Inorg. Chem. **2002**, *41*, 7072–7076

Inorganic Chemistry Article

Cage Compounds of Heterotrimetallic Mixed Phosphanediide/Silanolate Aggregates with an Alkaline Earth Metal-Centered Phosphorus Octahedron

Matthias Westerhausen,* Sabine Weinrich, Gernot Kramer, and Holger Piotrowski

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 9,
D-81377 Munich, Germany

Received March 28, 2002

The lithiation of potassium triisopropylsilylphosphanide yields the corresponding phosphanediide. The subsequent metathesis reaction with SrI_2 and BaI_2 in the presence of hexamethyldisiloxane gives hexalithium hexapotassium strontium hexakis(triisopropylsilylphosphanediide)bis(trimethylsilanolate) (**1**) and the corresponding barium derivative (**2**), respectively. The alkaline earth metal atoms are surrounded octahedrally by the phosphanediide ligands. Six P_3 faces of the octahedron are capped by the K atoms, and the P–P edges of two opposite P_3 faces are bridged by the lithium atoms. The Li cations are also bonded to the Me_3SiO substituents giving a coordination number of three for the alkali metals.

Introduction

Heterobimetallic amides of the alkali and alkaline earth metals form macrocycles that can function as superbases and are able to deprotonate arenes such as benzene and toluene.[1] The metalation of 2,2,6,6-tetramethylpiperidine (tmpH) with a mixture of butylpotassium and dibutylmagnesium gives the mixed heterobimetallic amides that appear to be a cationic host for deprotonated arene anions.[2] Even doubly deprotonated arenes can be generated and stabilized by the heterobimetallic dication $[Mg_2Na_4(tmp)_6]^{2+}$ with a $Mg_2Na_4N_6$ macrocycle.[3] A hydride encapsulation within a $Mg_2Na_2N_4$ macrocycle was also already observed employing the diisopropylamide substituents.[4] Furthermore, oxide and peroxide anions can be coordinated by inverse $Li_2Mg_2N_4$ as well as $Na_2Mg_2N_4$ crowns where tmp and $(Me_3Si)_2N$ anions were present.[5]

Heterobimetallic phosphanides and phosphanediides are only well-known for tin(II) and the heavy alkaline earth metals calcium,[6] strontium,[7] and barium.[8] Mixed magnesium and tin(II) phosphanides and arsenides are unknown because they dismutate into the homoleptic compounds.[9] Further differences between the magnesium and the homologous compounds affect the structures of the phosphanediides. Depending on the intramolecular strain of the magnesium trialkylsilylphosphanediides, tetrameric[10] or hexameric derivatives[11] were isolated. In contrast to this observation and because of the fact that the strong metalating reagents dialkylcalcium, -strontium, and -barium are not available,[12] homometallic phosphanediides of the heavy alkaline earth metals are unknown as of yet. Instead of spherical cage compounds as found for magnesium phosphanediides, mixed phosphanides and phosphanediides are observed as shown

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* Author to whom correspondence should be addressed. E-mail: maw@cup.uni-muenchen.de.

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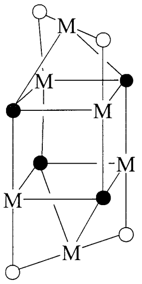
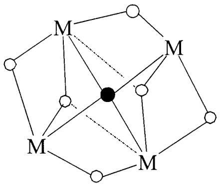
10.1021/ic0202413 CCC: $22.00

for A.[13] Because of the reduced reactivity of the homologous trialkylsilylarsane, another cage B with an even lower content of dianions was isolated.[14] Macrocyclic molecules with an inverse crown structure are unknown for the heavier alkaline earth metal phosphanides and phosphanediides.

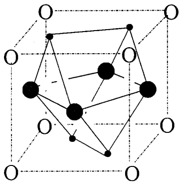


E = P
R = *i*Pr, *t*Bu
M = Ca, Sr, Ba
A



E = As
R = *i*Pr
M = Ca, Sr, Ba
B

○ = P(H)SiR$_3$
● = PSiR$_3$



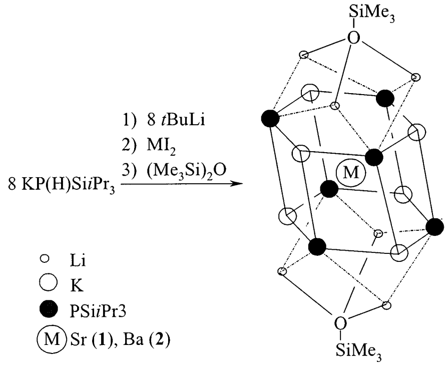
O = O-EMe$_3$ with
E = C/Si
• Li
● K

C

Because of the missing strong metalating reagents, we prepared mixed-metal phosphanediides via the metathesis reaction of alkali metal trialkylsilylphosphanediides with strontium and barium diiodide.

Results and Discussion

Synthesis. The metalation of triisopropylsilylphosphane with potassium bis(trimethylsilyl)amide yields nearly quantitatively KP(H)Si-*i*-Pr$_3$.[15] The lithiation of this phosphanide with *tert*-butyllithium gives a triisopropylsilylphosphanediide of lithium and potassium. The enhancement of the reactivity by combination of two different alkali metals is already well-known for oligomeric alkoxides[16] and mixed amides and alkoxides.[17] The metathesis reaction of KLiPSi-*i*-Pr$_3$ with SrI$_2$ and BaI$_2$, respectively, and the addition of hexamethyldisiloxane yield the heterotrimetallic cage compounds hexalithium hexapotassium strontium hexakis(triisopropylsilylphosphanediide)bis(trimethylsilanolate) (**1**) and the corresponding barium derivative **2** according to eq 1. The use of mixed lithium and potassium bases to cleave hexamethyldisiloxane was reported earlier for the super base system *n*-butyllithium/potassium *tert*-butoxide to prepare the cage Li$_4$K$_4$(OEMe$_3$)$_8$ (C) with E = C/Si.[18] Whereas the silanolate moieties are incorporated within the cages of **1** and **2**, it is not clear where the split off trimethylsilyl groups remains. In the ^{31}P NMR spectra of the reaction solution, broad signals of other but yet unknown compounds were detected between $\delta = -360$ and -390 and, however, are neither assignable to the simple phosphanides LiP(SiMe$_3$)(Si-*i*-Pr$_3$) ($\delta = -328$) or the corresponding potassium derivative ($\delta = -327$) nor to (Me$_3$Si)$_2$PSi-*i*-Pr$_3$ ($\delta = -267$).



(1)

Compounds **1** and **2** consist of six triisopropylsilylphosphanediide substituents that are arranged octahedrally and centered by an alkaline earth metal atom. The P$_3$ faces are capped by potassium atoms with the exception of two opposite ones. The P−P edges of these two faces are bridged by lithium cations. The trimethylsiloxy groups are bonded to three lithium atoms thus giving 3-fold coordinated alkali metal atoms.

The very similar structures of **1** and **2** also lead to nearly identical NMR data. Because of the coordination number of three at the lithium atoms, chemical shifts in the region of $\delta(^7\text{Li}) = 7$ were observed. The dianionic charge on the phosphorus atoms leads to a high-field shift of the ^{31}P resonance. A rather large ^1J(P,Si) coupling constant is observed, which is in agreement with the short P−Si bond lengths. Couplings between the phosphorus and the lithium nuclei were not detected.

Molecular Structures. The molecular structure of **2** is presented in Figure 1. The molecular structure of **1** is isotypic; therefore, no representation is given. Atoms generated by inversion symmetry ($-x + 1$, $-y$, $-z + 1$) are marked with apostrophes. The bond lengths are listed in Table 1; mean values are given in the last column. The alkaline earth metals Sr1 and Ba1 are in an octahedral environment with mean Sr−P and Ba−P distances of 310.4 and 317.4 pm, respectively. A comparison with the tetrakis-

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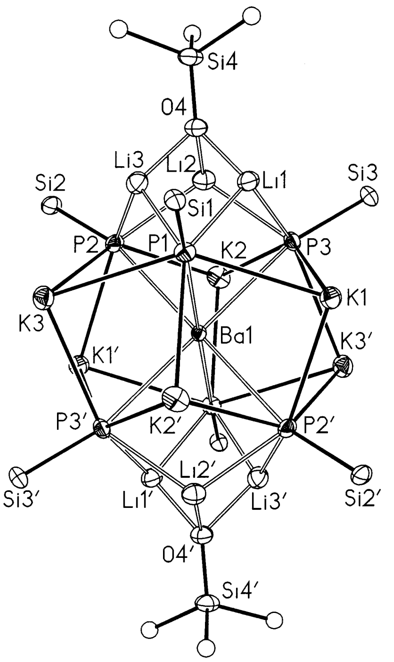

Figure 1. Perspective drawing of **2**. The ellipsoids represent a probability of 40%. The isopropylsilyl substituents and the H atoms are omitted for clarity reasons; the methyl groups of the $OSiMe_3$ ligands shown with arbitrary radii. Symmetry related atoms ($-x + 1$, $-y$, $-z + 1$) are marked with apostrophes. Selected bond angles of **2**: P1−Li1−P3 109.6(2), P1−Li1−O4 108.0(2), P3−Li1−O4 107.0(2), P2−Li2−P3 109.6(2), P2−Li2−O4 107.0(2), P3−Li2−O4 107.8(2), P1−Li3−P2 109.5(2), Li1−O4−Li2 82.9(2), Li1−O4−Li3 83.1(2), Li2−O4−Li3 83.0(2), Li1−O4−Si4 135.0(2), Li2−O4−Si4 127.6(2), Li3−O4−Si4 127.5(2).

Table 1. Selected Bond Lengths (pm) of 1 and 2

n	1	2	3	mv[a]
		1		
Sr1−P(*n*)	311.14(8)	311.06(8)	308.95(9)	310.4
P(*n*)−Si(*n*)	218.3(1)	217.9(1)	217.3(1)	217.8
K1−P(*n*)	342.8(1)[b]	326.9(1)	342.5(1)	336.7
K2−P(*n*)	333.3(1)	344.1(1)	321.0(1)	
K3−P(*n*)	329.0(1)	339.0(1)[b]	351.5(5)	
Li1−P(*n*)	259.2(6)		254.9(6)	256.9
Li2−P(*n*)	257.8(6)[b]	259.5(6)[b]		
Li3−P(*n*)		254.5(6)	255.3(5)	
Li(*n*)−O4	190.7(6)	190.3(7)	191.0(6)	190.7
O(4)−Si4	161.0(2)			
		2		
Ba1−P(*n*)	317.97(6)	316.74(6)	317.63(6)	317.4
P(*n*)−Si(*n*)	217.97(9)	217.62(9)	217.90(8)	217.8
K1−P(*n*)	336.34(9)	323.53(9)[b]	348.60(9)	340.2
K2−P(*n*)	332.90(9)[b]	355.49(9)	343.24(9)	
K3−P(*n*)	344.79(9)	346.38(9)	330.27(9)[b]	
Li1−P(*n*)	260.5(4)		260.0(4)	258.9
Li2−P(*n*)		258.1(4)	256.6(5)	
Li3−P(*n*)	261.3(5)	256.9(4)		
Li(*n*)−O4	188.8(5)	190.3(5)	190.6(5)	189.9
O(4)−Si4	161.6(2)			

[a] mv = mean value. [b] Atoms generated by inversion symmetry ($-x + 1$, $-y$, $-z + 1$).

(tetrahydrofuran) alkaline earth metal bis[bis(trimethylsilyl)-phosphanides (Sr−P 300.6 and 303.5 pm,[19] Ba−P 315.8 and 319.0 pm[20]) shows that the Ba1−P bond lengths of **2** fit very well into the characteristic range, whereas the Sr1−P values of **1** are larger than observed for the bis(phosphanides). On one hand, the Ba1−P distances should be rather short because of the electrostatic attraction between dianions and dications (i.e., in $[(\eta^6\text{-toluene})BaSn_3(PSi\text{-}t\text{-}Bu_3)_4]$ with a mean Ba−P bond length of 304.7 pm).[8] On the other hand, the stronger attraction is compensated by an electrostatic repulsion between the dianionic and the sterically crowded triisopropylsilylphosphanediide ligands. Because of the smaller radius of the strontium atom, the octahedral hole of **1** should contract; however, contraction of the octahedral hole would increase the electrostatic repulsion between the phosphanediide substituents. Therefore, the Sr1−P bond lengths of **1** are lengthened even as compared to $(THF)_4Sr[P(SiMe_3)_2]_2$. Because of this fact, very similar Sr1···Li and Ba1···Li contacts of 376.9 pm for **1** and 379.2 pm for **2** (average values) are observed. As a consequence of a very similar size of the P_6 octahedra of **1** and **2**, also nearly similar K−P and Li−P distances are found. A further lowering of the size of the alkaline earth metal by choosing calcium or magnesium dications destabilizes this structure; therefore, we were unable to isolate similar cage compounds for these small alkaline earth metals up until now.

The lithium atoms of **1** and **2** are bonded to two phosphanediide ligands and to the silanolate substituent. They are in a pyramidal environment because of the electrostatic repulsion between the lithium cations. Thus, the resulting fourth coordination site is sterically blocked by the bulky triisopropylsilyl groups, which prevents the coordination of additional donor molecules. The Li−P bond lengths lie in the characteristic region as observed for a wide variety of lithium phosphanides such as $(DME)_2LiPH_2$,[21] polymeric $[(DME)LiPH_2]_x$,[22] and organyl-substituted lithium phosphanides and phosphanediides.[23]

The potassium−phosphorus framework forms a distorted hexagonal K_6P_6 prism as shown in Figure 2; the distortion is caused by the electrostatic attraction between the phosphorus atoms and the alkaline earth metal center and leads to a widening of the K−P−K angles and to narrow angles at the potassium atoms. However, this deformation of the prism has no influence on the K−P bond lengths that lie in the expected region as observed for substituted potassium phosphanides.[24−26] The coordination numbers of the potas-

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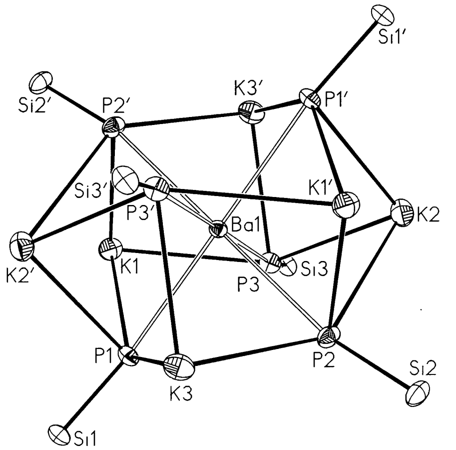

Figure 2. Representation of the distorted hexagonal K_6P_6 prism of **2**. The ellipsoids represent a probability of 40%. Only the silicon atoms of the triisopropylsilyl substituents are shown. Selected bond angles: P1−K1−P2′ 91.59(2), P1−K1−P3 76.76(2), P2′−K1−P3 89.86(2), P1′−K2−P2 86.77(2), P1′−K2−P3 88.60(2), P2−K2−P3 73.97(2), P1−K3−P2 75.49(2), P1−K3−P3′ 88.76(2), P2−K3−P3′ 89.14(2), K1−P1−K2′ 78.58(2), K1−P1−K3 139.28(2), K2′−P1−K3 76.96(2), K1′−P2−K2 77.08(2), K1′−P2−K3 79.03(2), K2−P2−K3 140.79(2), K1−P3−K2 139.73(2), K1−P3−K3′ 77.82(2), K2−P3−K3′ 77.52(2).

sium atoms of **1** and **2** are enhanced by agostic interactions to the triisopropylsilyl substituents with K···C contacts of 340 pm.

The metathesis reaction of alkali metal phosphanediides with strontium and barium diiodide and the cleavage of hexamethyldisiloxane yields heterotrimetallic cage compounds. The enhanced reactivity and the ether cleavage reactions could be a consequence of the heteropolymetallic cage compounds. A somewhat comparable reaction was performed by Izod et al.,[27] who reacted K−P[CH(SiMe$_3$)$_2$](C$_6$H$_4$-2-OMe) with calcium diiodide. During this metathesis reaction a C−O bond cleavage was observed, and tetrameric Ca{P[CH(SiMe$_3$)$_2$](C$_6$H$_4$-2-O)} with a central Ca_4O_4 heterocubane moiety precipitated; however, no heterobimetallic cage compounds were reported. A similar cage compound was already well-known from the reaction of K−P[CH(SiMe$_3$)$_2$](C$_6$H$_4$-2-OMe) with YbI_2; however, the metathesis reaction of YbI_2 with 2 equiv of the sterically more hindered KP[CH(SiMe$_3$)$_2$](C$_6$H$_3$-3-Me-2-OMe) in THF gave the corresponding ytterbium bis(phosphanide), which was also characterized by an X-ray structure determination.[28] A subsequent ether cleavage reaction suggests that not the heterobimetallic species induces the ether cleavage but the ytterbium or alkaline earth metal compound; the potassium derivative is stable, and no C−O bond cleavage reaction was observed by the authors.[28]

Summary

The metathesis reaction of the alkali metal triisopropylsilylphosphanediide yields heterotrimetallic cage compounds; homoleptic alkaline earth metal phosphanediides were not available in this reaction. The rather poor yield for the strontium derivative **1** originates from the size differences of the strontium atom and the octahedral hole formed by the phosphanediide ligands. This fact leads also to an enhanced reactivity of **1** in comparison to the barium derivative **2** toward moisture and air, which was noted during handling of these compounds. Similar cage compounds of the smaller alkaline earth metal cations are unknown thus far. No reaction was observed between calcium diiodide and lithium potassium triisopropylsilylphosphanediide in the presence of hexamethyldisiloxane.

These cage compounds are the first examples of a metal-centered alkali metal phosphanediide. The alkaline earth metal-free alkali metal phosphanediides tend to form spherical cages[29] that can be oxygen-centered[30,31] or can show a metal deficiency such as in {[Li$_2$PSi-*i*-Pr$_3$]$_8$[PSi-*i*-Pr$_3$]$_2$}.[31]

Experimental Section

General. All experiments and manipulations were carried out under purified argon. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting KP(H)Si-*i*-Pr$_3$ was prepared by a literature procedure.[15] NMR spectra were recorded on JEOL spectrometers GSX270 and EX400. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra.

Hexalithium Hexapotassium Strontium Hexakis(triisopropylsilylphosphanediide)bis(trimethylsilanolate) (1). Potassium triisopropylsilylphosphanide (1.54 g, 6.74 mmol) was dissolved in 20 mL of toluene, and 4.21 mL of a 1.6 M *t*-BuLi−hexane solution was added dropwise. The solution turned red. Thereafter, 1.43 mL of hexamethyldisiloxane (6.74 mmol) and 2.30 g of anhydrous strontium diiodide (5.03 mmol) were added. A colorless precipitate of iodides formed. The red solution was decanted, and its volume was reduced to approximately 15 mL. Within a few days, 0.19 g of colorless and pyrophoric crystals (0.10 mmol, 12%) precipitated. mp 286 °C dec. ^{1}H NMR δ: 1.21 (CH$_3$/*i*-Pr, ^3J(H,H) = 5.0 Hz), 1.20 (CH), −0.07 (OSiMe$_3$). ^{7}Li NMR δ: 6.9 (broad). ^{13}C{^{1}H} NMR δ: 20.7 (CH$_3$/*i*-Pr, ^3J(P,C) = 2.8 Hz), 16.6 (CH, ^2J(P,C) = 9.7 Hz), −2.3 (OSiMe$_3$). ^{29}Si{^{1}H} NMR δ: 22.0 (Si-*i*-Pr$_3$, ^1J(P,Si) = 57.8 Hz), −5.3 (OSiMe$_3$). ^{31}P{^{1}H} NMR δ: −315.7. IR: 1469 s, 1462 vs, 1377 m, 1363 m, 1355 w, 1290 vw, 1242 m, 1437 m, 1208 s, 1129 s, 1089 vs, 1070 s, 1060 s, 1004 vs, 973 vs, 963 vs, 919 m, 881 vs, 821 m, 738 vw, 660 m, 646 s, 639 s, 622 s, 566 s, 555 s, 521 m, 512 s, 472 m, 443 m, 429 w, 408 w, 385 w cm^{-1}. Elemental analysis ($C_{60}H_{144}K_6Li_6O_2P_6Si_8Sr$, 1856.43) Calcd: C, 43.09; H, 8.68. Found: C, 41.18; H, 8.87.

Barium Hexalithium Hexapotassium Hexakis(triisopropylsilylphosphanediide)bis(trimethylsilanolate) (2). To a solution of 1.15 g of KP(H)Si-*i*-Pr$_3$ (5.03 mmol) in 10 mL of toluene, 3.14 mL of a 1.6 M *t*-BuLi−hexane solution (5.03 mmol) was added at room temperature. The solution turned red immediately. Then 1.06

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mL of hexamethyldisiloxane (5.03 mL) and 1.96 g of anhydrous barium diiodide (5.03 mmol) were added. After 1 day, the solid materials (KI, excess of BaI_2) were removed, and the volume of the red solution was reduced to approximately 5 mL. After a few days, 0.67 g of colorless **2** (0.36 mmol, 57%) precipitated. mp 295 °C dec. ^{1}H NMR δ: 1.26 (CH_3/*i*-Pr, ^3J(H,H) = 5.1 Hz), 1.25 (CH), −0.07 ($OSiMe_3$). ^{7}Li NMR δ: 7.6 (broad). ^{13}C{^{1}H} NMR δ: 21.1 (CH_3-*i*-Pr, ^3J(P,C) = 2.7 Hz), 16.6 (CH, ^2J(P,C) = 8.8 Hz), −2.7 ($OSiMe_3$). ^{29}Si{^{1}H} NMR δ: 22.1 (Si-*i*-Pr_3, ^1J(P,Si) = 54.8 Hz), −3.1 ($OSiMe_3$). ^{31}P{^{1}H} NMR δ: −313.5 (broad). IR: 1494 m, 1469 s, 1453 s, 1380 m, 1363 m, 1350 m, 1290 vw, 1253 s, 1240 vs, 1207 m, 1127 m, 1082 s, 1069 vs, 1029 m, 1004 vs, 958 vs, 920 m, 880 vs, 825 vs, 741 vs, 729 m, 698 m, 666 m, 637 vs, 620 vs, 587 vs, 558 vs, 512 vs, 468 vs, 441 vs, 366 s, 307 vw cm^{-1}. Elemental analysis (crystalline material, $C_{74}H_{160}BaK_6Li_6O_2P_6Si_8$, 1906.14) Calcd: C, 45.95; H, 8.56. Found: C, 45.56; H, 7.94.

Crystal Structure Determinations of 1 and 2. The data were collected on a Nonius-Kappa CCD diffractometer with FR591 rotating anode (**1**) and a STOE-IPDS diffractometer (**2**) with graphite monochromated Mo Kα radiation (λ = 71.073 pm) using oil-coated[32,33] rapidly cooled single crystals. Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 2.

All structures were solved by direct methods with the program SIR97[35] and refined with the software package SHELXL-97.[36] Neutral scattering factors were taken from Cromer and Mann[37] and those of the hydrogen atoms were from Stewart et al.[38] The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms. The asymmetric unit of **1** and **2** contains also a toluene molecule that shows no short contacts to the potassium or lithium atoms because these alkali metal cations are sterically shielded by the demanding triisopropylsilyl substituents.

Table 2. Crystallographic Data of **1** and **2**

	1·2-toluene	**2**·2-toluene
chemical formula	$C_{74}H_{160}K_6Li_6O_2P_6Si_8Sr$	$C_{74}H_{160}BaK_6Li_6O_2P_6Si_8$
fw (g·mol^{-1})	1856.44	1906.14
T (K)	200(2)	200(2)
space group[34]	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	17.8124(3)	18.679(1)
b (Å)	16.0122(3)	16.0693(8)
c (Å)	18.5926(4)	17.744(1)
β (deg)	90.570(1)	90.904(8)
V (Å^3)	5302.6(2)	5325.4(5)
Z	2	2
ρ_{calcd} (g·cm^3)	1.163	1.189
λ (Å)	0.71073	0.71073
μ (mm^{-1})	0.961	0.823
wR2[a] (on F^2)	0.1045	0.0657
R1[a] ($I > 2\sigma(I)$)	0.0472	0.0307

[a] Definition of the *R* indices: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Acknowledgment. This paper is dedicated to Prof. Wolfgang Beck in honor of his 70th birthday. We thank the Deutsche Forschungsgemeinschaft for financial support.

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.

IC0202413

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