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A Copper Germanate Containing Potassium in Its Two-Dimensional Channel Network

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Single crystals of the new copper(II) germanate $K_2Cu_3Ge_5O_{14}$ have been grown. Conditions for the synthesis are reported. The crystal structure of this material has been established by single-crystal X-ray diffraction: triclinic, space group $P\bar{1}$ $a = 6.1859(4)$ Å, $b = 7.1484(5)$ Å, $c = 7.8491(5)$ Å, $\alpha = 82.150(1)°$, $\beta = 72.072(1)°$, $\gamma = 80.773(1)°$. The structure consists of layers of composition $[Ge_5O_{14}]_\infty^{8-}$ formed by GeO_4 tetrahedra and GeO_6 octahedra. The cohesion among them is established through chains of edge-sharing CuO_5 square pyramids and CuO_6 octahedra. This 3D structure contains a two-dimensional channel network were potassium ions are hosted. The downward deviation from Curie−Weiss behavior observed under 30 K in the molar magnetic susceptibility of $K_2Cu_3Ge_5O_{14}$ is attributed to the effect of the crystal field splitting of the ground term.

Introduction

The phosphates of 3d transition metals M form a huge family of compounds[1] (and references therein) showing many interesting properties. A mixed framework built up from MO_6 octahedra and PO_4 tetrahedra defining a great variety of polyhedral connectivities characterize most of them. The ability of germanates to form extended structures with GeO_4 tetrahedra, GeO_6 octahedra, and more rarely GeO_5 trigonal bipyramids, coupled with the different coordination polyhedra exhibited by transition metals, implies that a high number of possible structures could be reached for M-containing germanates. However while phosphates have been widely studied, the corresponding germanates remain poorly explored.

With regard to open-framework topologies, only a limited number of germanates have been reported.[2−4] Two of them, obtained by hydrothermal synthesis, with formula $Ge_9O_{19}[MNH_3]_2NH_4$ (M = Cu, Ag) have been recently reported by some of the authors.[5] In these compounds the transition metals are forming linear complexes without interacting with the framework. On the other hand, for Ge systems in which M is considered as involved in a mixed framework, the reported examples[6−8] show considerable variety in their polyhedra connectivities, with linkages involving Ge−O−Ge, M−O−M, and Ge−O−M bonds.

With the purpose of obtaining germanates of transition metals in which M is part of a mixed framework that also presents some kind of channels, as occurs in most phosphates, we have started an exploratory solid-state synthesis in the A/M/Ge/O system, A being an alkali metal. To study the interesting relations that can be found between structure and properties of materials containing A and d cations embedded in a matrix of p elements, we have tried to grow crystals of these materials. The Cu-containing title compound is the first result in this line. In this paper we report the new $K_2Cu_3Ge_5O_{14}$ structural type as well as the first results on the ionic conductivity and magnetization measurements.

Experimental Section

Crystal Growth. Previous attempts at growing crystals of germanate[7,8] showed the deep influence of the flux employed in order to avoid the high viscosity of the melts containing GeO_2. Nominal compositions near $K_2Cu_3Ge_5O_{14}$ in the absence of the right flux led to massive nucleation and to agglomerates of microcrystals showing aplitic structure.

Crystal used in this work were grown from mixtures of reagent-grade GeO_2, CuO, and K_2HPO_4 at Ge:Cu:K = 2:1:1 molar ratio, using KCl as a flux in nickel crucibles. These mixtures were heated to 900 °C, soaked for 3 h, and cooled to 850 °C at the rate of 1 °C h^{-1} and subsequently to room temperature after turning the power off. Greenish blue crystals were finally obtained after the excess of flux was completely removed with water.

Preparation of Powder Sample. The polycrystalline sample of $K_2Cu_3Ge_5O_{14}$ was prepared in a platinum crucible

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Table 1. Crystal Data and Structure Refinement for $K_2Cu_3Ge_5O_{14}$

empirical formula	$K_2Cu_3Ge_5O_{14}$
formula weight	855.77
temperature	296(2) K
wavelength	0.71073 Å
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 6.1859(4)$ Å, $\alpha = 82.150(1)°$ $b = 7.1484(5)$ Å, $\beta = 72.072(1)°$ $c = 7.846(1)$ Å, $\gamma = 80.773(1)°$
volume, Z	324.55(4) $Å^3$, 1
density (calcd)	4.38 Mg/m^3
absorption coefficient	16.945 mm^{-1}
$F(000)$	397
crystal size	0.1 mm × 0.1 mm × 0.01 mm
Θ range for data collection	2.74°−32.24°
limiting indices	(−9, −10, −11) (4, 8, 11)
reflections collected	2776
independent reflections	2020 ($R_{int} = 0.0286$)
absorption correction	SADABS (Bruker)
max. and min. effective transmission	1.0−0.393363
refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2020/0/102
goodness-of-fit on F^2	0.97
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.054$, w$R_2 = 0.1293$
R indices (all data)	$R_1 = 0.062$, w$R_2 = 0.1315$
Largest diff peak and hole	2.534 and −2.34 e$Å^{-3}$

from reagent grade GeO_2, CuO, and K_2CO_3, using for this last one a 50% excess over the stoichiometric amount required. The mixture was ground and heated in air at 800 °C during 2 days.

X-ray Structure Determination. Data of a greenish blue crystal of $K_2Cu_3Ge_5O_{14}$ were collected in a Siemens SMART-CCD diffractometer, over a hemisphere of the reciprocal space by a combination of three exposures. Unit cell dimensions were determined and refined by a least-squares fit of the strong reflections ($I > 10\sigma(I)$). Each frame exposure of 20s covered 0.3° in ω, using an ω scan over the range $3° < \theta < 32°$. The total number of reflections measured was 2776, of which 2020 were independent. The structure was solved by direct methods. Refinement was by full-matrix least-squares analysis with anisotropic thermal parameters for all atoms. The final residuals were $R_F = 0.054$ for $I > 2\sigma(I)$ and 0.062 for all data. A summary of the fundamental crystal and refinement data is given in Table 1. Most of the calculations were carried out with SMART software, for data collection and data reduction, and SHELXTL.[9,10] Further details of crystal structure determinations can be ordered from Fachinformationzentrum Karlsruhe, D-76344, Eggenstein-Leopoldshafen Germany, (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-410828.

X-ray and Neutron Diffraction Analysis of the Powder Sample. X-ray powder diffraction XRPD analysis of the polycrystalline sample was performed to test the crystal structure of the prepared compound, which appeared well crystallized and free of other phases. The data were collected at room temperature using a Siemens Kristalloflex 810 generator, Cu Kα radiation ($\lambda = 1.540598$ Å), and a computer-controlled D-500 goniometer equipped with a graphite monochromator, over an angular range of $5° \leq 2\theta \leq 100°$, scanning in steps of 0.025° with a counting time of 4 s each step. A neutron powder diffraction NPD pattern was collected at 1.7 K, in the angular range $5° \leq 2\theta \leq 85°$, on the D1B powder diffractometer at the Institut Laue-Langevin de Grenoble, using a wavelength of 2.52 Å. Both XRPD and NPD patterns were analyzed by the Rietveld profile analysis method.[11]

Table 2. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [Å × 10^3] for $K_2Cu_3Ge_5O_{14}$

	x	y	z	U(eq)[a]
K	−2724(3)	4858(3)	1597(3)	27(1)
Cu(1)	3433(2)	275(2)	−3280(1)	10(1)
Cu(2)	0	0	0	10(1)
Ge(1)	2076(1)	2602(1)	3162(1)	8(1)
Ge(2)	1733(1)	7312(1)	3055(1)	8(1)
Ge(3)	5000	0	0	8(1)
O(1)	−531(9)	8181(8)	2194(7)	12(2)
O(2)	2283(9)	1722(8)	1159(7)	12(1)
O(3)	2606(10)	4971(8)	2439(8)	19(2)
O(4)	4310(9)	8275(8)	2177(7)	10(1)
O(5)	3963(9)	1588(8)	4350(6)	12(2)
O(6)	−813(9)	2705(8)	4546(7)	14(2)
O(7)	3147(9)	−1071(7)	−930(7)	9(1)

[a] U(eq) is defined as one third of the trace of the orthogonal U_{ij} tensor.

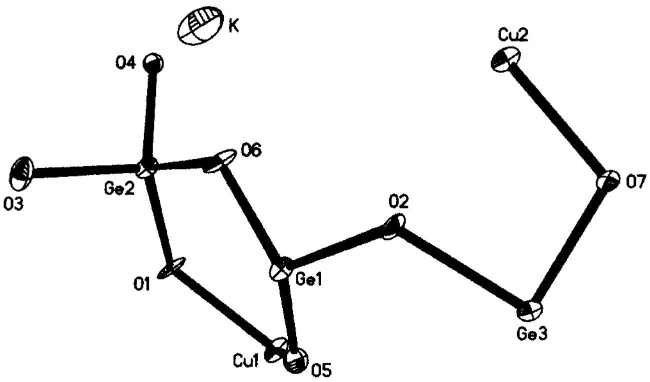

Figure 1. Labeled ORTEP plot of the asymmetric unit in $Cu_3Ge_5K_2O_{14}$.

Starting values of the unit cell and positional parameters used in refinements were those previously obtained in the single-crystal X-ray determination. Further details concerning the refinement process can be found elsewhere.[12]

Magnetic Measurements. Direct current magnetic measurements were carried out on the powder sample using a SQUID (Quantum Design) magnetometer operating from 300 to 2 K at 2000 Oe. Diamagnetic corrections were taken into account.[13]

SEM and EDS. Scanning electron microscopy and energy dispersive spectroscopy were employed to determine the amount of Cu in the single crystals using a PHILIPS XL-30 electron microscope operating at 20 kV with an Edax-Dx4i detector.

Results and Discussion

The crystal structure indicated that the composition is $K_2Cu_3Ge_5O_{14}$. Table 2 includes the atomic parameters and main interatomic distances and angles, and Figure 1 is an ORTEP drawing of the asymmetric unit. Two germanium atoms are tetrahedrally coordinated [Ge−O bond lengths range 1.724(5)−1.790(5) Å; O−Ge−O bond angles 100.6(3)°−119.6(2)°] and the remaining is octahedrally coordinated to oxygen atoms [Ge(3)−O bond lengths range 1.838(5)−1.967(5) Å; O−Ge−O bond angles between 87.8(2) and 92.2(2)°]. There are two kinds of copper atoms in the structure, one of them, Cu(1), is bonded to five oxygen atoms forming a square

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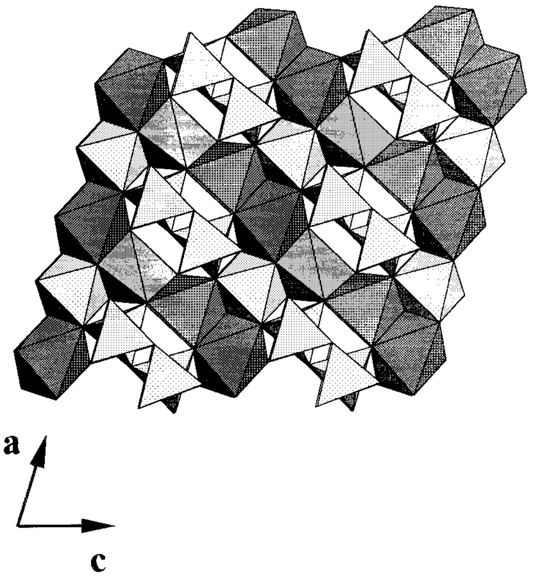

Figure 2. View along the [010] direction of polyhedra arrangement: $[Ge_5O_{14}]_\infty^{8-}$ layers (in gray), and the connectivity among them through Cu chains (in black).

pyramid, with four distances averaging 1.94 Å and the apical one at 2.286(5) Å. The other, Cu(2), situated in a inversion center, forms octahedra which are elongated but not to such an extend as those present in $CuGeO_3$[14] since Cu–O apical distances in $K_2Cu_3Ge_5O_{14}$ are both 2.448(5) Å versus 2.77 Å in $CuGeO_3$. There are twice the square pyramids in the unit cell as octahedra because Cu(1) is situated in a general position (Figure 2). The structure can be envisaged in terms of a $[Ge_5O_{14}]_\infty^{8-}$ sheet that is repeated by translation along the [101] stacking direction to generate the full three-dimensional structure. This sheet is thus perpendicular to the [101] direction, being formed by GeO_6 octahedra and Ge_4O_{12} cyclotetragermanates. These four-rings, with −1 internal symmetry and built up only by two independent GeO_4 tetrahedra, are interconnected through GeO_6 octahedra by sharing vertexes. These sorts of connections give rise a second class of rings formed by six polyhedra in the 1Oh−2Th−1Oh−2Th sequence (Figure 3a). Along the [10−1] direction, chains of edge-sharing CuO_6 and CuO_5 polyhedra are running in such a way that one of every three polyhedra is an octahedron and the remaining two are square pyramids. Cu–Cu distances are 2.7937(9) and 2.833(2) Å between pyramids or an octahedron and a square pyramid, respectively. These chains establish the cohesion among neighboring $[Ge_5O_{14}]_\infty^{8-}$ sheets (Figure 3b). From this linkage comes up a new kind of six-ring, formed by four GeO_4 tetrahedra and two CuO_6 octahedra. This 3D structure contains three types of intersecting tunnels, two of them running in the [101] direction, as a consequence of the stacking of both four- and six-germanium rings, and the third one, which involves Cu chains, along [10−1]. The shape and size of the windows are shown in Figure 4. It is in this last channel where the potassium atoms are guests. The only independent potassium atom in the asymmetric unit is 7-fold coordinated by oxygen atoms, with an average distance K–O of 2.960 Å, a value quite similar to those found in other potassium containing germanates.[6] Every two KO_7 polyhedron related by an inversion center form pairs via O(3)–O(3) common edge (Figure 5).

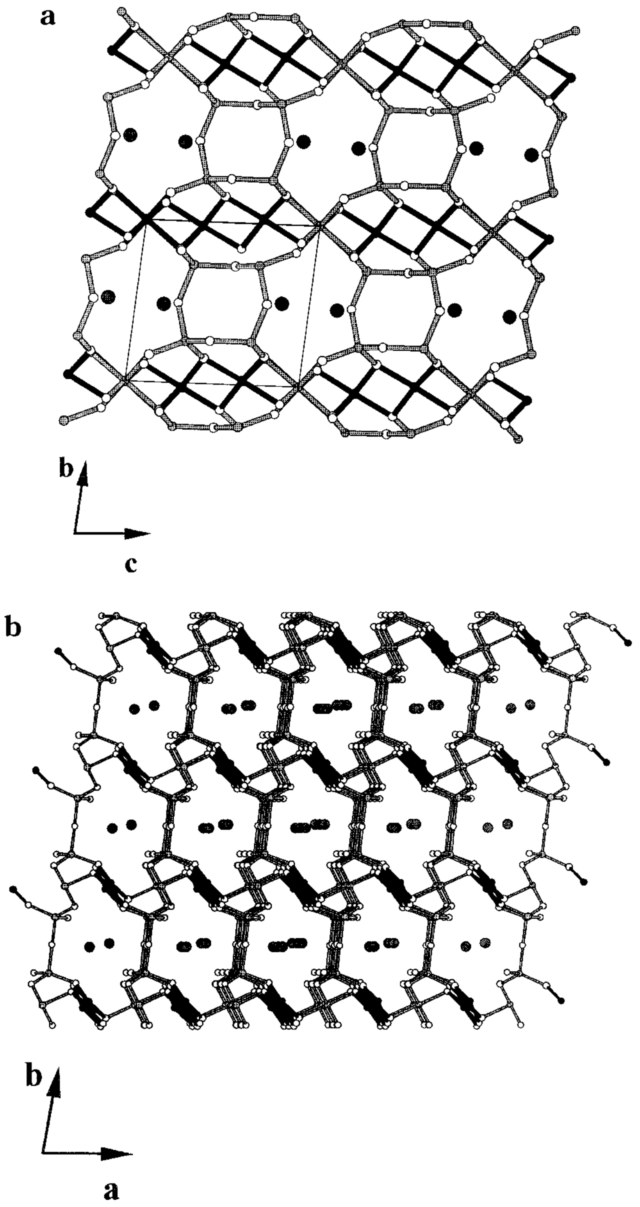

Figure 3. View of the structure of $Cu_3Ge_5K_2O_{14}$: (a) in the bc plane; (b) along the [10−1] direction. Ge atoms are in gray, O in white, Cu in black, and K in larger black circles.

Results of the RXPD Rietveld analysis showed a single-phase sample with parameters quite similar to those obtained from the single crystal: $a = 6.1729(3)$ Å, $b = 7.1244(4)$ Å, and $c = 7.8281(4)$ Å, $\alpha = 82.135(3)°$, $\beta = 71.995(3)°$, and $\gamma = 80.693(3)°$. As expected from the magnetic susceptibility curve (Figure 6) the NPD data Rietveld analysis at 1.7 K did not indicate any signs of magnetic interactions, i.e., magnetic ordering of the d^9 Cu^{2+} magnetic moments at low temperature (Figure 7). The obtained parameters in this refinement were $a = 6.173(2)$ Å, $b = 7.132(3)$ Å, and $c = 7.834(3)$ Å, $\alpha = 82.07(2)°$, $\beta = 72.07(3)°$, and $\gamma = 80.72(2)°$.

Taking into account the relatively open framework of $K_2Cu_3Ge_5O_{14}$ and the location of the K ions at the intersecting tunnels, this material could be a good ionic conductor. In other tunnel-containing materials that

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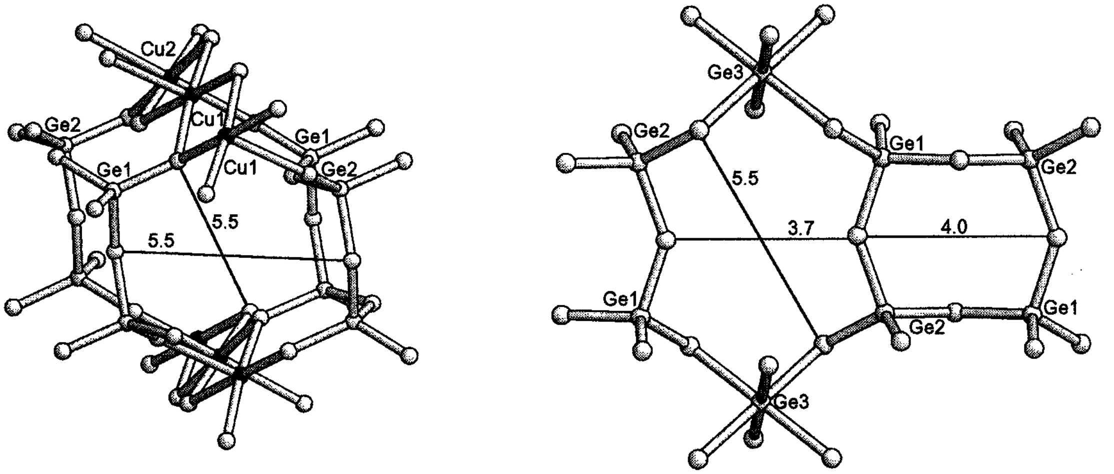

Figure 4. Shape and size of the windows corresponding to the three different kinds of channels present in $K_2Cu_3Ge_5O_{14}$. Distances, in Å, to the centers of atoms are given.

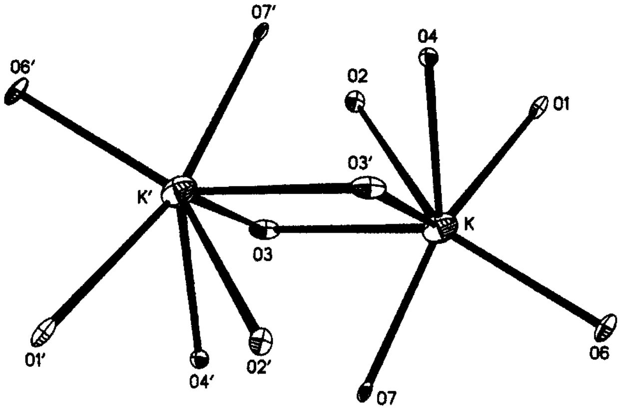

Figure 5. ORTEP view of the pairs formed by two KO_7 polyhedra.

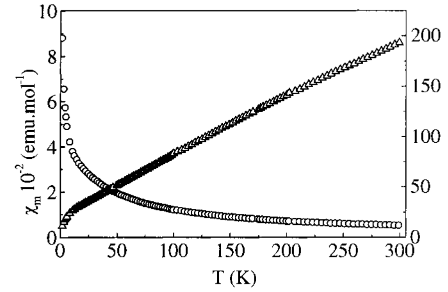

Figure 6. Molar paramagnetic susceptibility (circles) and its reciprocal (squares) as a function of temperature for $Cu_3Ge_5K_2O_{14}$.

own this property[15] the amplitude of thermal vibration of the K ions in the direction of the tunnels is associated with the unhindered motion of those ions and with high ionic conductivity. However, the anisotropic thermal parameter of the K atom in the present compound is not larger than usual, which agrees with the high value of the activation energy $E_a = 1.45$ eV as determined from a routinely measured Arrhenius-type conductivity plot. This fact can be explained by the stoichiometric nature of this compound; consequently the tunnels are "filled up" by potassium ions. This may produce strong electrostatic interactions between K cations occupying the same tunnel that would be responsible for the limitation of their mobility. Partial extraction of potassium atoms in order to improve the ionic conductivity of this material is under way.

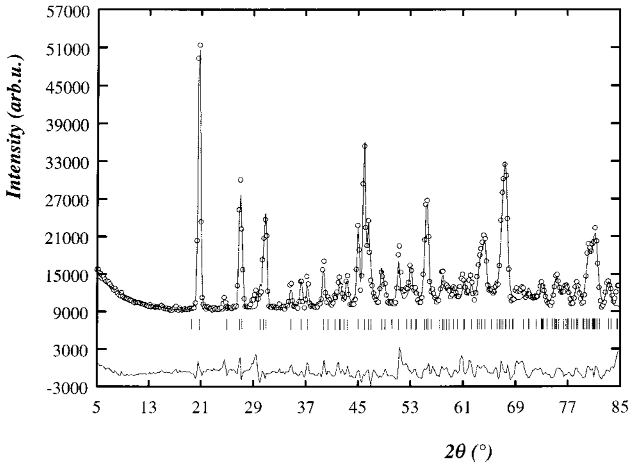

Figure 7. Observed (symbol), calculated (solid line), and difference (at the bottom) profiles for $K_2Cu_3Ge_5O_{14}$, from NPD at 1.7 K. Vertical marks correspond to the position of the allowed Bragg reflections.

Many studies trying to establish relations between crystal structure and the magnetic behavior derived from different metallic interactions inside the germanate matrix are being lately carried out.[12,16] Figure 6 shows the temperature dependence of the molar magnetic susceptibility, and its reciprocal, for $K_2Cu_3Ge_5O_{14}$. Above $T \sim 30$ K, the plot follows a Curie–Weiss type law, $\chi_m^{-1} = 24.1(4) + 0.578(2)T$ mol emu^{-1} ($r = 0.9994$), with $\theta_c = -42$ K being the calculated magnetic moment 3.7 μ_B per formula unit, which corresponds to 2.1 μ_B per Cu^{2+}. This value is similar to that observed for other d^9 Cu^{2+} compounds and agrees with the expected value, considering the mixing in of the excited states $^2T_{2g}$ to the ^2E_g ground state which result of the crystal-field splitting of the ^2D free ion ground term. Since at low temperatures neither maxima in χ_m nor magnetic ordering is observed from NPD measurements (Figure 7), no cooperative interactions are present in

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$K_2Cu_3Ge_5O_{14}$, and consequently, under 30 K the effect of the crystal-field splitting of the ground term is the only thing responsible for the observed downward deviation from linearity in the χ_m^{-1} vs T plot.

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Supporting Information Available: Anisotropic temperature factors and a listing of structure factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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