICMM-2Ag.

To establish the stability of the ICMM-2 framework without the intratunnel complex and study the structural modifications, the cation $[Cu(NH_3)_2]^+$ was removed by stirring of the copper sample (ICMM-2Cu) in a 0.1 M HCl solution for four hours. After determining the crystal structure of the resulting product, $(NH_4)^+(H^+)(Ge_9O_{19})^{2-} \cdot 2\,H_2O$ (ICMM-2H), by single-crystal X-ray diffraction, we can conclude that: 1) the framework does not suffer any significant change upon loss of the metal complex (Table 1), which makes sense when the lack of interaction between the complex cations is taken into account; 2) the NH_4^+ cations remain unaltered inside the cages, and compensated for one-half of the framework charge; and 3) two water molecules are in the interblock space, one of them at the site previously occupied by the Cu atom and the other in the middle of the $8R_c$ channels. Since compensation of the framework charge requires an extra H^+ ion in addition to the ammonium cation, this H^+ ion could give either a hydroxonium ion or a hydroxyl group by association with a water molecule or an oxygen atom from the framework, respectively. Unfortunately, the crystals became slightly damaged during the interchange procedure, which made it impossible to obtain data good enough to locate these hydrogen atoms by Fourier techniques. Further studies to determine the acidity and catalytic activity of this material are under way.

Thermogravimetic analysis coupled with differential thermal analysis (TGA-DTA) of ICMM-2Cu shows two weight losses accompanied by two endothermic energy changes between 200 and 400 °C as well as by a change of color from beige to turquoise blue. The first of these changes, a 3.3 % weight loss between 200 and 300 °C, corresponds to the loss of the NH_3 molecules of the $[Cu(NH_3)_2]^+$ complex cations situated in the open channels. The second weight loss of 1.4 % between 350 and 400 °C corresponds to the decomposition of the compound with loss of the NH_4^+ cations in the cages. X-ray powder diffraction measurements show that the structure is maintained after heating to 350 °C and collapses at 400 °C to crystalline GeO_2 and $CuGeO_3$.

A preliminary study of the catalytic activity of ICMM-2Cu in cyclopropanation reactions of styrene with ethyl diazoacetate[25] showed the following results: The ethyl (phenylcyclopropyl)carboxylate was isolated in greater than 80 % yield with a *trans*:*cis* ratio of 1.98:1. The reaction involving ICMM-2Cu gives rise to relatively low amounts of polymeric side products, which are assumed to be formed at the outer zeolite surface. The polymers consisted exclusively of (ethoxycarbonyl)carbene residues. Polymer formation inside the zeolite would probably lead to its gradual deactivation due to pore blocking by the polymers. Hence, ICMM2 can be a promising catalyst for the cyclopropanation of olefins by ethyl diazoacetate. The activity and selectivity are in about the same range as found for other copper catalysts.

Given that in the structure of ICMM-2 the only connection between blocks is through one oxygen atom (O(9)), these compounds seem to be good candidates for layered zeolite precursors that are to be delaminated.[26] In this way, they will allow access for larger molecules to the catalytic sites, thus increasing the range of reactions that they can catalyze in the present state.

In conclusion, the first microporous germanate containing a transition metal complex, presented here, shows four remarkable features: the presence of GeO_6 octahedra, which allows the framework to become negatively charged without doping with trivalent cations; the housing of isolated molecules of a metal complex inside their tunnels, which makes these materials a good point of departure for designing new catalysts; a stable framework after removal of the transition metal complex; and large distances between the active metal centers, which allows unhindered access of reactants to these centers through uniformly sized 8Rc channels.

Experimental Section

X-ray structure analysis of ICMM-2Cu, ICMM-2Ag, and ICMM-2H: Orthorhombic, space group *Pnna*, $Mo_{K\alpha}$, dimensions of crystals: $0.2 \times 0.1 \times 0.05$, $0.02 \times 0.08 \times 0.2$, and $0.04 \times 0.16 \times 0.2$ mm, respectively; see Table 1 for the cell parameters. Data were collected in a Siemens SMART-CCD diffractometer using ω scans over the range $3 < \theta < 26°$. Of 4663, 5159, and 3518 reflections, 1301, 1651, and 1187 were independent for Cu, Ag and H compounds, respectively. The structures were solved by direct methods. In the Cu and Ag compounds, all the hydrogen atoms were located in difference Fourier maps and those of the NH_4 cation refined with a model of disorder due to the special position of this N atom. Refinement was by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms.[27] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410751 (ICMM-2Cu), -410752 (ICMM-2Ag), and -410753 (ICMM-2H).

Cyclopropanation reactions: The sample of ICMM-2Cu was previously dried at 100 °C. Ethyl diazoacetate (4.11 mmol) was added dropwise over a period of 2 h in a N_2 atmosphere at 50 °C to a stirred mixture of styrene (3 mmol) and the catalyst (0.04 mmol). After the N_2 evolution had ceased, the chemical yields were determined by gas chromatography.

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Donor/Acceptor Metallocenes: A New Structure Principle in Catalyst Design[**]

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Dedicated to Dr. Pol Bamelis
on the occasion of his 60th birthday

Soon after their discovery and structure elucidation[1] metallocenes were being applied as well-defined organometallic species in transition metal catalyzed polymerization with alkylaluminum halide cocatalysts.[2] However, it was only after spectacular work by Sinn, Kaminsky, Brintzinger, Ewen, and others on the increase in catalyst activity in olefin polymerization by aluminoxanes[3] and on the realization of stereospecificity in propene polymerization with homogeneous stereorigid C_2-symmetric *ansa*-metallocenes[4] that the new era of worldwide polyolefin catalyst research began. The results have an impact on a current world market of more than 170 million tonnes of polymers, of which almost half are polyolefins.[5]

The metallocene catalysts developed up to now can be divided into two large classes: 1) unbridged and 2) covalently bridged sandwich compounds.[6]

The catalysts of the first group are highly active in the polymerization of the small ethylene molecule.[7a] A limited

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