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A Hybrid Metalloarsenate 3D Framework–1D Interrupted Metal Oxide

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Complex metal arsenates of the stoichiometry $M_{1-x}M'_6(OH)_3(AsO_4H_{2x/3})_3(HAsO_4)$, M = M′ = Co, Ni, have been synthesized under hydrothermal conditions. The two compounds display a very similar structural topology to that of the mineral dumortierite, an uncommon complex oxyborosilicate of aluminum. The hybrid structures consist of well separated, vacancy interrupted chains of face sharing MO_6 octahedra, with short M•••M distances near 2.5 Å, embedded in a metalloarsenate 3D framework having the topology of the aluminosilicate cancrinite. The framework also contains a quadruply bridging hydroxide ion. Magnetic susceptibility measurements reveal a strong antiferromagnetic interaction and magnetic transition to low temperature spin canted phases below 51 K (Co) and 42 K (Ni). The material may be considered as a zeotype framework structure templated by an interrupted one-dimensional metal oxide.

Introduction

The integration of different functionalities within a single material is a topic of considerable recent interest. Work in this general area includes studies of materials such as hybrid organic−inorganic structures,[1,2] molecular materials exhibiting electronic and magnetic properties,[3,4] and porous framework materials that potentially have magnetic interactions between metal centers.[5,6] Perhaps the two key properties currently of interest are, on one hand, porosity, in structures such as zeolites and related frameworks based on linked polyhedra, and, on the other, cooperative electronic and magnetic properties, as commonly exhibited by extended, transition metal oxide structures. In both cases, dimensionality, due to structural elements such as chains and sheets, is of crucial importance in defining properties. Thus, one-dimensional magnetic/electronic materials include the AMX_3 type systems,[7] two-dimensional systems include the cuprate superconductors,[8] and three-dimensional structures include the manganate perovskite magnetoresistance materials, such as $Ln_{1-x}Ca_xMnO_3$.[9]

Formally, the porous structures of zeolites contain channels that have distinct dimensionality, and filling of these pores with various functional species leads to constrained, oriented, and directional properties. This behavior has been reported with various materials such as those of selenium groups and chains in cancrinite[10] and fluorescent and dye compounds aligned in various zeolite channels.[11] Some zeolite structures, e.g., the JBW structure type, have dense regions which may be considered to be oxide as in SiO_2 and therefore lie on the borderline between dense oxide and porous framework structures.[12] Furthermore, the incorporation of some transition metal species, especially Co, into the frameworks of zeolite-like structures is well-known.[13,14] This formally gives porous structures constructed from magnetically active ions though in many cases these transition metal centers are well separated and magnetic interactions are weak or not observed. Such metallo-framework formation is common in materials constructed from tetrahedra such as transition metal (M)

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phosphates, silicates, and arsenates where tetrahedral BO_4 (B = Si, P, As) units cross link MO_n ($n = 4-6$) polyhedra.[15,16]

One example of a material that might be considered as a hybrid framework/oxide is the mineral dumortierite.[17] This mineral, an uncommon complex oxyborosilicate of aluminum, has a structure that, when idealized, consists of two sections; the first part is made up of a fully occupied 1D chain of face sharing octahedra, and the second is based on a perfect 3D network of cancrinite topology. Dumortierite itself is far from ideal, containing both a distorted 3D network and a partially occupied face sharing chain that reduces symmetry from a hypothetical $P6_3mc$ polymorph to the recognized *Pmcn*. Other materials that also share the structural connectivity are a copper/iron vanadate,[18] iron/cobalt molybdates,[19,20] and a cobalt/nickel hydroxytellurite.[21] These few materials are either naturally occurring or do not show any magnetic properties at all.

The combination of a framework, possibly magnetically active itself, with a metal oxide unit within its channels or interlayer spacing would provide a key stage in controlling dimensionality in magnetic or electronic materials. In this article, we report the synthesis of two new inorganic materials in which MO_n polyhedra are linked into interpenetrating 3D and 1D structures.

Experimental Section

Caution. Arsenic compounds are highly toxic.

Materials. $(NH_4)H_2AsO_4$ (Alfa Aesar, 98%), $M^{II}(NO_3)_2{\cdot}6H_2O$ (M = Co or Ni, both Aldrich, 98%), and $LiOH{\cdot}H_2O$ (Aldrich, 98%) were used.

$(NH_4)H_2AsO_4$ and $M^{II}(NO_3)_2{\cdot}6H_2O$ in molar ratio 1:1 were dissolved in 12 mL of H_2O. An equimolar amount of solid $LiOH{\cdot}H_2O$ was added to raise the pH, causing precipitation of $M^{II}(OH)_2$ particles. The mixture was sealed in a 23 mL, Teflon lined Parr autoclave and heated at 200 °C for 24 h. After cooling, the crystalline product, $M_{1-x}M'_6(OH)_3(AsO_4H_{2x/3})_3(HAsO_4)$, was purified by sonication. Product **1** (Co) occurred as purple spearlike crystals, and product **2** (Ni) as hexagonal blocklike crystals.

Crystallographic Determination. Suitable crystals, for **1** and **2**, were selected for data collection on a Nonius Kappa CCD area detector diffractometer (Mo Kα radiation) at 120(2) K. The unit cell obtained, for **1**, was trigonal with $a = 12.8279(6)$ Å, $b = 12.8279(6)$ Å, $c = 5.0919(2)$ Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 120.00°$, $V = 725.64(6)$ Å^3, $Z = 6$, $2\theta_{\max} = 27.48°$ to give 3327 measured reflections and 607 unique. For **2**, the unit cell was again trigonal with $a = 12.7021(18)$ Å, $b = 12.7021(18)$ Å, $c = 4.9966(10)$ Å, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 120.00°$, $V = 698.16(2)$ Å^3, $Z = 6$, $2\theta_{\max} = 27.37°$. These isostructural materials were solved and refined by least-squares method using SHELXS/L-97[30] in the space group $P6_3mc$. Hydrogen atoms were not located by this method to any certainty. All calculations were performed using the WINGX system (version 1.64.03)[31] giving final anisotropic values R1 = 0.0334 and wR2 = 0.0798 for **1** and R1 = 0.0396 and wR2 = 0.0976 for **2**. Some data collection and refinement information is given in Table 1. Additional data are supplied in the Supporting Information.

Table 1. Crystal Data for Compounds **1** and **2**

empirical formula	$H_{1.57}As_{1.22}Co_{2.22}O_{6.33}$	$H_{1.68}As_{1.33}Ni_{2.16}O_{6.33}$
fw	333.43	329.83
space group	$P6_3mc$	$P6_3mc$
Z	6	6
T, K	120(2)	120(2)
a, Å	12.8279(6)	12.7021(18)
b, Å	12.8279(6)	12.7021(18)
c, Å	5.0919(2)	4.9966(10)
V, Å^3	725.64(6)	698.2(2)
μ, mm^{-1}	16.583	18.087
D_x, Mg m^{-3}	4.578	4.707
data/restraints/params	607/0/56	497/0/56

Magnetic Susceptibility. Magnetic measurements were performed on polycrystalline powder samples using a Quantum Design MPMS SQUID magnetometer, between 2 and 300 K and in a range of field up to ±5.5 T. A diamagnetic correction for both **1** and **2** was determined from Pascal's constants as -51×10^{-6} cm^3 mol^{-1}, per M^{2+} ion.[22]

Infrared Spectroscopy. IR spectra (KBr pellet) were recorded using a Perkin-Elmer Spectrum One system operating between 4000 and 450 cm^{-1}. The main bands were observed at 3573 (w), 3510 (w), 3456 (w), 905 (s), 842 (s), 724 (s), and 448 (s) cm^{-1} for **1**. (For **2**, 3574 (w), 3505 (w), 3444 (w), 917 (s), 839 (s), 776 (s), and 492 (s) cm^{-1}.)

SEM/EDX. Energy-dispersive X-ray spectra were recorded using a Phillips XL30 ESEM scanning electron microscope operating in high vacuum mode. Several crystals of **1** and **2** were selected for analysis using the backscattered X-ray detector.

Results and Discussion

The underlying "structure type", if fully occupied, could be given by the formulation $MM_6'(OH)_3(AsO_4)(AsO_4H)$ where M lies on a 2a Wyckoff position and M′ on a 12d site along with two crystallographically distinct arsenate groups. This would possess the same topology with the hypothetical idealized structure of the mineral dumortierite.

Figure 1 shows an ORTEP representation of the asymmetric unit of **1** from which the structure is built; it consists of two types of distorted Co(Ni)O_6 octahedra and AsO_4 and $AsO_3(OH)$ tetrahedra. Important bond length data for the two compounds are summarized in Table 2. The structure can

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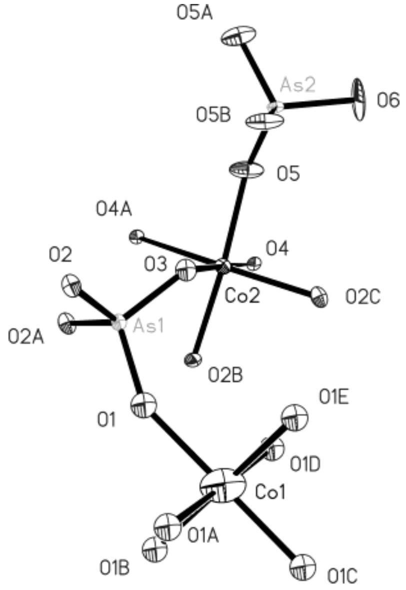

Figure 1. Asymmetric unit and selected symmetry equivalent atoms present in $M_{1-x}M'_6(OH)_3(AsO_4H_{2x/3})_3(HAsO_4)$, M = M′ = Co, showing the coordination geometries to cobalt (nickel) and arsenic. The quadruply bridging hydroxide ion is O4 which has the attached hydrogen disordered over two sites and is hydrogen bonded to O5 and O6. O6 is the hydroxide unit in the (AsO_3OH) group with the hydrogen disordered over three equivalent sites and which is hydrogen bonded to O5. Ellipsoids are at the 30% probability level.

Table 2. Important Bond Lengths (Å) for $M_{1-x}M'_6(OH)_3(AsO_4H_{2x/3})_3(HAsO_4)$, M = M′ = Co, Ni[a]

	Co	Ni		Co	Ni
As1−O2	1.674(8)	1.645(10)	As2−O5^{ii}	1.667(13)	1.650(17)
As1−O2^{i}	1.674(8)	1.645(10)	As2−O5	1.667(13)	1.650(17)
As1−O3	1.674(11)	1.664(16)	As2−O5^{iii}	1.667(13)	1.650(17)
As1−O1	1.675(12)	1.673(15)	As2−O6	1.69(2)	1.69(4)
M−O1^{iv}	2.111(13)	2.11(2)	M′−O2^{v}	2.028(8)	2.016(11)
M−O1^{v}	2.111(13)	2.11(2)	M′-O5	2.048(10)	2.026(13)
M−O1^{vi}	2.111(13)	2.11(2)	M′−O2^{x}	2.064(8)	2.044(11)
M−O1	2.119(3)	2.13(2)	M′−O3	2.079(6)	2.055(8)
M−O1^{vii}	2.119(3)	2.13(2)	M′−O4^{xi}	2.146(8)	2.121(12)
M−O1^{viii}	2.119(3)	2.13(2)	M′−O4	2.238(9)	2.174(12)
M−M^{ix}	2.54595(10)	2.4843(5)	M′−M′^{xii}	2.875(3)	2.797(4)

[a] Esd’s are given in parentheses. Symmetry codes: (i) $x, 1 + x - y, z$; (ii) $1 - y, x - y, z$; (iii) $1 - x + y, 1 - x, z$; (iv) $1 - x, 1 - y, {}^1/_2 + z$; (v) $2 - x, 2 - y, {}^1/_2 + z$; (vi) $1 + x - y, x, {}^1/_2 + z$; (vii) $y, 1 - x + y, {}^1/_2 + z$; (viii) $1 - x + y, 2 - x, z$; (ix) $2 - y, 1 + x - y, z$; (x) $2 - x, 2 - y, z - {}^1/_2$; (xi) $y, x, {}^1/_2 + z$; (xii) $1 + x - y, x, z - {}^1/_2$; (xiii) $1 - y, 1 - x, z$; (xiv) $y, x, z - {}^1/_2$; (xv) $1 - x, 1 - y, z - {}^1/_2$.

be divided to show two key component elements: a three-dimensional framework consisting of strongly distorted $M'O_6$ octahedra, interlinked on the basis of four vertices only, and terminated by arsenate groups and a partially occupied chain of face sharing MO_6 octahedra. Each of these motifs is considered in detail in turn.

The topology of the framework can be visualized by considering just the metal centers and the shortest M′−O−M′ interactions, as shown in Figure 2. This arrangement is identical to that of the cancrinite zeolite structure consisting of an AB sequence of stacked six rings[23] in the space group $P6_3/mmc$. This generates two cavities within the structure. The smaller cavity (so-called 11-hedral cage) contains one type of arsenate group linking six $Co(Ni)O_6$ octahedra with three doubly bridging oxygen atoms; in cancrinites such as $Na_8[SiAlO_4]_6.(CO_3)\cdot nH_2O$, this cavity contains just sodium ions and water molecules. The larger cavity is formed from a 12 tetrahedral atom membered ring in the cancrinite structure where it encloses sodium ions and the trigonal carbonate groups. In $MM_6'(OH)_3(AsO_4)_3(AsO_4H)$, this channel is decorated around its internal surface by arsenate groups; these arsenate groups again link the $Co(Ni)O_4O_2$ octahedra with three common oxygen atoms leaving one additional oxygen that is directed toward the center of the 12-ring and then forms part of the partially occupied $Co(Ni)O_6$ chain.

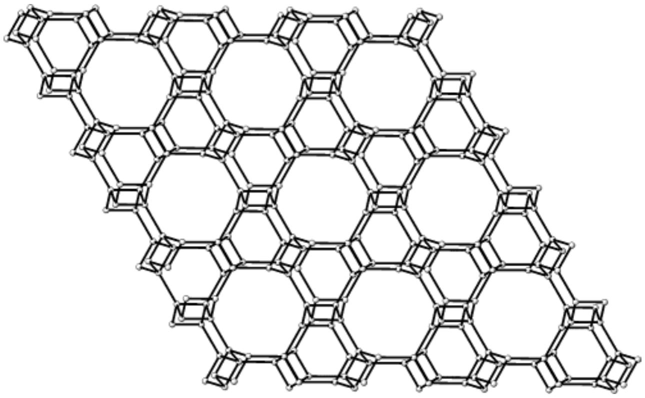

Figure 2. Framework structure shown in terms of the connectivity between M′ (M2) centers though M′−O−M′ bonds.

However, a free occupancy refinement of the data shows that the metal occupying the 6-fold site is only partially occupied with the percentage occupancy of this site roughly ${}^2/_3$ for **1** and ${}^1/_2$ for **2**. This partial occupancy in the 1D oxide chain has also been observed in many other materials that have the same structural topology.[24,25] These compounds, as well as the naturally occurring mineral dumortierite, are varied with respect to composition. The partial occupancies range considerably from about 50% up to 75% in the molybdates, vanadates, and the natural minerals, in which our values lie also.

The compositions are confirmed by the EDX results. For **1**, assuming ${}^2/_3$ occupancy of the 6-fold site we would expect to see a 5:4 ratio of cobalt to arsenic. The average value from analysis of several crystals gives a ratio of 5:4.19. For **2**, with ${}^1/_2$ occupancy the calculated ratio is 4:4, and EDX results average out at 4:3.76 nickel to arsenic.

For charge neutrality, the unit cell needs a total of 9.4 hydrogen atoms for **1** and 10.06 for **2**; therefore, to best describe the formula $M_{1-x}M'_6(OH)_3(AsO_4H_{2x/3})_3(HAsO_4)$ is used. Other refinements on this structure type, that contains hydrogen, have failed to locate the positions of these atoms merely stating that they are present in order to balance the charges. Due to the disorder in the structure, the hydroxide species are very difficult to find using solely X-ray techniques.

Through the loss of every 1 in 3 cobalt sites, and 1 in 2 nickel sites, the remaining oxygen, O(1), requires protonation. Bond valence calculations were used to locate the sites that were most likely to contain the hydroxy groups. This study has shown that when the partially occupied model of the 1D chain is used, three unique OH groups are observed. First,

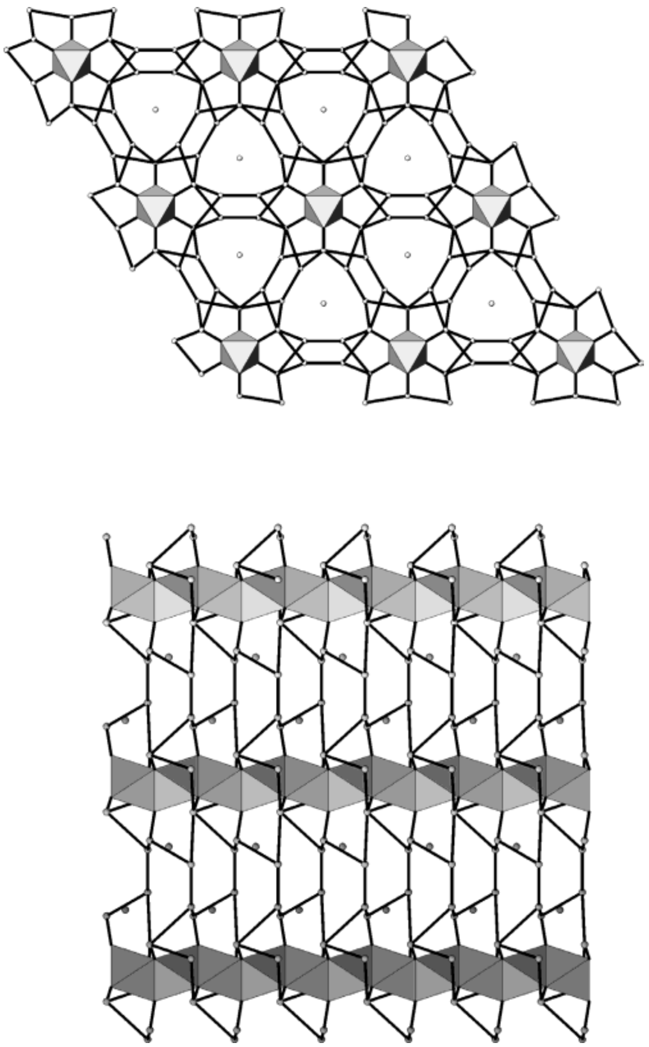

Figure 3. Interrupted chain of face sharing octahedra. Top: the structure viewed down *c*. Bottom: the structure viewed perpendicular to *c*. The framework is represented as linked Co and As centers, and the As atoms in the 11-hedral cages as isolated spheres.

a terminal hydroxide is found on O(6), giving rise to an AsO_3-OH group. Second, the presence of hydroxide is spread about O(1) and occupies these sites only at the cobalt vacancies. The final hydrogen is located on O(4) which is bonded to four Co(Ni)(2) atoms forming a μ^4-hydroxide species.

The unusual feature of the framework is the presence of a quadruply bridging hydroxide ion which weakly links four $M'(2)O_6$ octahedra with M′(2)−OH distances in the range 2.15−2.24 Å (Co) and 2.12−2.17 Å (Ni). Further evidence of the hydroxide groups can be seen in the IR spectra, with three weak bands at 3573, 3510, and 3456 cm^{-1} for **1** (3574, 3505, and 3444 cm^{-1} for **2**).

The position and orientation of the interrupted one-dimensional chain formed from face sharing $Co(Ni)O_6$ octahedra are shown in detail in Figure 3. This arrangement of face sharing octahedra results in short M···M contacts of 2.5460(1) Å for Co and 2.4843(5) Å for Ni. Such a short contact in divalent metal oxide systems is extremely rare. $BaNiO_2$ has short Ni−Ni interactions at 2.378 Å formed in zigzag chains of edge sharing square planes[26] while K_2CoO_2 has a Co−Co distance of 2.537 Å, again between edge sharing square planes.[27] Infinite one-dimensional chains formed from face sharing octahedra are unknown in oxide structures for Ni and Co but are well-known in fluorides, for example in the materials AMF_3, where A = Rb and Cs and M is a divalent transition metal.[7]

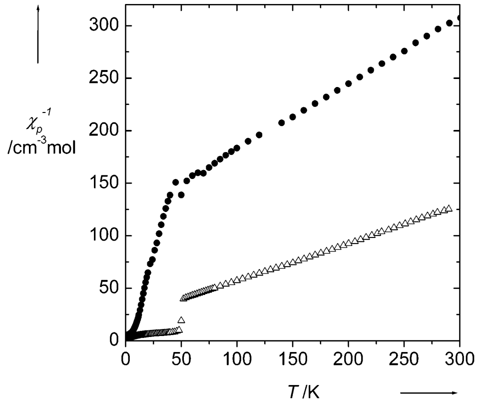

Figure 4. Plot of reciprocal susceptibility for Co (△) and Ni (●), showing the Curie−Weiss behavior of the high temperature paramagnetic phases and the transitions to magnetically ordered states.

Other transition metal arsenates all contain linked arsenate tetrahedra and metal octahedra, though the latter are only vertex or edge shared. Presumably, the unusual structural features present in $MM_6'(OH)_3(AsO_4)_3(AsO_4H)$ result from the synthesis method where the metal hydroxide is precipitated prior to the hydrothermal reaction; formally, a strand of metal hydroxide formed from condensed $M(OH)_6$ octahedra could act as a template for the main channel of the structure.

The magnetic behaviors displayed by $MM_6'(OH)_3(AsO_4)(AsO_4H)$ where M = M′ = Co and Ni are very similar, Figure 4. At high temperatures, both obey the Curie−Weiss law well: Curie constants are 2.89(1) (Co) and 1.67(2) (Ni) $cm^3\ K\ mol^{-1}$, $\mu_{eff} = 4.80\ \mu_B$ (Co) and 3.66 μ_B (Ni), values typical for octahedrally coordinated high spin M^{II}, and Weiss constants $\theta = -59.9(5)$ (Co) and $-191(5)$ (Ni) K. On cooling both materials, they order to a state with a small moment at 50.5(5) (Co) and 42(1) (Ni) K. The susceptibility below T_N is found to be strongly field dependent. This behavior is consistent with canted antiferromagnetic ordering and is supported by hysteresis measurements.[28] At 5 K, the cobalt compound requires a coercive field of 1580(10) G and has a remnant magnetization of 84(1) G $cm^3\ mol^{-1}$, while for the nickel derivative these values are 1620(10) G and 74(2) G $cm^3\ mol^{-1}$. Assuming a two sublattice model, these deviations from collinearity correspond to cant angles of 0.23° and 0.25° for Co and Ni compounds, respectively.

This cooperative magnetic behavior is determined by the single ion properties and the topology of the spin-coupled network. This is defined by the strongest (usually shortest) superexchange pathways. In this case, all M^{2+} ions are connected by M−O−M bridging pathways, but in two interpenetrating networks, the 3D zeotype framework potentially can contain isolated chains of metal ions, although partial occupancy on this site breaks the chain into mostly isolated ions, dimers, and trimers. Although the M···M distances within these short chain fragments are very small,

∼2.5 Å, and a strong coupling should be expected, the low dimensional nature of this structural component cannot undergo a conventional magnetic ordering.[29] In fact, the 3D M′···M′ interactions in the framework dominate, allowing the whole material to undergo a transition to an ordered magnetic state, without evidence of short-range correlations above T_N.

Conclusions

Two new complex metal arsenates have been synthesized which show interesting structural features: the metal oxide framework that shares a zeolite topology and the quadruply bridging μ^4-hydroxide ion. This hybrid structure type of a framework containing an interrupted metal oxide chain is one that could produce materials showing unusual properties such as multiple sublattice and low dimensional magnetism.

Further work is in progress to determine the range of transition metal ions that can be incorporated into this structure type and to see whether it is possible to synthesize a material with a fully occupied metal oxide chain. Clearly, it may be possible to segregate metal ions between the two sites, the framework and metal oxide chain. Materials such as $NiZn_6(OH)_3(AsO_4)_3(HAsO_4)$ where the framework metal is nonmagnetic would allow a more detailed study of the magnetic properties of the chain portion of the hybrid material.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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