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$(CuI)_3P_4Se_4$: β-P_4Se_4 Cages between Columns of Copper Iodide[†]

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Pure orange $(CuI)_3P_4Se_4$ was prepared by reaction of stoichiometric amounts of CuI, red P, and Se in evacuated silica ampules. The crystal structure was determined from single crystals at room temperature. $(CuI)_3P_4Se_4$ crystallizes in the hexagonal system, space group $P6_3cm$ with $a = 19.601(2)$ Å, $c = 6.7196(6)$ Å, and $Z = 6$. The compound consists of β-P_4Se_4 cages that are embedded between columns of copper iodide. These columns can be considered as sections of a wurtzite-type structure, which is not yet known for copper iodide. Three of four phosphorus atoms are coordinated by copper, whereas selenium is exclusively bonded to phosphorus.

Introduction

The molecular structures of numerous binary phosphorus−selenium cage molecules have not yet been determined by X-ray crystallography apart from a limited number of exceptions. Thus, precise structural data are available only for P_4Se_3,[1,2] P_4Se_5,[3] and P_2Se_5.[4] In addition, *polymeric* phosphorus selenides with the compositions $P_{14}Se$[5] and *catena*-P_4Se_4[6] were described. The molecular structure of *monomeric* P_4Se_4, which was first prepared by Monteil and Vincent,[7] is not known to date and is discussed controversially.[8,9] Four different P_4Se_4 cages were suggested: *exo*-P_4Se_4-I (derived from P_4Se_3 with an exo-bonded Se atom at one of the basal P atoms), *exo*-P_4Se_4-II (derived from P_4Se_3 with an exo-bonded Se atom at the apical P atom), α-P_4Se_4 (with a realgar analogous structure), and β-P_4Se_4 (P_4Se_3 with a Se atom inserted into a basal P−P bond).[8,9] The α-/β-nomenclature is used analogously to the corresponding phosphosulfides. The reason for the problems occurring during the structure determination of monomeric P_4Se_4 is the strong tendency of glass formation and polymerization of P−Se mixtures. Thus, to date no single crystals suitable for a structure determination could be obtained, and the reaction products turned out to be insoluble in the common solvents.[10] Recently, we successfully applied copper(I) halides as solid solvents for the synthesis of new phosphorus polymers,[11] heteroatomic chalcogen molecules,[12] thiometalates,[13] and polychalcogenides.[14] Most of these materials exhibit a high copper ion conductivity.[13b,15] Herein, we report the synthesis and the molecular structure of P_4Se_4 in a matrix of copper iodide.

Experimental Section

Synthesis and Characterization. $(CuI)_3P_4Se_4$ was prepared by reaction of CuI (>98%, Merck), Se (99.999%, Chempur), and P (99.9999%, Hoechst) in the molar ratio CuI:Se:P = 3:4:4. Prior to use, CuI was purified by recrystallization from concentrated aqueous HI. The white microcrystalline powder was filtered from the solution, subsequently washed with demineralized water and ethanol, and then dried in a vacuum for several days. The starting materials were sealed in evacuated silica ampules, slowly heated up to 600 °C, and then kept at 400 °C for 5 days. Orange needle-shaped crystals were grown on the tube and on the surface of the shiny solidified reaction product. The pure reaction product is neither air nor moisture sensitive. X-ray powder techniques (Siemens D5000, Cu Kα_1 ($\lambda = 1.54051$ Å), Si as an external standard) and differential thermal analysis (DTA) measurements (Linseis L62, Al_2O_3 as reference material) were employed for characterization. $(CuI)_3P_4Se_4$ has a melting point of 429 ± 2 °C. Impedance spectroscopic investigations in the frequency range 100 mHz to 4 MHz (IM6, Zahner elektrik) show an enhanced copper ion mobility and a corresponding activation energy of $E_A = 0.33$ eV. Solid state NMR spectra were recorded on a Bruker CXP-300 NMR spectrometer at room temperature. The measuring frequency was 121.5 MHz, and the magic angle spinning frequency was 12 kHz.

X-ray Studies. The crystal structure of $(CuI)_3P_4Se_4$ at room temperature was determined from single crystal of suitable size, i.e., $0.5 \times 0.03 \times 0.03$ mm^3. The crystal was glued on a glass capillary and mounted on an IPDS (STOE) single crystal diffractometer, providing monochromatic Mo Kα ($\lambda = 0.71073$ Å) radiation. The orientation matrix and lattice constants were determined from 5000 reflections (see Table 1). A total of 37 790 reflections with $-25 \le h \le 25$, $-25 \le k \le 25$, and $-8 \le l \le 8$ up to $2\theta_{max} = 56.3°$ were collected in the range $-2 \le \varphi \le 360°$ with $\Delta\varphi = 1.5°$. Each image was exposed for 25 min. Absorption was corrected numerically. The reflections were merged to give 1903 symmetry independent reflections

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[†] Dedicated to Professor H.-D. Lutz on the occassion of his 65th birthday.

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(1) Vos, A.; Keulen, E. *Acta Crystallogr.* **1959**, *12*, 323.

(2) Rollo, J. R.; Burns, G. R.; Robinson, W. T.; Clark, R. J. H.; Dawes, H. M.; Hoursthouse, M. B. *Inorg. Chem.* **1990**, *29*, 2289.

(3) Penney, G. J.; Sheldrick, G. M. *J. Chem. Soc.* **1971**, 245.

(4) Blachnik, R.; Lönnecke, P.; Boldt, K.; Engelen, B. *Acta Crystallogr., Sect. C* **1994**, *50*, 659.

(5) von Schnering, H.-G.; Hönle, W. *Chem. Rev.* **1988**, *88*, 243.

(6) Ruck, M. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1832.

(7) Monteil, Y.; Vincent, H. *Z. Anorg. Allg. Chem.* **1975**, *416*, 181.

(8) Lathrop, D.; Eckert, H. *J. Phys. Chem.* **1989**, *93*, 7895.

(9) Lister, G. M. S.; Jones, R. *J. Phys.: Condens. Matter* **1989**, *1*, 6039.

(10) Blachnik, R.; Lönnecke, P.; Nuss, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 160.

(11) (a) Pfitzner, A.; Freudenthaler, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1647. (b) Pfitzner, A.; Freudenthaler, E. *Z. Kristallogr.* **1995**, *210*, 59. (c) Freudenthaler, E.; Pfitzner, A. *Z. Kristallogr.* **1997**, *212*, 103. (d) Pfitzner, A.; Freudenthaler, E. *Z. Naturforsch, B: Chem. Sci.* **1997**, *52*, 199.

(12) (a) Pfitzner, A.; Zimmerer, S. *Z. Anorg. Allg. Chem.* **1995**, *621*, 969. (b) Pfitzner, A.; Zimmerer, S. *Z. Anorg. Allg. Chem.* **1996**, *622*, 853. (c) Pfitzner, A.; Zimmerer, S. *Z. Kristallogr.* **1997**, *212*, 203.

(13) (a) Pfitzner, A.; Zimmerer, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 982. (b) Pfitzner, A. *Chem.−Eur. J.* **1997**, *3*, 2032. (c) Pfitzner, A. *Inorg. Chem.* **1998**, *37*, 5166.

(14) Pfitzner, A.; Baumann, F.; Kaim, W. *Angew. Chem.* **1998**, *110*, 2057.

(15) (a) Freudenthaler, E.; Pfitzner, A.; Sinclair, D. C. *Mater. Res. Bull.* **1996**, *31(2)*, 171. (b) Freudenthaler, E.; Pfitzner, A. *Solid State Ionics* **1997**, *101−103*, 1053.

10.1021/ic981042f CCC: $18.00

Table 1. Crystallographic Data for $(CuI)_3P_4Se_4$

chem. formula	$Cu_3P_4Se_4I_3$	fw [g mol^{-1}]	1011.09
a [Å]	19.601(2)	space group	$P6_3cm$ (No. 185)
c [Å]	6.7196(6)	T [°C]	25
V [Å^3]	2235.7(4)	λ [Å]	0.71073
Z	6	ρ_{calc} [g cm^{-3}]	4.504
μ(Mo Kα) [cm^{-1}]	206.1	R (all reflections)[a]	0.0613
		R_w (all reflections)[a]	0.1450

[a] $R = (\sum||F_{obs}| - |F_{calc}||)/\sum|F_{obs}|$, $R_w = [\sum w(|F_{obs}|^2 - |F_{calc}|^2)^2/\sum w|F_{obs}|^4]^{1/2}$, $w = 1/[\sigma^2(I) + (0.0001I^2)]$.

Table 2. Fractional Atomic Coordinates, Displacement Parameters U_{eq}[a] [Å^2], and Site Occupancy Factors (SOF)[b] for $(CuI)_3P_4Se_4$

atom	Wyckoff position	x	y	z	SOF	U_{eq}
Cu1	6c	0.12356(8)	x	0.3135(3)	1.0	0.0222(5)
Cu2	12d	0.3360(1)	0.5417(1)	0.1826(4)	0.555(6)[c]	0.032(1)
Cu2′	12d	0.3350(1)	0.5413(1)	−0.0052(5)	0.445[c]	0.024(1)
I1	6c	0.12944(4)	x	0.701070	1.0	0.0158(2)
I2	12d	0.20185(3)	0.53358(3)	0.0875(1)	1.0	0.0240(2)
P1	6c	0.2327(1)	x	0.2153(6)	1.0	0.0189(9)
P2	12d	0.3382(1)	0.4311(1)	0.0879(5)	1.0	0.0261(8)
P3	6c	0.3978(1)	x	0.3218(5)	1.0	0.0196(9)
Se1	6c	0.29987(6)	x	0.4847(2)	1.0	0.0258(4)
Se2	12d	0.21648(5)	0.32459(5)	0.0507(2)	1.0	0.0290(3)
Se3	6c	0.42058(7)	x	−0.1331(2)	1.0	0.0265(4)

[a] U_{eq} is defined as one-third of the trace of the anisotropic $\mathbf{U}_{ij}$ tensor. [b] The SOF is equal 1 for a fully occupied position. [c] The SOFs for Cu2 and Cu2′ were constrained to sum up to 1. A SOF (Cu2) = 0.1581(7) and a SOF (Cu2′) = 0.471(7) are obtained if the occupancies are refined independently.

Table 3. Selected Interatomic Distances [Å] and Angles [deg] for $(CuI)_3P_4Se_4$

Cu1−I1	2x	2.594(2)	Cu2−Cu2′		1.262(5)
−I1		2.607(2)	P1−Se1		2.238(4)
−P1		2.239(3)	−Se2	2x	2.267(4)
Cu2−I2		2.599(2)	P2−Se2		2.265(2)
−I2		2.633(3)	−Se3		2.278(3)
−I2		2.724(3)	−P3		2.241(5)
−P2		2.280(4)	P3−Se1		2.210(3)
Cu2′−I2		2.609(2)	−P2	2x	2.241(5)
−I2		2.612(3)			
−I2		2.740(4)			
−P2		2.281(4)			
Se1−P1−Se2	2x	101.7(1)	Se1−P3−P2	2x	104.3(1)
Se2−P1−Se2		108.1(2)	P2−P3−P2		89.4(2)
Se2−P2−S3		108.2(1)	P1−Se1−P3		96.3(1)
Se2−P2−P3		105.8(1)	P1−Se2−P2		100.2(1)
Se3−P2−P3		86.2(1)	P2−Se3−P2		87.6(1)

(R_{int} = 0.0553). A starting model for the structure refinement was obtained by direct methods (NRCVAX[16]). Structural data were refined against F^2 by full matrix least squares methods, using the JANA98 program package[17] and scattering factors therein. During the refinement, no hints for twinning were detected. After introduction of anisotropic displacement parameters for all atoms and an isotropic extinction coefficient, the refinement of 83 parameters converged to $R = 0.0613$ and $R_w = 0.1450$ for all reflections. The largest peak in the final difference Fourier calculation was 3.63 e Å^{-3}. Table 2 contains the refined atomic coordinates and the displacement parameters. The z parameter of I1 was not refined in order to define the origin. Selected interatomic distances and angles are summarized in Table 3.

Results and Discussion

Crystal Structure. We obtained the orange compound $(CuI)_3P_4Se_4$ by reaction of copper iodide with red phosphorus and selenium. Contrary to an older publication,[18] no organic solvents with a relatively low boiling point were used. Thus, this new compound was obtained as very thin needle-shaped single crystals. The X-ray structure analysis shows that $(CuI)_3P_4Se_4$ is analogous to the compounds described in refs 11−12 insofar as it can be described as an adduct of a copper(I) halide with a formally neutral ligand. However, $(CuI)_3P_4Se_4$ contains *isolated monomeric* P_4Se_4 cages contrary to $(CuI)_8P_{12}$,[19] $(CuI)_3P_{12}$,[11a] and $(CuI)_2P_{14}$,[11d] which all have *polymeric* main-group molecules as a basic building unit in common. Figure 1 shows the P_4Se_4 cage in $(CuI)_3P_4Se_4$, which could be characterized by X-ray structure analysis for the first time. It is the so-called β-cage with C_s symmetry. Selected interatomic distances and angles are given in Table 3. The P−P bond length is 2.241 Å, and the average of the P−Se bond lengths is 2.25 Å. Both are in a typical range for single bonds between these elements. The experimentally determined bond lengths P−Se are slightly smaller than those obtained by ab initio calculations[9] for β-P_4Se_4, whereas the P−P distances take the same value as calculated. By contrast, the experimental angles show some pronounced discrepancies to the predicted values, amounting up to 18°. As discussed elsewhere, these differences are rather due to the use of a limited basis for the ab initio calculations than to the influence of the copper halide matrix.[20] Similar to $(CuI)_3P_{12}$ and $(CuI)_2P_{14}$, there is no significant influence on the neutral main-group molecule by the surrounding copper atoms to be observed.[11a,d] Interestingly, only the phosphorus atoms P1, P2, and P2′ are coordinated by copper ($\bar{d}$ (P−Cu) = 2.26 Å), whereas P3 and the selenium atoms bear exclusively intramolecular covalent bonds. The P_4Se_4 cage molecules in $(CuI)_3P_4Se_4$ are stacked along [001] within the crystal structure. The shortest intermolecular distance (3.49 Å) in this direction, that is, within one stack, is found between Se1 and Se3. This distance is significantly smaller than the van der Waals distance (3.8 Å). Each stack of P_4Se_4 molecules is surrounded by three columns formed by copper iodide and three further stacks of P_4Se_4 molecules. Figure 2 shows the resulting motif, which can be rationalized as a hexagonal rod packing. The shortest intermolecular distance between the stacks of P_4Se_4 molecules in the a−b plane is 3.57 Å (Se3−P3). The copper atoms have a distorted tetrahedral environment of iodine and phosphorus, with an average Cu−P bond length of 2.27 Å and an average Cu−I distance of 2.63 Å. The coordination spheres for the copper atoms can be rationalized as [$CuPI_3$], taking the disorder of Cu2 and Cu2′ into account. During the refinement of the crystal structure, the site occupancy factors of Cu2 and Cu2′

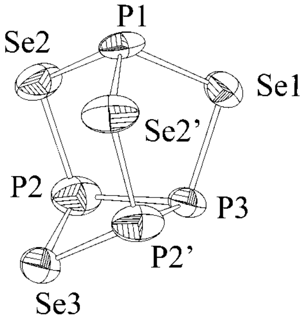

Figure 1. Molecular structure and labeling scheme of the β-P_4Se_4 cage in $(CuI)_3P_4Se_4$, symmetry-related atoms are marked by a (′). The ellipsoids represent a probability of 90%.

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(16) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(17) Petricek, V. JANA98, Institute of Physics, Academy of Sciences of the Czech Republic, Prag, Czech Republic, 1997.

(18) Ibáñez, W. F.; González, M. G.; Clavijo, C. E. *Z. Anorg. Allg. Chem.* **1977**, *432*, 253.

(19) Möller, M. H.; Jeitschko, W. *Solid State Chem.* **1986**, *65*, 178.

(20) Pfitzner, A.; Reiser, S.; Panthöfer, M. To be published.

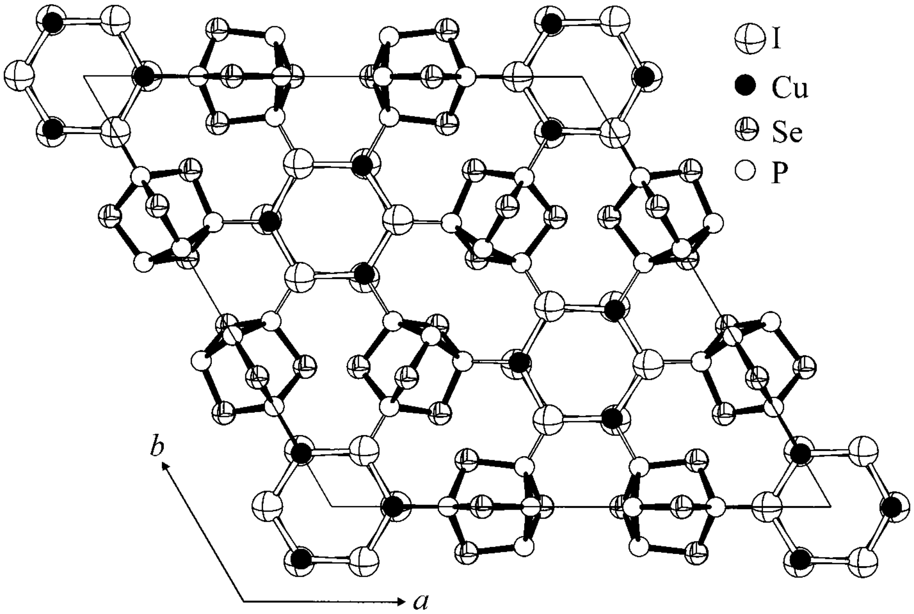

Figure 2. Projection of the crystal structure of $(CuI)_3P_4Se_4$ along [001]. The P_4Se_4 cages are stacked along the *c*-axis. They are surrounded by three further stacks and three columns of CuI. The CuI columns are surrounded by six P_4Se_4 stacks. A hexagonal rod packing results.

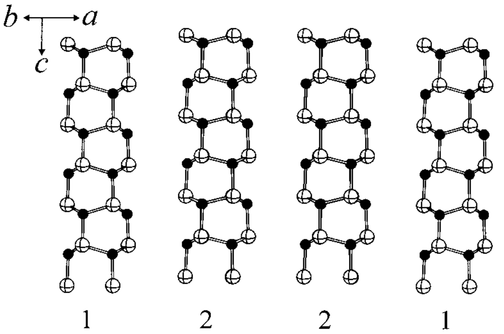

Figure 3. Arrangement of the wurtzite analogous CuI columns in $(CuI)_3P_4Se_4$ as seen along [210]. The columns of type 1 and of type 2 occur in a ratio of 1:2 and are shifted for 0.77 Å along the *c*-axis. In the columns of type 2, only the positions of Cu2 are drawn for clarity. The representation of the atom types is the same as in Figure 2.

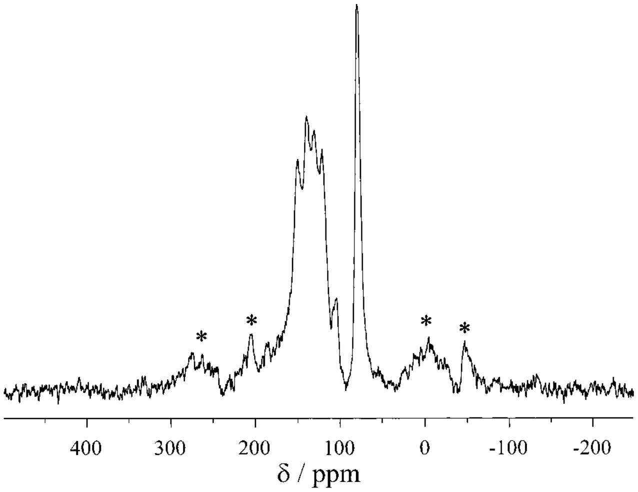

Figure 4. ^{31}P solid state NMR spectrum of $(CuI)_3P_4Se_4$. The narrow signal at 79.1 ppm is assigned to P3 and the unresolved multiplet with maxima at 149, 138, 130, 121, and 105 ppm is assigned to P1, P2, and P2′. The asterisks mark rotational side bands.

were constrained to sum up to 1. These two positions are located in a trigonal bipyramid of four iodine atoms and one phosphorus atom, which results from two face-sharing tetrahedra. Both tetrahedron centers are occupied to nearly 50% with a distance of 1.262 Å between them. If the occupancies of Cu2 and Cu2′ are refined independently, a slight surplus of 0.052 copper atoms is obtained. A similar observation was made for $(CuI)_2P_{14}$, where a copper atom is located in a trigonal bipyramid of three phosphorus and two iodine atoms.[11d] The iodine atoms of the CuI columns build up face sharing octahedra. As expected, copper is not located within these octahedral voids. These columns can be regarded as sections of a wurtzite-type structure; cf. Figure 3. In the title compound, two different columns are found, and they are shifted against each other for 0.77 Å along the *c*-axis. The reason for this displacement is the coordination of the copper atoms to P1 (column 1) and to P2 (column 2), respectively. To date, no wurtzite-type modification is known for pure CuI,[21,22] which crystallizes in the zinc blende type at room temperature.

In $CuBrS_4N_4$, which might be regarded as a lighter homologue of $(CuI)_3P_4Se_4$ with a similar composition, the S_4N_4 cage molecules have almost D_{2d} symmetry.[23] From this compound, molecular S_4N_4 can be separated by a thermolysis reaction. Because of the tendency of P_4Se_4 to undergo polymerization at higher temperatures, a similar experimental procedure will probably not yield crystalline β-P_4Se_4. While attempts to synthesize transition-metal complexes with phosphochalcogenide ligands have only resulted in fragmentation products,[24] the present contribution shows that the β-P_4Se_4 cage can be stabilized in a copper iodide matrix. Thus, its molecular structure could be determined by X-ray methods for the first time.

^{31}P-MAS-NMR Spectra. $(CuI)_3P_4Se_4$ was investigated by solid state ^{31}P-NMR in order to confirm the structural results obtained by X-ray crystallography. The spectrum is shown in Figure 4. It shows one narrow signal at 79.1 ppm and a broad, unresolved multiplet with maxima at 149, 138, 130, 121, and 105 ppm vs 85% H_3PO_4. The ratio of the integrated signals is 1:3. The narrow signal is assigned to P3, which is not

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(21) Yude, Y.; Boysen, H.; Schulz, H. *Z. Kristallogr.* **1990**, *191*, 79.
(22) Keen, D. A.; Hull, S. *J. Phys.: Condens. Matter.* **1995**, *7*, 5793.
(23) Thewalt, U.; Müller, B. *Z. Naturforsch., B: Chem. Sci.* **1982**, *37*, 828.
(24) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 750.

coordinated to copper. The ^{31}P signals of the three other phosphorus atoms (P1, P2, P2′) are drastically broadened because of heterodipolar interactions with the quadrupolar nuclei ^{63}Cu and ^{65}Cu, as also predicted by theoretical considerations.[25]

Note added in Proof: β-P_4S_4 coordinated to two $NbCl_5$ molecules has very recently been reported. The metal atoms are bonded to those phosphorus atoms which are equivalent to P2 and P2′ in $(CuI)_3P_4Se_4$.[26]

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Supporting Information Available: X-ray crystallographic files, in CIF format, providing more details regarding data collection and structure refinement for $(CuI)_3P_4Se_4$, a listing of *d*-values, and an X-ray powder pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Olivieri, A. C. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 345.

(26) Nowottnick, H.; Stumpf, K.; Blachnik, R.; Reuter, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 693.